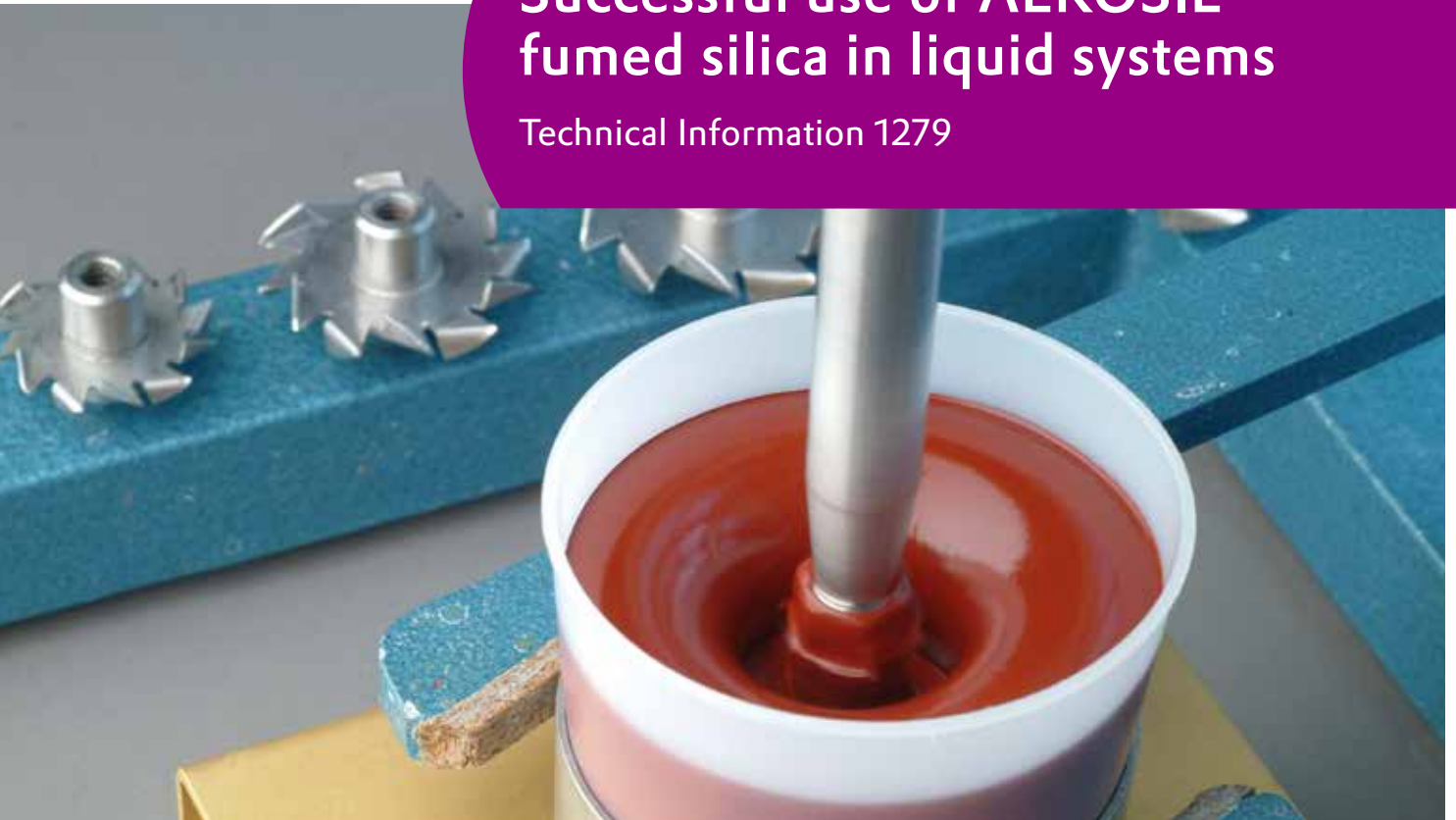


Successful use of AEROSIL[®] fumed silica in liquid systems

Technical Information 1279



AEROSIL[®]

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1 Introduction

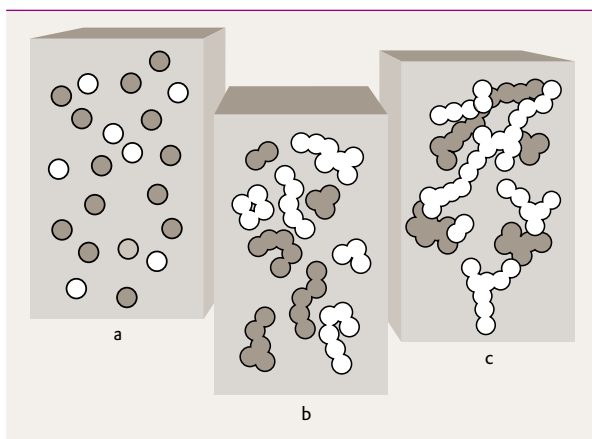
Hydrophilic and hydrophobic AEROSIL® grades are used in many liquid systems for viscosity control, anti-sag and anti-settling behavior and for general processing enhancement. All of these effects are based on the ability of dispersed AEROSIL® fumed silica particles to form a network of aggregates via hydrogen bridge linkage and/or VAN DER WAALS attractive forces in liquid media.

AEROSIL® fumed silica is highly pure, very fine silicon dioxide. The primary nano-scale particles do not exist as isolated primary particles (**Figure 1a**) since during the high-temperature manufacturing process, these sinter together in chains known as aggregates (**Figure 1b**).

Upon further cooling, aggregates form larger agglomerates by means of hydrogen bonds and other weak forces of attraction (e.g. van der Waals forces). Agglomerates (**Figure 1c**) may be broken down to aggregates during dispersion, but under typical dispersion conditions, aggregates cannot be broken down to individual primary particles. In general, the higher the specific surface area of the AEROSIL® product, the greater the degree of agglomeration.

The surface of AEROSIL® fumed silica is characterized by the presence of silanol (Si-OH) groups. These groups are responsible for the effects of AEROSIL® in liquid systems. When the fumed silica is dispersed in a liquid,

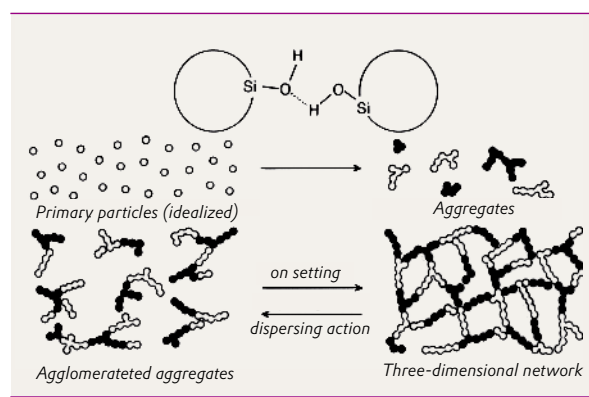
Figure 1



Schematic representation of AEROSIL® fumed silica

these silanol groups interact with each other either directly or indirectly via the molecules in the liquid. This affinity is attributed to hydrogen bonding and results in a reversible, three-dimensional lattice structure that is visible macroscopically as thickening. Under mechanical stress, for example stirring or shaking, the structure is broken down again, the system becomes more fluid, and the viscosity drops. Once again at rest, the lattice builds up again and the viscosity returns to its original value. This process is known as thixotropy and it is represented schematically in **Figure 2**.

Figure 2



Schematic representation of the interaction between AEROSIL® fumed silica particles in liquids.

Hydrophobic AEROSIL® (“R”) grades have been treated during manufacture to obtain a hydrophobic surface. During this process, silanol groups are reacted. Depending on the coating system hydrophilic or hydrophobic AEROSIL® results in the best rheological effects. With hydrophobization we are able to offer tailor made types of AEROSIL®. In pure deo-gels, such as lippgloss, hydrophobic AEROSIL® types often exhibit lower thickening efficiency compared to hydrophilic types. However, hydrophobic grades have other advantages and so may also be an option when maximum viscosity is not required. Furthermore agglomerates of hydrophobic fumed silica are more easily broken up, leading to better grind values. Hydrophobic types also have improved flow and leveling properties, suspension without the higher resulting viscosity, better skin feel, maintain better gloss and give water-repellency and anti-corrosion properties.

To optimize efficiency and consistency of behavior for all AEROSIL® grades, the following steps are important for success:

I. Finding desired addition level

II. Applying proper dispersion

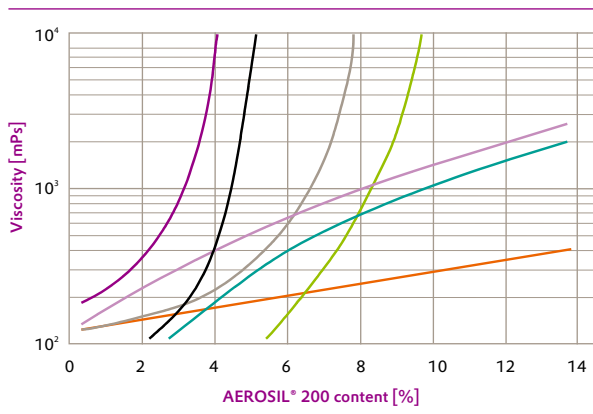
- Equipment and design features
- Tip speed considerations
- Length of shearing time
- Temperature build-up
- Sequence of addition
- Masterbatch vs direct addition
- Grind values vs dispersion
- Preventing under/over shearing

III. Completing the formulation

2 Finding the Desired Addition Level

In cosmetic applications, hydrophilic AEROSIL® 200, 300 and 380 grades are used routinely for rheology improvement in non-polar to semi-polar systems. In semi-polar to polar cosmetic systems, hydrophobic AEROSIL® R 972, R 974, R 812, R 812 S, R 202 and R 805 grades may be used. There are many systems where hydrophobic grades are less efficient rheology adjusters, but impart other properties to the system such as water resistance, improved leveling, better skin feel, and suspension of pigments with less viscosity increase.

Figure 3



— Carbontetrachloride — Dibutylphthalate — Benzene
 — Methylacetate — Acetone — Water — Butanol

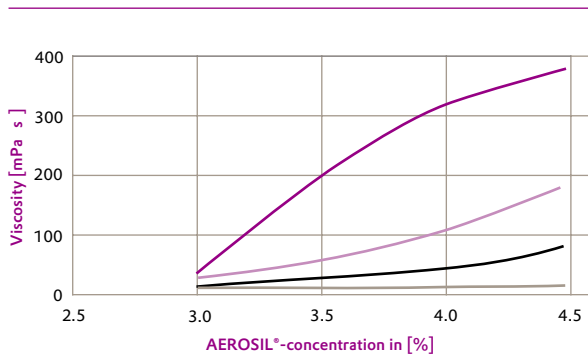
Thickening of various solvents with AEROSIL® 200

The type of liquid medium used is an important consideration. In general, higher viscosities can be achieved in non-polar systems, compared to polar oils/solvents/resins. In this sense, the term “polar” is used to mean the ability of the molecules in the liquid to form hydrogen bonds. **Figure 3** shows the viscosities that can be achieved with AEROSIL® 200 in solvents of varying polarity. AEROSIL® fumed silica is in general not an efficient thickening agent for aqueous systems.

Another important consideration is whether to use a hydrophilic or hydrophobic AEROSIL® fumed silica type. As discussed before, hydrophobic AEROSIL® R-types are often less efficient thickeners for oleo-gels than are hydrophilic grades. However, especially in personal care applications, they have the advantage of a better skin feel. As suspension stabilizers they function similarly, and they can also impart hydrophobicity to a formulation (water- and sweat resistance in cosmetic emulsions, for instance). In many cases, use of hydrophobic grades results in better gel stability due to the better wetting of the silica by the non-polar medium.

Figure 4 shows the differences in the viscosity of mineral oil (PKWF 4/7 from Dow, a printing ink oil) obtained with hydrophilic AEROSIL® 200 and various hydrophobic AEROSIL® types.

Figure 4



— AEROSIL® 200 — AEROSIL® R 974
 — AEROSIL® R 972 — AEROSIL® R 805

Viscosity increase achieved in mineral oil using hydrophilic AEROSIL® 200 and various hydrophobic AEROSIL® types

Whatever the use, loading levels in most coating and ink applications are relatively low. In the final formulation, less than 1 % by weight (based on the total system) is usually suggested as a starting point. AEROSIL® loading levels for anti-settling properties may approach 2.0 % if the formulation contains high loadings of other pigments and fillers. For adhesives, sealants and some personal care applications, loading levels are or can be considerably higher, 4 %–8 % by weight (based on the total system), because the desired thickening and thixotropy is higher. The actual percentage is dependent on the initial viscosity condition of the system, the desired condition and the desired length of storage stability. The optimum loading is determined by trial and error and is very system specific.

3 Applying Proper Dispersion

Low and high shear dispersion

To maximize the efficiency of AEROSIL® fumed silica and to ensure performance consistency, proper dispersion is required. Low shear dispersion (LSD) with a propeller or stirring blade is insufficient shear for fumed silica in general. Peripheral velocity (tip speed) for this type of mixing is 1.5–6 m/s (5–20 ft/s). At these rates, minimal energy is used to wet the fumed silica. The results are inconsistencies in thickening from batch-to-batch, loss of efficiency whereby more AEROSIL® fumed silica needs to be added, poor grind behavior, settling, and poor storage stability.

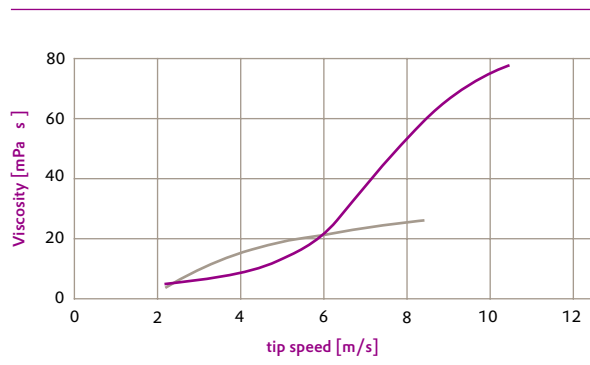
High shear dispersion (HSD) utilizing an aggressive saw-tooth type blade (also known as a dissolver, see **Figure 5**) is the minimum shear that is required for AEROSIL® grades with surface areas of 50–200 m²/g (both hydrophilic and hydrophobic). Higher surface area AEROSIL® grades (such as AEROSIL® 300, AEROSIL® 380, AEROSIL® R 812 and R 812 S) usually require more energy intensive equipment for optimizing dispersion. Peripheral velocity for HSD equipment can be more than 7 m/s (25 ft/s).



Figure 5: Dissolver blades

For most industrial applications, Evonik suggests tip speeds ranging from 8 - 10 m/s (26 - 32 ft/s) for sufficient shear (**Figure 6**).

Figure 6



- 2.5 % AEROSIL® 200 in silicone oil AK 10
- 3 % AEROSIL® 200 in dibutylphthalate

Influence of tip speed in m/s on the viscosity of two systems of different polarity.

Table 1

Calculation: $\frac{d \text{ in mm} \cdot \pi \cdot \text{rpm}}{60 \cdot 1000} = \text{m/s}$								
Blade diameter in mm	Blade circumference in mm	1000 rpm	1500 rpm	2000 rpm	2500 rpm	3000 rpm	4000 rpm	5000 rpm
... m/s Peripheral Velocity								
30	94.25	1.571	2.356	3.142	3.927	4.712	6.283	7.854
40	125.67	2.095	3.142	4.189	5.236	6.284	8.378	10.473
50	157.08	2.618	3.927	5.236	6.545	7.854	10.472	13.090
60	188.50	3.142	4.712	6.283	7.854	9.425	12.566	15.708
70	219.91	3.665	5.498	7.330	9.163	10.996	14.660	18.326
75	235.62	3.927	5.891	7.854	9.818	11.781	15.708	19.635
80	251.33	4.189	6.283	8.378	10.472	12.566	16.755	20.944
90	282.74	4.712	7.068	9.425	11.781	14.137	18.849	23.562
100	314.16	5.236	7.854	10.472	13.090	15.708	20.944	26.180

Calculation of peripheral velocity as related to blade diameter and revolutions per minute (rpm)

As a rule of thumb, calculate the maximum production scale tip speed first, and do not exceed this in laboratory trials. This will help avoid scale-up problems later.

Relation of blade size to vessel size in batch processes

Critical aspects for high shear dispersion also include the blade : vessel ratio (see **Figure 7**). The blade:vessel diameter ratio should be 1 : 2 to 1 : 3. Using this ratio, a strong vortex should be observed straight down to the dispersing blade. When the ratio approaches 1 : 4, material often clings to the sides of the tank. In this case, a clear vortex is not observed down to the blade. When

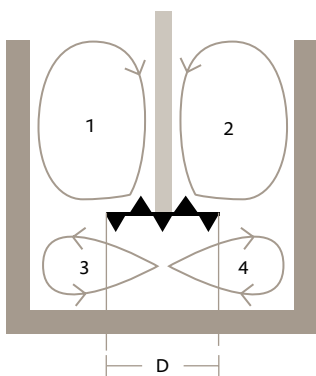
blades are too small, only the shaft may be visible, and wet-in of powders takes longer. The blade should be positioned such that material is pulled from the bottom of the vessel up into the dispersing blade (normally 0.5–1 blade D). Optimal blade positioning creates four mixing zones (see **Figure 7**).

The top two mixing zones are pulled down into the dissolver blade and the bottom two mixing zones are pulled up into the dissolver blade. Blade sharpening and tightening of belts should be part of routine maintenance as both contribute to efficiency and consistency of dispersion.

High intensity mills, sand mills, media mills and roller mills are sufficient and are suggested for dispersing high surface area (> 300 m²/g) AEROSIL[®] grades and for all products requiring the highest thickening efficiency, best long term stability, best grind values and best gloss (coatings, nail polish, etc.). Performance of all AEROSIL[®] grades improves with increasing external and internal shear forces (**Figure 8**).

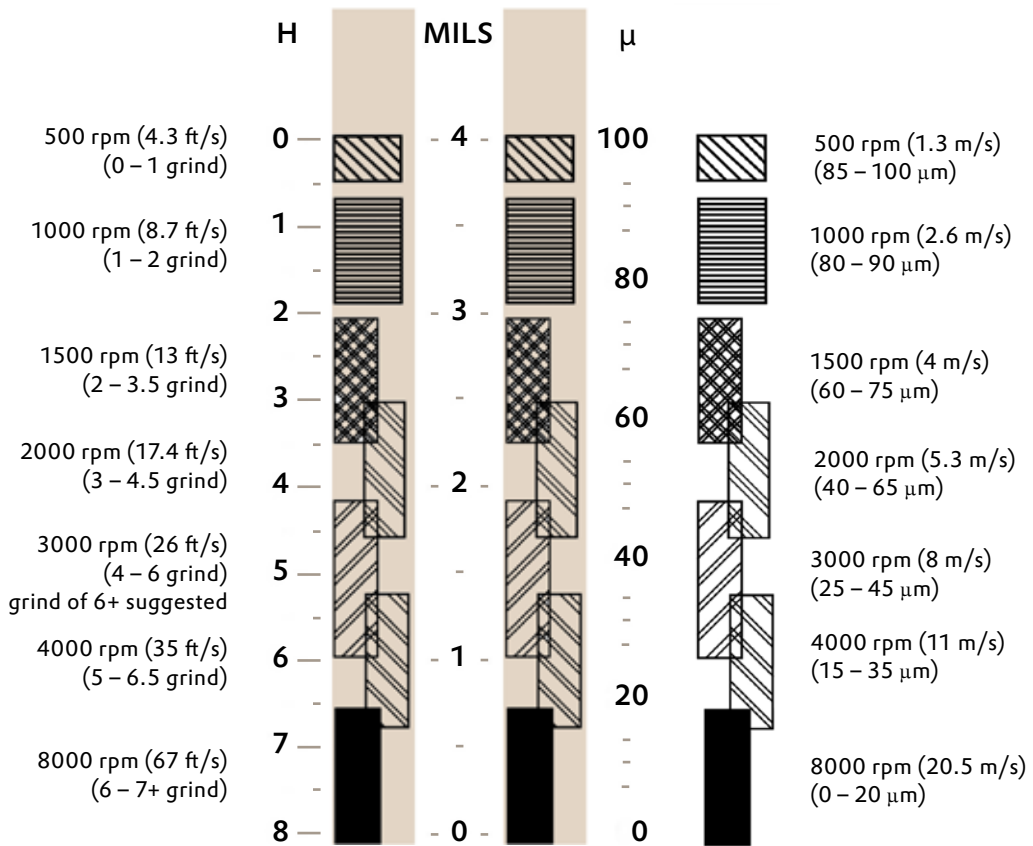
Rotor-stator systems are another type of high shear dispersion equipment that is suitable for dispersing AEROSIL[®] fumed silica. This type of equipment can have either one or two rotating heads. For singlehead equipment, the tip speed is calculated from the diameter of the inner rotor (**Figure 9**).

Figure 7



Importance of blade: vessel size ratio. 1 + 2 = axial material stream, 3 + 4 = radial material stream

Figure 8



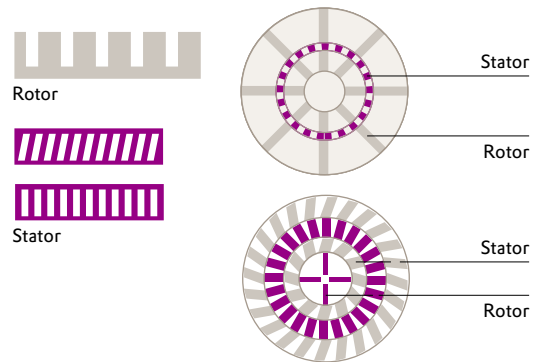
Typical grind values vs. dispersion (tip) speed. The left scale shows US units and Hegman grind, the right scale shows metric units and μ grind.



Figure 9: Single rotor-stator mixing head

In systems with two rotors (**Figure 10**) there are really two “tip speeds”, an inner one and an outer one, based on the diameter and rotational speed of each rotor. The tip speed should be calculated for both. The calculation is the same as for a toothed-blade (dissolver) system. On a large scale, rotor-stator systems can offer continuous production.

Figure 10



Schematic view of a double rotor-stator mixer showing the inner and outer revolving part and the stationary stator(s). The slit geometry of the stators as well as the geometry of the rotor tips vary by manufacturer.

Some systems can pull the AEROSIL® fumed silica directly from the packaging into the mixer, so that dust is minimized (**Figure 11**). The equipment manufacturer should be consulted for details.

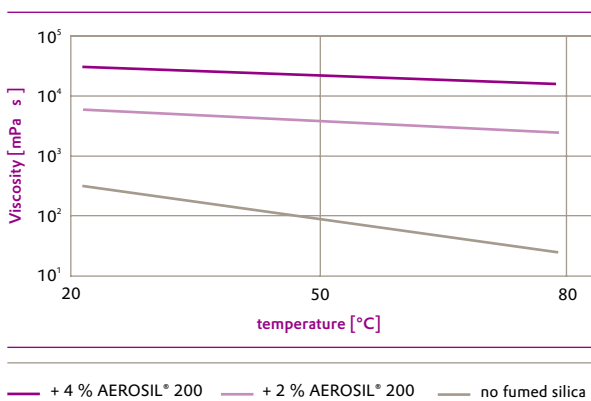


Figure 11: Continuous rotor-stator mixer showing the inlets for the AEROSIL® (A) and the liquid (B), and the outlet for the product (C). This system is practically dust-free.

Dispersing time

Length of dispersing time should be kept to a minimum to prevent excessive temperature build-up. Longer dispersing times result in lower mixing viscosity due to the higher mixing temperatures. Continued mixing at higher temperatures does more harm than good to many systems. However, some systems are not negatively influenced by dispersion temperature (Figure 12).

Figure 12

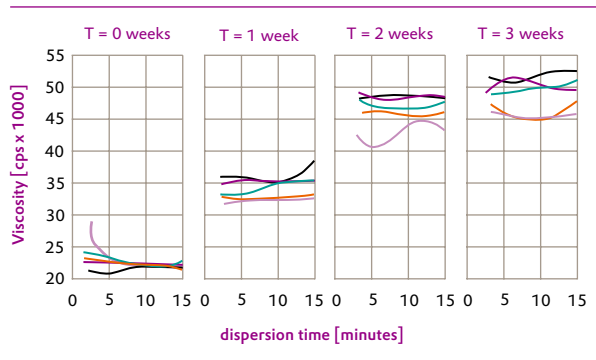


Influence of temperature on the viscosity of paraffin oil thickened with AEROSIL® 200 (identical dispersion conditions, except for temperature).

Optimum mixing time and temperature are system specific and must be established empirically for each formulation. Results from tests show that once sufficient energy is put into the system (rpm/tip speed), processing time becomes less critical (see Figures 13

and 14 for examples using two different types of unsaturated isophthalic polyesters). Also, when dispersion is optimized, slight changes in processing procedures or parameters have less of an impact on the consistency of the final product.

Figure 13 a

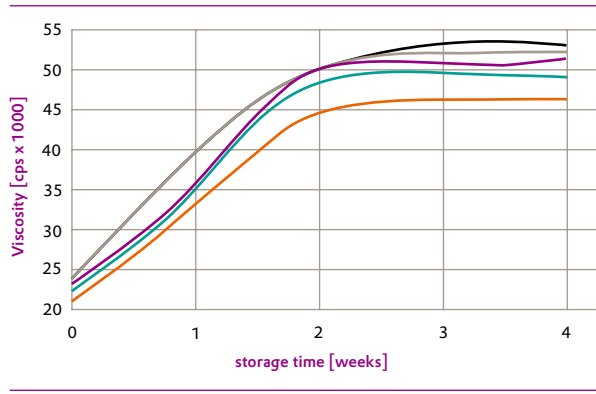


— 8000 rpm — 4000 rpm — 3000 rpm
— 2000 rpm — 1200 rpm

Viscosity vs. dispersion in Polyester Resin 1

When insufficient energy is put into systems, all changes in processing can drastically affect the efficiency of AEROSIL® fumed silica and the consistency of the final product.

Figure 13 b

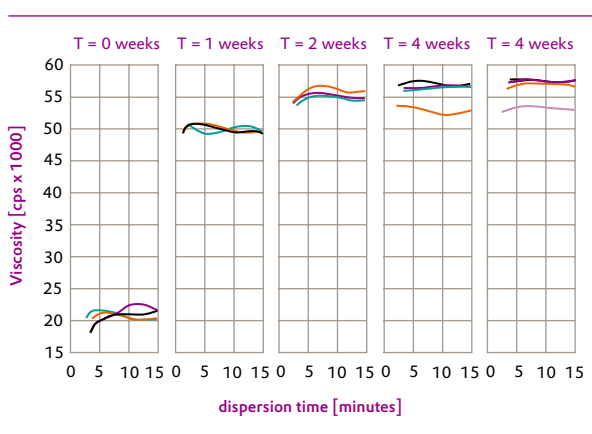


— 8000 rpm / 67.0 ft/s — 4000 rpm / 34.8 ft/s
— 3000 rpm / 25.9 ft/s — 2000 rpm / 17.4 ft/s
— 1200 rpm / 10.4 ft/s

Viscosity stability vs. dispersion in Polyester Resin 2

Sufficient time should be allotted for batch preparation, especially if bags of AEROSIL® fumed silica are used in the process. Batch preparation involves the time needed to open all the bags necessary to complete the batch.

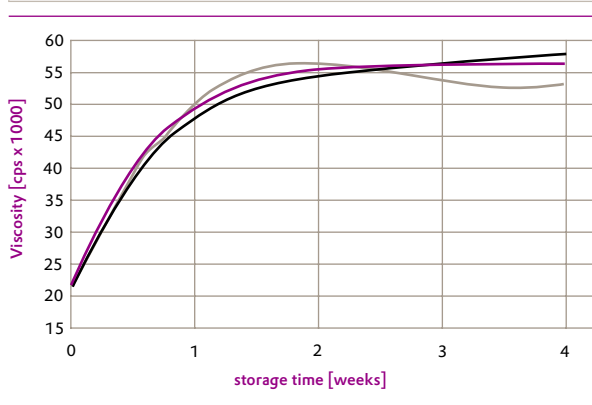
Figure 14 a



— 8000 rpm — 4000 rpm — 3000 rpm
 — 2000 rpm — 1200 rpm

Viscosity vs. dispersion in Polyester Resin 2

Figure 14 b



— 8000 rpm / 67.0 ft/s — 4000 rpm / 34.8 ft/s
 — 1200 rpm / 10.4 ft/s

Viscosity stability vs. dispersion in Polyester Resin 2

Wet-in time is considered the time required for all the fumed silica to be wetted by the vehicle or liquid medium. At this stage, low shear mixing is most often used. Once all the fumed silica is wetted, the mixing speed is increased and only then does dispersion begin. The time it takes bags to be broken and material to wet-in can be operator dependent. Different operators can be faster or slower at this point. If time is not allowed for each of these periods, some batches may receive more or less dispersion time depending on the operator. Systems for the automated addition of AEROSIL® fumed silica from a hopper or FIBC (Flexible Intermediate Bulk Container, or “big bag”) are possible. In general, the feed rate (either manual or automatic) should be adjusted to the wet-in capacity of the material for the fumed silica. This minimizes the wet-in time so that dispersion can begin. If all of the AEROSIL® fumed silica is added to the top of the liquid at once, wet-in time is increased significantly.

Addition sequence and wet-in

The sequence of AEROSIL® addition is critical in many processes. Tests show that AEROSIL® fumed silica should be one of the first components added after the oil/resin. AEROSIL® fumed silica should not be pre-dispersed into solvent first, but dispersed in film forming liquid components. It also should be wetted in at the highest viscosity condition possible, with as little solvent as possible. Some resins or oils show preferential wetting of AEROSIL® fumed silica. In these cases, it is best to disperse AEROSIL® fumed silica into the better wetting vehicle as a masterbatch, then bring this AEROSIL® concentrate into other systems where wetting may not be as good. In water-reducible systems, the sequence of addition is especially critical for hydrophobic AEROSIL® grades. It is suggested that the AEROSIL® fumed silica be added into the vehicle first, without the water adjustment.

Once the AEROSIL® fumed silica is wetted in, the other pigments, fillers, and additives can be added. If water encapsulates unwetted hydrophobic AEROSIL® fumed silica, further dispersion becomes very difficult. In emulsion systems, both AEROSIL® 200 and AEROSIL® R 972 are successfully used for improving pigment suspension and anti-sag properties. Incorporation is suggested at the highest resin solids state, preferably higher than 40%.

Incorporation of hydrophobic grades becomes very difficult once the resin solids drop under 38%. After wet-in and proper dispersion, final letdowns with water can be conducted. Dispersion of AEROSIL® fumed silica in the pigment grind portion is always recommended. Making concentrated masterbatches of AEROSIL® fumed silica, pigments and fillers has proven to give the best long term storage stability and higher overall thickening and thixotropy versus direct addition into the letdown. Evonik Industries does not recommend AEROSIL® fumed silica be added into the letdown or as a “post-add”, due to lower shear forces used for mixing.

Under- and overshear

Undershear is more common than overshear due to inadequate energy input at the dispersing stage. However, overshear may occur in cases where very long dispersing times are used or where very high temperatures in the process are generated which give added wetting characteristics to the resins. Under these circumstances, AEROSIL® fumed silica can be too randomly dispersed.

These longer distances may not be bridged by hydrogen bonding. In these instances, more AEROSIL® fumed silica is needed to increase rheology. An indication of overshear is there is no viscosity and thixotropy rebound after shearing. An indication of undershear is poor grinds, lower viscosity achieved and poor long term stability.

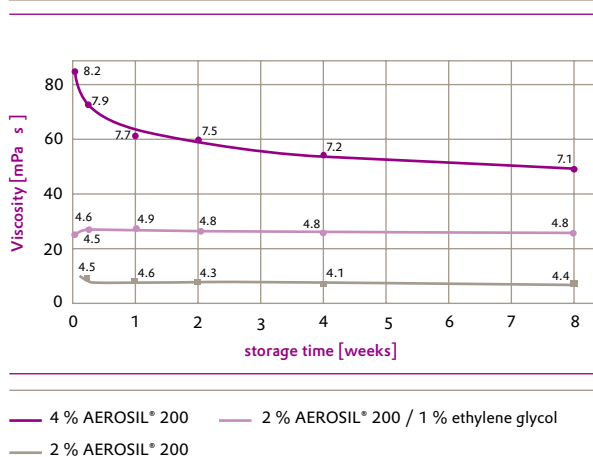
4 Completing the Formulation

After dispersion is complete, remaining components can be added under letdown/low shear mixing. At this point, application tests need to be conducted to ensure that the loading level and dispersion process was adequate to meet performance requirements. Long term stability testing is also needed to ensure a proper dispersion procedure is established. Poor long term stability can be an indication that dispersion, loading level and/or sequence of addition have not been optimized.

Effect of additives

Certain common types of additives that might be a part of the formulation (examples include aminoalcohols, polyols, polyamines and surfactants) can have an influence on the rheology of a system thickened with AEROSIL® fumed silica. However, the effect cannot be predicted in advance, and has to be determined by trial and error. As part of any testing program, to determine the influence of additives, long-term stability of systems must be checked. See **Figure 15** for an example. Some additives (like ethylene glycol) are successfully used as synergists in non-polar to semi-polar systems with hydrophilic grades of AEROSIL® fumed silica only.

Figure 15



Effect of ethylene glycol on the rheology and storage stability of polybutene (Indopol H-7, BP Chemicals) thickened with AEROSIL® 200.

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