SIPERNAT® specialty silica
and AEROSIL® fumed silica
for defoamer

Technical Information 1313

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This technical information provides an overview of

- Theoretical aspects of foam and defoaming
- Evonik silica that can be used to produce defoamers
- How they are used
- What functionality they deliver, and
- Which application-technology tests are conducted in our laboratory.

In this technical information TI 1313, the term „defoaming" will be used synonymously for all possible variations of defoaming, foam prevention, foam control and deaeration.

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1 Introduction

Foam occurs in many natural and industrial processes as well as everyday life. Whipped cream and many other products from food technology like ice cream, cappuccino, mousse au chocolat, etc. are impressive examples where foam is desired. Important technical applications include heat-insulating polymer foams like Styropor® and the use in flotation processes. In cosmetic products, foam is often a desirable side effect.

On the other hand, the formation of stable foams causes problems in most industrial processes. Examples are found in the **paint and coating, textile, paper, detergent** and the **chemical industries**. Here foam will either affect the quality of the final product directly or impede the manufacturing process, for example, by reducing the carrying capacity of containers or by causing pumping problems. For this reason a number of foam control processes have been developed. The first group includes mechanical and thermal procedures for destroying foam. However, these are normally linked to high investment costs and high energy demands and they need to be optimized for each particular process. On the other hand, they do have the inherent advantage that the product will contain no foreign substances that can affect the quality of the finished product.

A second approach is to use cost-effective defoamers for which the requirements are very high. The demand is for such products that have **no negative impact** on the manufacturing process or final product, work in **low concentrations** and are **highly efficient under extreme conditions (high temperature, high pH, high shearing forces)**, and have **high environmental compatibility**. Key components used in the production of these highly effective foam control agents are dispersions made of oils and hydrophobic silica, with a great variety of oils and silica being used.

Evonik defoamer silica have been established components in foam control agents for many years.

Evonik Industries, a leading manufacturer of synthetic amorphous silica, offers the following product groups for the formulation of silica-based defoamers:

• SIPERNAT® Specialty Silica and
• AEROSIL® Fumed Silica.

Foam is detrimental to most production processes. The use of foam control agents containing Evonik SIPERNAT® and AEROSIL® grades is a cost-effective method preventing for foam problems.

In addition to their use as highly **effective active components in foam control agents** (as hydrophobic solid, SIPERNAT® and/or AEROSIL® products), these silica also find applications as **anti-settling agents** (primarily AEROSIL® products) and in the manufacture of **antifoam powders** (SIPERNAT® carrier silica).

2 Theoretical considerations and defoaming principles

2.1 General properties of foam systems

Foam is a two-phase system where gas bubbles, such as air, are dispersed in a liquid. Often, they show a cellular structure in which cells that contain gas are surrounded by liquid films (**Figures 1** and **2**). (Meta)stable foams always require the presence of interfacially active substances like surfactants. From a thermodynamic point of view, the large interface of the foam represents an unfavorable state, with every foam system consequently attempting to achieve a structure in which the films expand as little as possible. However, any change in the film structure firstly requires an energy input because the surfactants stabilize the foam structure by means of different stabilization mechanisms. For example, the foam stability is a function of the surface elasticity, surface viscosity, and steric interactions in the foam films. In the case of aqueous foam systems, electrostatic interactions in the foam films also play an important role.

Foam is a two-phase system in which gas bubbles are dispersed within a continuous phase like a liquid.

Depending on the proportion of the liquid phase, it is possible to distinguish between "wet" spherical foams and relatively dry polyhedral foams. Polyhedral foams arise from spherical foams when the liquid in the foam lamellae flows downwards under the influence of gravity.
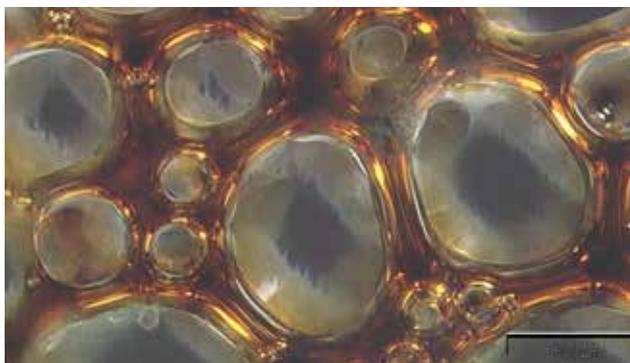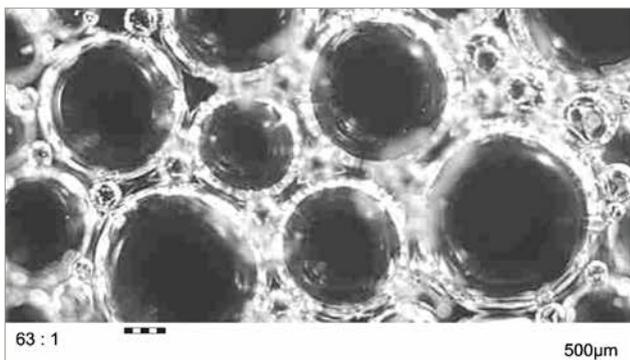

Figure 1 Photomicrograph of black liquor foam

Figure 2 Photomicrograph of detergent foam

2.2 Stabilization mechanisms for foam

Foam becomes a problem in practice only when it is metastable, that is, when it fails to decompose immediately. This kinetic stability comes from interfacially active substances which are enriched in the air/liquid interface. In pure two-component systems on the other hand, such as air in pure water, very rapid coalescence will occur. The kinetic stabilizing effect of low-molecular interfacially active substances, that is, surfactants, is based on the Gibbs film elasticity and the Marangoni effect[1]. A local change or stretching of the foam film consequently gives rise to a reduction in the number density of surfactant molecules in the interface, leading to a surface tension difference. As a result of this, the foam film pulls itself together again due to the local increase in the surface tension (Gibbs film elasticity). The fact that the movement of surfactant molecules from the solution to the interface is diffusion-controlled, i.e. time-dependent (Marangoni effect), further intensifies this effect. This stabilizing effect of low-molecular interfacially active substances is conceptually different from the stabilizing mechanism of high-molecular interfacially active substances, such as proteins. Simplified, some proteins tend to form a two-dimensional network structure[2] in the foam film with elastic components that counteract the change in the foam-film structure. The main difference between protein-stabilized and surfactant-stabilized foams can thus be found in the viscoelastic properties of the interfacial phases involved.

2.3 Defoaming and foam control

As already stated, foams are not thermodynamically stable but are characterized by a metastable state that cannot be maintained indefinitely. In general, the destabilization processes involved can be subdivided into the following categories:

- Foam destabilization based on pressure differences between foam bubbles of different sizes (Ostwald ripening)
- Drainage of the foam film, meaning that the foam liquid flows downward in the foam lamellae due to the gravitational force; this process is inversely proportional to the viscosity of the liquid
- Rupture of the foam film.

Foam control agents make particular use of the latter of these principles.

The properties required of a defoamer can be summarized as follows:

- Insolubility in the foam medium
- (Easy) dispersibility in the foam medium
- Chemical inertness
- Lower surface energy/surface tension than the foam medium.

[1] P. R. Garrett, *Defoaming, Theory and Industrial Application* (1993), Surfactant Science Series Vol 45
[2] Benjamins J., Cagna A. & Lucassen-Reynders E. H., *Colloids and Surfaces A: Physicochemical and Engineering Aspects* (1996) 114, 245-254.
Viscoelastic properties of triacylglycerol/water interfaces covered by proteins.

Explanation: If the defoamer, which generally features a lower surface tension than the foam film, were soluble in the foam film, this would lead to reinforced foam formation. Easy dispersibility means that the defoamer can be quickly transformed into an appropriate droplet size distribution by stirring. Chemical inertness and compatibility are important to ensure that the defoamer will not deteriorate the properties of the product into which it is introduced.

2.4 Defoaming mechanism

No general, quantitative defoaming mechanism has yet been published in the literature. On the contrary, it appears that different destabilization mechanisms play a role due to the large number of different defoamers and foam systems that have been studied. Nevertheless several qualitative principles of actions have been identified.

It is possible to schematically divide the defoaming mechanism for aqueous foams into four sub processes. The importance of each process step will vary greatly depending on the foam system:

1 Entry of the defoamer into the foam interface
2 Bridging between two neighboring foam films
3 Dewetting or pin-effect, and
4 Rupture of the foam film.

The entry and spreading of the defoamer plays a decisive role for nonaqueous foams. **Figure 3** illustrates these processes schematically. In the next section we will discuss the defoaming steps of aqueous foams in more detail.

2.4.1 Entering and spreading

In the first step of the defoamer mechanism oil droplets from the oil phase are enriched in the water/air interface, that is, into the foam lamella. From a thermodynamic (energetic) perspective, this process can be described in terms of the entering coefficient E with the following equilibrium condition being valid[3] where:

$$E = \gamma_{W/A} + \gamma_{W/O} - \gamma_{O/A}$$

$\gamma_{W/A}$ – surface tension at the water/air interface
$\gamma_{W/O}$ – surface tension at the water/oil interface
$\gamma_{O/A}$ – surface tension at the oil/air interface.

Evidently, it is necessary for a defoamer droplet to enter ($E > 0$) the foam film for film rupture of the foam lamella. This condition is not sufficient, however, because practical systems are rarely at equilibrium.
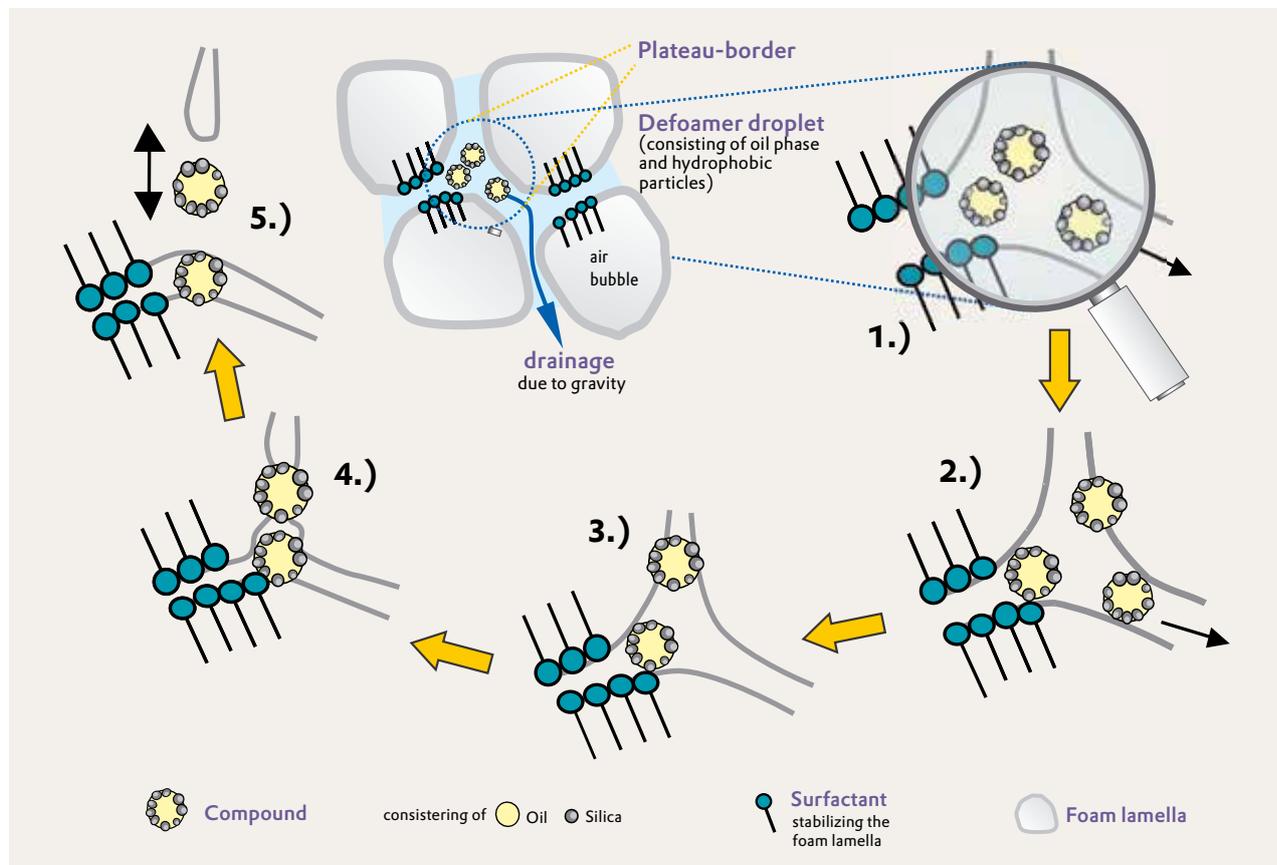

Figure 3 Illustration of the defoaming mechanism of silica/oil droplets in an aqueous foam:
   1 Draining foam **2** Entry of the defoamer droplet into the foam interface and spreading **3** Bridging between adjacent foam films
   4 Dewetting **5** Rupture of the foam film *(Source: Silicone surfactants in Surf. Sc. Series, Marcel Dekker)*

Moreover, a closer inspection shows that oil droplets approaching the interface give rise to the formation of an asymmetrical three-phase film (oil/water/air). The literature also refers to this thin film as a "pseudoemulsion film".

The ability of the defoamer droplet to spread on the foam lamella is also important. This causes the liquid to flow radially around the oil droplet, resulting in local thinning of the foam film (Marangoni flow). The spreading coefficient[3] is given by:

$$S = \gamma_{W/A} - \gamma_{W/O} - \gamma_{O/A}$$

It is positive for spreading systems. For aqueous foams, however, no clear correlation can be found between the value of S and the ability to cause film rupture. For the defoaming of nonaqueous systems, spreading of the defoamer droplet on the foam lamella obviously plays a larger role[3].

In summary, it can be concluded that positive values of the entering and spreading coefficients do not generally predict effective defoaming, but they may be useful in choosing an appropriate oil for the foam system to be defoamed.

2.4.2 Bridging and dewetting

Bridging by the oil droplets is another important factor in defoaming. Here the speed of the bridging process, droplet size, and lamella thickness are all functions of the oil/water contact angle and drainage velocity. The ability for bridging and dewetting is given by

$$B = \gamma^2_{W/A} + \gamma^2_{W/O} - \gamma^2_{O/A}$$

which has been proposed by Garrett[3]. Here B is the bridging coefficient and must be greater than zero for bridging to occur. This also implies that the oil/water contact angle must exceed 90°[3]. It was consequently reported that the contact angle for good hydrophobic defoamer particles should exceed 110°[4]. However, it must be pointed out that it is very difficult to make quantitative interpretations about contact angles on rough surfaces.

2.4.3 Kinetics of film rupture

The entering, spreading, and bridging coefficients describe the energetic conditions, in other words the necessary thermodynamic equilibrium conditions for the foam film to rupture. We have already pointed out that often practical systems are not in the state of equilibrium. Specifically, this means that foam bubbles are continuously formed due to mechanical intermixing so that the actual effectiveness of the defoamer also depends on the rate at which

the foam film ruptures. The number of defoamer droplets (droplet size distribution) and the kinetics of the entering, spreading, and bridging processes are consequently the decisive factors in the macroscopic defoaming effect.

2.5 Defoaming mechanism for non-aqueous foam systems

As mentioned in the introduction, the working mechanism for non-aqueous foam systems significantly differs from that for aqueous systems. The reason can be found in the corresponding colloidal interactions. Aqueous foam films are generally characterized by long-range electrostatic, repulsive interactions that result in (kinetic) energy barriers that limit the rate at which oil droplets can penetrate the foam lamella and thereby restrict bridging. The film stability of non-aqueous films is primarily a function of its Gibbs elasticity. A strong correlation between surface-rheological properties and foam stability has thus been established for liquid hydrocarbons[5].

2.6 Synergism between oil and hydrophobic particles

Dispersions of hydrophobic particles in oil are significantly more effective than the individual components themselves. This effect is known as synergism[6]. Garrett's monograph[3] states that this defoaming synergism is fairly universal. This is the reason why the patent literature describes a large number of mixtures of oil/hydrophobic particles.

The main effect of hydrophobic particles can obviously be attributed to the fact that they destabilize the thin pseudo-emulsion film (which consists of oil/water/air) more rapidly. This greatly facilitates the penetration of defoamer droplets (pin-effect, booster).

The effect of hydrophobic particles can be understood by assuming that they drastically increase the depth and rate of penetration of the defoamer droplets into the foam lamella.

The critical factor for this is that the hydrophobic particle need to be located on the surface of the oil droplet. Besides the hydrophobic nature of the particle themselves, it is also possible for an emulsifier or surfactant to affect the spatial distribution of the hydrophobic particle in the oil droplet[7]. Moreover, it has also been discussed that dynamic conditions (here we mean mechanical intermixing during the defoaming process) can also contribute to the formation of a special spatial configuration of the oil/silica system so that the hydrophobic silica is primarily localized on the surface of the oil. It must also be taken into consideration that irregularly shaped, i.e. rough hydrophobic particles in the oil/water/air three-phase interface can reduce the contact angle and thereby the dewetting conditions[8].

[3] P. R. Garrett, *Defoaming, Theory and Industrial Applications* (1993), Surfactant Science Series Vol. 45
[4] Lichtman, I. A., Sinka, J. V., Evans, D. W., de Papel Boletin, 15, 26 (1975)
[5] I. C. Callaghan in P. R. Garrett, *Defoaming, Theory and Industrial Application* (1993), Surfactant Science Series Vol 45, 119-151
[6] Garrett, P. R., Davis, J., Rendall, H. M. Colloids Surf. A 85, 159 (1994)
[7] Wang, G., Pelton, R., Shawafaty, N., Heng, Y. M. Langmuir 1999, 15, 2202-2208
[8] N. J. Jarvis , J. Phys. Chem. 70, 3027 (1966)

In summary, the synergetic effect of oil and hydrophobic particles on the defoaming process obviously depends on the hydrophobic (silica) particles protruding from the interface of the oil droplet into the foam film. **This results in a substantially faster entry (pin-effect) of the defoamer droplets into the foam film and thus to film rupture.** All things considered, the presence of hydrophobic silica significantly boosts the defoaming effect.

2.7 Important factors on the defoaming effect

The lamella thickness of most foam systems ranges between 0.01–1 μm. Effective foam control agents, on the other hand, have an average droplet size of 5–40 μm[9,10]. This leads us to the conclusion that for some foam systems, the defoaming process takes place in the Plateau border, as illustrated in **Figure 1**[11,12]. However, there are good reasons to believe that it is not possible to generalize this conclusion since rupture of the foam lamella is assumed for other foam systems, too[13]. It is obvious that the size of the defoamer droplet must be similar to that of the Plateau border or lamella thickness to cause rapid destruction of the foam bubble.

If the oil droplets are too small, they may become effective only after the foam film has reached a particular, smaller lamellae thickness by means of drainage. On the other hand, larger particles are effective, but the respective number density is much lower at a given silica concentration. The defoamer droplet size distribution is therefore critically important for formulations used in practice[14]. For example, the viscosity of the carrier oil substantially determines the droplet size distribution of the resulting emulsion[15].

The effectiveness of foam control agents is largely determined by the droplet size distribution of the defoamer. The type and manner of its dispersion and production therefore have a decisive effect.

Likewise, it is possible to use the considerations valid for the defoamer droplets for the size and shape of the hydrophobic particles: The larger and rougher these are and the further they protrude from the oil droplets, the more effective and rapid the destabilization of the pseudoemulsion film in the foam lamella (knock-down). However, at a constant solid concentration, this certainly leads to a significant change in the number of particles (for example, if the particle size is cut down to one third the particle number increase by factor 27!). In the end, application technology tests are necessary to determine an optimum size and particle density for a particular system. Finally, it must also be emphasized that coarse particles are much more prone to sedimentation than smaller particles.

3 Defoamer composition

It is possible to divide foam control agents into various categories based on composition. Some of the categories that are important for practical applications are as follows:

- Homogeneous single component systems like
  - polyethylene oxides (these act by means of phase separation above the polymer's cloud point, resulting in the formation of insoluble hydrophobic droplets through dehydration) and
  - polysiloxanes
- Oil-based defoamer dispersions with a hydrophobic solid (compounds)
- Defoamer emulsions
- Foam control agents in solid form: here the actual active defoamer is applied to an absorbing solid.

The emulsifiers used in the emulsions can substantially reinforce the defoaming effect. They first of all facilitate the defoamer's dispersibility and enable appropriate particle size distributions as well as stabilize them. Secondly, they have been said to have a positive effect on the spatial distribution of the silica in the oil droplets.

Most high-quality defoamers are manufactured on the basis of water-insoluble liquids, such as mineral oils (paraffinic, napthenic), the full range of silicone oils in terms of viscosities, polyether siloxanes, natural oils (e.g., rapeseed oil) or fatty alcohols. The addition of one or more hydrophobic solids improves the defoaming effectiveness of the above oils drastically because of the synergetic effect. Foam control agents based on hydrophobic solids also have the advantage that temperature has little effect on their defoaming performance. The hydrophobic solids (e.g., hydrophobized silica, waxes or amides, fatty acids and their salts, amines or polyurea) may be used in defoamers either separately or in combination. Silicone oil defoamers mainly contain silica as hydrophobic solids, whereas systems based on mineral oil, for example, might contain waxes in addition to the silica.

The use of synthetic hydrophobic silica as solids in defoamers has the following advantages compared to the use of other solids, such as waxes or metal soaps

- Rough, porous surface
- Defined particle size
- Temperature insensitivity and/or temperature stability
- Insensitivity to water hardness
- Optimized degree of hydrophobicity.

[9] Randal M. Hill, Kenneth C. Fey *Silicone Surfactants in Surfactant Science* Series Vol 86, 159-181, (1999)
[10] K. Koczo, J. K. Koczone, D. T. Wasan, J. Colloid Interface Sci. 166, 225, (1994)
[11] Randal M. Hill, Kenneth C. Fey *Silicone Surfactants in Surfactant Science* Series Vol 86, 159-181, (1999)
[12] K. Kozco, J. K. Koczone, D. T. Wasan, J. Coll. Interface Sci., 166, 225-238, (1994)
[13] N. D. Denkow, P. Cooper, Langmuir *"Mechanisms of Action of Mixed Solid- Liquid Antifoams"*. 1. Dynamics of Film Rupture, 15, 8514, (1999)5, 8514
[14] P. R. Garrett, Langmuir, 11, (1995) 3576
[15] V. Bergeron, P. Copper, C. Fischer, J. Giermanska-Kahn, D. Langevin, A. Pouchelon, *Colloids Surfaces A: Physico-chemical and Engineering Aspects* 122 (1997), 103-120

4 Evonik silica for use in defoamers

4.1 Evonik processes for manufacturing synthetic amorphous silica

Evonik Industries produces two different product groups of synthetic amorphous silica that are used in defoamers:

- SIPERNAT® Specialty Silica and
- AEROSIL® Fumed Silica.

SIPERNAT® grades are produced from sulfuric acid and water glass solutions (sodium silicate solutions) under particular conditions (temperature, pH value, concentration ratios, agitation)[16]. The following equation describes the overall reaction:

$$Na_2O \cdot 3.3\ SiO_2 + H_2SO_4 \rightarrow 3.3\ SiO_2 + Na_2SO_4 + H_2O.$$
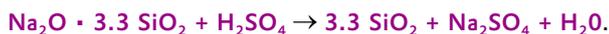
Silica of different property profiles are obtained once the product has been washed, filtered, and dried. For some products, a grinding step follows the drying.

AEROSIL® products are produced in a high-temperature flame hydrolysis process[17] in which silicon tetrachloride is hydrolyzed in an oxyhydrogen flame. The following chemical overall equation describes the overall reaction:

$$SiCl_4 + 2\ H_2 + O_2 \rightarrow SiO_2 + 4\ HCl.$$
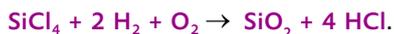
Different reaction conditions are used to control the chemico-physical properties of the resulting silica. In contrast to SIPERNAT®, AEROSIL® products are not ground.

Both grades of silica show a **hydrophilic** character after manufacture. This means that they can be wetted by water. They differ greatly in their other chemico-physical properties, however. Hydrophilic SIPERNAT® grades have a moisture content of approximately 6 %, whereas the moisture content of AEROSIL® products are below 1.5 %. Because of the strongly branched structure of fumed silica, their tapped density is only about 50 g/l, whereas that of SIPERNAT® may be well over 200 g/l.

Details regarding silica manufacture and the differences caused by processing are thoroughly covered in the Technical Overview: AEROSIL®–Fumed Silica[17].

As already mentioned in the second section of this Technical Bulletin, it is particularly important for the defoaming effectiveness, that the silica has a **hydrophobic** surface character. Particular SIPERNAT® and AEROSIL® grades are after-treated in an additional production step called hydrophobization to modify the surface chemistry of the silica. This greatly changes their wetting behavior with regard to water. Hydrophilic silica becomes **hydrophobic** (**Figure 4**). The underlying process is a real chemical reaction, such as reactions between appropriate polysiloxanes and the silanol groups on the silica surface.

Figure 4 Wetting behavior towards water:
left: SIPERNAT® D 10 (hydrophobic)
right: SIPERNAT® 383 DS (hydrophilic)

SIPERNAT® D 10, a classic hydrophibic **SIPERNAT®** type for use in defoamers has often been proven useful in practice. Depending on their property profile, very different hydrophobic AEROSIL® products, which all carry the letter "R" in their name, can be added to defoamer as either defoaming components or as suspending agents.

Several methods are available to determine the hydrophobicity of silica. First of all, it is possible to quantify a silica hydrophobicity by determining its wettability in various methanol-water mixtures. This is based on the fact that hydrophobic silica can not be wetted by water but by methanol. The amount of methanol that is necessary to wet the hydrophobic silica is consequently a measure of its hydrophobicity. Another method is water-vapor adsorption under defined conditions. This is based on the fact that highly hydrophobized silica shows a low water absorption and that low water adsorption thus correlates with a high hydrophobicity.

The following Sections 4.2–4.4 discuss in more detail which SIPERNAT® and AEROSIL® grades in particular can be recommended for use in defoamers. This is compiled in tabular form in Section 4.5.

4.2 Defoamer dispersions using hydrophobic silica

SIPERNAT® and AEROSIL® products can generally increase the performance of many foam control agents. However, to get best results with synthetic silica several important factors must be considered.

Due to attractive interactions and their large surface areas, finely divided silica particles tend to form agglomerates of different sizes even when they are stored in their dry state. The more finely divided the chosen silica, the greater its tendency to agglomerate. Specifically, this

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[16] Brochure "Specialty silica", Evonik company publication
[17] Technical Overview: AEROSIL®–Fumed Silica, Evonik company publication

means that AEROSIL® grades tend to agglomerate more strongly than SIPERNAT® grades. Surface texture also plays an important role. Hydrophilic silica agglomerate particularly strongly. Optimum **dispersion** in the chosen oil is therefore very important when using a silica. This applies all the more as the viscosity of the oil rises. In general, any sort of simple mixing operation will not suffice to disperse the silica homogeneously and, therefore, can not substitute an effective dispersion step. Dispersing units, such as rotor-stator units like those made by *Silverson Machines LTD. (U.K.)* [A] and Ultra Turrax by *Janke & Kunkel* [B], high-pressure homogenizers (e.g., by *Invensys APV* [C] or *Christison*[D]) and ball mills have proven themselves in the manufacture of silica-containing defoamer dispersions.

Finely divided silica, especially finely divided hydrophilic silica, has a pronounced tendency to agglomerate, making careful and proper dispersion a basic requirement for effective foam control agents. Simple agitation is no substitute for a dispersion step! A temperature rise during dispersion is not generally necessary.

It is important to take into account that, besides the shearing force and applied pressure (**Figure 5**), other factors also affect the particle size of the silica and the particle size distribution in the oil, such as the viscosity of the oil, the concentration of silica, and other additives. If an Ultra Turrax is used, for example, a higher filler content may result in a finer particle distribution. However, at the end, application technology tests need to be carried out to determine what particle distribution will produce the best defoaming performance.
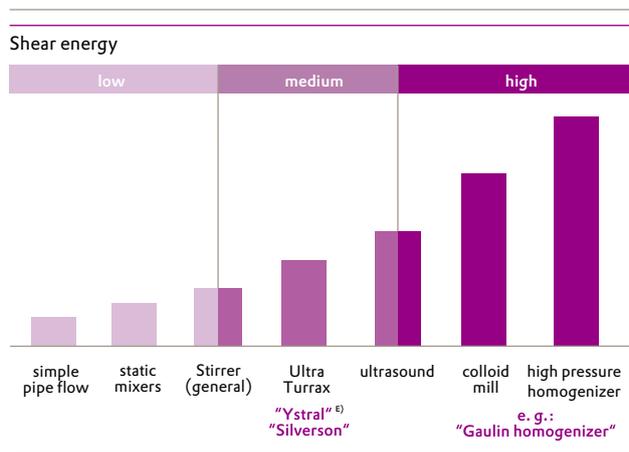

Figure 6 The Ultra Turrax T 50 from IKA® has been proven as an appropriate dispersion unit for the preparation of homogeneous defoamer dispersions containing silica

Starting formulation for silica-based defoamers:

  5–10 % e.g., SIPERNAT® D 10
  90–95 % paraffinic or naphthenic mineral oil or silicone oil or vegetable oil or other nonpolar liquids

Lipophilic dispersing agents as well as emulsifiers are often added to oil-based defoamer dispersions to improve their dispersibility or to produce self-emulsifiable formulations. Moreover, it is possible to add rheological additives, such as fumed silica and organic high-molecular thickeners to impart sedimentation stability to the dispersion and improve its application-technology properties.

Section 5.3 "Application technology testing of sedimentation stability" thoroughly covers the topic of using fumed silica to improve storage stability.

SIPERNAT® grades recommended as defoaming components[F]:

SIPERNAT® D 10 is a milled hydrophobic (i.e., not wettable by water) silica. It is used in a great variety of defoamers due to its high effectiveness and ease of dispersion.

SIPERNAT® D 13 * is a milled, hydrophobic (i.e., not wettable by water) silica, high methanol wettability and low surface. It is used in a great variety of technical defoamers due to its high effectiveness and ease of dispersion.

SIPERNAT® D 17 is a hydrophobic (i.e., not wettable by water) silica also used in defoamers. Its primary application is as a free flow and anticaking agent.

Figure 5 Shear energy of different dispersion units

Example: In our application technology laboratory, we disperse a 60 g batch with an Ultra Turrax T 50 (shear head G 45 M, **Figure 6**) at 10,000 rpm for 5 minutes.

A Silverson Machines LTD., Waterside, Chesham Bucks, England, HP 51 PQ, Tel.: +44-1494-786331, **sales@silverson.co.uk**
B Janke und Kunkel GmbH & Co. KG, IKA-Labortechnik, Janke & Kunkel-Str. 10, D-79219 Staufen, Tel.: +49-7633-831-0, **www.ika.net**
C Invensys AVP, Zechenstr. 49, D-59425 Unna, Tel.: +49-2303-108-0
D Christison Particle Technologies LTD., Albany Road, Gateshead, NE 8 3 AT, UK, Tel.: +44-191-478-8120, **sales@christison.com**
E Ystral GmbH, Maschinenbau + Prozesstechnik, Wettelbrunner Str. 7, D-79282 Ballrechten-Dottingen, Tel.: +49-7634-5603-0, **ystral@ystral.de**
F under certain preconditions
* Regionally restricted availible

AEROSIL® grades recommended as defoaming agents:

AEROSIL® R 202 is a hydrophobic fumed silica grade, treated with a polydimethylsiloxane. This product can be used in defoamer formulations for sedimentation stabilization and due to its high hydrophobicity as defoaming component.

AEROSIL® R 812 is hydrophobic fumed silica grade treated with HMDS (Hexamethyldisilazane). It can be used for sedimentation stabilisation and due to its high hydrophobicity as defoaming agent.

AEROSIL® R 812 S is hydrophobic fumed silica grade treated with HMDS (Hexamethyldisilazane). It is even more hydrophobic than AEROSIL® R 812 and convenient for stabilizing a defoamer and well suitable as a component of foam control agents.

AEROSIL® R 8200 is a structurmodified hydrophobic silica grade treated with HMDS (Hexamethyldisilazane). It is characterized by an extremely low thickening effect and high compacted bulk density. Its high hydrophobicity makes it suitable as a defoamer silica.

AEROSIL® R 972 and **AEROSIL® R 974** are hydrophobic fumed silica grades treated with DDS (Dichlordimethylsilane). The moderate hydrophobicity of these AEROSIL® products is suited for defoaming properties in the presence of appropriate hydrophobic liquids. They are recomended for improving the sedimentation stability of defoamer dispersions as well.

AEROSIL® R 104 and **AEROSIL® R 106** are hydrophobic fumed silica treated with D4 (Octamethylcyclotetrasiloxane). They have very good performance as defoamer silica, especially in silicone oil based formulations.

The precise physico-chemical data are compiled in section 6. The physico-chemical data (such as hydrophobicity or particle size) are helpful in preselecting silica for particular defoamer systems. When a very alkaline foam medium is under consideration, for example, it is necessary that the silica has a very high hydrophobicity (SIPERNAT® D 10, AEROSIL® R 8200). On the other hand, if the defoamer is intended for use in paints that will be applied in thin coats, the particle size may be the limiting factor. AEROSIL® products deliver the best results in this case. The type of silica most suitable for a particular defoamer must ultimately be examined in application technology tests.

For AEROSIL® and SIPERNAT® use in coating defoamer formulations, please refer to our technical information TI 1381: "AEROSIL® and SIPERNAT® – Efficient booster for defoamer in paints and coatings"

4.3 *In-situ* hydrophobization with hydrophilic silica

In addition to applying a ready-to-use hydrophobized silica in an oil-based defoamer, there is another way to employ silica in defoamers. For it, hydrophilic silica, e.g. SIPERNAT® 35 or SIPERNAT® 383 DS is used as a raw material and after-treated by means of the so-called *in-situ* hydrophobization process. Basically, the modification agent such as silicone oil is chemically grafted to the silica surface at an elevated temperature during this process. The high temperature causes the silicone oil chains to break down into shorter fragments that bond to the surface of the silica irreversibly. A slightly alkaline silica surface facilitates this process significantly.

At the same time, this method will produce, after dispersion, an already finished, albeit simple defoamer base formulation. For this reason hydrophilic silica is usually incorporated into silicone oil, which initially leads to a very high-viscous, sometimes even gel-like dispersion. Hydrogen bonds between the silanol groups of the hydrophilic silica are the cause of the high viscosity. This dispersion, which is also called α-dispersion in the literature, does not yet display any defoaming properties[18].

The dispersion is then heated for several hours under continuous shearing at temperatures between 100 and 200 °C (212 and 392 °F) in order to render the silica surface hydrophobic. This dispersion, which now has defoaming action, is also called β-dispersion in the literature.

The hydrophilic silica **SIPERNAT® 383 DS** and **SIPERNAT® 35** have often been proven a good choice because they are particularly suitable for the *in-situ* process. Key properties of this SIPERNAT® include small particle size and slightly alkaline pH value, which greatly accelerates the hydrophobization process. Due to the fact that the base catalyst is where it is supposed to be, namely on the surface where the reaction happens, it is possible to spare the addition of an additional alkaline catalyst.

In-situ Hydrophobization using SIPERNAT® 383 DS

SIPERNAT® 383 DS (5 %)	SIPERNAT® 383 DS (5 %)
silicone oil (95 %)	silicone oil (1 %)
mixing and stirring at approx. 200 °C	mineral oil (94 %)
one to several hours	mixing and stirring at 100 - 150 °C
	several hours

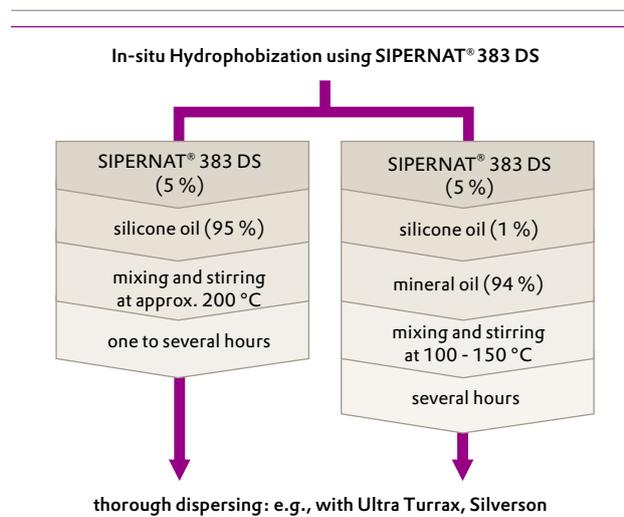**thorough dispersing: e.g., with Ultra Turrax, Silverson**

Figure 7 Principle of in-situ hydrophobization using SIPERNAT® 383 DS (same procedure applies to SIPERNAT® 35)

[18] S. Ros a. Gary Nishioka, Experimental Research on Silicon Antifoarms in „Emulsiion, Latices and Dispersions", P. Becher and M. N. Yudenfreund (Editors), Marcel Dekker, 1978

If silicone oil has been selected as the dispersion medium, this oil is used both as the carrier oil and as hydrophobization agent. If silicone oil is inappropriate due to application technology constraints, other oils can be used as carrier for the silica. A small amount of silicone oil will then be necessary (approx. 15–20 % relative to the SIPERNAT® used for example) to ensure that the hydrophilic silica will be hydrophobized (**Figure 7**).

4.3.1 Factors affecting *in-situ* hydrophobization

The **time** that it takes to complete the hydrophobization process is a function of the temperature, the viscosity of the batch as well as the efficiency of the catalyst used, to mention a few factors. It may therefore range between one and several hours and must be tested for the particular case. The **viscosity** of the silicone oil as a hydrophobization agent should preferably be in the range of 50–500 mPa·s at 25 °C in order to complete the hydrophobization in the shortest possible time. The longer the silicone-oil chains, the longer the process of breaking them down into fragments.

The **hydrophobization temperature** must be adjusted to the thermal stability of the respective oil. In principle, a higher temperature will naturally accelerate the hydrophobization process, but should not exceed 140–150 °C (284-302 °F) in the case of a paraffinic mineral oil, such as Shell Ondina 913 [G]. Silicone oils, on the other hand, can generally withstand temperatures up to 200 °C (392 °F).

4.3.2 When can we expect the hydrophobization process to be complete?

The declining viscosity of the batch provides a clear indication for the degree of conversion of the hydrophobization process.

As the silica is gradually rendered more and more hydrophobic, fewer interactions between silica particles will take place through hydrogen bonds which makes the dispersion viscosity drop substantially. To be specific, this means that the dispersion, initially of high viscosity, is irreversibly converted into a low viscous dispersion (**Figure 8**).

Figure 8 Viscosity of the batch prior to and after hydrophobization
　　　　　left: SIPERNAT® 383 DS dispersion prior to hydrophobization
　　　　　right: SIPERNAT® 383 DS dispersion after hydrophobization

Other indications may come from application technology testing of the defoaming performance in comparison to a reference product (e.g., dispersing **SIPERNAT® D 10** in the same oil without heating). See also [19].

To achieve an optimum defoaming effect, sufficient dispersion is mandatory immediately after the hydrophobization!
Evonik silica recommended for *in-situ* hydrophobization:

SIPERNAT® 383 DS is a very finely milled, hydrophilic, slightly alkaline silica. It is particularly well suited for the production of *in-situ* hydrophobized defoamers. Due *to an optimum pH value of 8.3* it facilitates the hydrophobization process and produces a homogeneous result. It is **not** necessary to add any other catalyst.

SIPERNAT® 35 [*] is a very finely milled, hydrophilic, slightly alkaline silica. It is particularly well suited for the production of *in-situ* hydrophobized defoamers. Due *to an optimum pH value of 8.3* it facilitates the hydrophobization process and produces a homogeneous result. It is **not** necessary to add any other catalyst.

SIPERNAT® 320 DS is a very finely milled, hydrophilic silica. Due to its slightly acidic pH value, it is recommended that an *alkaline catalyst* be added to optimize the hydrophobization process.

SIPERNAT® 22 S is a finely milled, hydrophilic silica; it is primarily used as a free-flow agent in other applications. SIPERNAT® 22 S can also be used *in-situ* hydrophobized in defoamers. The use of an *alkaline catalyst* is recommended.

SIPERNAT® 22 LS is a very finely milled, hydrophilic silica; it is primarily used as a free-flow agent in other applications.SIPERNAT® 22 LS can also be used *in-situ* hydrophobized in defoamers. The use of an *alkaline catalyst* is recommended.

AEROSIL® 200 is hydrophilic. If a *particularly finely divided silica* is required, it may be possible to use AEROSIL® 200 (or even other hydrophilic AEROSIL® products) *in-situ* hydrophobized as a defoamer silica.

This chapter has made it clear that the use of *in-situ* hydrophobization in the manufacture of defoamers requires empirical knowledge and comes at high cost in terms of time and equipment. It is often easier to use silica that have already been optimized and hydrophobized for defoaming, like those sold by Evonik (see 4.2).

For *in-situ* hydrophobization of AEROSIL® and SIPERNAT®, please refer to our technical information TI 1382: "Comparison of SIPERNAT® D10 with *in-situ* hydropho-bized fumed silica"

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* 　Regionally restricted availible
[G] 　Shell, Suhrenkamp 71–77, D-22284 Hamburg, Tel.: 040-632 40
[19] Technical Information 1382, Evonik company publication

4.4 Production of defoamer emulsions

Defoamer **emulsions** have proven particularly suitable for a range of applications. An emulsion is a two-phase system that has been produced from defoamer dispersions and water using emulsifiers and dispersing agents. A major advantage of emulsions is that it is possible to specifically set the defoamer droplet size distribution by means of the emulsifying process and the surfactants used. This comes along with a better dispersibility of the foam control agent in the foam system. The use of emulsions is consequently preferred, for example, where only weak agitation takes place. Particular end uses, such as paints and coatings, represent another field of application for defoamer emulsions. A wide range of surfactants and emulsifiers is used in the manufacture and stabilization of emulsions, but their discussion would greatly exceed the scope of this publication. The reader is referred to the literature for further details [20].

4.5   Production of anti-foam powders

Some products, like cement mixtures, require defoamers in powdered form. For this purpose, Evonik offers a range of SIPERNAT® grades that can be used to produce free-flowing powders from defoamer dispersions or defoamer emulsions. The production of the antifoam powder requires that the defoamer dispersion or emulsion be applied to the carrier silica as homogeneously as possible, with the absorption capacity of the SIPERNAT® grade being taken into consideration. For optimal mixing, we recommend a **low-shear mixer**, such as a **paddle mixer** (e.g., Dinnisen [H]), a **plough-share mixer** (e.g., Lödige [I]) or a **cone mixer** (e.g., Nauta Hosokawa [J]).

To guarantee optimum flowability and performance as well as to prevent caking and formation of agglomerates of the antifoam powder, the defoamer must be applied to the silica as finely distributed as possible.

The following principles generally apply to the loading of SIPERNAT® grades:
- Dripping is better than pouring
- Spraying is better than dripping
- Atomizing is better than spraying.

Which SIPERNAT® type is most suitable for manufacturing a powder defoamer depends, among other things, on the desired characteristics such as absorption capacity and particle size distribution. The DOA number is used as a measure of the absorption capacity [16]. The desired maximum particle size also plays a role. Evonik offers SIPERNAT® for carrier applications with mean agglomerate sizes of 7–320 µm. Detailed recommendations about this topic can be found in Technical Information 1360 [21] or obtained from our Technical Service department (**at-silica-chemicals@evonik.com**).

The following SIPERNAT® grades are recommended for the carrier application:

SIPERNAT® 22 is a hydrophilic, coarse silica combining a high absorptive capacity with a good flowability. It is well suited to transform any type of liquid, including defoamers, into dry, free flowing powder concentrates.

SIPERNAT® 2200 is a hydrophilic, microgranular, dust-free silica with spherical particles. It combines a high absorptive capacity with a narrow and optimized particle size distribution leading to a very good flowability of the final powder concentrates.

Chemical industry in general

Pulp industry

Textile industry

Petrochemistry

Detergent and cleaning industry

Paint and coating industry

H Dinnissen BV, Horsterweg 66, NL-5975 NB Sevenum, Tel.: +31-77-467 3555, **www.dinnissen.nl**
I Lödige, Gebr. Lödige, Maschinenbau GmbH, Elsener Str. 7 - 9, D-33102 Paderborn. Tel.: 05251 - 309-0, **info@loedige.de**
J Hosokawa Micron BV, P. O. Box 98, NL-7000 AB Doetinchen

20 P. Becher, Editor, Encyclopaedia of Emulsion Technology, Marcel Dekker, New York 1996
16 Brochure "Specialty silica", Evonik company publication
21 Technical Information 1360: "SIPERNAT® and AEROSIL® –an essential in industrial powder technology", Evonik company publication

SIPERNAT® 22 S is a hydrophilic, finely milled silica of high absorptivity which is primarily used for improving flowability of powders or as anticaking agent. SIPERNAT® 22 S may also be used as carrier in case a fine particle size is required.

SIPERNAT® 33 is a hydrophilic silica combining a very high absorptive capacity with good flowability and a coarse particle size. It is well suited to transform any type of liquid, including defoamers, into dry, free flowing powder concentrates.

SIPERNAT® 50 is a hydrophilic, coarse silica with the highest absorptive capacity and a high surface area. It is capable of transforming any liquid solution, water- or oil-based systems into dry powder concentrates of up to 75%.

SIPERNAT® 50 S is a hydrophilic, finely milled silica. Besides its application as flow aid and highly effective anticaking agent it also may serve as carrier of especially high absorptive capacity in case particle fineness is required.

SIPERNAT® 120 is a hydrophilic silica with medium particle size, medium oil adsorption (DOA) and low surface area.

SIPERNAT® 320 is a hydrophilic silica of medium particle size and moderate absorptive capacity. Among others applications it can be used as carrier for defoamers.

SIPERNAT® 360 is a hydrophilic silica with a relatively low surface area, medium particle size, and a slightly alkaline pH value. It is recommended as carrier for formulations which are sensitive to acids.

SIPERNAT® 820 A is a very fine particle aluminiumsilicate with an aluminium content of app. 9.5% in the form of Al_2O_3 and app. 8% sodium in the form of Na_2O. SIPERNAT® 820 has a medium oil adsorption (DOA) and a high whiteness level.

The high **absorption capacity** of Evonik synthetic SIPERNAT® types make them ideal carriers for transforming liquids or pastes (including defoamers) into powder with up to 75–80% active agent. In this case, it is important to use a low-shear mixer and to apply the defoamer to the liquid as finely distributed as possible. Some important carrier properties of SIPERNAT® when manufacturing powdered defoamers are as follows:

- Absorption capacity
- Particle distribution
- Specific surface area
- pH value

Usually, silica with larger particle size result in better flowing absorbates. More finely divided silicas make a good choice when higher **particle fineness** is needed.

The **surface** of carrier silica can play a role when easily oxidizable liquids must be applied. In this case a silica with a surface area as low as possible is recommended. High surface areas normally result in accelerated oxidation. In general, Evonik SIPERNAT® types have a weakly acidic to neutral **pH value**.

4.6 Application Fields of Silica-based Defoamers
Evonik SIPERNAT® and AEROSIL® grades are used for defoaming applications, to prevent settling of defoamers and for the manufacture of powder defoamers. They are employed for instance in the following branches of industry:

Food industry

Pharmaceutical industry

Building materials industry

Paper industry

4.7 Product recommendations

	Defoaming		Anti-settling	Powder defoamer production(carrier silica)
	Hydrophobic silica	In-situ-hydrophobization		
SIPERNAT®				
SIPERNAT® D 10	●●			
SIPERNAT® D 13 *	●●			
SIPERNAT® D 17	●			
SIPERNAT® 383 DS		●●		
SIPERNAT® 35 *		●●		
SIPERNAT® 320 DS		●		
SIPERNAT® 22				●●
SIPERNAT® 2200				●●
SIPERNAT® 50				●●
SIPERNAT® 22 S		●		●
SIPERNAT® 22 LS		●		
SIPERNAT® 33				●●
SIPERNAT® 50 S		●		●
SIPERNAT® 120		●		●
SIPERNAT® 320				●
SIPERNAT® 360				●
SIPERNAT® 820 A				●
AEROSIL®				
AEROSIL® 90			●●	
AEROSIL® 130			●	
AEROSIL® 150			●	
AEROSIL® 200		●	●	
AEROSIL® R 972	●		●●	
AEROSIL® R 974	●		●●	
AEROSIL® R 816			●●	
AEROSIL® R 202	●●		●	
AEROSIL® R 104	●●		●	
AEROSIL® R 106	●●		●	
AEROSIL® R 812	●●		●	
AEROSIL® R 812 S	●●		●	
AEROSIL® R 8200	●●			

●● very well suited   ● well suited

* Regionally restricted availability

5 Application technology tests

The preceding discussion shows that practical tests are absolutely necessary for an effective foam control agent. A series of test procedures that assess defoamer performance have been put forward in conjunction with systematic studies. In principle, it is necessary to choose a test in which it is possible to simulate the cause of the foam formation. We shall now discuss in detail the application technology tests that Evonik uses. These are the so-called circulation test and the latex test.

Figure 9 Circulation test unit Contifoam (capacity of the glass vessel: 600 ml)

5.1 Circulation test

This defoamer test is particularly suited to the study of agitated foaming systems.

The circulation test requires a glass vessel with water jacket, a tempered oil bath, a (for example, gear-type) pump, and a photocell system for measuring the foam height (**Figure 9**). To run the test, carefully pour 600 ml of the foam medium used for the application into the glass vessel. Having adjusted the desired temperature, foam is generated by turning on the pump. The foam solution is pumped from the bottom to the top of the vessel and is sprayed onto the foam surface. Start the measurement at the same time. After the maximum foam height has been attained, use a microliter syringe to inject the defoamer dispersion or emulsion to be tested through a septum. The foam height as a function of time is automatically recorded. The quantities, knock-down and hold-down have proven to be meaningful, characteristic parameters for assessing defoaming performance. While the first of these parameters describes the capability of the defoamer to reduce the foam height to a particular height immediately after addition, hold-down characterizes the defoamer's persistence, that is, the time that it remains effective. Specifically, it is the time that elapses until the foam again reaches a particular foam level (**Figure 10**).
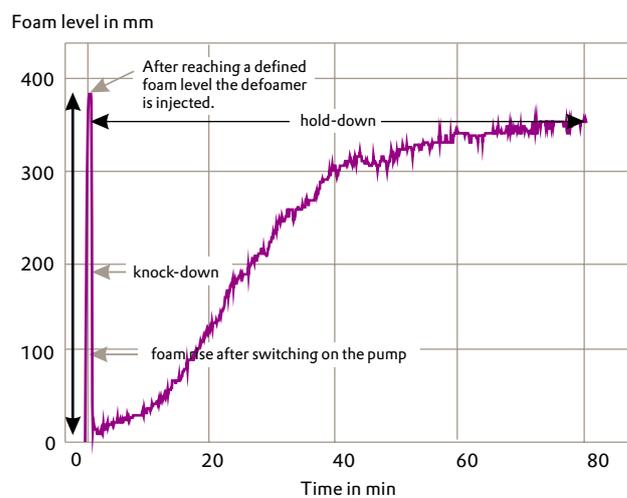

Figure 10 Characteristic parameters of the circulation test

The extent of foam formation is controlled, among other things, by the flow rate and the shape and width of the nozzle. The advantage of this test method is that different aqueous foam solutions can be tested under practical, dynamic, temperaturecontrolled conditions. Also, the action of the defoamer is investigated over a particular time period. Not only is it possible to say whether the defoamer has an immediate effect, but also how fast the effect takes place, how strong it is, and how long it lasts.

It is well known that the defoaming action diminishes over time. This is accelerated under extreme conditions (high temperature, high alkalinity, high shearing forces). Since these conditions can all be modeled with the circulation test, it is possible to say which silica will provide the best defoamer characteristics in combination with a given oil under practical conditions.

We run the circulation test as a standard test method to compare the defoaming performance of silica. Moreover, we also carry out this application technology test for our customers if they don't have the appropriate equipment to do it themselves.
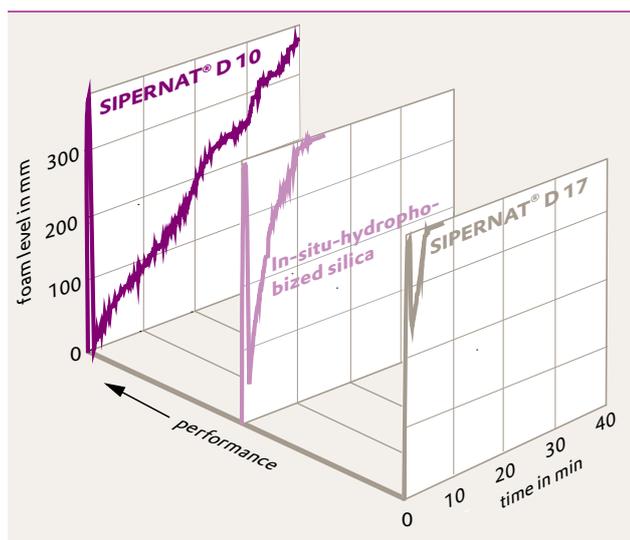
--- SIPERNAT® D 10   --- in-situ hydrophobized silica
--- SIPERNAT® D 17

Figure 11   Comparison of different defoamer silica
(5% SIPERNAT® in mineral oil, 80°C, 80 ppm dosage)

Figure 11 shows a comparison of the defoaming effects of the hydrophobic silica SIPERNAT® D 10, SIPERNAT® D 17 and an *in-situ* hydrophobized SIPERNAT®, which have been incorporated into the mineral oil to give a 5% dispersion (test medium: black liquor, temperature: 80°C (176°F)). The mineral oil dispersion with SIPERNAT® D 10 shows the best knock-down and hold-down.
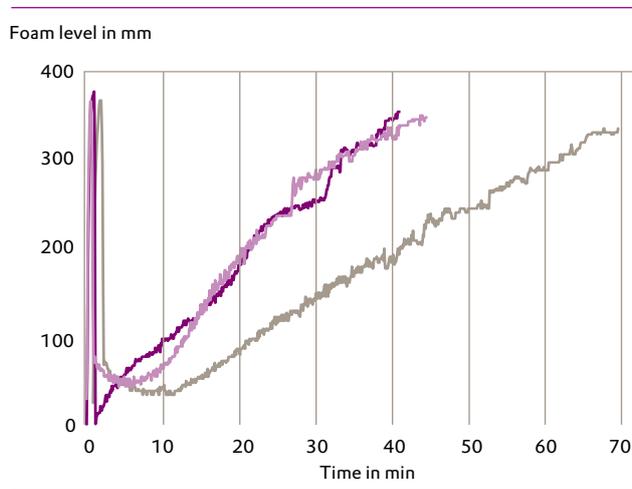
--- mineral oil   --- silicone oil 100 mPas   --- silicone oil 1000 mPas

Figure 12   Effect of different oils on defoaming performance
5% SIPERNAT® D 10, 80°C, 80 ppm dosage

Figure 12 clearly demonstrates that the oil used for producing the defoamer has a major effect, especially on the hold-down. 5% SIPERNAT® D 10 was dispersed in a mineral and a silicone oil of viscosity of 100 mPas as well as a silicone oil of viscosity 1000 mPas, and tested in the test medium black liquor. All three SIPERNAT® D 10 dispersions provide a very good knockdown. While the foam level begins to rise again steadily shortly after its collapse in case of the mineral oil dispersion, especially the more viscous silicone dispersion is able to hold the foam at a low level for quite a while. It can be generally said that more viscous silicone oils lead to a better hold-down of SIPERNAT® D 10 dispersion.

5.2 Testing the sedimentation stability

In general, particles that are larger than 1 micrometer are strongly inclined to settle down provided that their density is larger than that of the dispersion medium. The reason is that Brownian motion, which is universally present, is significantly smaller than gravitational forces in the micrometer range. From this it follows that hydrophobic SIPERNAT® is normally prone to settle in nonpolar dispersion media, that is, dispersions of defoamer silica in oils. Besides the viscosity of the system the rate of sedimentation greatly depends on the particle size and concentration of the settling particles, the sedimentation rate generally being smaller at higher concentrations.

There are generally two different approaches to formulating a suspension that is sufficiently sedimentation-stable under the given conditions. First, it is possible to influence the rate of sedimentation directly through the viscosity of the dispersion medium, that is, the continuous phase. This is based on the fact that the sedimentation rate drops as the viscosity rises. However, application technology constraints often greatly reduce the latitude for this approach.

A second, more general option is to selectively impart a gel-like structure upon the suspension by adding suitable additives. This means that the dispersion behaves like a gel at rest but has relatively low viscosity when it flows due to external forces imposed (stirring, pumping, etc.). It is thus possible to prevent or at least greatly reduce the undesired phase separation of defoamer dispersions by adding an AEROSIL® product.

The effect of the AEROSIL® product is based on the formation of a three-dimensional physical network with viscoelastic properties based on hydrogen bonds. Rheologically speaking, a yield point is formed. It is possible to make a rough estimate of the amount of AEROSIL® product needed to stabilize the dispersion against sedimentation, provided that the size of the settling particles, their density ρ, and the yield point τ_y of the dispersion can be measured. The minimum yield point that is needed to prevent settling from happening is then given by the theoretical equation:

$$\tau_y = \frac{a}{3} \cdot \Delta\rho \cdot g,$$

where a is the particle radius, $\Delta\rho$ is the density difference between the particles and the dispersion medium, and g is the gravitational acceleration. The rheologically determined yield point must consequently exceed this value for no sedimentation to occur. This assumes that the formulation is resistant to certain influences (vibrations, shaking) that might occur during handling and storage.

To test the effectiveness of the AEROSIL® grades, disperse fumed silica together with the hydrophobic defoamer silica in the oil or defoamer formulation of interest. Then pour the dispersion into a (100 ml) graduated cylinder while it is still warm and place it in a vibrationless location. Measure the sedimentation volume at regular intervals and define the storage stability on the basis of these amounts (**Figure 13**).

Figure 13 Settling behavior of 5 % SIPERNAT® D 10
left: With 0.5 % AEROSIL® R 974
right: Without AEROSIL® R 974

Accelerating the test (e.g., applying centrifugal forces) is not recommended, because the shearing or centrifugal forces would destroy the three-dimensional network and could falsify the test result. Due to the large number of defoamer formulations and possible (interfacially active) additives in defoamers, it is difficult to draw general conclusions about which AEROSIL® grade is particularly appropriate. **AEROSIL® R 972** and **AEROSIL® R 974** often prove effective, but they do not produce the best results in all formulations. See also [22].

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[22] Technical Information 1381: "Improving sedimentation stability of SIPERNAT® D 10 in mineral oil based defoamer formulations"
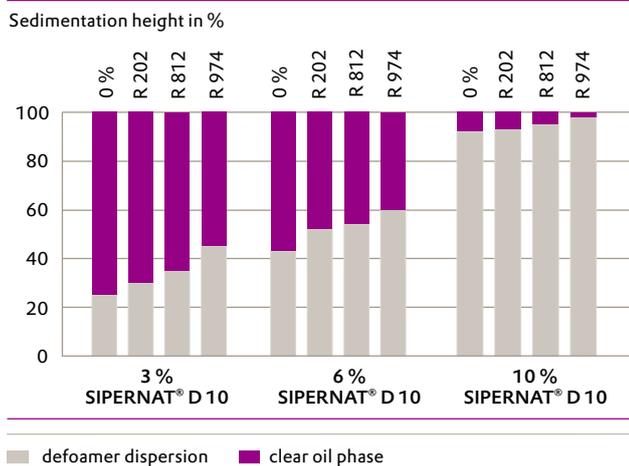
Figure 14 Storage stability: test period 6 months; 3, 6 and 10 % SIPERNAT® D 10 mineral oil dispersions with 0.5 % AEROSIL® products

Figure 15 Storage stability: test period 6 months; 5 % SIPERNAT® D 10 in mineral oil and silicone oil dispersions with 0.5 % AEROSIL® product added

As **Figure 14** demonstrates, that higher solids contents (e.g., a combination of SIPERNAT® and AEROSIL® grades) appear advantageous with respect to sedimentation stability. A dosage of at least 10–15 % AEROSIL® product in relation to the defoamer silica should be used for stabilization. However, if the dosage of SIPERNAT® is very small (e.g., only 3 %), then a dosage of 30 % AEROSIL® product or more in proportion to the silica (i.e., an AEROSIL® product percentage of at least 0.9 % in our example) may be needed. Therefore, an increase in the fraction of SIPERNAT® is also useful from an economic point of view, because it also improves the defoaming effect in addition to increasing sedimentation stability.
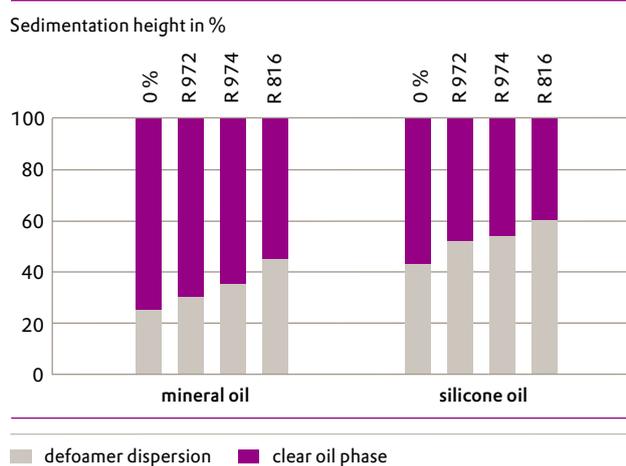
Figure 15 demonstrates that the same AEROSIL® grade has a good, but different stabilizing effect in two different oils. AEROSIL® R 974 and AEROSIL® R 816 exhibit the best results, AEROSIL® R 974 in a mineral oil suspension and AEROSIL® R 816 in a silicone oil suspension, respectively, each consisting of 1 % AEROSIL® product related to total formulation and 5 % SIPERNAT®. It must be kept in mind, however that, in addition to the hydrophobic liquid, all other additives of the defoamer, such as emulsifiers, may also affect the stabilization capability of the AEROSIL® product. For all defoamer components, besides the components themselves, the way they are processed and order they are added also make a difference. Our application technology laboratory also runs tests to determine which AEROSIL® grade shows the best anti-settling effect in the customer's defoamer formulations.

AEROSIL® products recommended for the storage-stabilization of defoamers:

AEROSIL® R 972 is hydrophobic and is very suitable for improving the sedimentation stability of defoamer dispersions.

AEROSIL® R 974 is hydrophobic and can be used like AEROSIL® R 972. It has a larger surface and often produces a higher thickening effect.

AEROSIL® R 816 is surface treated, however water-wettable, and was specially developed as a rheological agent for water-based varnishes. It is also suitable for stabilizing sedimentation in defoamer dispersions.

AEROSIL® 200 is hydrophilic and consequently water-wettable. It is used as a rheological additive and for improving the flowability of powders. AEROSIL® 200 is also suitable for stabilizing hydrophobic defoamer dispersions.

AEROSIL® 90 is a hydrohpilic fumed silica with specific surface of 90 m^2/g. It is used as a rheological additive and well suited for stabilizing hydrophobic defoamer dispersions.

AEROSIL® 130 is a hydrohpilic fumed silica with specific surface of 130 m^2/g. It is used as a rheological additive and suited for stabilizing hydrophobic defoamer dispersions.

AEROSIL® 150 is hydrophilic and consequently water-wettable. It is used as a rheological additive and for improving the flowability of powders. AEROSIL® 150 is also suitable for stabilizing hydrophobic defoamer dispersions.

The anti-settling properties of AEROSIL® products are governed by

- the balance of hydrophilic and hydrophobic surface fractions and the consequent capability to form physical networks,
- the particle size,
- the structure.

6 Characteristic physico-chemical data*

6.1 Recommended SIPERNAT® grades

Test methods	Unit	D 10	D 13	D 17	383 DS	35	320 DS	22	2200	50	22 S	33	50 S	120	320	360	820 A**
Behaviour towards water		hydrophobic			hydrophilic												
Specific surface area (N2) Multipoint *following ISO 9277*	m²/g	–	–	–	175	170	180	190	190	500	190	185	500	130	180	55	≤105
Particle size. d_{50} Laser diffraction *following ISO 13320*	µm	6.5	10.5	10.0	7.5	9.0	7.5	120	320	50	13.5	≤90	18	–	–	18.5	7.0
Loss on drying *(2 h at 105 °C) following ISO 787-2*	wt. %	≤4.0	≤4.0	≤6.0	≤6.0	≤7.0	≤6.0	≤7.0	≤7.0	≤7.0	≤7.0	≤6.5	≤7.0	≤6.0	≤7.0	≤7.0	≤7.0
pH value. *5 % in water following ISO 787-9*		–	–	–	8.3	8.6	6.2	6.5	6.0	6.0	6.5	7.0	6.0	6.9	6.2	9.0	10.1
DOA absorption[1,4]	ml/100g	–	–	–	–	245	210	235	225	295	240	≥260	280	200	195	190	155
pH value. *5 % in water/methanol =1:1 following ISO 787-9*		10.3	10.0	8.0	–	–	–	–	–	–	–	–	–	–	–	–	–
Wettability by methanol *internal method*	wt. %	≥56	≥58	≥52	–	–	–	–	–	–	–	–	–	–	–	–	–
Carbon content elemental analyser LECO *following ISO 3262-19*	wt. %	3.0	3.3	1.7	–	–	–	–	–	–	–	–	–	–	–	–	–
Sieve residue 45 µm Spray *following ISO 3262-19*	wt. %	≤400	≤600	–	≤300	≤0.1	≤300	–	–	–	≤1.5		≤5.0	–	–	–	≤0.2
Sieve residue 63 µm Alpine *following ISO 8130-1*	wt. %	–	–	≤1.0	–	–	–	≥75	–	≥15	–	≥72	–	≤8.0	≤10	≤10	–
Tamped density not sieved *Following ISO 787-11*	g/L	80	120	150	90	75	90	260	250	175	90	215	105	180	160	180	215
Loss on ignition[2] **2 h at 1000 °C** *following ISO 3262-1*	wt. %	≤8.0	≤8.0	≤6.0	≤6.0	≤6.0	≤6.0	≤6.0	≤6.0	≤6.5	≤6.0	≤6.0	≤6.5	≤5.5	≤6.0	≤6.0	≤12.5
SiO_2 content[3] *following ISO 3262-19*	wt. %	≥97	≥97	≥97	≥97	≥97	≥97	≥97	≥97	≥97	≥97	≥98	≥97	≥97	≥97	≥97	≥77
Na content[3] *internal method*	wt. %	≤1.2	≤1.2	≤1.2	≤1.5	≤1.4	≤1.0	≤1.0	≤0.80	≤0.6	≤1.0	≤0.6	≤0.6	≤1.0	≤1.0	≤1.0	4.5
Fe content[3] *internal method*	wt. %	≤400	≤400	≤400	≤400	≤400	≤400	≤400	≤400	≤400	≤400	≤200	≤400	≤400	≤400	≤400	≤400
Sulfate content[1] *internal method*	wt. %	≤1.0	≤1.5	≤1.0	≤1.8	≤1.5	≤1.5	≤1.5	≤1.0	≤1.0	≤1.5	≤1.2	≤1.5	≤1.0	≤1.5	≤0.7	≤1.0

[1]   based on original substance
[2]   based on dry substance (2 h/105 °C)
[3]   based on ignited substance (2 h/1000 °C)
[4]   internal method
*   The given data are typical values. Specifications on request
**   Al content 6,0 % (internal method)

The given physico-chemical data are typical values.
All values apply at the time of leaving the delivering works.
Specifications on request.

6.2 Recommended AEROSIL® grades

Test methods	Unit	AEROSIL®													
		R 972	R 974	R 816	R 202	R 812	R 812 S	R 104	R 106	R 8200	90	130	150	200	380
Behaviour towards water		hydrophobic									hydrophilic				
Specific surface area (BET) *Multipoint*	m²/g	90-130	150-190	170-210	80-120	230-290	195-245	125-175	220-280	135-185	75-110	105-155	135-165	175-225	350-410
Loss on Drying *2 h at 105 °C following ISO 787-2*	wt. %	≤0.5	≤0.5	≤1.0	≤0.5	≤0.5	≤0.5	≤1.5	≤0.5	≤0.5	≤1.0	≤1.5	≤1.5	≤1.5	≤2.0
pH value** **in 4% dispersion** *following ISO 787-9*		3.6-5.5	3.7-4.7	4.0-5.5	4.0-6.0	5.5-8.0	5.5-9.0	≥4.0	≥3.7	≥5.0	3.7-4.7	3.7-4.5	3.7-4.5	3.7-4.5	3.7-4.5
C content	wt. %	0.6-1.2	0.7-1.3	0.9-1.8	3.5-5.0	2.0-3.0	–	1.0-2.0	1.5-3.0	2.0-4.0	–	–	–	–	–
Tamped density *ex plant*	g/L	approx. 50	approx. 50	approx. 60	approx. 60	approx. 60	approx. 60	approx. 50	approx. 50	approx. 140	approx. 80	approx. 50	approx. 50	approx. 50	approx. 50
SiO₂ content *based on ignited material*	wt. %	≥99.8	≥99.8	≥99.8	≥99.8	≥99.8	≥99.8	≥99.8	≥99.8	≥99.8	≥99.8	≥99.8	≥99.8	≥99.8	≥99.8

* The given data are typical values. Specifications on request
** Narrower pH possible, depending on region

The given physico-chemical data are typical values.
All values apply at the time of leaving the delivering works.
Specifications on request.

7 References

[1] P. R. Garrett, Defoaming, Theory and Industrial Application (1993), Surfactant Science Series Vol. 45

[2] Benjamins J., Cagna A. & Lucassen-Reynders E. H., Colloids and Surfaces A: Physicochemical and Engineering Aspects (1996) 114, 245-254. Viscoelastic properties of triacylgly cerol/water interfaces covered by proteins.

[3] P. R. Garrett, Defoaming, Theory and Industrial Applications (1993), Surfactant Science Series Vol. 45

[4] Lichtman, I. A., Sinka, J.V., Evans, D. W., de Papel Boletin, 15, 26 (1975)

[5] I. C. Callaghan in P. R. Garrett, Defoaming, Theory and Industrial Application (1993), Surfactant Science Series Vol. 45, 119-151

[6] Garrett, P. R., Davis, J., Rendall, H. M. Colloids Surf. A 85, 159 (1994)

[7] Wang, G., Pelton, R., Shawafaty, N., Heng, Y. M. Langmuir 1999, 15, 2202-2208

[8] N. J. Jarvis , J. Phys. Chem. 70, 3027 (1966)

[9] Randal M. Hill, Kenneth C. Fey Silicone Surfactants in Surfactant Science Series Vol. 86, 159-181, (1999)

[10] K. Koczo, J. K. Koczone, D. T. Wasan, J. Colloid Interface Sci. 166, 225, (1994)

[11] Randal M. Hill, Kenneth C. Fey Silicone Surfactants in Surfactant Science Series Vol. 86, 159-181, (1999)

[12] K. Kozco, J. K. Koczone, D. T. Wasan, J. Coll.Interface Sci., 166, 225-238, (1994)

[13] N. D. Denkow, P. Cooper, Langmuir "Mechanisms of Action of Mixed Solid-Liquid Antifoams". 1. Dynamics of Film Rupture", 15, 8514, (1999)

[14] P. R.Garrett, Langmuir, 11, (1995) 3576

[15] V. Bergeron, P. Copper, C. Fischer, J. Giermanska-Kahn, D. Langevin, A. Pouchelon, Colloids Surfaces A: Physico-chemical and Engineering Aspects 122 (1997), 103-120

[16] Brochure "Specialty silica", Evonik company publication

[17] Technical Overview: AEROSIL® – Fumed Silica, Evonik company publication

[18] S. Ross u. Gary Nishioka, Experimental Research on Silicon Antifoams, in "Emulsions, Latices and Dispersions", P. Becher and M.N. Yudenfreund (Editors), Marcel Dekker, 1978

[19] Technical Information 1382, Comparison of SIPERNAT® D 10 with *in-situ* hydrophobized fumed silica, Evonik company publication

[20] P. Becher, Editor, Encyclopaedia of Emulsion Technology, Marcel Dekker, New York 1996

[21] Technical Information 1360: " SIPERNAT® and AEROSIL®–an essential in industrial powder technology", Evonik company publication

[22] Technical Information 1381: "AEROSIL® and SIPERNAT® – Efficient booster for defoamer in paints and coatings", Evonik company publication

8 Glossary

Agglomerates:
According to DIN 53206, loose clusters of primary particles and/or aggregates that can be separated by dispersion.

Aggregates:
Joined particles whose the surfaces are attached to each other. Aggregates usually cannot be separated by a dispersion process.

Coalescence:
The merging of droplets, an example being an emulsion coalescing into larger droplets.

Contact angle:
The contact angle between a solid and a liquid is a measure of the ability of the liquid to wet the solid. In general, the wetting tendency rises as the surface tension declines.

Dispersing agents:
Term for interfacially active substances that greatly facilitate the distribution of particles in a continuous (liquid) phase. The effect of these substances is based on improving the wetting by reducing the surface tension.

Dispersion:
Term for a multiphase system in which at least one continuous phase, the dispersing agent, and a finely distributed phase, the dispersed phase are present.

Electrostatic interaction:
Electrical interaction, which is caused by charged groups and is governed by Coulomb's laws.

Emulsifiers:
Term for interfacially active substances which are capable of making emulsions out of insoluble liquids, such as an emulsion of oil and water.

Hydrophobicity:
Hydrophobic means water-repellent, or not wettable by water. But all hydrophobic silica are wettable by methanol.

Hydrophilic:
Wettable by water.

In-situ **hydrophobization:**
Chemical reaction between surface silanol groups of the silica and the hydrophobization agent.

Interfacially active:
Feature of surfactants that tend to enrich in the interface of multiphase systems, thereby reducing the surface tension.

Kinetic conditions:
Describe the boundary conditions for the rate of a process. The rate of a process is generally determined by its driving force and the resistance against the process.

Metastable:
Term for an apparent state of equilibrium.

Ostwald ripening:
Phenomenon occuring in emulsions and dispersions in which large particles grow at the expense of small particles. Minimization of surface energy is the driving force behind this process.

Plateau border:
(named after the Belgian physicist J. A. Plateau, 1801-1883). The principle behind the Plateau border can be understood using monodisperse polyhedral foams as an example. A Plateau border is formed when three foam films meet at an angle of approximately 120°. A concave triangle represents the cross section of such a Plateau border. Four such liquids containing channels will meet in a tetrahedral angle.

Rheology:
Field of physics where the flow and deformation behavior of materials is studied.

Silanol groups:
Hydroxyl groups on the surface of silica: $\equiv SiOH$.

Silicone oils:
Polydimethyl siloxanes and other organosilicone compounds.

Spreading:
Term for the property of an insoluble solid or liquid substance to expand on a surface (e.g., in a monomolecular layer). The spreading ability of defoamers is particularly high.

Steric stabilization:
Term for the stabilizing interaction of bulky, mostly polymer groups on the surface of disperse materials.

Surface elasticity:
It is possible to assign an elasticity to the interfacial phase, in analogy to the viscoelastic properties of the volume phase of substances.

Suspensions:
Term for dispersions that contain finely dispersed solids in a liquid continuous phase.

Thermodynamics:
Field of physics in which the behavior of physical and chemical systems is studied when thermal energy is added or removed or the temperature changes. Chemical thermodynamics is the study of the direction, but not the rate of processes.

Viscoelasticity:
Term from rheology. Term for the behavior of solids and liquids that feature viscous and elastic components in their properties (material functions).

Yield point:
Term from rheology. Minimum shear stress that needs to be imposed on a material so that it will flow, thus deforming it irreversibly.

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