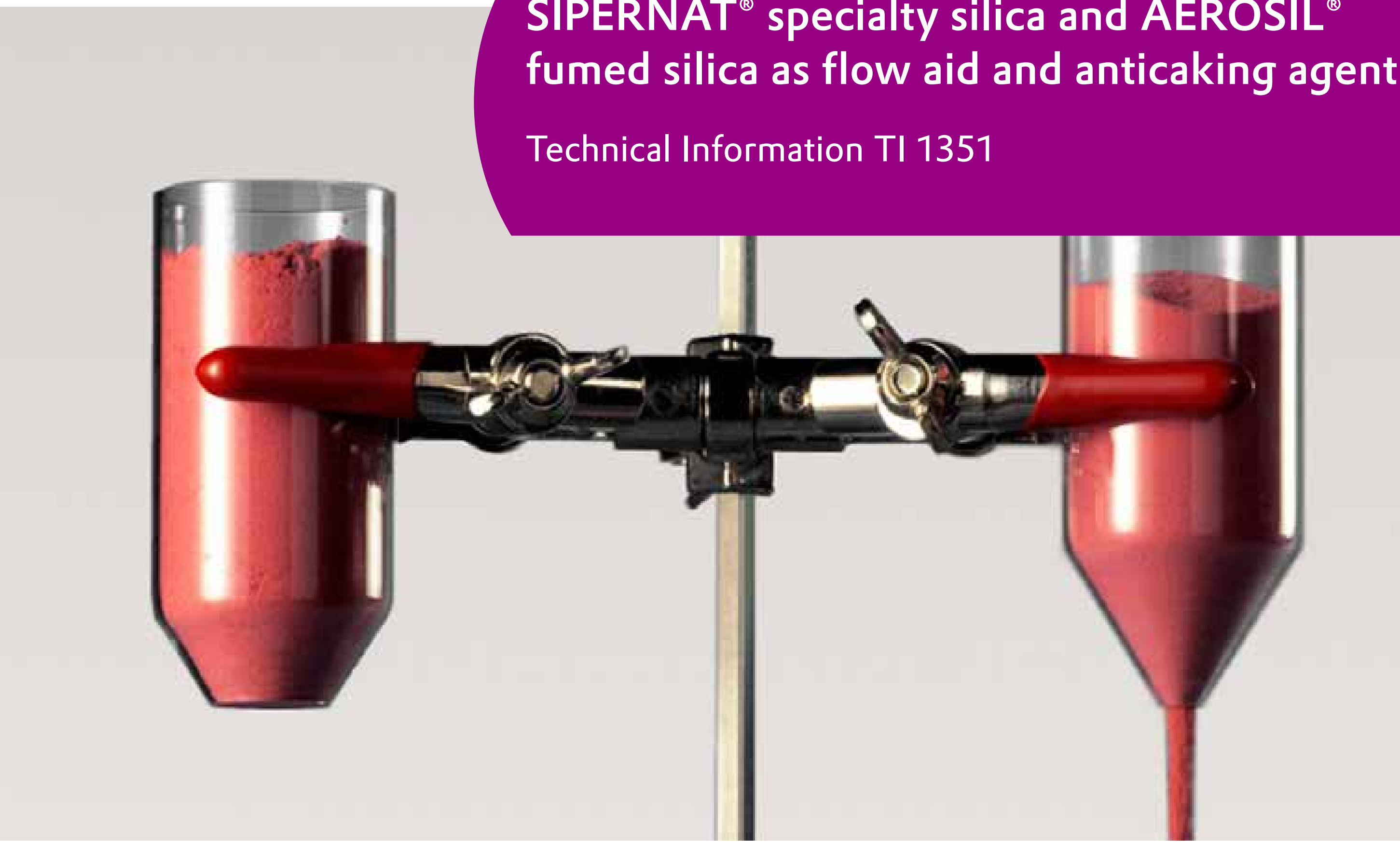
SIPERNAT® specialty silica and AEROSIL® fumed silica as flow aid and anticaking agent

Technical Information TI 1351



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1 Introduction

Powdered ingredients are used increasingly in many industries. A good flowability is the prerequisite for handling powders properly, discharging them easily out of a silo and dosing them exactly. However, many powders are highly cohesive and the proper processing therefore is a challenge. Additionally many powders tend to cake on storage or while being transported due to climate conditions or pressure.

2 Measuring the flowability

To characterize the flow behavior of powders, several methods can be used. One of these methods is called the 'Angle of Repose'. The powder passes through a sieve and falls on the top of a metal cylinder which causes the powder to form a cone. When particles fall on the cone, they either stick or roll-off based on the angle of the cone and the stickiness of the particles. As more particles stick, the cone grows steeper until gravity overcomes the cohesiveness. This in turn leads to a cone that has a fixed height and slope. Measuring the height, or the angle of the slope, gives the 'Angle of Repose'. Needless to say, the stickier the particles, the higher the cone will rise and therefore the higher the 'Angle of Repose', as shown on the left in **Figure 1**. A lower angle indicates, however, a better flow, which is shown on the right side.

Figure 1 The cone height indicates bad (**left**) or good (**right**) flowability

Figure 2 Set of glass funnels for measuring the flowability

Another method for quick determination of flowability is to use a series of glass funnels with different outlet diameters. The measurement consists of determining whether the powder is still flowing out of one of the funnels without interruption. An alternative to this method is to measure the length of time that a powder needs to flow through a funnel with a specific outlet diameter.

A more sensitive but still easy method to perform is to use a nest of sieves. In this test the powder is poured onto the sieve with the largest meshes being at the top of the nest. The nest is then vibrated for a given time and part of the powder falls down onto the lower sieves. If the powder is very cohesive, a large amount will stay in the top sieve, however the more flowable the powder, the more material will fall through onto the lower sieve levels and eventually onto the sieve pan. After vibrating the carry over on each sieve is weighed. The mass is multiplied by a given factor for each sieve and the results are added together. The final result yields the measurement for the flowability.

Shear cell measurements are more elaborate and allow for calculating the dimensions of a silo, in order to ensure that a powder may be discharged easily. According to Jenike[1], the ratio between consolidation stress and bulk material strength is defined as the flowability ff_c. A modification to the classical shear cell is the ring shear cell according to Schultze[2].

Equation
Flowability ff_c according to Jenike

$$ff_c = \frac{\sigma_1}{f_c}$$

ff_c = flowability
σ_1 = consolidation stress
f_c = bulk material strength

According to Zimmermann[3], the tensile strength test is another method that can be used to quantify the cohesion forces within a powder in a low densified state. In this measurement, a probe which bears a thin Vaseline film touches the flat surface of a powder and then is lifted up again. The force that is needed to separate the upper layer of powder from the bottom layers is recorded by a sensitive tensile strength tester[4].

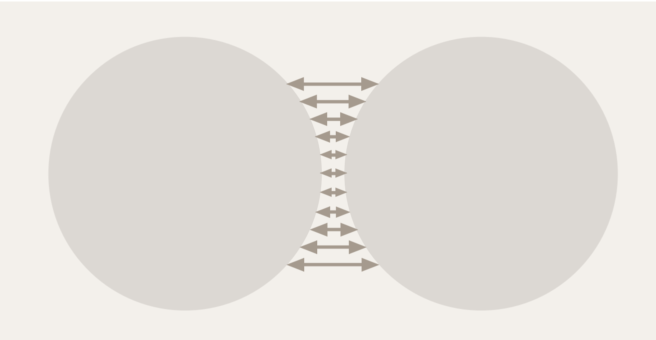
[1] Jenike, A. W.: Storage and flow of solids, Bulletin No 123, Utah Eng. Exp. Station, Univ. of Utah, Salt Lake City, 1970
[2] Dr. Dietmar Schultze, Schüttgutmesstechnik, Am Forst 20, 38302 Wolfenbüttel, Germany
[3] I. Zimmermann, M. Eber, K. Meyer, Z. Phys. Chem. 218, 2004, 51 – 102
[4] Tensile strength tester, developed by Schweiger, modified by Anstett

3 Mode of action of flow aids

3.1 Fundamentals on flow aids

All particles stick together by Van-der-Waals forces as shown in **Figure 3**. For small particles these Van-der-Waals forces are much stronger than the gravitational forces which pull the particles apart and produce the powder flow. Therefore fine powders flow badly.

Figure 3
Particles sticking together by Van-der-Waals forces



Flow aids are very fine powders that can cover the surface of the host powder to create a surface roughness on the powder particle. A surface roughness reduces the attraction forces between two powder particles as shown in **Figure 4**.

AEROSIL® fumed silica and SIPERNAT® specialty silica are perfectly suited to cover the surface of particles, keeping them apart, and thus reducing the attraction forces. This is one of the reasons why they are highly efficient flow aids and anticaking agents. This effect is shown in **Figure 5**. In this brochure the term 'caking' is used as a time related decrease in flowability, which in extreme cases can lead to the formation of one solid 'cake' after a long storage time. Correspondingly the term 'anticaking agent' is used in the sense of a flow agent which can preserve a good flowability for powders that are stored over a long period of time.

Figure 4
Influence of a surface roughness on the attraction between powder particles[5]

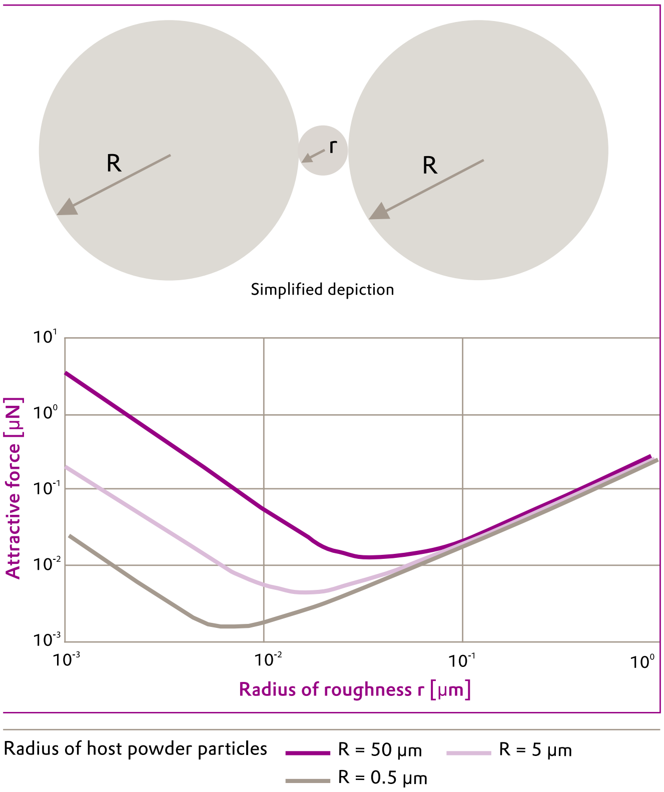
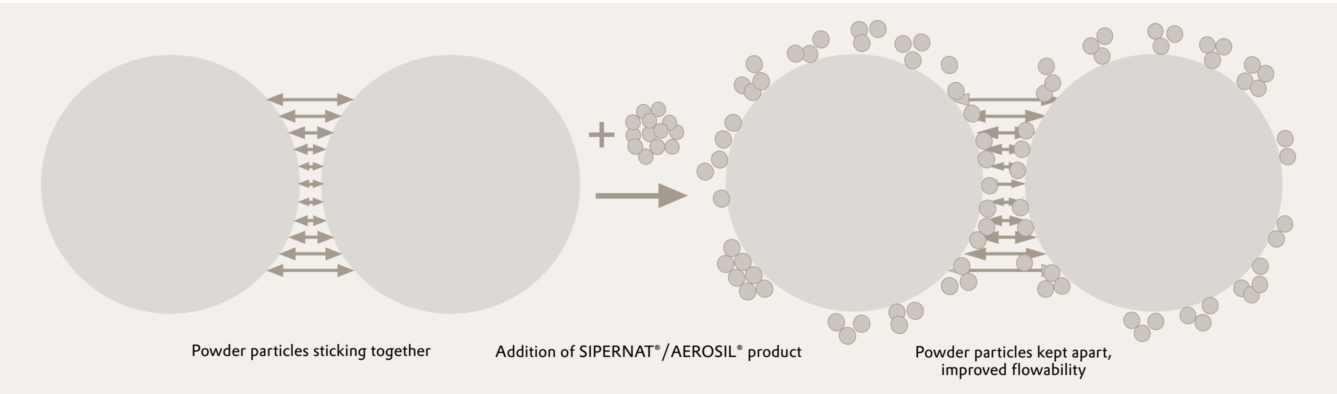


Figure 5
AEROSIL® fumed silica resp. SIPERNAT® specialty silica cover the host powder's surface and act as a spacer



[5] H. Rumpf, Die Wissenschaft des Agglomerierens, Chemie Ingenieur Technik, 46, 1974, 1–11

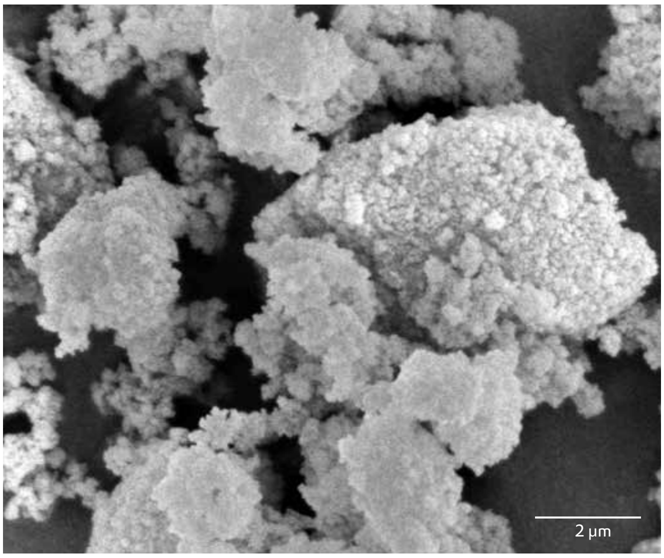
3.2 Flow aids for dry, hard powders

In order to achieve the optimum result in flow improvement, the flow aid must be dispersed finely on the host powder's surface. With SIPERNAT® specialty silica and AEROSIL® fumed silica this fine dispersing can be attained by simply mixing it with the host powder. Suitable mixers are e. g. Ploughshare® mixers, paddle mixers or ribbon blenders.

The following SEM pictures prove this dispersibility. The left picture shows pure SIPERNAT® 320 DS, the right picture shows the surface of a corn starch particle covered with SIPERNAT® 320 DS.

Some SIPERNAT® and AEROSIL® types, however, are easier to disperse than others. This effect was investigated in depth by Prof. Zimmermann, University of Wurzburg, with many different SIPERNAT® and AEROSIL® grades as well as with tricalcium-phosphate, another flow aid which is frequently used in the industry.

Figure 7 shows some of the results. In these tests corn starch was used as a model substance, and mixed with different types of AEROSIL® and SIPERNAT® at different mixing times in a Turbula® tumbler mixer. Afterwards the tensile strength was measured to evaluate the flowability. High values for the tensile strength refer to bad flowability, low values show good flowability. One can see that after a short mixing time the flowability improved with all of the used flow aids. However some, for example, the hydrophobic SIPERNAT® D 17, showed especially good results. With a long mixing time the flowability deteriorates again. This could be caused by a loss in surfaces roughness due to the extremely fine dispersing of the flow aid on the corn starch surface.



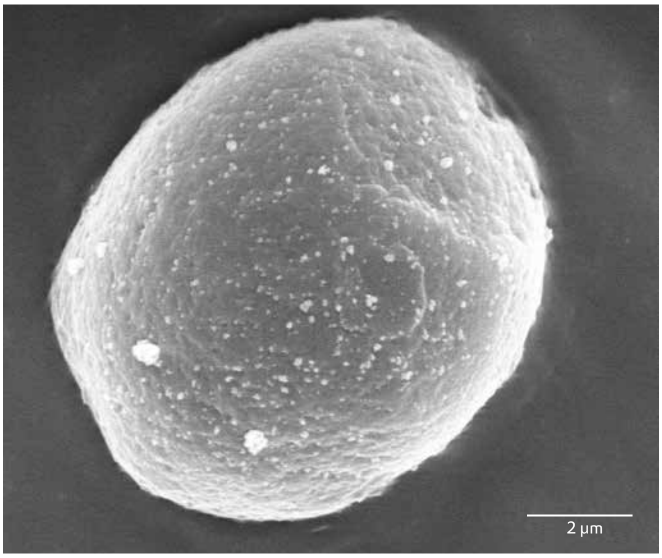
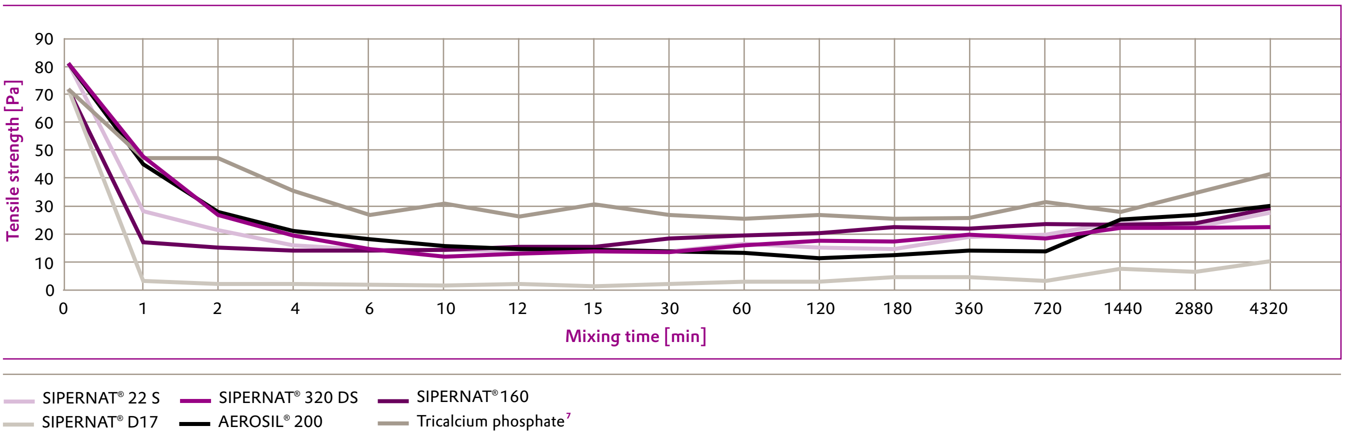


Figure 6 SEM pictures of pure SIPERNAT® 320 DS (left) and a corn starch particle covered with SIPERNAT® 320 DS (right)

Figure 7
Tensile strength of corn starch with 0,2% flow aid according to mixing time[6]



[6] A.-K. Peter, PhD-Thesis, 2007, University Würzburg
[7] Tricalcium phosphate, Cafos M, Budenheim, Germany

3.3 Flow aids for wet powders

Wet powders flow badly due to the liquid film at the surface of the powder particles which glues them together. This liquid may be water, an aqueous solution or oil. A flow aid can improve the flowability by absorbing the liquid film. This process is shown in **Figure 8**.

For absorbing the liquid, a flow aid of high porosity is a prerequisite as it absorbs the liquid into the pores by capillary action. That is one of the reasons why SIPERNAT® specialty silica with their high porosity are excellent flow aids in wet powders.

Depending on the mixing conditions, however, part of the porosity of the flow aid can be lost. The disintegration of the silica agglomerates to the submicron range as shown in **Figure 6**, contributes to a loss in absorption capacity. In other words: A very good dispersion of the flow aid, which is beneficial for the efficiency in dry powders, may reduce the efficiency in wet powders. For wet powders highly porous and mechanically more stable silica types are an advantage. Thus different types of SIPERNAT® specialty silica and AEROSIL® fumed silica which meet the requirements for the different host powders that need flow improvement were developed by Evonik.

Figure 9 shows a comparison between SIPERNAT® 50 S and SIPERNAT® 22 S being used as a flow aid in a wet salt mixture. The wet salt mixture itself shows a poor flowability. (Flow grade 7, measured according to the flow funnel method.) Directly after addition of 0.6 % of SIPERNAT® 22 S or SIPERNAT® 50 S the flowability improves within 1 minute of mixing to flow grade 2.

After longer mixing, however, the silica is too finely dispersed and subsequently the porosity is reduced and the flowability becomes worse again. Depending on the mixing intensity this overmixing effect can happen within a few minutes with SIPERNAT® 22 S, whereas SIPERNAT® 50 S can resist for a much longer period of time without loosing efficiency.

Figure 9
Resistance against overmixing for SIPERNAT® 22 S and SIPERNAT® 50 S at 400 rpm

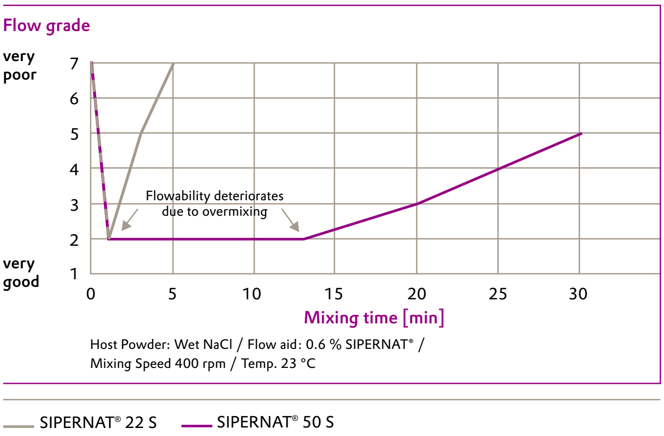


Figure 10
Resistance of SIPERNAT® 22 S against overmixing depending on mixer speed

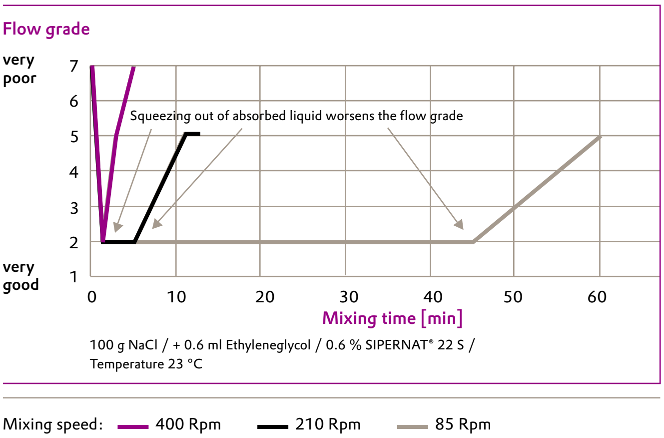
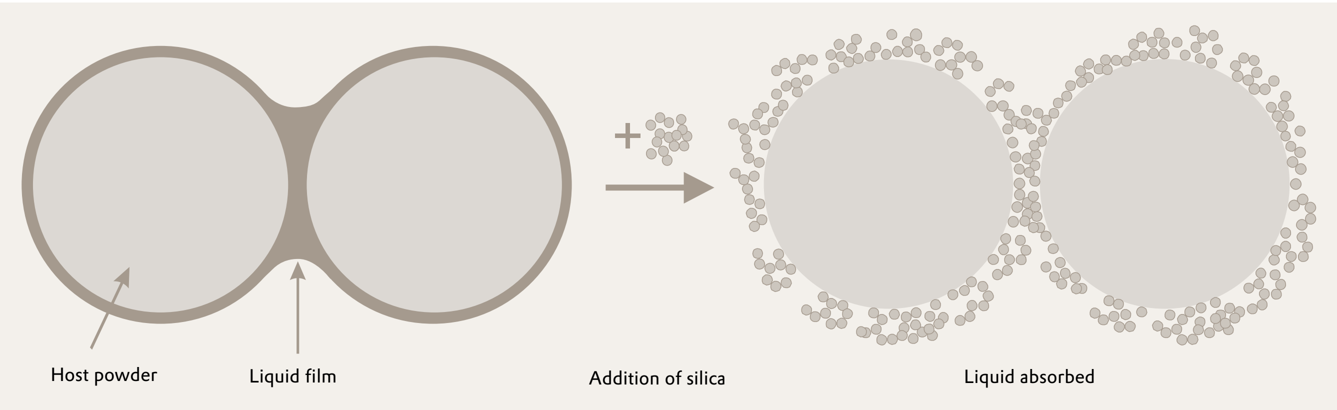


Figure 8
Silica absorbs liquid from a wet powder's surface



Applying lower shear resp. reducing mixing speed and intensity the efficiency of SIPERNAT® 22 S can be kept for a longer time, which is shown in **Figure 10**.

The liquids that make a wet powder sticky can be either water- or oil-based. In case it is water there is another possibility how to improve the flowability besides the absorption of the liquid. Hydrophobic silica have proven to be very efficient flow aids especially for hygroscopic substances.

Hydrophobic silica do not absorb the water film but float on it, spacing the particles apart, as shown in **Figure 11**. They improve the flowability at lower addition levels, as their efficiency is not limited to the absorption capacity. Hydrophobic silica can also be sensitive to overmixing as they can be wetted by water if too high shear forces are applied. The more hydrophobic a silica is the less sensitive it is to overmixing.

Figure 12 shows the effect of the hydrophobic silica SIPERNAT® D10 and SIPERNAT® D17 on a wet salt mixture. The flowability of the salt is improved immediately by addition of 0.4 % of the resp. SIPERNAT® type. By longer periods of mixing the flowability deteriorates because the silica can be wetted due to too high shear energy. This overmixing effect happens after 3 minutes with SIPERNAT® D17 whereas SIPERNAT® D10 is more resistant and can be mixed up to 12 min at a given shear rate without reduction in flowability.

Figure 12
Sensitivity of hydrophobic SIPERNAT® types to overmixing

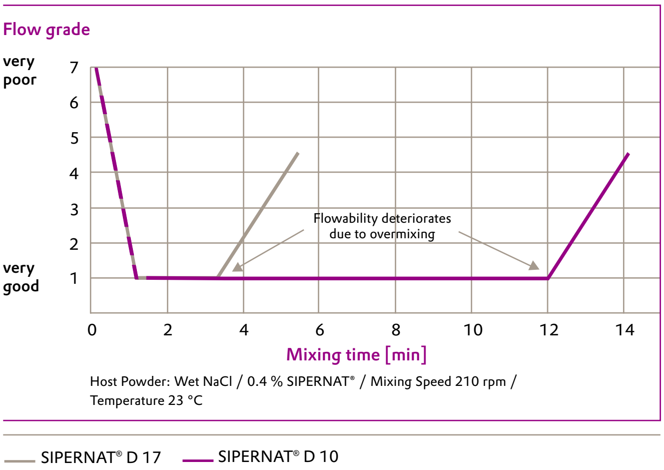
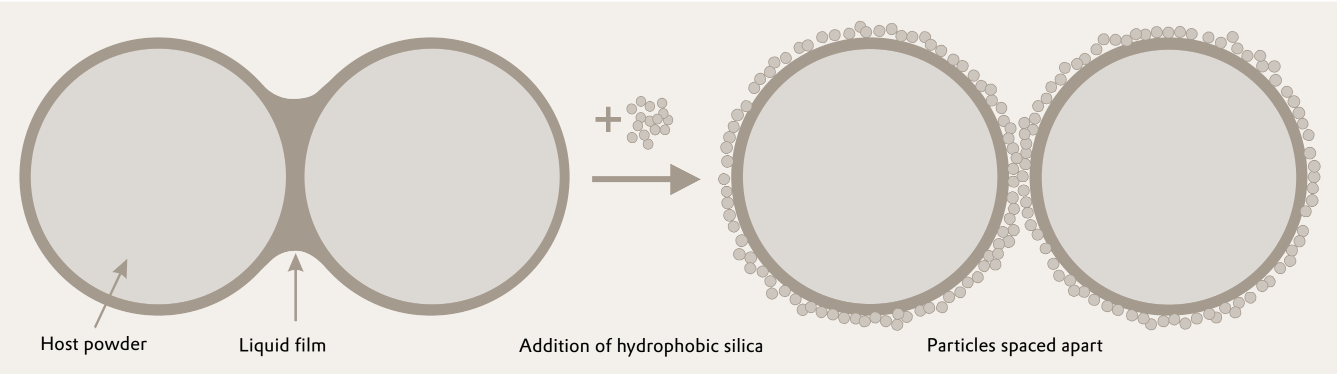


Figure 11
Hydrophobic silica separate water films on hygroscopic substances



3.4 Conclusion for dry and wet powders

Deagglomeration of the flow aid during mixing with the host powder…

+ … Leads to a better coverage of the host powder and therefore increases the efficiency of silica as a flow aid in a **dry** powder.

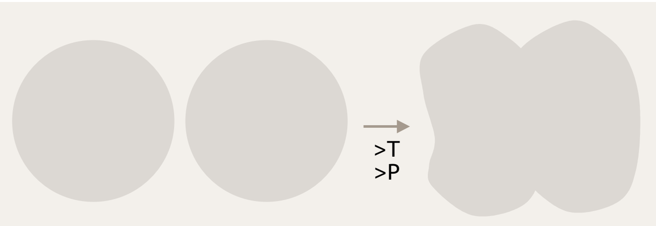
– … Reduces the porosity of silica and therefore reduces the efficiency of silica as a flow aid in a **wet** powder.

> Depending on the type of powder, different mixing procedures and different silica types are recommended.

3.5 Flow aids / Anticaking aids for soft powders

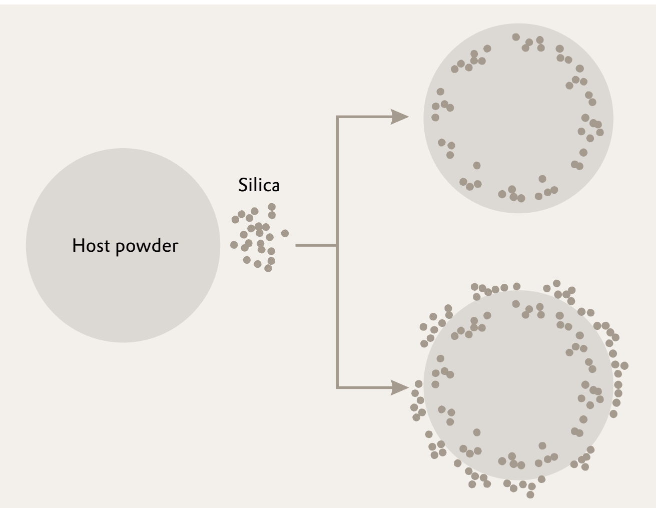
Powders of soft materials such as fats, waxes or emulsifiers are especially challenging in handling and transport. Especially on long term storage or transport time they tend to cake heavily. The problem becomes even worse when the product is exposed to changing temperatures – which can easily happen during sea transport. An efficient anticaking aid is therefore a prerequisite when such powders are shipped for long distances. Soft or thermoplastic powders are deformed at rising temperature or when pressure is applied and stick together as shown in **Figure 13**.

Figure 13
Soft or thermoplastic particles stick together as they are deformed on pressure and rising temperature.



Silica can cover the soft powders' surface and prevent the particles from sticking together. In contrast to hard powders, however, higher addition levels of silica are needed to achieve this effect, especially when a long lasting anticaking effect is required. Usually addition levels of silica in soft powders can be up to 5 %, whereas in hard, dry powders addition levels below 1 % are often sufficient. The reason is that part of the anticaking agent may penetrate into the soft powder's surface on storage and thus loose its efficiency. When an adequate amount of anticaking aid is added, enough will stay on the surface of the soft powder particle and the efficiency is preserved. This effect is shown in **Figure 14**.

Figure 14
Soft powders capture part of the anticaking aid



4 Mixing technology

The mixing technology has a major influence in the efficacy of a flow aid. As explained in the previous chapters concerning hard, dry powders the mixing must be intense enough to disperse the silica agglomerates, as intense mixing leads to better results. For wet powders, on the other hand, mixing too intensely partially destroys the silica porosity and reduces the efficacy as anticaking aid. For soft powders the mixing intensity has to be adapted to the individual characteristics of the powder to avoid the soft powders structure being damaged.

Tumble mixers provide a very gentle mixing; they can be used for very soft powders. Cone mixers like the Nauta® mixer are also very gentle, but require longer mixing times. Paddle mixers are very gentle and at the same time homogenize the mixture very well on a macroscopic scale. They are a very good choice for all soft powders as well as for hygroscopic powders where the porosity of the silica needs to be preserved. Ploughshare® mixers apply more mixing energy but still are gentle enough not to press the flow aid into the soft powder's surface. Ploughshare® mixers can be used for a wide range of different powders. Generally, Ploughshare® or paddle mixers need shorter mixing times. Depending on the individual needs, mixing can be adapted to shorter times for hygroscopic powders and longer times for dry, hard powders. Ribbon blenders are even more intense and are suitable for hard, dry powders. **Figure 15 – 17** show a selection of the described mixers.

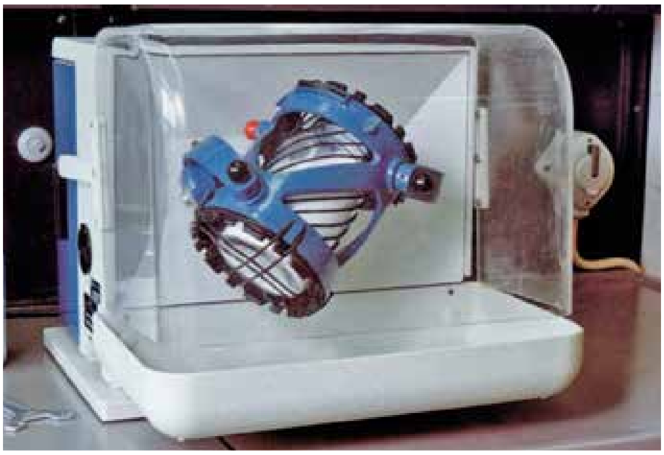


Figure 15
Laboratory scale TURBULA® mixer, Willy A. Bachofen AG, Switzerland

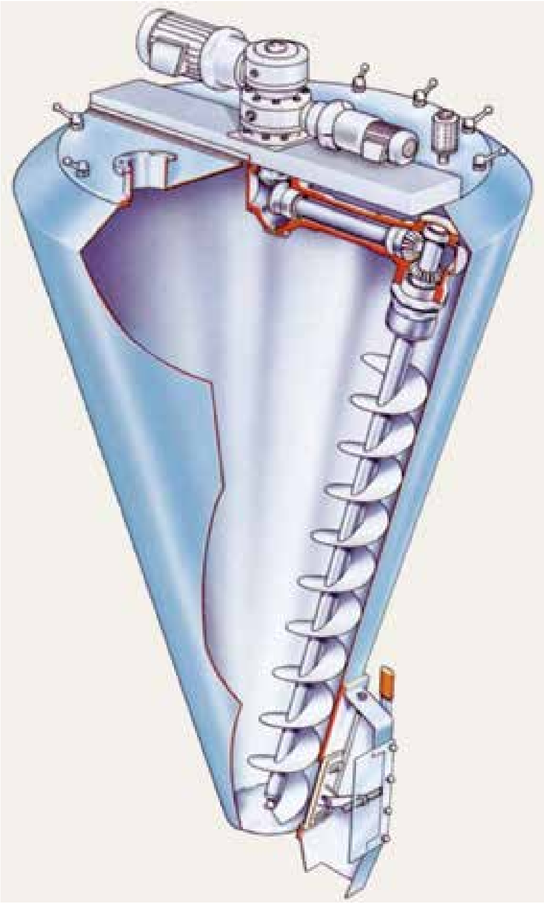


Figure 16
Schematic illustration of a Nauta® Mixer, Hosokawa Micron B. V., The Netherlands

Figure 17
Ploughshare® mixer, Gebr. Lödige Maschinenbau GmbH, Germany

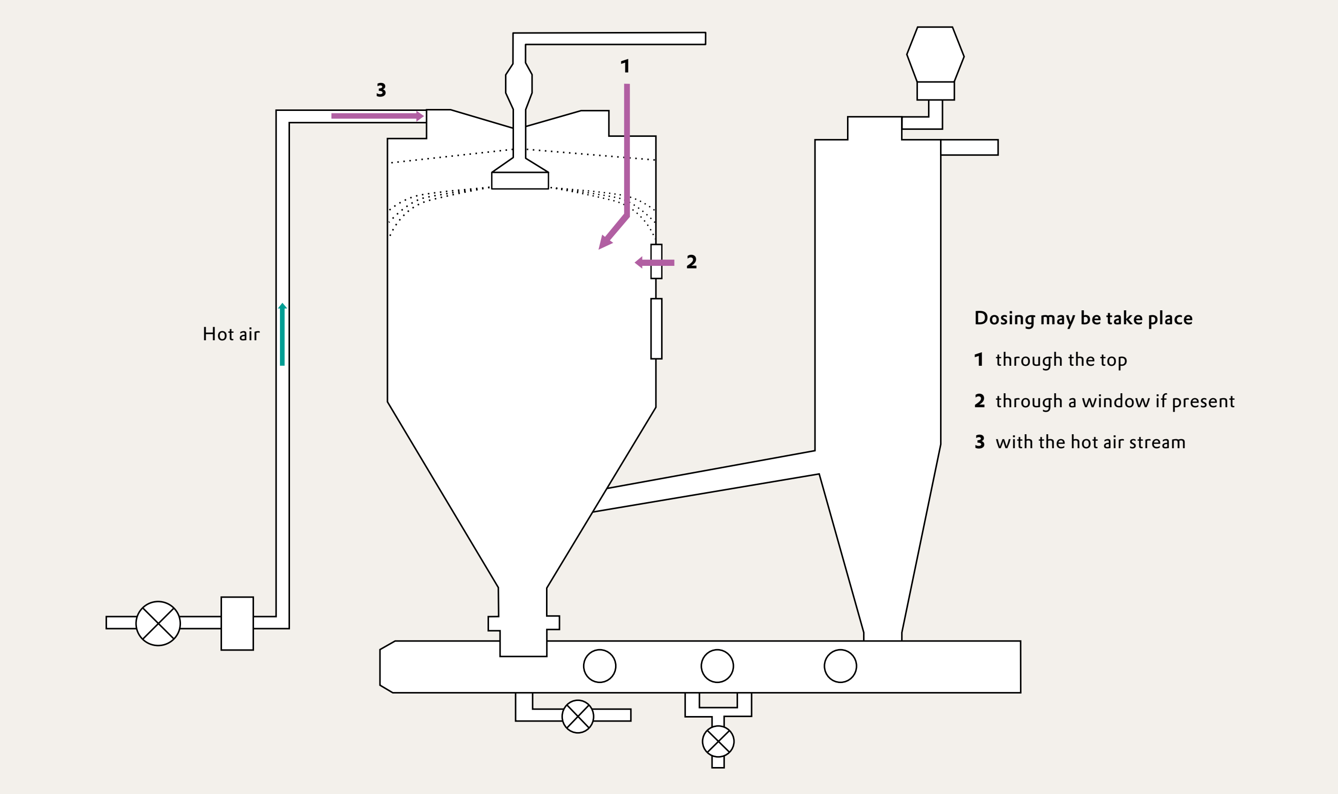
A special case is the flow improvement of spray dried products. The addition of silica directly into the spray drier, separately from the slurry, results in a fine dispersion of the silica at the particles' surface by the air stream while not mechanically stressing the spray dried powder.

Figure 18 shows possible addition points for silica in a spray drying process, of which points 1 and 2 are the most effective ones. A more comprehensive description of mixing technology is given in our Technical Information, TI 1213[8], for silica applications in spray drying processes see TI 1365[9].

[8] AEROSIL® fumed silica and SIPERNAT® specialty silica as flow aid, anticaking agent and carrier – Recommended mixing procedures for powders and granulates, Evonik Resource Efficiency GmbH.

[9] SIPERNAT® specialty silica and AEROSIL® fumed silica in spray drying applications, Evonik Resource Efficiency GmbH.

Figure 18
Addition of silica during spray drying



5 Recommendation matrix

Table 1 summarizes our recommendations on the use of flow aids/anticaking agents in different types of powders.

In real systems, different characteristics of a powder can often be combined. Fruit or vegetable powders may contain hard, dry, non-hygroscopic components like starches as well as hygroscopic components like sugars. Dairy powders may contain hygroscopic lactose as well as soft components like fat. Due to the wide range of applications for flow aids there are many more examples like these. The behavior of such systems often combines the single characteristics from **Table 1** in a complex way.

Thus, individual substances require individual solutions. We look forward to answering your questions and would gladly assist you in finding the proper SIPERNAT® or AEROSIL® product for your individual demand, which not only includes consultancy but also assistance in handling and processing of any of our silica products.

Table 1
Recommendation matrix for flow aids / anticaking agents in different types of powders

	Dry, Hard powders	Wet, Hard powders	Soft powders
Type of silica	Use silica which can be dispersed easily	Use mechanically stable, highly absorptive silica	Use silica which can be dispersed easily
Addition level	Low addition level, often < 1 %	Addition level adapted to the amount of liquid	High addition level, especially if anticaking is needed; up to 5 %
Mixing	Intensive mixing	Gentle mixing	Moderate mixing: Disperse the silica, but do not destroy the soft powder

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