



Improving Sedimentation Stability of SIPERNAT® D 10 in Mineral Oil based Defoamer Formulations

Technical Information 1391

1. Introduction and Summary

SIPERNAT® D 10 is well known in the industry as excellent booster silica for liquid and powder defoamer formulations (Lit. 1). During long term storage of liquid defoamer containing hydrophobic booster silica, however, sedimentation may occur. This is especially the case when carrier oils of low viscosity like mineral oil are used.

AEROSIL® fumed silica is often used to increase the viscosity and thixotropy of liquid formulations such as epoxy resins and special polyurethane systems (Lit. 2). Therefore, we systematically studied the effect of selected AEROSIL® fumed silica grades on the sedimentation stability of different defoamer formulations containing SIPERNAT® D 10 as booster silica. Within the test program, we varied the type of mineral oil and surfactant and evaluated the influence of small amounts of water. The test program was set up and interpreted according to a systematic design of experiments (DOE).

From our experimental design, we were able to draw the following conclusions for the development of long term stable defoamer formulations:

- SIPERNAT® D 10 alone is more stable against sedimentation in higher viscosity naphthenic oil than in lower viscosity white oil.

- Higher SIPERNAT® D 10 concentrations reduce the separation of the oil phase. Furthermore, the defoamer activity is significantly enhanced.
- Addition of AEROSIL® fumed silica generally elevates the sedimentation stability of SIPERNAT® D 10 containing defoamer formulations. Most common AEROSIL® grades can be used although hydrophobic and/or high surface area grades are usually the more effective anti-settling agents.
- Hydrophilic AEROSIL® grades provide an additional boosting effect and further enhance defoamer activity.
- The presence of surfactants and/or water can have a detrimental effect on the sedimentation stability of booster silica containing defoamer formulations.

Among the grades investigated, AEROSIL® 90, AEROSIL® 150, and AEROSIL® R 972 are particularly recommended. AEROSIL® 200, AEROSIL® 300, AEROSIL® R 974 and AEROSIL® R 812 – even though not investigated in this study – should always be considered as well since they are very powerful anti-settling and gelling agents.

2. Experimental Part

2.1 Design of Experiment (DOE)

Experimental designs were set up and evaluated with help of the design of experiment (DOE) program Modde 9 from Umetrics, Sweden. All results discussed in this study (linear and interaction terms between two variables) were statistically significant. A separate set of experiments were performed to investigate the influence of water and surfactants.

2.2 Experimental Details

2.2.1 Preparation of Samples

The following silica grades from Evonik Industries were used: SIPERNAT® D 10, AEROSIL® 50, AEROSIL® 90, AEROSIL® 150, AEROSIL® R 972 and AEROSIL® R 106.

Tabelle 1

Silica grades used in this investigation

Product Name	Silica type	Surface treatment	Behavior towards water	BET specific surface area (m ² /g)*	Carbon Content (wt.-%)*
SIPERNAT® D 10	precipitated	Polydimethyl-siloxane	hydrophobic	90	3.0
AEROSIL® 50	fumed	no surface treatment	hydrophilic	50	–
AEROSIL® 90	fumed	no surface treatment	hydrophilic	90	–
AEROSIL® 150	fumed	no surface treatment	hydrophilic	150	–
AEROSIL® R 972	Fumed	Dimethyl-dichlorosilane	hydrophobic	110	0.9
AEROSIL® R 106	Fumed	Octamethyl cyclotetra-siloxane	hydrophobic	250	2.3

* typical values

Naphthenic mineral oil (Shell Gravex® 917 with a kinetic viscosity at 20 °C of 31 mm²/s), white oil (Shell Ondina® 913 with a kinetic viscosity at 20 °C of 15 mm²/s) and a 1:1 (v/v) mixture of both oils (Lit 3.) were used as carrier oils.

It was observed that different ways of silica incorporation influence the sedimentation stability. Most importantly, introduction of air bubbles at high sheer must be avoided: The AEROSIL® grade selected for a specific experiment was first wetted in 100 ml of carrier oil and then dispersed with a laboratory rotor-stator ULTRA Turrax® T25 at 10,000 rpm for one minute. Subsequently, the sample was agitated in a Dispermat® CN 10 unit at 200 rpm under reduced pressure to remove air bubbles. SIPERNAT® D 10 was then added to the AEROSIL® / mineral oil mixture and deaerated for 5 minutes before dispersing it with the Dispermat® CN 10 unit at 2,500 rpm for 10 minutes followed by another deaeration under vacuum for 5 minutes.

For additional experiments to investigate the effect of water and/or surfactants, water (2% to 4% by weight) and/or surfactant (BASF, Lutensol® TO3, TO8, ON30 or ON80, 2% to 4% by weight) were dissolved in mineral

oil at 1,500 rpm with the Dispermat® CN 10, followed by 5 minutes of deaeration in vacuum without stirring before adding silica as described before.

Samples were divided for determination of sedimentation stability and defoamer activity and separately stored at room temperature for defined time intervals of up to 6 months.

2.2.2 Sedimentation Stability

Sedimentation stability of the defoamer samples was determined visually by measuring the clear mineral oil supernatant in 50 ml glass cylinders.

2.2.3 Defoamer Activity

Defoamer activity was measured with the semi-automatic Contifoam® equipment (Manufacturer: Raab, Austria) between one and three weeks after sample preparation. Knock-down values for the evaluation of initial (fast acting) defoamer activity and hold-out values for antifoam persistence were recorded.

3. Results

3.1 Mineral Oil Formulations without Surfactant

3.1.1 Sedimentation

3.1.1.1 Influence of SIPERNAT® D 10 concentration

The amount of SIPERNAT® D 10 itself plays a major role in the sedimentation stability of a mineral oil defoamer formulation: Increasing the concentration of SIPERNAT® D 10 from 2% to 6% by weight reduces the phase separation significantly (Figure 1). However, within the normal application range from 2 to 6 weight % of SIPERNAT® D 10, the hydrophobic booster silica by itself is not able to form a stable three-dimensional network necessary to achieve long term sedimentation stability. Especially low viscosity mineral oil formulations need gelling/anti-settling agents such as AEROSIL® fumed silica.

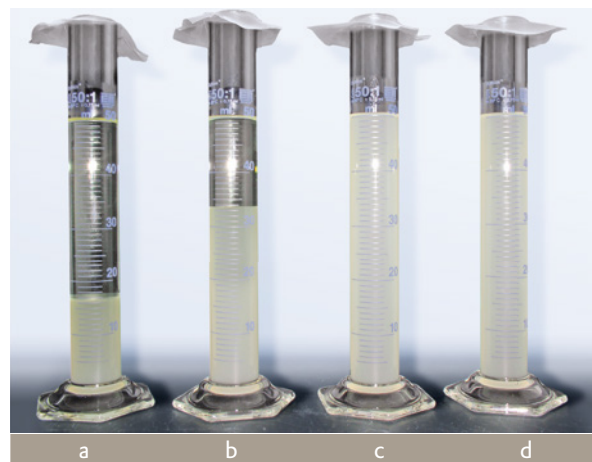


Figure 1

Sedimentation of SIPERNAT® D 10 in naphthenic oil (Shell Gravex® 917) after three months of storage at room temperature. Glass cylinders contain:

- a) 2% SIPERNAT® D 10,
- b) 4% SIPERNAT® D 10,
- c) 4% SIPERNAT® D 10, stabilized with 1.5% AEROSIL® R 972,
- d) 4% SIPERNAT® D 10, stabilized with 1.5% AEROSIL® R 106 (all % by weight).

Glass cylinders c) and d) do not show any clear oil supernatant

3.1.1.2 Type of Oil

The clear mineral oil supernatant – as seen in samples a) and b) in Figure 1 – was read from the glass cylinder scaling in milliliters to assess the sedimentation stability of a defoamer formulation. Smaller readings were therefore preferred and indicated better sedimentation stability. Samples c) and d) were perfectly stable towards sedimentation since no clear oil supernatant at all was formed during storage.

In Figure 2 a) and b) calculated values from the DOE are depicted in colored contour-plots. Further dimensions are visualized by showing a series of these plots, including the type of the respective AEROSIL® grade and the specific oil type. The coefficient of determination of the mathematical model is $R^2 = 0.8494$.

In general, the sedimentation stability of SIPERNAT® D 10 was better in the higher viscosity oil with higher polarity Shell Gravex® 917 than in the lower viscosity, less polar white oil Shell Ondina® 913 (compare to the contour plots in Figure 2 a) and b), top row to bottom row).

3.1.1.3 Type of AEROSIL® Fumed Silica

Five AEROSIL® fumed silica types with different surface areas and surface treatments were investigated. All grades resulted in an enhanced sedimentation stability of SIPERNAT® D 10. As can be seen from the comparison between the Figures 2 a) and 2 b) the hydrophobic types AEROSIL® R 972 and AEROSIL® R 106 were more efficient than the three hydrophilic grades AEROSIL® 50, AEROSIL® 90 and AEROSIL® 150.

3.1.1.4 Concentration of AEROSIL® Fumed Silica

The performance of all AEROSIL® grades was evaluated within the concentration range 0.5 – 1.5% by weight (x-axis of all contour plots in Figure 2). After seven days of storage, it was observed that in all cases the sedimentation stability of SIPERNAT® D 10 improved with increasing AEROSIL® concentration.

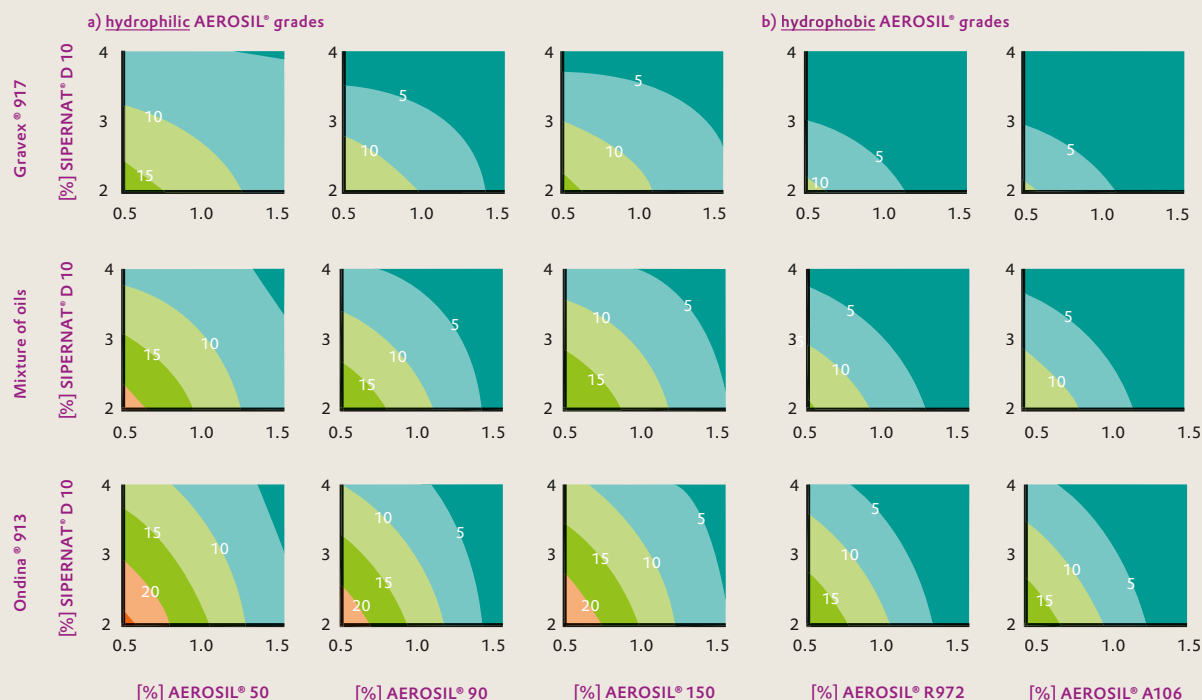


Figure 2 a) and b)

Contour plots illustrating the sedimentation stability of SIPERNAT® D 10 containing defoamer formulations without surfactant after 7 days of storage as a function of SIPERNAT® D 10 concentration (y-axis), AEROSIL® type, and AEROSIL® concentration (x-axis) in three different oils (top row to bottom row). Blue colors indicate areas of good sedimentation stability (supernatant readings 0–5 ml), while green colours shows insufficient and red colours poor sedimentation stability.

a) Hydrophilic AEROSIL® grades with increasing surface area: AEROSIL® 50 ($\sim 50 \text{ m}^2/\text{g}$), AEROSIL® 90 ($\sim 90 \text{ m}^2/\text{g}$), and AEROSIL® 150 ($\sim 150 \text{ m}^2/\text{g}$) from left to right

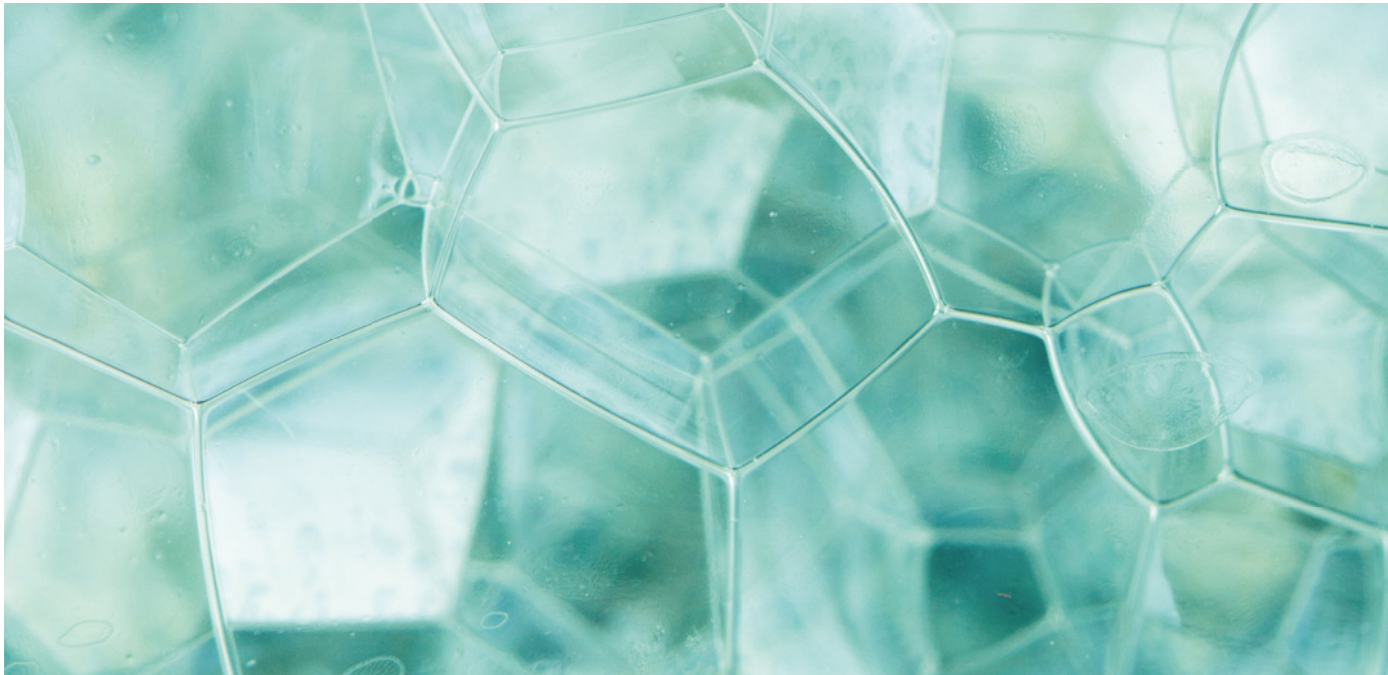
b) Hydrophobic AEROSIL® grades with different surface areas and surface treatments: AEROSIL® R 972 ($\sim 110 \text{ m}^2/\text{g}$, DMDS-treated, Lit. 2) and AEROSIL® R 106 ($\sim 270 \text{ m}^2/\text{g}$, octamethyl cyclo tetrasiloxane-treated, Lit. 2) from left to right.

3.1.2 Defoamer Activity

Defoamer activity was determined in a Contifoam equipment as foam knock-down and foam hold-out. Foam knock-down describes the fast destruction of foam. The resulting foam height immediately after addition of the defoamer was measured whereby high defoamer activity leads to foam heights of below 10 mm. The hold-out time in minutes is the persistency of the defoaming effect. The longer the hold-out time the more effective is a defoamer formulation.

From the results of individual experimental plans the following conclusions can be drawn (see figure 3a and 3b):

- Increasing SIPERNAT® D 10 content considerably improves the knock-down and hold-out of all defoamer formulations.
- Surprisingly, hydrophilic AEROSIL® provides an additional boosting effect and further enhances the defoamer activity while hydrophobic AEROSIL®-grades have little effect on the defoamer activity.
- Small amounts of water (< 3%) increase the knock-down defoamer activity, whereas higher amounts of water (> 3%) will decrease the knock-down activity (figure 3a).



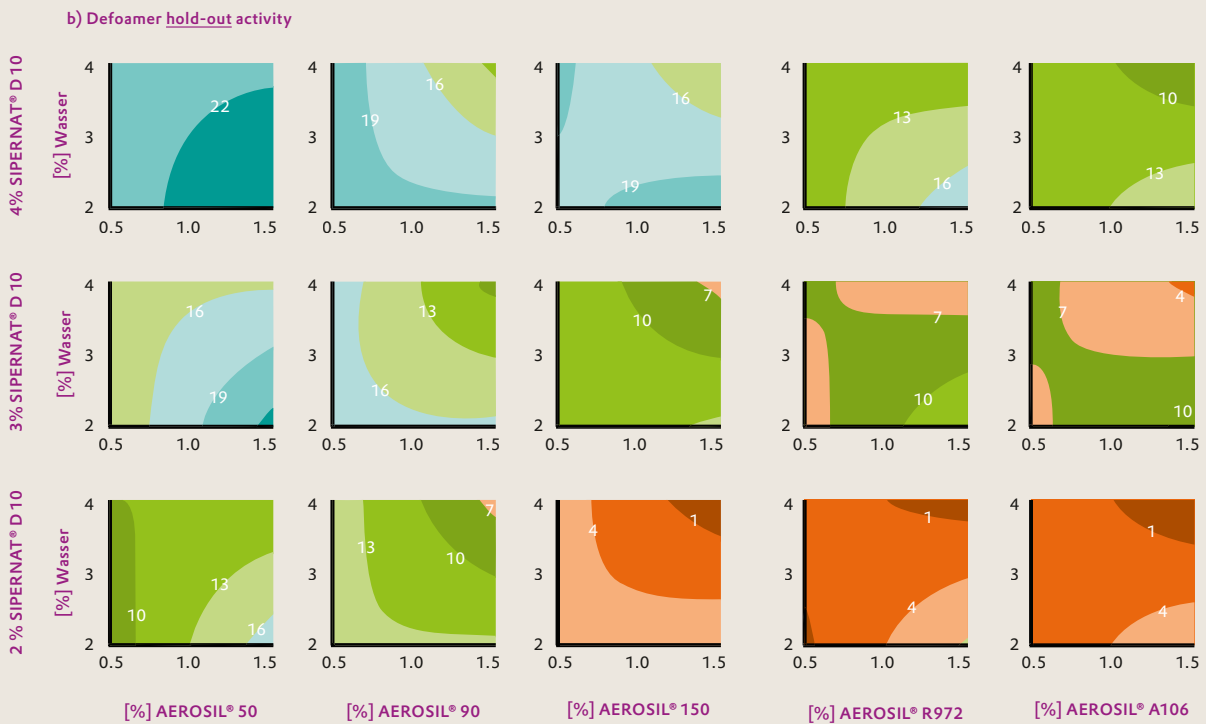
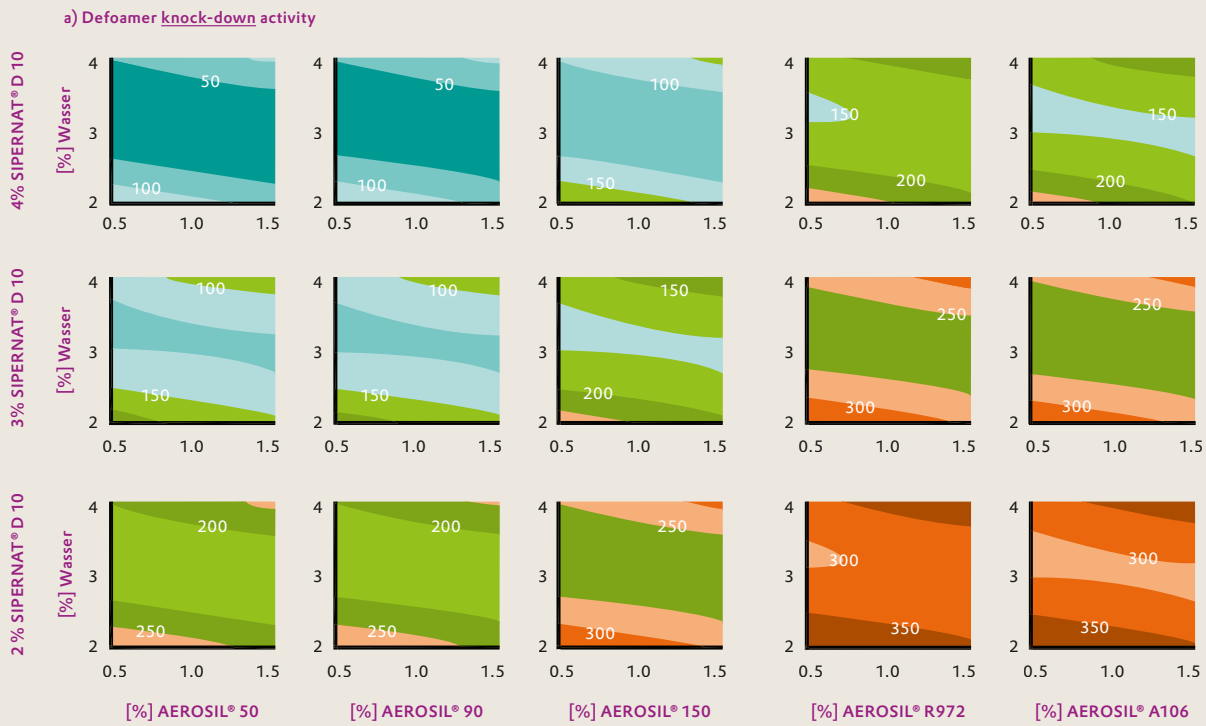


Figure 3 a) and b)

Contour plots illustrating the defoamer activity of SIPERNAT® D 10 containing defoamer formulations (without surfactant, after 7 days of storage) as a function of SIPERNAT® D 10 concentration, water content (y-axis), AEROSIL® type, and AEROSIL® concentration (x-axis) in Shell Ondina 913 oil. Blue represents areas of good defoamer activity, medium activity is shown in green, while low defoamer activity is depicted in red.

3.2 Formulations in White Oil Ondina® 913

Containing Surfactants

3.2.1 Sedimentation Stability

3.2.1.1 Surfactant

Surfactants are often added to defoamer formulations to increase their compatibility with the system to be defoamed. For this study, four different Lutensol® grades were selected with varying degrees of ethoxylation (between 3 and 8 EO) and oxoalcohol carbon-chain lengths (from C 10 and C 13) corresponding to HLB-values from 8 to 14 (Lit 4).

Interestingly, the specific type of surfactant was not critical at the low concentration of 2%. Surfactant concentrations above 2%, however, had a negative influence on the sedimentation stability of SIPERNAT® D 10. It can be speculated that the surfactant somehow "disrupts" the three-dimensional network formed by the AEROSIL® particles.

3.2.1.2 AEROSIL® fumed silica grades

Like in the defoamer formulations without surfactant, the hydrophobic AEROSIL® grades increased the sedimentation stability also in the presence of surfactants even

though a clear correlation between surface area of the AEROSIL® and sedimentation stability was only found for a 2% surfactant concentration.

3.2.1.3 Addition of Water

Addition of water to a formulation has usually a detrimental effect on defoamer stability especially in the presence of surfactants.

3.2.2 Defoamer Activity

3.2.2.1 Knock-Down

Variation of the AEROSIL® grades showed that in the presences of surfactants the knock-down activity of hydrophilic AEROSIL® was slightly better compared to the hydrophobic grades while a higher surface area had a slightly positive influence on the defoamer knock-down activity. Interestingly, all four surfactant-types do not have a significant effect on the defoamer activity.

3.2.2.2 Hold-Out

Neither the five evaluated AEROSIL®-grades, nor the four tested surfactants had a significant influence on the hold-out activity of the defoamer formulation.

4 Literature:

- 1 Technical Information TI 1313 "SIPERNAT® and AEROSIL® for Defoamer".
- 2 "AEROSIL® – Invented to Improve. Product overview".
- 3 Shell 2001.04, Industrial Brochure "Fabrikationsöle".
- 4 BASF AG 2007/12 brochure "Tenside und Polyalkylenglycole."
- 5 T. Mezger, 2002, Vincentz Verlag, "The Rheology Handbook" ed. U. Zorll.

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

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



EVONIK
INDUSTRIES

**Europe/Middle-East/
Africa/Latin America**

Evonik Resource Efficiency GmbH

Business Line Silica
Rodenbacher Chaussee 4
63457 Hanau-Wolfgang
Germany

PHONE +49 6181 59-8118

FAX +49 6181 59-78118

ask-si@evonik.com

www.evonik.com

North America

Evonik Corporation

Business Line Silica
299 Jefferson Road
Parsippany, NJ 07054
USA

PHONE +1 800 233-8052

FAX +1 973 929-8502

ask-si-nafta@evonik.com

Asia / Pacific

Evonik (SEA) Pte. Ltd.

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

PHONE +65 6 809-6877

FAX +65 6 809-6677

ask-si-asia@evonik.com

Evonik. Power to create.