

**AEROSIL® and SIPERNAT® –
Efficient booster for defoamer
in paints and coatings**

Technical Information 1381

1 Summary

Hydrophobic silica products are well known as efficient booster for defoamer formulations which are used in a variety of industries and applications. This Technical Brochure describes how Evonik's AEROSIL® fumed silica and SIPERNAT® specialty silica products effectively enhance the performance of polyether-siloxane based defoamer formulations in three different latex binder systems commonly used in waterborne paints and coatings.

Our results show that all hydrophobic AEROSIL®-grades were compatible with and effective in the polyurethane binder system. However, in the acrylate-methacrylate and polyvinylacetate binder systems strongly hydrophobic silica grades were superior. In all model formulations AEROSIL® R 202, AEROSIL® R 812 S, AEROSIL® R 8200 and AEROSIL® R 812 S are therefore particularly recommended.

Furthermore, in thick layered architectural coatings hydrophobic specialty silica SIPERNAT® D 10 and SIPERNAT® D 17 can be used with good results. For help in choosing the best hydrophobic silica for your system, please contact our Evonik application specialists.

2 General

Today's industrial manufacturing and processing of liquid paints and coatings are impossible to imagine without the help of mechanical and/or chemical defoamers. This is true for application of coatings with brush, roller or more sophisticated application methods e.g. spray and curtain coating. Environmental considerations have led to the replacement of solvent based systems by waterborne coating systems. The increased amount of special surfactants in waterborne coatings has induced the need for even more efficient defoamer, antifoam, and/or deaerator formulations.

2.1 The function of defoamers, antifoams, and deaerators

Defoamers destroy macro-foam on the surface and combat large air-entrapments, i. e. by initiating the collapsing of foam lamella. Antifoams are substances which "inhibit" the formation of foam from the very beginning. Deaerators are used to remove finely dispersed air from a paint film by quick coalescence of the gas bubbles.

Since the exact distinction between defoamers, antifoams and deaerators is not always possible, the expression "defoamer" used in this brochure is not meant to be exclusive, but rather includes antifoams and deaerators as well.

There is still scientific discussion on the precise mode of action of defoamers in waterborne coatings. However, it is possible to define some prerequisites for an effective defoamer formulation which are described in more detail by P. R. Garrett¹.

The most important are:

- Low surface tension of the defoamer carrier oil
- Insolubility of the defoamer oil in the liquid to be defoamed
- Positive entering coefficient into the water/air interface
- Positive spreading coefficient at the water/air surface
- Dewetting/bridging mechanism at the water/air interface

2.2 Composition of a defoamer

Liquid defoamer formulations are rather complex. Main component is a carrier oil, for example, mineral oil, silicone oil, or polyethersiloxane, which is insoluble in the final paint or coating. Emulsifiers help to adjust the compatibility of the carrier oil with the binder system. Additional components could include antissettling agents and rheology modifiers. Depending on the application, defoamer formulations can be further diluted with solvents or with aqueous media to form emulsions. These dilutions and emulsions eventually require chemicals for stabilization and rheological adjustment of the final defoamer formulation.

3 Design of experiments

To boost the performance of defoamer formulations, hydrophobic particles are used, such as metal soaps (Al-, Mg-, and Ca-stearate), waxes, polymeric substances (e. g. polyamide, polypropylene, polyurethanes) or hydrophobic silica. Since hydrophobic silica is temperature stable, can be milled to a specific particle size and consists of a fractal structure allowing for a variety of contact angles at the air/water interface, AEROSIL® fumed silica and SIPERNAT® specialty silica are particularly preferred boosters.

2.3 Role of hydrophobic silica

The role of hydrophobic silica for combating foam and entrained air is described in detail by N. D. Denkov². Two main factors should be mentioned here: The rapid collapse of macro-foam in the presence of hydrophobic silica due to a reduction of the activation energy (entering coefficient) required for the defoamer to enter the air/liquid interface. This is also known as the “pin-effect”. Secondly, a dewetting/bridging mechanism of the hydrophobic silica is described by P. R. Garret¹.

This technical brochure focuses on hydrophobic silica, its sedimentation stability in a defoamer model formulation, performance as defoamer, antifoam, and/or deaerator, and compatibility with different binder systems.

3.1 Why design of experiments?

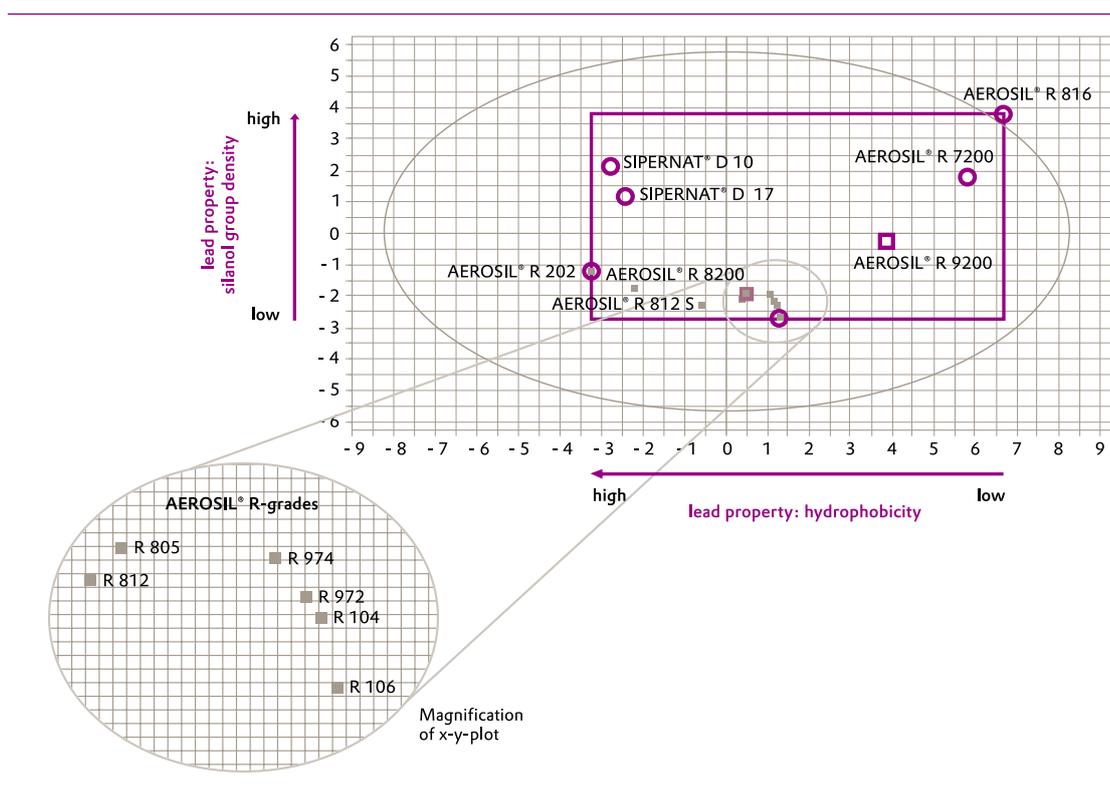
Comprehensive evaluation of the entire line-up of hydrophobic Evonik silica products in different defoamer formulations and binder systems would have resulted in an enormous laboratory program. Therefore, a design of experiment study was carried out based on the physico-chemical properties of selected commercially available Evonik hydrophobic silica grades. The experiments were planned, recorded and calculated by “Design-Expert®”- software.

3.2 Physico-chemical properties of selected silica products

Evonik offers a broad range of surface treated silica products, which are either based on SIPERNAT® precipitated silica or AEROSIL® fumed silica. Based on the properties of the hydrophilic starting material and different surface treatment agents applied in the surface treatment process, these products vary in their physico-chemical properties, for example, specific surface area (BET), surface silanol group density, methanol-wettability and C-content⁴.

The two-dimensional diagram shown in Figure 1 was created based on these physico-chemical data. While positioning of a silica type on the x- axis is predominantly influenced by its hydrophobicity (lead property 1), its positioning on the y-axis is mainly determined by its surface silanol group density (lead property 2). Throughout this technical brochure, the silica grades investigated have the same relative position within the square.

Figure 1
Graphic depiction of the physico-chemical properties of the evaluated hydrophobic AEROSIL®- and SIPERNAT®- grades



4 Sedimentation stability of defoamer formulations

To prepare the model defoamer formulations, 2 weight-% each of the silica products listed above were incorporated in a mixture consisting of polyethersiloxane (38 weight-%, TEGO 5861, Evonik Goldschmidt GmbH and mineral oil (60 weight-%, ONDINA® 913, Shell). For incorporation of the silica we used a rotor-stator system Ultra-Turrax® at 10.000 rpm for 1 minute.

The quality of dispersion and the sedimentation stability of the defoamer formulations obtained was recorded at intervals of 7, and 31 days and 6 months by means of a) microscopic evaluation and /or b) rheological measurements (see **Figure 2** and **4**) and subsequently visual inspection.



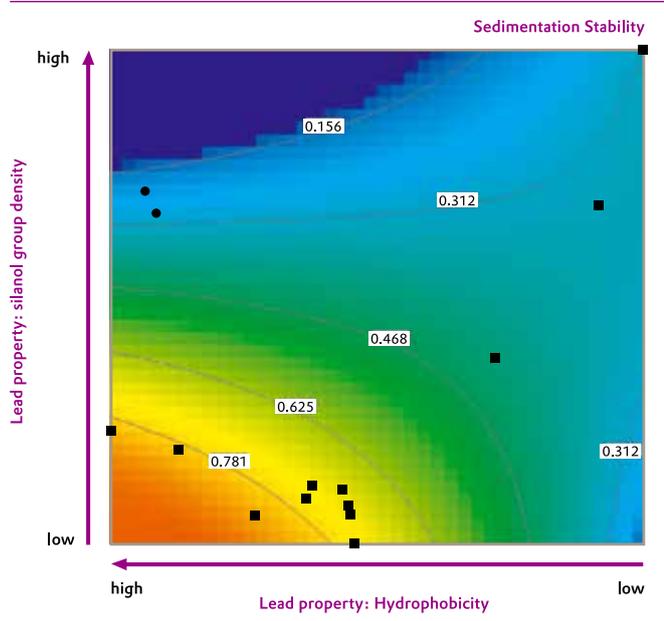
Figure 2

Methods used for evaluation of the dispersion and sedimentation stability of the model defoamer formulation

- a Microscopy for checking the quality of the dispersion
- b Rheology for viscosity measurements

Figure 3

Sedimentation stability of hydrophobic AEROSIL® and SIPERNAT® containing model defoamer formulations. The higher the number of an isoline, the more stable the model defoamer formulation is expected to be against settling. The relative position of the black dots in this and the following figures represent the same silica grades as shown in Figure 1.



On the other hand, the rather hydrophobic precipitated silica products SIPERNAT® D 10 and SIPERNAT® D 17, the structure modified fumed silica grades AEROSIL® R 9200 and AEROSIL® R 7200, and the slightly hydrophilic AEROSIL® R 816 are located in the upper (green and blue colored) part of the diagram in Figure 3. They are therefore not expected to have sufficient sedimentation stability in the tested model defoamer formulation. Combinations of precipitated and fumed silica may improve the stability of the formulation considerably; however, this is beyond the scope of this brochure and will be explored in the future.

Every black dot represents the same silica grade as shown in Figure 1. The higher the number of an isoline, the more stable the respective model defoamer formulation is expected to be against settling. For example, a silica grade positioned in the red or yellow area means that the model defoamer it is based on should have very good or good sedimentation stability. The following hydrophobic AEROSIL® fumed silica products were actually found to have good or very good sedimentation stability:

AEROSIL® R 202, AEROSIL® R 8200, AEROSIL® R 812 S, AEROSIL® R 812, AEROSIL® R 972, AEROSIL® R 104, AEROSIL® R 974, AEROSIL® R 106 and AEROSIL® R 805.

5 Performance / compatibility of the model defoamer formulation in various latex systems as a function of the silica grade

It is well known that defoamer formulations behave differently in distinct binder systems. Therefore, the following three latex binder systems were evaluated as model systems:

- 1 Acrylate/methacrylate – Mowilith® 7717, Celanese
- 2 Polyurethane-dispersion – APU® 1035, Alberdingk Boley,
- 3 Polyvinylacetate – Airflex® CEF 10, (now) Wacker.

In order to estimate performance and compatibility of the various model defoamer formulations based on different silica grades, 0.25 weight-% of a defoamer formulation was added to each one of the latex binder systems. The mixture was stirred with a dissolver blade at 1000 rpm for one minute at room temperature in order to obtain a homogeneous dispersion. Subsequently, the mixture was agitated with the same dissolver blade at 3000 rpm for one minute in order to introduce air under defined conditions (aeration). Directly afterwards, the mixture was poured into a graduated cylinder and the resulting density was determined by pycnometric measurement (see Figure 4 a and b). Due to the agitation with the dissolver blade at high speed, the density of the latex dispersion was reduced by incorporating of air, increasing the volume of the sample. The density of this sample was then compared to samples treated without agitation and samples agitated the same way but without defoamer. The relative air content was calculated to get an indication about the effectiveness of the defoamer applied and, more importantly in this study, the silica it contains.

Directly after the pycnometric measurement, the respective latex/defoamer mixture was evaluated in a flow-out test on a polyethylene (PE) covered slope (see Figure 5 a, b, and c). Density, macrofoam, microfoam, sagging, haze, pinholes and cratering were assessed for all latex/defoamer mixtures before and after drying to rank their compatibility with the hydrophobic silica used.

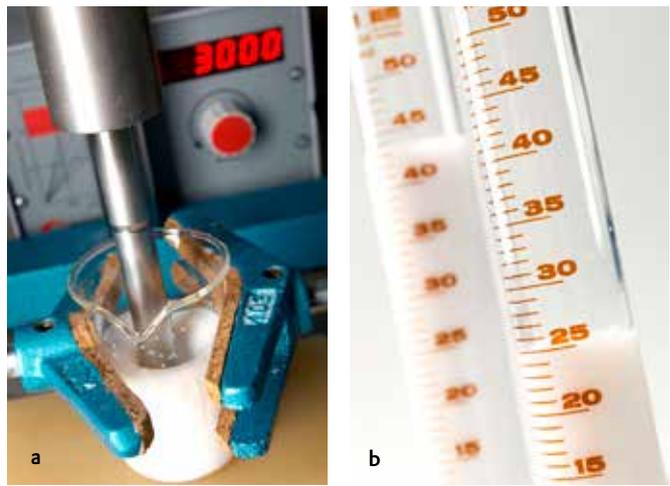


Figure 4
Methods used for air introduction and measurement of the binder system:
a Introduction of air into the latex/defoamer mixture
b Determination of the defoamer activity: difference in volume after aeration (same weight of latex mixed with and without defoamer)

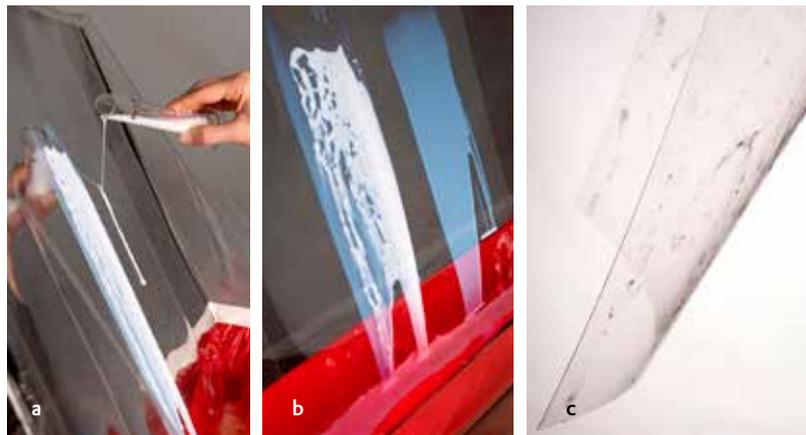


Figure 5
Testing of the deaeration properties and compatibility after application of the latex/defoamer sample onto a PE sheet
a Flow out test
b Visual inspection of the latex/defoamer mixture film before drying
c Visual inspection of the latex/defoamer mixture film after drying

Figure 6

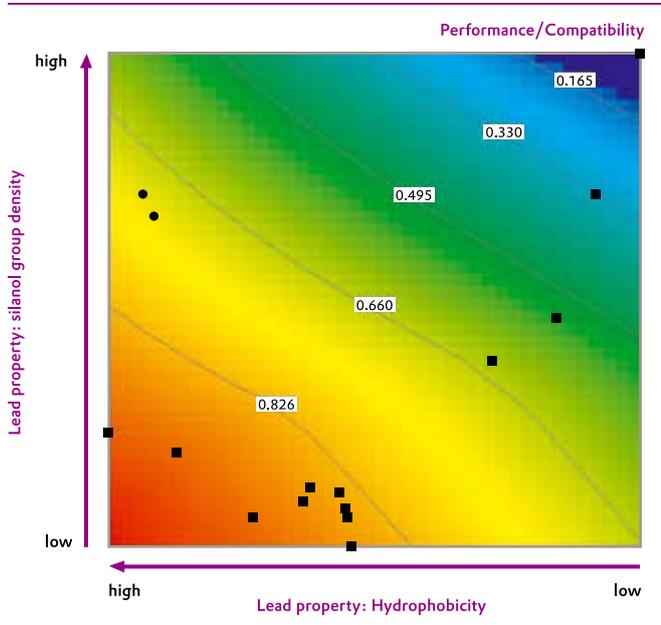
Performance/compatibility of hydrophobic AEROSIL® and SIPERNAT® containing defoamer formulations in

a acrylate/methacrylate binder system Mowilith® 7717

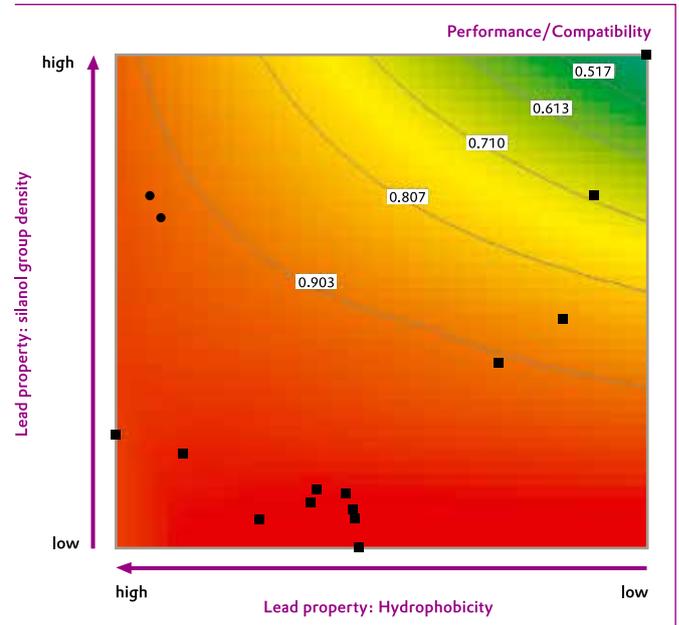
b polyurethane binder system APU®1035.

c polyvinylacetate binder system Airflex® CEF 10.

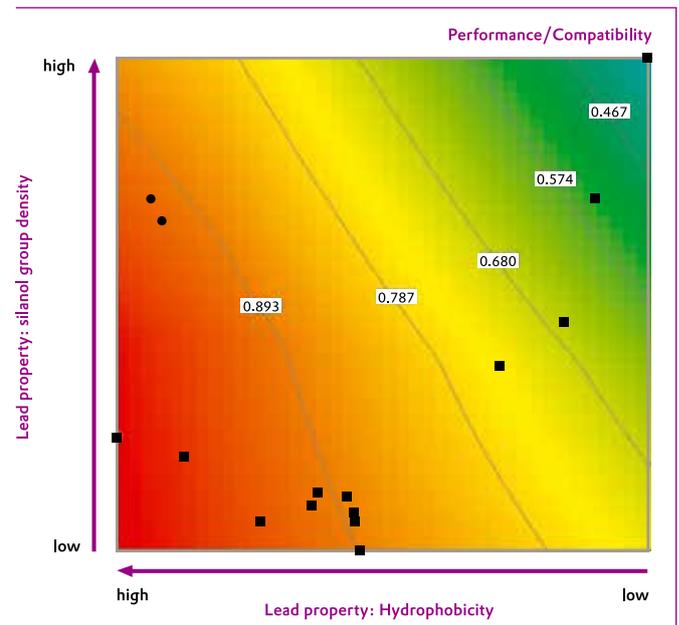
The higher the number of an isoline in the diagrams below, the better is the expected performance/compatibility of the respective silica in the model defoamer formulation. For example, a silica (black dots, as in Figure 1) in the yellow or red area means that the performance and/or compatibility of the defoamer formulation containing the respective silica is expected to be good or even very good.



a Acrylate/methacrylate binder system Mowilith® 7717



b Polyurethane binder system APU®1035



c Polyvinylacetate binder system Airflex® CEF 10

Surprisingly, as was the case with the stability of the silica in the defoamer formulation itself (Figure 3), it was found, that in the model latex systems applied (Figures 6 a–c) the silica in the lower left corner of the diagram had better performance/compatibility behavior than the other silica. Therefore, the ranking of the silica resulted in expecting a number of good or even very good AEROSIL®- types with rather high hydrophobicity and a rather low silanol group density on the surface:

**AEROSIL® R 972, AEROSIL® R 104, AEROSIL® R 974,
AEROSIL® R 106, AEROSIL® R 805, AEROSIL® R 812,
AEROSIL® R 812 S, AEROSIL® R 8200, and AEROSIL® R 202.**

It should be emphasized again, that the ranking of the silica may change considerably with the model defoamer formulation and the model binder systems applied. Therefore our results can only give a first indication for comparable systems and are not meant to predict stability and performance/compatibility data of other defoamer formulations or even other latex systems.

6 Literature

- 1 P. R. Garrett, *Silicone surfactants in Surfactant Science, Series Vol. 45*, Marcel Dekker (1993)
- 2 N. D. Denkov, *Langmuir* Vol. 20, 9463-9505 (2004)
- 3 Evonik Industries AG, Technical Information 1313
–Specialty Silica for Defoamer.
- 4 Evonik Industries AG, AEROSIL® Product Overview

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