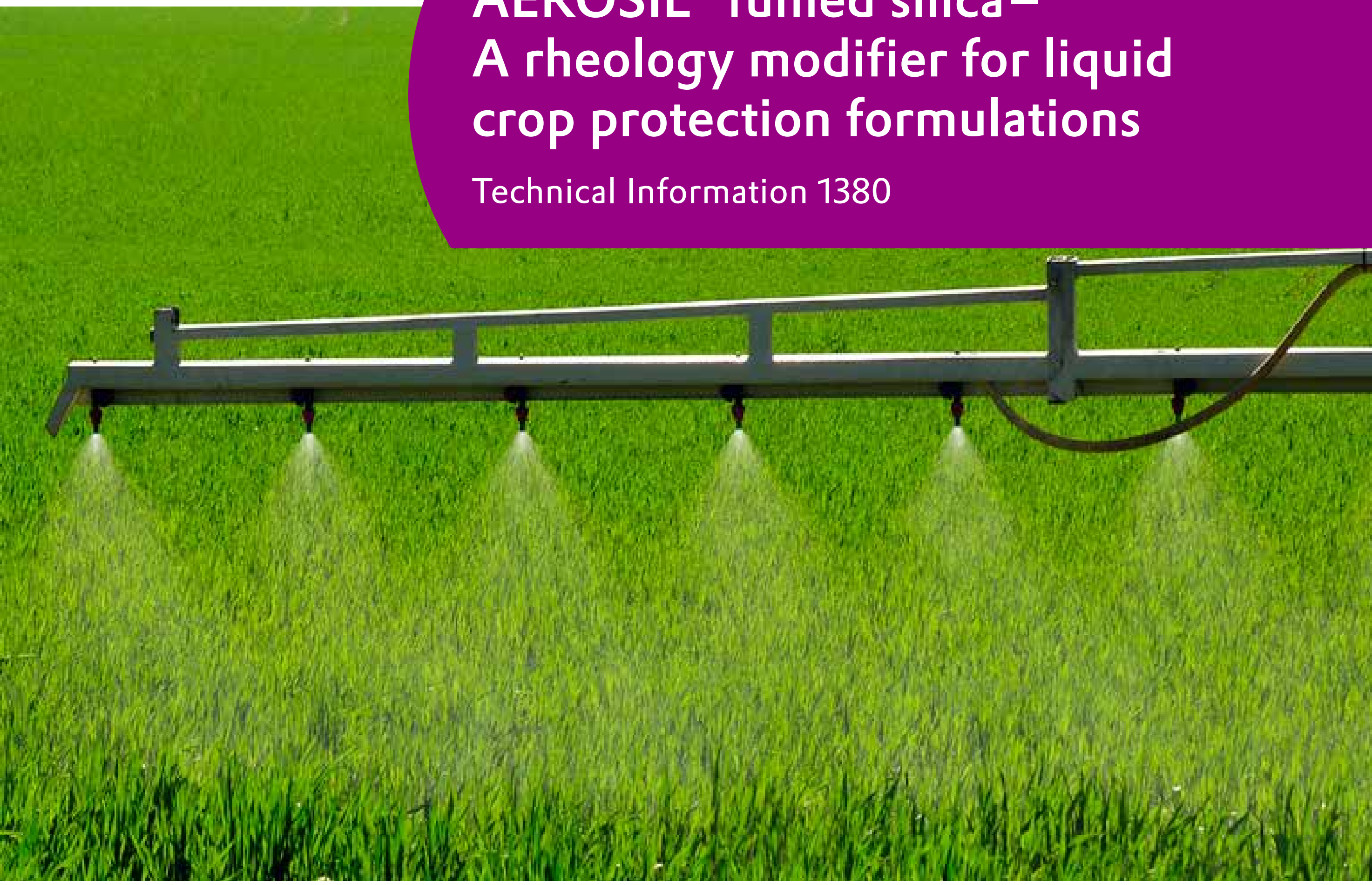
AEROSIL® fumed silica – A rheology modifier for liquid crop protection formulations

Technical Information 1380



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1 Introduction

The increasing demand for food to satisfy the nutritional needs of the world's growing population drives the crop protection industry to change its production processes and products. The use of liquid formulations such as oil dispersions (OD) is of prime importance. Effective formulations based on natural or mineral oils are essential to preserve sustainable resources.

Therefore the development of more effective liquid crop protection formulations like herbicides, fungicides, insecticides and biocides is the challenge of today and the future. A stable formulation with homogeneously dispersed active ingredients, protected against moisture, combined with good pourability and simple package cleaning is needed to optimize the effectiveness of such formulations.

Evonik Industries has addressed these challenges and offers a wide range of products for rheology modification and anti-settling effects in liquid systems based on OD formulations.

AEROSIL® fumed silica....

- **inhibits settling of solid active ingredients in liquid formulations.**
- **surrounds the active ingredient and prevents re-agglomeration.**
- **is incorporated within short dispersing time at room temperature without water activation.**
- **does not promote the growth of mould and bacteria.**
- **makes the formulation easy to disperse in water.**
- **can be dispersed using equipment that is customary in the crop protection industry.**

2 How does AEROSIL® fumed silica prevent settling in liquid crop protection formulations?

The improvement of the stability and therewith the efficiency of crop protection formulations is related to the prevention of settling.

The end-user needs to disperse the concentrate containing an active ingredient in the solvent well before applying the liquid crop protection formulation directly on the field. This enhances the availability of the active and leads to homogeneous distribution in the tank before spraying. The use of the right antisettling agent is crucial in order to obtain a perfect balance of a low viscosity and a moderate yield point (see page 4) to prevent settling of active ingredients.

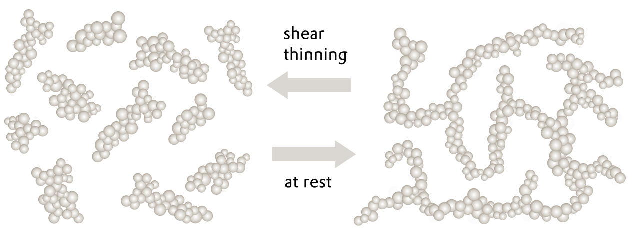
On one hand a pourable OD is necessary for good handling properties in practice permitting an easy cleaning of the canisters and containers, but on the other hand a certain yield point is needed to prevent settling of the active ingredient. In Newtonian fluids a suspended particle will settle over a certain period of time if the viscosity is low enough to allow sufficient flow ability for discharging the container. The sedimentation of particles in "easy to handle" liquids can only be prevented reliably in non-Newtonian fluids.

Therefore a combination of both, moderate shear viscosity and a sufficient yield point adjusted by the use of AEROSIL® fumed silica are crucial for stabilizing an OD showing good pourability and drained packages.

The effectiveness of AEROSIL® fumed silica in a liquid is achieved through a reversible three-dimensional network that is generated by the incorporated silica (see **Figure 1**). The silanol groups on the surface of the silica interact with each other building up a loose but elastic network which increases the viscosity and therewith the yield point at rest. Under mechanical stress (e.g. stirring or shaking) the structure is broken down, the system becomes more fluid and the viscosity drops.

Furthermore the silica particles surround the active ingredient and prevent it from re-agglomeration.

Figure 1
Shear thinning effect of AEROSIL® fumed silica



At a certain point, the so called yield point, the extrinsic forces are just higher than the bonding forces of the network – the substance begins to flow because the visco–elastic network starts to break down and the viscosity decreases. The higher the shear forces the lower the viscosity.

This process is described as a shear thinning effect. After resting the substance should recover its original level of viscosity in order to keep the suspended particles in balance. According to the bead-spring model, the elastic part of a non-Newtonian fluid is described through the spring and the viscous part is given through the damper.

The ratio of the viscous part divided by the elastic part is defined as the loss factor. Generally the elastic part should prevail in contrast to the viscous part to achieve a stable formulation.

3 AEROSIL® fumed silica enables stable formulations within a broad temperature range

The long term stability of a formulation is defined by its visco-elastic properties and the homogeneous distribution of the active ingredient. The visco-elastic properties are given through both the yield point and the loss factor.

Table 1 shows the composition of an OD guide formulation based on an organic solvent containing the active ingredient Nicosulfuron which was stabilized through the addition of 4% AEROSIL® 380. A constant performance in terms of unique values characterizes the performance of Evonik's AEROSIL® fumed silica in the given OD formulation. Excellent pourability and a fast build-up of the elastic network of AEROSIL® fumed silica assure a convenient handling in combination with the homogeneous dilution of the OD concentrate before spraying on the field.

In addition to an appropriate shear thinning behavior and comparable loss factors at different storage conditions, a good anti-settling behavior is characteristic for a strong network of dispersed silica particles.

Table 1
Guide formulation containing AEROSIL® 380

Component	Chemical structure	wt.-%
Hydrocarbon Fluid	Organic solvent	66.5
BREAK-THRU® DA 655	Dispersing agent	5.0
TEGO® SMO V 80	Emulsifying agent	10.0
BREAK-THRU® EM TD 6	Emulsifying agent	10.0
Nicosulfuron	Active ingredient	4.5
AEROSIL® 380	Thickening agent	4.0

Manufacturing procedure: Premixing of all components (excluding thickening agent) in a 1000 ml bottle; generating vacuum in order to remove incorporated air bubbles at 500 rpm; 5.3 h milling time at 1500 rpm/ 20 °C in a bead mill (VMA-Getzmann GmbH/Germany) - grinding balls ZrO_2/Y_2O_3, size = 1–1.2 mm ((VMA-Getzmann GmbH/Germany); incorporation of thickening agent AEROSIL® 380 at 500 rpm; dispersion of thickening agent for 10 min at 1500 rpm.

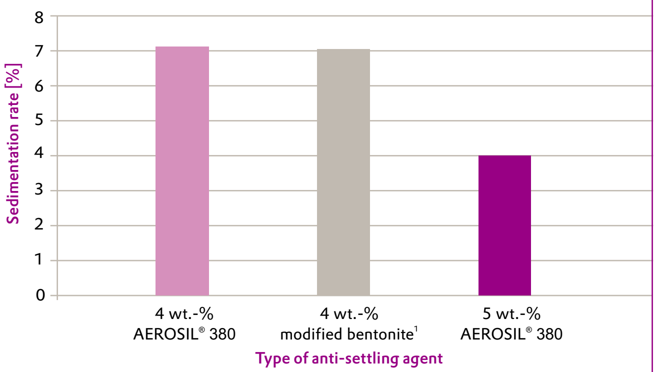
Generally one of the most important values for the estimation of an OD formulation's stability is the above mentioned loss factor. Acceptable values are lower than 1 and indicate that the elastic part prevails in contrast to the viscous part. **Table 2** illustrates the unique values for the loss factor achieved by the addition of 4 % AEROSIL® 380 for rheology control at both room temperature (RT) and 54 °C after a storage time of 14 days. The values of the loss factor obtained with AEROSIL® fumed silica are on a good level after the storage period of 14 days at RT as well as at 54 °C.

Table 2
Loss factors from OD formulations stored for 14 days at 54 °C and RT

Rheology modifier	Concentration [%]	Loss factor at RT	Loss factor at 54 °C
AEROSIL® 380	4	0.29	0.29
AEROSIL® 380	5	0.27	0.32
Organically modified bentonite[1]	4	0.89	0.35

Measurement methods: Sample measurement by MCR 300 – **M**odular **C**ompact **R**heometer 300 – (Anton Paar GmbH/Germany); Loss factor was calculated by the method of amplitude sweep at 23 °C (Rheoplus Software RHEOPLUS/32 V 3.40; Anton Paar GmbH/Germany).

Figure 2
Sedimentation rate of different batches stored for 14 days at 54 °C



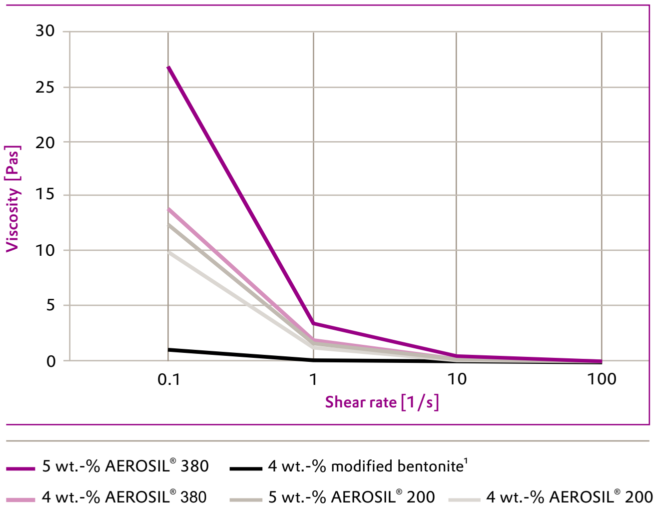
The sedimentation rate was measured by a slide gauge and calculated in percent relating to the height of sample bottles Schott Duran 50 ml (SCHOTT AG/Germany) minus the height of the bottom (30 mm) of the sample bottles.

Figure 2 shows the settling rate of AEROSIL® 380 added in certain concentrations. Increasing the amount of AEROSIL® fumed silica results in a lower settling rate.

A higher addition of AEROSIL® 380 leads to an optimal visual result as well as to an easy to disperse OD formulation.

The test results showed clearly that the formulation containing AEROSIL® fumed silica show both, the described effect of shear thinning in combination with moderate yield point even at low shear rates as shown below in **Figure 3**.

Figure 3
Viscosity values for AEROSIL® fumed silica vs. bentonite[1] after storage at RT



Moreover the stabilizing structure of AEROSIL® fumed silica in the present OD formulation doesn't depend on the addition of any activator and does not require a certain temperature increase during the storage period.

Furthermore, the dispersing time of AEROSIL® 380 is very short with 10 to 15 minutes (q. v. **Figure 8**).

The lower dispersing time saves resources and costs in the manufacturing of liquid crop protection formulations.

[1] NANOFIL® SE 3000 (organically modified nanodispersible layered silicate) Typical properties: Product form: Powder; Bulk density: 450 kg/m³; Median particle size D_{50} < 10 µm; Moisture content: < 3 %.

Benefits of AEROSIL® fumed silica at different storage temperatures

AEROSIL® fumed silica …

- Results in a moderate yield point
  Benefit: Easy emptying and cleaning of packaging

- Builds up a stable structure at 54 °C as well as at RT
  Benefit: Long term stability over a wide temperature range

- Shows optimal dispersibility for dispersion in water
  Benefit: Effective distribution on the field of the OD formulation

4 Rheology control for mineral- and vegetable oils using AEROSIL® fumed silica

Mineral and natural oils containing active ingredients are easy to stabilize by hydrophilic or hydrophobic AEROSIL® grades. The right grade for preventing the settling of an active ingredient depends amongst other things on the polarity and the character of the oil used. Generally higher viscosities can be achieved in non-polar systems with hydrophilic silica products. Hydrophobic AEROSIL® grades are easier to disperse in oils and may be an option when maximum viscosity is not required. In non-polar to semi-polar systems hydrophilic types are routinely used, in semi-polar to polar systems hydrophobic AEROSIL® types may be used.

As an example **Figure 4** shows various concentrations of AEROSIL® 200 dispersed in soybean oil resulting in different viscosity levels. The diagram demonstrates clearly the typical shear thinning behavior of AEROSIL® fumed silica.

Figure 4
AEROSIL® 200 in soybean oil, measured at RT

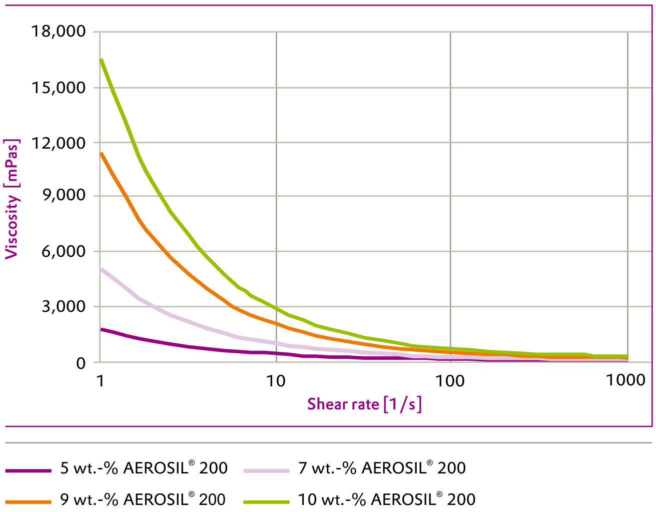
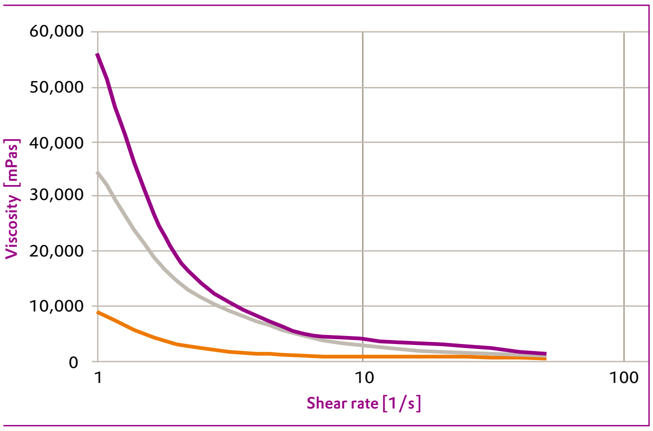


Figure 5 shows the thickening performance achieved using the basic type AEROSIL® 200 in paraffin oil. The higher viscosity level in the non-polar oil is reached with lower AEROSIL® 200 concentrations compared to the viscosity level in the more polar soybean oil.

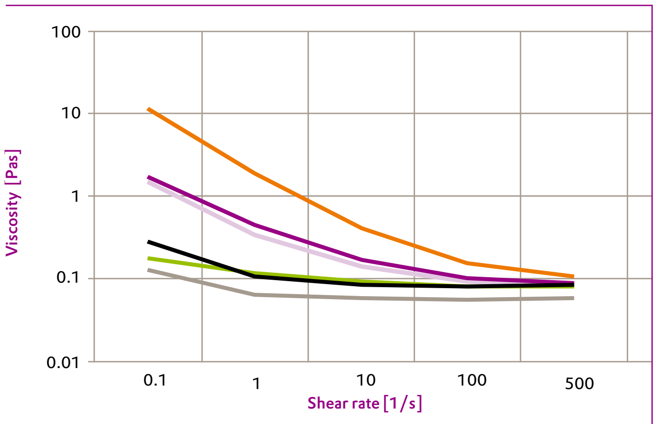
Figure 5
AEROSIL® 200 in paraffin oil measured at RT



In contrast to the hydrophilic AEROSIL® types recommended in non-polar to semi-polar systems, Evonik's hydrophobic grades like AEROSIL® R 974, AEROSIL® R 812 S or AEROSIL® R 202 are especially suitable for rheology control in polar systems. In general hydrophobic types create a distinctively lower viscosity at a given concentration compared to the hydrophilic types because of their surface treatment. It is therefore possible to achieve stable formulations with a minimum shear viscosity for easy handling in the manufacturing process.

Another example of the efficient use of hydrophobic AEROSIL® types is demonstrated in the diagram in **Figure 6**. In each case except the pure corn oil an addition of 2.0 wt. percent of different types of hydrophobic AEROSIL® grades leads to a higher viscosity level. The viscosity curve was measured after 3 days storage time. But also after a storage period of minimum 14 days at RT (in case of adding AEROSIL® R 812 S) almost no viscosity increase was detected. Furthermore

Figure 6
Hydrophobic AEROSIL® fumed silica in corn oil stored for 3 days and measured at RT



comparable viscosity levels were measured after storage time of 35 days by using AEROSIL® R 202 and even the same viscosity level after 63 days if adding AEROSIL® R 805 and AEROSIL® R 816. The huge range of different hydrophobic and hydrophilic grades of AEROSIL® fumed silica to be used in a number of different solvents like vegetable or synthetic oils offers a unique solution in order to stabilize formulations at nearly all viscosity levels on customers request without undesired post thickening effects.

With the addition of hydrophobic AEROSIL® fumed silica in corn oil the yield point can be distinctively increased and therewith a stabilization of incorporated solid active ingredients takes place. High values of the storage modulus which means a greater elastic part along with low values of the loss modulus indicate a loss factor on a low level even after 35 and 63 days storage time. In the following table 3 the results by using AEROSIL® R 805 and AEROSIL® R 202 dispersed in corn oil are summarized.

Table 3
Visco-elastic properties of AEROSIL® fumed silica in corn oil measured and stored at RT

AEROSIL® type	Concentration [%]	Yield point [Pa]	Storage modulus [Pa]	Loss modulus [Pa]	Loss factor
Corn oil	100	< 0.01	0.092	0.577	6.05
AEROSIL® R 805[1]	5	1.272	119.6	37.14	0.31
AEROSIL® R 202[2]	5	4.252	404.8	115	0.28

[1] Sample stored for 63 days at RT [2] Sample stored for 35 days at RT

5 How to disperse AEROSIL® fumed silica in liquid formulations

This chapter provides a short overview of proper dispersing conditions and incorporating steps to be considered when AEROSIL® fumed silica is used as a rheology modifier. Best performance can be achieved by taking into account the following instructions.

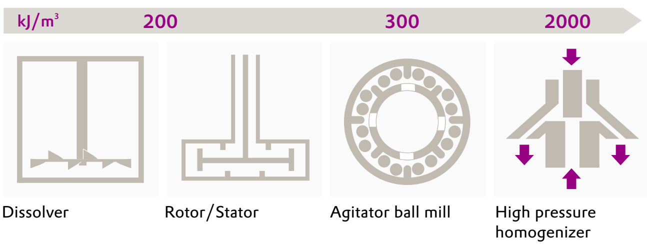
Influencing factors

- **Shear intensity during the dispersing process**
- **Dispersing time**
- **Dispersing equipment**
- **Type of AEROSIL® fumed silica**
- **Addition sequence and wet-in**
- **Relation of blade size to vessel size in batch processes**
- **Air bubbles incorporated during the dispersing step**

First of all the energy input into the liquid is of great importance. On the one hand too high shear intensities may damage the structure of the AEROSIL® fumed silica which is the reason for the network-building characteristics of the silica. On the other hand, too low shear intensity leads primarily to a poor distribution of silica particles in the liquid and additionally to insufficient wetting of the AEROSIL® product. A consequence of insufficient shear would be a higher concentration of thickening agent required to obtain the desired viscosity.

Suitable devices for dispersing AEROSIL® products are high speed mixers such as a dissolver, rotor-stator mixer or bead mill. But the user has to keep in mind the differences in the energy input on the system generated by the respective dispersing devices. The energy input increases beginning with the dissolver, increasing over rotor-stator systems, followed by ball mill and lastly homogenizer like depicted in **Figure 7**. If longer dispersing or milling times are needed – for example to mill down the active ingredient – the order of addition has to be adjusted and the right type of AEROSIL® fumed silica has to be chosen.

Figure 7
Possible energy input of different dispersing devices

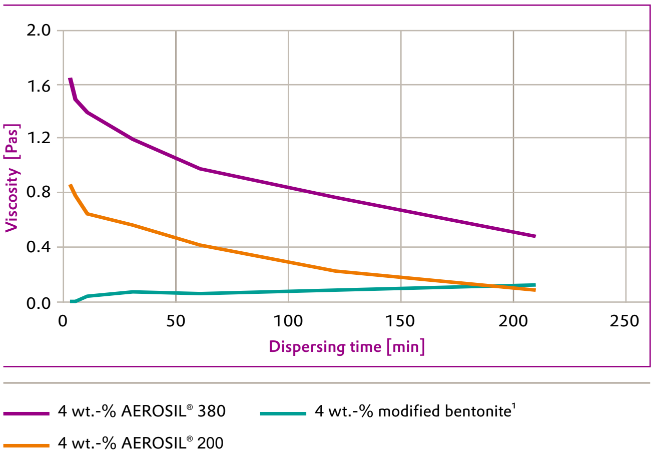


The dispersing time and the rotational speed of the dispersing equipment should be adjusted as well as the type of AEROSIL®. Some types such as AEROSIL® 380 are more resistant against high shear forces than AEROSIL® 200. Higher surface area AEROSIL® grades such as AEROSIL® 300, 380, and AEROSIL® R 812 S require more energy-intensive mixing equipment for optimized dispersion. For most applications peripheral velocity can be more than 7 m/sec using a dissolver or a rotor stator system.

In case of using a bead mill, a rough rule of thumb is that the dispersing time should be around 10 minutes at a tip speed of 4.6 m/s at the given ratio of blade to vessel size of 1 : 2 to 1 : 3. The amount of AEROSIL® fumed silica should be incorporated stepwise at a rotation speed of 500 rpm to predisperse it before high shear is applied. It is recommended that incorporation and dispersing step of AEROSIL® fumed silica should be the last step of the manufacturing process.

Figure 8 shows the influence of the dispersing time using a bead mill for dispersion of certain types of AEROSIL® fumed silica vs. dispersing time of modified bentonite[1].

Figure 8
Dispersing time of different thickening agents using a bead mill



The figure shows clearly the advantage of shorter dispersing time when AEROSIL® fumed silica is used. This reduces production time and therewith manufacturing costs. Air bubbles incorporated during the dispersion process should be removed by generating a vacuum. If a higher viscosity level is needed, this can be obtained through increasing the concentration of AEROSIL® fumed silica.

A more comprehensive description of the successful use of AEROSIL® fumed silica in liquid systems is given in our Technical Information 1279.

[1] NANOFIL® SE 3000 (organically modified nanodispersible layered silicate)
Typical properties: Product form: Powder; Bulk density: 450 kg/m³; Median particle size D_{50} < 10 µm; Moisture content: < 3 %.

6 Selection of the right type of AEROSIL® fumed silica

Based on the broad range of Evonik's portfolio of AEROSIL® fumed silica for rheology control the selection of the right type is of vital importance.

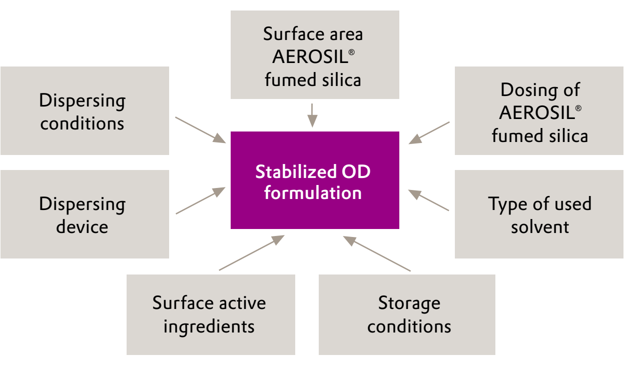
The most effective AEROSIL® grade for a particular liquid crop protection formulation depends on a number of parameters, such as

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

These parameters should be considered when using our products for viscosity control in liquid crop protection formulations in order to get the best performance with AEROSIL® fumed silica.

In **Figure 9** the influencing factors to be considered for the stabilization of an OD are summarized.

Figure 9
Influencing factors on stability of OD formulations



7 Product overview

A selection of recommended types of Evonik's AEROSIL® fumed silica grades and their typical properties are given in the tables below. Please contact us for more specific and detailed information as well as to request samples.

Table 4
Recommended products

AEROSIL® type	Description
AEROSIL® 200 AEROSIL® 300 AEROSIL® 380	Hydrophilic AEROSIL® fumed silica to be used as rheology modifier, anti settling agent in SC's and OD's, o/w emulsion
AEROXIDE® Alu C	Highly dispersed metal oxide with high specific surface area especially used in polar, water based SC's.
AEROSIL® COK 84	Mixture of fumed silica and fumed aluminum oxide, especially used in water based SC's, o/w emulsions
AEROSIL® R 202 AEROSIL® R 805 AEROSIL® R 812 S AEROSIL® R 816 AEROSIL® R 972 AEROSIL® R 974	Hydrophobic AEROSIL® fumed silica to be used as rheology modifier and as anti settling agent in OD's

Product overview

Table 5
Properties of recommended hydrophilic AEROSIL® fumed silica, fumed aluminium oxide and mixed oxide grades

Properties	Unit	AEROXIDE® Alu C	AEROSIL® 200	AEROSIL® 300	AEROSIL® 380	AEROSIL® COK 84
Specific surface area[1] (BET)	m²/g	100 ± 15	200 ± 25	300 ± 30	380 ± 30	185 ± 30
pH value[1] 4% in water method		4.5–5.5	3.7–4.7	3.7–4.7	3.7–4.7	3.6–4.3
Loss on drying[1] 2 h at 105 °C method	wt. %	≤ 5.0	≤ 1.5	≤ 1.5	≤ 2.0	≤ 1.5
Loss on ignition[1] Based on dry substance 2 h at 1000 °C	wt. %	≤ 3.0	≤ 1.0	≤ 2.0	≤ 2.5	≤ 1.0
Tamped density[1] (approximate value)	g/l	appr. 50	50	50	50	50
SiO_2 content[1] (based on ignited substance)	wt. %	≥ 99.8[2]	≥ 99.8	≥ 99.8	≥ 99.8	82–86[3]

[1] ex plant
The data represent typical values (no product specification)
[2] Al_2O_3 content: Pure aluminum oxide
[3] Al_2O_3 content: 14–18%

Table 6
Properties of recommended hydrophobic AEROSIL® fumed silica grades

Properties	Unit	AEROSIL® R 202	AEROSIL® R 805	AEROSIL® R 812 S	AEROSIL® R 816	AEROSIL® R 972	AEROSIL® R 974
Specific surface area[1] (BET)	m²/g	100 ± 20	150 ± 25	220 ± 25	190 ± 20	110 ± 20	170 ± 20
pH value[1] 4% in water method		4.0–6.0	3.5–5.5	5.5–7.5	4.0–5.5	3.6–5.5	3.7–4.7
Carbon content[1] method ISO 3262-20	wt. %	3.5–5.0	4.5–6.5	3.0–4.0	0.9 – 1.8	0.6–1.2	0.7–1.3
Loss on drying[1] 2 h at 105 °C	wt. %	≤ 0.5	≤ 0.5	≤ 0.5	≤ 1.0	≤ 0.5	≤ 0.5
Loss on ignition[1] Based on dry substance 2 h at 1000 °C	wt. %	4.0–6.0	5.0–7.0	1.5–3.0	not determined	≤ 2.0	≤ 2.0
Tamped density[1] (approximate value)	g/l	60	60	60	60	50	50
SiO_2 content[1] (based on ignited substance)	wt. %	≥ 99.8	≥ 99.8	≥ 99.8	≥ 99.8	≥ 99.8	≥ 99.8

[1] ex plant
The data represent typical values (no product specification)

8 Literature

1 Technical Information TI 1279, Successful use of AEROSIL® fumed silica in liquid systems

2 Industry Information II 2241, AEROSIL® and SIPERNAT® products for optimized crop protection formulations

3 The rheology handbook: for users of rotational and oscillatory rheometers, Thomas Mezger, Hannover: Vincentz, 2000

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