EVONIK INDUSTRIES

AEROSIL® and SIPERNAT® Products for Optimized Crop Protection Formulations

Industry Information

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AEROSIL® SIPERNAT®

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Contents

1 Introduction

An increasing population, the need for natural and sustainable resources in our energy, material life cycles and a changing world climate make it obligatory for us all to improve with greater urgency the efficiency of agricultural production processes. Applying efficient crop protection formulations is one of the most important measures to meet these requirements.

By providing a wide range of silica grades, we support our customers to meet the following challenges:

- Optimize biological activity and availability
- Reduce dose of active ingredient used
- Offer user-friendly systems, improve handling and application
- Maximize long-term dispersion and emulsion stability
- Guarantee safety in manufacture and handling
- Reduce waste and effluent of all kinds
- Reduce solvent emission (VOC)

With the choice of AEROSIL® fumed silica, SIPERNAT® precipitated silica and BREAK-Thru® Oil Enhancers, Dispersing Agents, Emulsifiers, Wetting Agents and Antifoams we provide a broad portfolio enabling the agrochemical industry to enhance the functionality of their liquid and solid crop protection formulations.

This selection from one supplier combined with the corresponding application support is unique. We provide products for solid and liquid formulations with different functionalities summarized in the following paragraphs.

1.1 Basic Principles of AEROSIL® Fumed Silica and SIPERNAT® Precipitated Silica

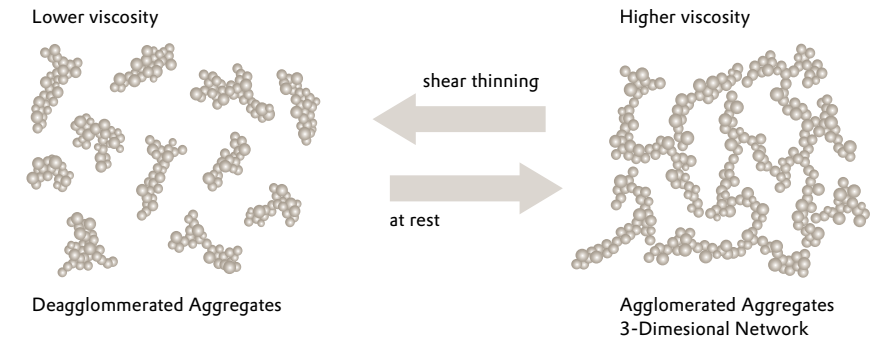
Hydrophilic and hydrophobic AEROSIL® grades are widely used in many liquid systems e. g. for viscosity control and anti-settling behavior. AEROSIL® fumed silica is a highly pure, very fine silicon dioxide and its manufacturing process can be described essentially as a continuous flame hydrolysis of silicon tetrachloride ($SiCl_4$) according to the following reaction:

$$SiCl_4 + 2\,H_2 + O_2 \xrightarrow{> 1000\,°} SiO_2 + 4\,HCl$$

Tetra-chlorosilan	Hydrogen	Oxygen	Fumed silica	Hydrochloric acid

During the manufacturing process the primary particles sinter together in chains known as aggregates. The surface of AEROSIL® fumed silica is characterized by the presence of silanol (Si-OH) groups. These groups are responsible for the above mentioned effects of AEROSIL® products in liquid systems. When the fumed silica is dispersed in a liquid the silanol groups interact with each other and build up a reversible three dimensional network. Under mechanical stress (e. g. stirring or shaking) the structure is broken down again, the system becomes more fluid, and the viscosity drops. Once again at a rest, the three dimensional network builds up again and the viscosity returns to its original value. This process is known as thixotropy and it is represented schematically in the following figure 1:

Figure 1
Shear thinning effect of AEROSIL® fumed silica



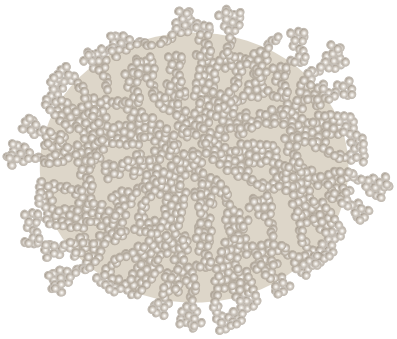
In contrast to AEROSIL® fumed silica the SIPERNAT® precipitated silica grades are manufactured in a wet process based on sodium silicate and sulfuric acid. The reaction of the precipitation process is shown schematically below.

$$Na_2O * 3.3\,SiO_2 + H_2SO_4 \longrightarrow 3.3\,SiO_2 + Na_2SO_4 + H_2O$$

Sodium water glass	Sulfuric acid	Precipitated silica	Sodium sulfate	Water

All SIPERNAT® products consist of primary particles which are linked together to larger agglomerates. The agglomerates form a highly porous sponge-like structure which can absorb liquids (e. g. water) into the pores thus converting a moist and sticky powder into a free-flowing powder. The porous structure of the SIPERNAT® grades enables them to absorb up to three times their weight in liquid. Figure 2 shows the porous structure of SIPERNAT® precipitated silica.

Figure 2
Porous SIPERNAT® structure



The different SIPERNAT® types are frequently used as carriers for liquid active ingredients, as flow and anti–caking aids for agrochemical formulations and in particular the hydrophobic types as humidity regulators in seed pellets as well as grinding aids.

1.2 BREAK-THRU® Additives

BREAK-THRU® is a registered trademark of Evonik-Goldschmidt GmbH for certain organomodified siloxanes and other specialty surfactants*. BREAK-THRU® additives are used e.g. as super-spreaders and penetrants in order to enhance the bio-efficacy by increasing the deposition and uptake of pesticides. As a further benefit BREAK-THRU® enables a safeguarded pesticide performance at low water volumes and high application speeds. Besides the above mentioned applications BREAK-THRU® adjuvants are also used as oil enhancers as well as dispersants, antifoams or emulsifiers in pesticide formulations.

* Technical Information Evonik Goldschmidt GmbH: "Additives for Pesticides Fomulations"

2 Liquid Formulations

Liquid formulations of agrochemical products occupy an important share in the pesticides market. These formulations are developed to improve safe handling of the active ingredients. Examples for liquid formulations are Emulsifiable Concentrates (EC), Oil Dispersions (OD) or Suspension Concentrates (SC). Whereas EC formulas usually require organic solvents causing high VOC emissions, SC formulas are based on water whereas OD's often can be formulated based on vegetable oils. Oil based dispersions (OD) are furthermore protecting water sensitive actives from premature decomposition.

In liquid formulations (such as SC's or OD's) there is a general need to protect dispersed, insoluble active ingredient particles against sedimentation. This can be achieved by adjusting suitable viscoelastic properties. In addition, their viscosity has to be low enough to make sure packages can easily be emptied without residue.

The use of AEROSIL® fumed silica supports very much these functionalities as a rheology modifier and anti-settling additive. As an efficient stabilizer AEROSIL® products prevent the agglomeration of active ingredients helping to ensure that they are evenly distributed and show a long-term stability.

The performance of AEROSIL® fumed silica in liquid formulations is based on two mechanisms. First, the silica envelops the active ingredient and prevents re-agglomeration. Second, AEROSIL® fumed silica creates a three dimensional network giving visco-elastic properties to the liquid formulation and thus avoiding the sedimentation of solid particles. Furthermore, the proper choice of AEROSIL® fumed silica combines an excellent anti-settling effect with a low shear viscosity.

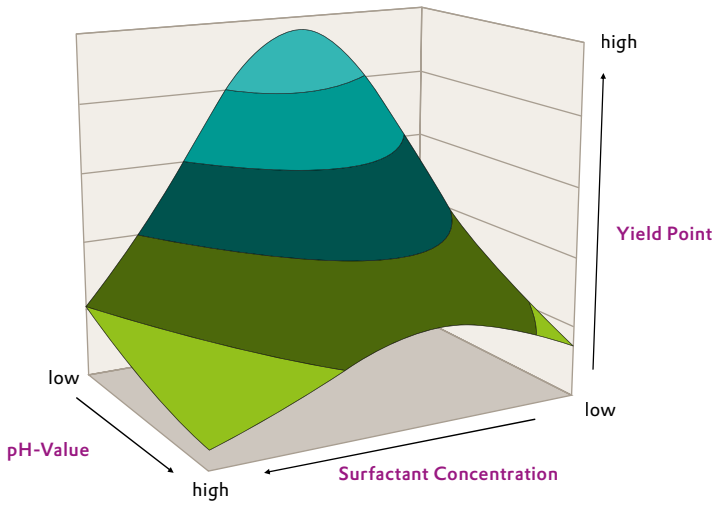
The most effective AEROSIL® grade for particular liquid crop protection formulations depends on a number of parameters, such as

- Concentration and type of
  - Active ingredient
  - Surfactant
  - Other ingredients
- Particle size of active ingredient
- Temperature during dispersing process
- Shear intensity of the mixing process (time and shear rate)
- Polarity of oil matrix

2.1 Suspension Concentrates, SC Formulations

To demonstrate the influence of some of the above mentioned parameters Figure 3 shows how the yield point of a water-based AEROSIL® 200 suspension depends on the pre-adjusted pH-value and the surfactant concentration (sorbitan mono-oleate). At a given surfactant concentration the yield point increases with lower pH values. At a given pH-value, there is an optimum surfactant concentration leading to the maximum yield point.

Figure 3
Dependance of the yield point of a waterbased AEROSIL® 200 suspension on the pH-value and the surfactant concentration



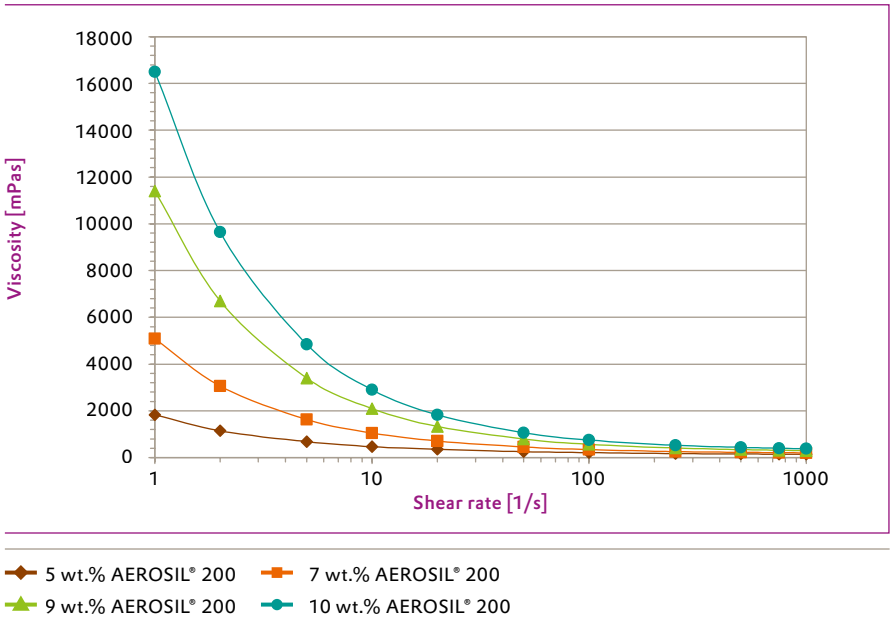
AEROSIL® fumed silica can be used in SC-formulations as single thickener as well as in combination with organic thickeners such as xanthan gum to improve their temperature stability*. In contrast to organic thickeners silica does not promote any microorganism growth due to its fertilizer free mineral character.

* Tadros, Th. F. "Surfactants in Agrochemicals" 1994 (Surfactant Science Series: 54)

2.2 Oil Dispersions, OD Formulations

Mineral and natural oils containing active ingredients are easy to stabilize using hydrophilic or hydrophobic AEROSIL® products. Figure 4 shows the strong shear thinning effect of different AEROSIL ® 200 concentrations in soybean oil.

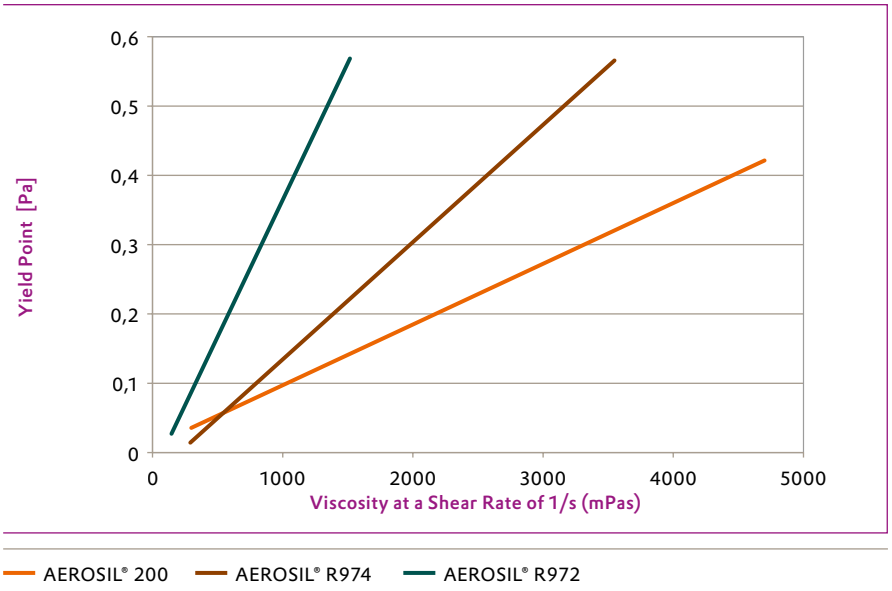
Figure 4
AEROSIL® 200 in soybean oil



Similar to SC-formulations, AEROSIL® fumed silica establishes a yield point and prevents settling of active ingredients. Hydrophobic AEROSIL® types in particular combine a moderate shear viscosity with a sufficient yield point. These properties provide excellent suspension stabilization whilst enabling the formulation to be poured easily and ensuring a proper rinsing of the container.

The correlation of the viscosity and the yield point in a model formulation is depicted in Figure 5. The hydrophobic AEROSIL® grades AEROSIL® R 974 and AEROSIL® R 972 lead to a lower viscosity at a given yield point than the hydrophilic AEROSIL® 200.

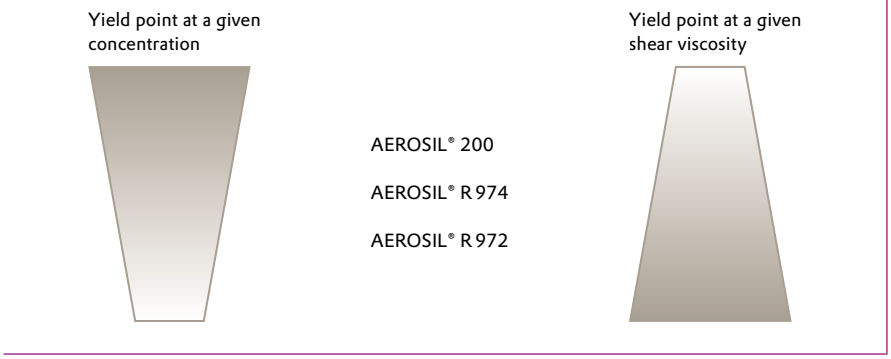
Figure 5
Yield point versus viscosity of a mixture based on a vegetable oil derivative with different grades of AEROSIL® fumed silica



Describing the results obtained in the vegetable oil system (soybean oil methyl ester) schematically, Figure 6 shows the correlation between yield point and viscosity resp. concentration. Based on the selected AEROSIL® grades, the use of the hydrophilic AEROSIL® 200 leads to a distinct yield point at a low concentration. However, this is at the expense of a relatively high viscosity. If one defines a certain viscosity as the maximum that is acceptable, the hydrophobic AEROSIL® grades AEROSIL® R 974 and AEROSIL® R 972 are both beneficial. The more hydrophobic AEROSIL® R 972 achieves the highest yield point at a given viscosity.

In contrast to clay thickeners, AEROSIL® fumed silica can be used in OD formulations without being activated by water. AEROSIL® fumed silica is an amorphous synthetic product of consistently high quality that does not contain any dangerous crystalline impurities. Therefore it is less prone to quality fluctuations compared to natural products. This leads to a highly reliable quality in the production process of agrochemical formulations.

Figure 6
Correlation yield point and viscosity resp. concentration



2.3 Emulsions, Emulsifiable Concentrate, EC Formulations

AEROSIL® fumed silica can also be used in emulsions as an effective particle stabilizer. Hydrophilic types are used for the particle stabilization in oil in water emulsion and the hydrophobic types are used as particle stabilizer in water in oil emulsion.

Table 1
Overview of AEROSIL® fumed silica types for liquid crop protection formulations

AEROSIL® type	Description
AEROSIL® OX 50 AEROSIL® 200 AEROSIL® 300 AEROSIL® 380	Hydrophilic fumed silica, can be used as anti-settling agent/ rheology modifier in SC's and OD's, o/w emulsion
AEROSIL® COK 84	Mixture of fumed silica and fumed aluminium oxide, especially used in water based SC's, o/w emulsion
AEROSIL® R 202 AEROSIL® R 812 S AEROSIL® R 972 AEROSIL® R 974	Hydrophobic fumed silica. Especially recommended in OD's for viscosity control

3 Summarized Features of AEROSIL® Fumed Silica Containing Liquid Agrochemical Formulations

AEROSIL® fumed silica

- prevents the active ingredient from settling
- facilitates cleaning of packaging and recipients
- has a double functionality as milling aid and additive for liquid concentrates
- makes the formulations easy to disperse in water
- shows compatibility and synergies with cationic and non-ionic surfactants
- is not promoting growth of mould and bacteria (inorganic substance)
- is suited to stabilize even highly acidic formulations
- can be dispersed using equipment that is customary in the crop protection industry

AEROSIL® products can be incorporated at room temperature and without water activation.

Water-based AEROSIL® fumed silica and Xantham gum containing formulations are less sensitive to temperature variations.

Evonik Degussa provides competent support by selecting the right grades of AEROSIL® fumed silica combined with recommendations regarding processing parameters.

4 Solid Formulations

Free Flow / Anti-caking / Carrier

Solid agrochemical formulations have been known for many years in the industry. Examples for solid formulation types are wettable powders (WP), granules (GR) and water dispersible granules (WG).

A clear advantage of granulated formulations is that they leave almost no contamination in the empty package. Additionally powders may create dust, which is undesirable in terms of user safety. Therefore, powder formulations are more and more replaced by granule formulations or liquid systems.

SIPERNAT® precipitated silica and AEROSIL® fumed silica are used in solid formulations as flow aid, anti-caking aid, milling aid and as carrier for liquid active ingredients. WP formulations treated with SIPERNAT® or AEROSIL® products are dry, free-flowing and do not tend to cake on storage.

In formulations which need to be dispersed in water before use, finely ground SIPERNAT® precipitated silica or AEROSIL® fumed silica have to be chosen, as the silica must stay suspended from the moment of dispersing the formulation until it is sprayed onto the field. Besides, particles which are too big may also block the spray nozzles.

In granules for direct application in the field, however, large particle size silica can be advantageous. Those grades can be used as carrier for liquid or low melting actives providing both a free flowing as well a non-caking absorbate. The granular shape of the absorbate is already predesigned with the silica. No additional granulation step is necessary.

4.1 Wettable Powder (WP) and Water Dispersible Granules (WG)

SIPERNAT® precipitated silica provides three main functionalities to wettable powder and water dispersible granule formulations:

- Highly efficient absorption of liquid actives: Solid formulations containing up to 75 % of liquid active ingredient can easily be prepared using suitable SIPERNAT®-grades.
- Free flow additive / anti-caking additive: 1 – 3 % of SIPERNAT® precipitated or AEROSIL® fumed silica added to powder or granule formulations enhance the flowability greatly and avoid caking during storage.
- Milling aid: Adding up to 10 % of SIPERNAT® precipitated silica facilitates the milling of low melting ingredients.

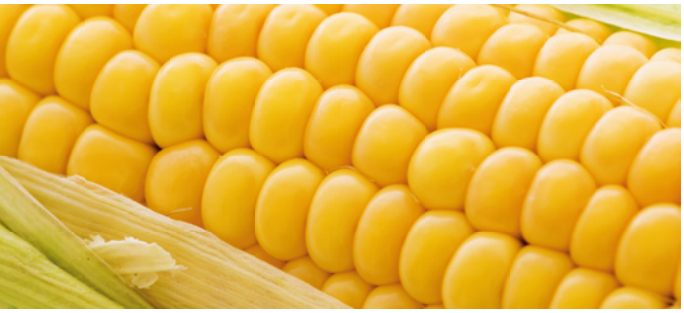
As a positive side effect, the suspensability of the WP and WG at the point of use is much improved with the use of SIPERNAT® and AEROSIL® products.

4.2 Granules (GR)

Hydrophobic silica on the surface of granulates or dusts enables the formulator to increase stability in humid environments or to delay ("slow release") the diffusion of the active ingredient.

Hydrophilic SIPERNAT® 2200 is an ideal carrier for liquid or low melting actives to be converted to granules. Such carried actives are easy to be applied directly to the soil, will not create dust and reduce direct skin contact which facilitates their handling. SIPERNAT® 2200 is able to absorb 190 ml liquid / 100 g silica still providing a dry and free flowing formulation.

4.3 Seed Coatings



During production of coated seeds the rheological behavior of the liquid seed coating can be adjusted as required by AEROSIL® fumed silica as a process aid. In the coated seeds hydrophobic AEROSIL® fumed silica or SIPERNAT® precipitated silica can control and slow down the penetration of moisture to the grain.

Table 2
Overview of SIPERNAT® precipitated silica types for solid crop protection formulations

SIPERNAT® resp. AEROSIL® type	Description
SIPERNAT® 22[1)] SIPERNAT® 50[1)] SIPERNAT® 22 S SIPERNAT® 50 S SIPERNAT® 320 SIPERNAT® 350	Hydrophilic precipitated silica can be used as carrier in WP and WG formulations
SIPERNAT® 22 S SIPERNAT® 50 S SIPERNAT® 350 AEROSIL® 200	Hydrophilic precipitated silica and hydrophilic fumed silica provide good properties as flow aid and anti caking agent in WP's and WG's.
SIPERNAT® 22 SIPERNAT® 50	Hydrophilic precipitated silica especially appropriate as grinding aid in WP and WG formulations
SIPERNAT® 2200	Micro-granular hydrophilic silica can be used as carrier for granules, which are directly applied to the field.
SIPERNAT® D 17	Hydrophobic precipitated silica, can slow down the penetration of moisture, e. g. in seed coatings.

1) Grinding of the whole formulation is necessary

5 Regulation and Registration

The following table gives an overview on the listing of our products in the EPA lists 4 a and 4b, as well as in 40 CFR § 180.xxx.

Table 3
Listing of AEROSIL® and SIPERNAT® products

CAS-No	Products	EPA-List	40 CFR
1344-28-1	AEROXIDE® Alu C	4b	180.910
67762-90-7	AEROSIL® R 202 SIPERNAT® D 10	4b	180.960
68611-44-9	AEROSIL® R 972 AEROSIL® R 974 SIPERNAT® D 17	4b	180.960
68909-20-6	AEROSIL® R 812 AEROSIL® R 812 S AEROSIL® R 8200	4b	180.960
1344-28-1 + 112945-52-5	AEROSIL® COK 84 AEROSIL® MOX 80 AEROSIL® MOX 170	4b + 4 a	180.910 + 180.950
1344-00-9	SIPERNAT® 820 A	4 a	180.910
1318-02-1	SIPERNAT® 44	4 a	180.910
1344-95-2	SIPERNAT® 880	4 a	180.910
112926-00-8	SIPERNAT® 160 SIPERNAT® 22 SIPERNAT® 22 S SIPERNAT® 22 LS SIPERNAT® 2200 SIPERNAT® 310 SIPERNAT® 320 SIPERNAT® 325 C SIPERNAT® 320 DS SIPERNAT® 50 SIPERNAT® 50 S SIPERNAT® 500 LS SIPERNAT® 350 SIPERNAT® 360 SIPERNAT® 383 DS	4 a	180.950
112945-52-5	AEROSIL® OX 50 AEROSIL® 90 AEROSIL® 130 AEROSIL® 150 AEROSIL® 200 AEROSIL® 300 AEROSIL® 380 AEROPERL® 300/30	4 a	180.950

6 Handling, Packaging and Storage

6.1 Packaging & Handling

AEROSIL® and SIPERNAT® products are delivered in multiply bags of various weights, depending on the product and market. We also offer certain silica products in semi-bulk packaging – the FIBC (Flexible Intermediate Bulk Container). The FIBC option offers dust-free discharge, requires less manual labor (compared to paper bags) and eliminates any possible risk of external contamination in a closed system. Bulk deliveries are available as well. For more information on packaging, please request our Technical Information 1232 " Types of Packaging for Performance Silica, the Technical Information 1231 "Packaging Forms for AEROSIL®", the Technical Information 1219 "Semi-bulk Packaging for AEROSIL®" or the Technical Information 1321 "Semi Bulk Packaging for fine particle SIPERNAT® products". Several options for dust free and automated handling (conveying, dosing, feeding etc.) into both solid or liquid systems are possible. For more detailed information regarding the handling of silica, please request our Technical Bulletin Fine Particles No 28 "Handling of synthetic silica and silicate".

Please contact a sales agent in your area for detailed product / packaging / handling specific information.

6.2 Storage

Although AEROSIL® and SIPERNAT® products are largely chemically inert and their composition does not change chemically over time, their high specific surface area could result in the adsorption of volatile substances (in the case of moisture, this adsorption is reversible). For this reason, we recommend storing all AEROSIL® and SIPERNAT® products in a dry place, protected from moisture and organic vapors. For more detailed information regarding the stability of silica please request the corresponding Product Information. During prolonged periods of storage, AEROSIL® fumed silica and SIPERNAT® precipitated silica may become slightly compacted. This can lead to a minor increase in tamped density, affecting the related product properties.

7 Information and Internet service

You may also use our website www.evonik.com to access specific Product Information sheets directly through the Product Finder database, or request our Technical Information publications.

Relevant Literature

- Technical Bulletin Fine Particles, No. 28
  The Handling of Synthetic Silicas and Silicates
- Technical Information TI 1360, SIPERNAT® and AEROSIL®
  – An Essential in Industrial Powder Technology
- Technical Information TI 1213, Performance Silica as Flow Agent and Carrier Substance.
- Technical Bulletin Fine Particles, No. 62
  Synthetic Silica and Electrostatic Charges
- Technical Information 1219
  New Semi Bulk Containers for AEROSIL®
- Technical Information 1279
  Successful Use of AEROSIL® Fumed Silica in Liquid Systems
- Tadros, Th.F. "Surfactants in Agrochemicals"
  1994 (Surfactant Science Series; 54)
- Technical Information Evonik Goldschmidt GmbH
  Additives for Pesticides Formulations

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