

FLOWABILITY TECHNIQUES IN THE PROCESSING OF POWDERED EXPLOSIVES, PROPELLANTS,
AND PYROTECHNICS

ALLEN J. TULIS

IIT Research Institute, Chicago, Illinois, U.S.A.

ABSTRACT

A very effective flowability additive developed by Dow Corning Corporation is obtained by converting a hydrophilic silica aerogel to a hydrophobic colloidal silica by reacting with hexamethyldisilazane. This additive has been used to prepare homogeneous powder mixtures with a minimum of mixing, to mill difficult materials, and to obtain amazing flow properties in troublesome powders. This hydrophobic silica has an exceedingly light bulk density of about 0.05 g/cc, and a particle size of about one millimicron. It can be premixed before milling and will allow milling of waxy materials. After treatment the powder becomes water repellent and the bulk density increases. Hydrophobic silica additive in amounts less than one percent by weight has often proven effective.

INTRODUCTION

A major problem in the processing of powdered formulations is agglomeration. This problem can be compounded when one or more of the powdered constituents are: (1) hygroscopic, such as ammonium perchlorate or sodium nitrate; (2) waxy or oily, such as nitroguanidine or TNT; or (3) unusually shaped, such as needle-type or flake particles. The agglomeration increases as the particle size decreases. In addition, moisture content directly increases agglomeration and leads to caking of the powder. Therefore, most fine-particled powders, and particularly those that are hygroscopic, oily, or oddly shaped, must be specially handled in all processing and handling operations. This means drying the powders at elevated temperatures, screening to break up or remove agglomerates, and desiccating to prevent moisture uptake.

Another, related problem is created by the milling of powdered formulations necessary to reduce particle size. Hygroscopic, waxy, and oddly shaped particles are difficult to mill except by extreme, and often very expensive, operations. For example, the milling of hygroscopic materials must be done under near-absolute dryness. As the particle size is reduced, the surface area increases and moisture

absorption becomes extensive. As another example, waxy materials can be milled only at reduced temperatures, so that the waxy particles "freeze" and become sufficiently brittle to fragment. Other techniques, such as milling under an appropriate liquid, have also been utilized.

This paper addresses these problems from the point of view of powder flowability. Flowability techniques are described that permit preparing homogeneous mixtures, particularly of explosive, propellant, and pyrotechnic powders, with a minimum of mixing, milling difficult materials, and obtaining amazing flow properties in troublesome powders.

POWDER CONDITIONING

Powder conditioning to overcome agglomeration problems generally involves the use of flow-conditioner additives. These are usually very fine powders of subsieve particle size and include various types of silicates, stearates, phosphates, diatomaceous earth, starch, magnesium oxide, talcum, and fatty amines (ref. 1,2). Calcium stearate and aluminum silicate have been utilized in the food industry where such additives have to conform to food legislation. The mode of action of these conditioners in inhibiting agglomeration and improving flowability has been explained in three ways (ref. 3):

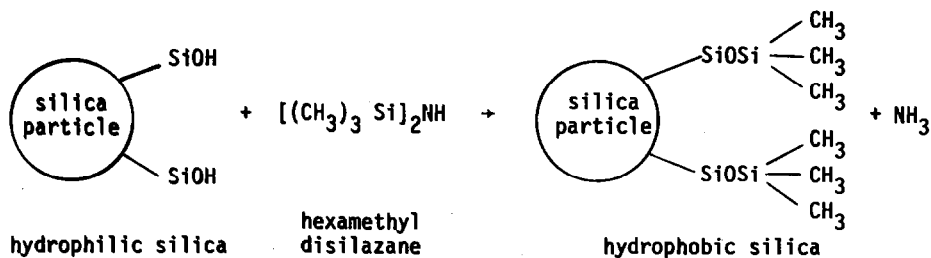
- (1) a solid barrier between the powder particles, reducing their attractive forces
- (2) lubricants of the solid surfaces, reducing the friction between the particles
- (3) neutralizers of electrostatic charges

For powders that are not destined to be consumed as foods, however, a potential solution to this problem was developed by Dow Corning Corporation (ref. 4). In their technique, a hydrophobic fumed silica powder is prepared from a hydrophilic colloidal silica by reacting the latter with hexamethyldisilazane. The effectiveness of this product has been shown in a dry-grinding process to prepare a free-flowing, readily dispersible powder of CN (tear gas), an oily, sticky solid with a low boiling point (ref. 5).

The advantages of this flowability conditioner are many:

- it has an exceedingly light bulk density, about 0.05 g/cc
- the particle size is about one millimicron
- the conditioner can be premixed before milling and will allow milling of waxy or oily materials
- the treated powder becomes water repellent, even if initially hygroscopic
- on a weight basis, less than one percent is often adequate
- the resultant powder generally has a higher bulk density after adding the conditioner
- it is chemically inert, even with sensitive propellants, explosives, and pyrotechnics

The powder is commercially available as SilanoxTM* or TullanoxTM** . The silica aerogel is converted from the hydrophilic to the hydrophobic state by replacing the hydroxyl groups on the surface of the silica particle with siloxane groups:



It is the steric methyl field upon the particles that causes the particles to become hydrophobic.

POWDER PREPARATION

Moisture absorption by powders is an ever-present problem, not restricted to hygroscopic materials. The use of molecular sieves (ref. 6) for near-absolute drying of powders is an excellent procedure. (Molecular sieves are crystalline zeolites that have Angstrom-sized pores for selective and polar adsorption of gases and liquids.) Direct contact of molecular sieves with sensitive materials, such as explosives, however, must be avoided--the heat of moisture adsorption by molecular sieves is sufficiently great that it could cause ignition of sensitive materials.

In some situations, where the addition of an inert material will not degrade the system, the direct admixture of molecular sieves to a powder--particularly before a milling operation if size reduction is required--is advantageous. In the preparation of a water-ignitable pyrotechnic composition of boron and AgF₂, adequate size reduction of the AgF₂ was difficult even under the most sophisticated "dry" conditions. By adding various amounts of molecular sieves to the mixture before milling, however, the dryness of the AgF₂ powder was optimized. (The powders were dried under vacuum over P₂O₅ prior to milling, whether or not molecular sieves were used.) Subsequent ignition tests proved that the molecular-sieve additive system was much faster in ignition, with time delays reduced, for example, from 650 to 220 msec (ref. 7). Even after 24 hours the time delays remained low in the molecular-sieve additive system, actually decreasing to 200 msec. Some of these items were

*SilanoxTM is manufactured by Cabot Corp., Boston, Mass., and is currently not available. It was, however, the hydrophobic silica used in the work described here.

**TullanoxTM 500 is a super-hydrophobic fumed silica manufactured under licensing arrangements with Cabot Corporation, Boston, Mass., by Tulco, Inc., North Billerica, Mass.

stored for several years and remained about as effective as the systems without molecular sieves were initially. (These latter systems did not function after such storage). The amount of molecular sieve additive in this example was 10 percent by weight, although much smaller amounts would have been adequate (ref. 7).

Molecular sieves can be obtained as fine powders. They readily absorb and hold up to 70 percent of their weight in moisture. It should be noted that when the molecular sieves are added to powders they simply transfer the moisture from such powders to themselves in an equilibrium process. Hence the moisture is not removed from the total system but simply from the powder. Their use in this manner is recommended only when a "continuous" drying action of very small amounts of moisture is desired, as in the AgF_2 milling operation. They can, however, be added to powders that are nearly dry and not sensitive to rapid temperature excursions in order to remove tightly bound moisture; they can then be removed by sieve separation. In this case molecular sieve pellets should be used rather than molecular sieve powder.

In certain milling operations we have found it advantageous to use both molecular sieves and hydrophobic silica: the molecular sieves achieve near-absolute dryness of the particles in the milling process so that, as the particles are fragmented, the hydrophobic silica instantly coats their surfaces. This minimizes subsequent absorption of moisture and greatly aids the milling action. This is particularly effective when one of the milled components is hygroscopic and the other is waxy; e.g., ammonium perchlorate and nitroguanidine.

The hydrophobic characteristic of powders treated with hydrophobic silica can be readily illustrated. Figure 1 illustrates ammonium perchlorate powder, with about 3 percent SilanoxTM additive, floating on the surface of water. (Ammonium perchlorate is readily soluble in water.) Figure 2 illustrates how this ammonium perchlorate powder now repels water even when submerged under the water. Figure 3 shows two samples of ammonium perchlorate, one with SilanoxTM added and the other untreated, after extended exposure to a humid atmosphere. There is no agglomeration in the SilanoxTM-treated sample, whereas the untreated sample is agglomerated badly.

The exceedingly high water repellency of powders conditioned with hydrophobic silica is attributed to air entrapment upon the surface of the powder particles. The water surface actually rests on the millions of points of the hydrophobic silica projections coating the surface of the powder particles. This same effect occurs in nature, with insects and foliage which repel water so efficiently that a sheen from the surface air film is observed when they are totally submerged under water. Such a sheen is also observed on the submerged powder in Figure 2. Hence both steric hydrophobicity and physical separation of the water surface from the powder particle surface by the air film combine to create a super-hydrophobic condition. This effect is fully described in a TullanoxTM product bulletin published by Tulco, Inc. (see footnote on page 2).

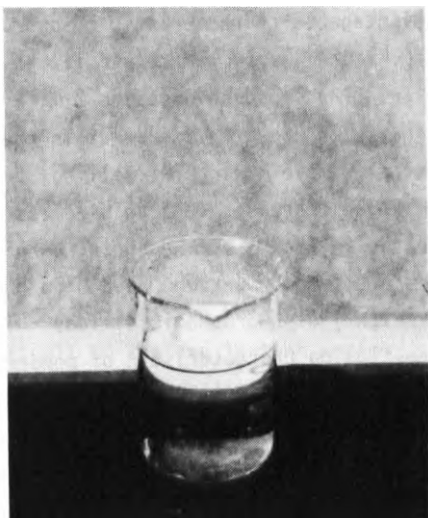


Fig. 1. Ammonium perchlorate powder floating on surface of water after being mixed with about three percent hydrophobic silica additive.

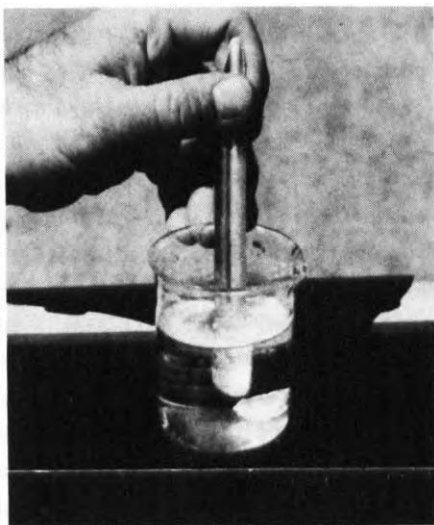


Fig. 2. Dry hydrophobic silica additive ammonium perchlorate powder submerged under water.

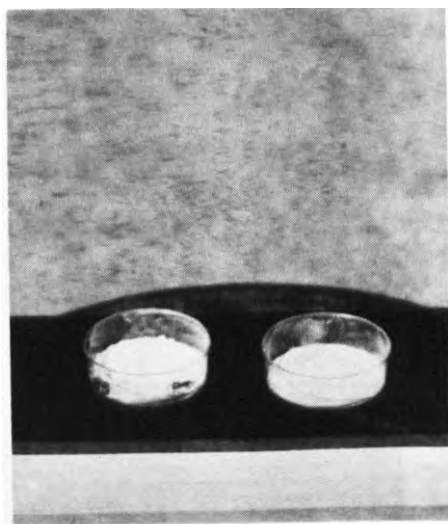


Fig. 3. Comparison of the effect of humidity on (left) ammonium perchlorate powder and (right) ammonium perchlorate powder with about three percent hydrophobic silica additive.

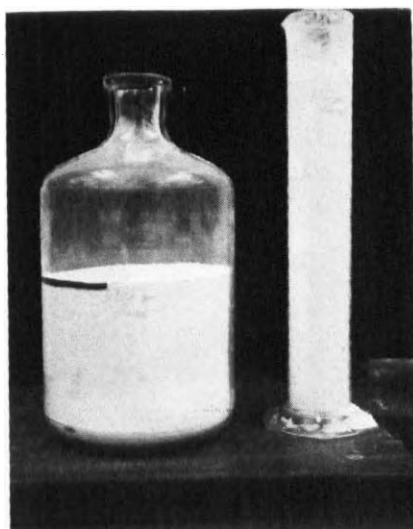


Fig. 4. Six liters BoraxTM powder in a jar and two liters of SilanoxTM in a graduate before mixing.

Figures 4 through 6 illustrate another advantageous characteristic of hydrophobic silica. The powder used was Borax. In Figure 4 approximately 6 liters (5905 g) of Borax is contained in the glass jar. The graduate contains 2 liters (100 g) of Silanox.TM In Figure 5 SilanoxTM has been added to the Borax in the jar for a total of 8 liters material. However, after simple mixing (no milling) for about 15 minutes the overall volume for the mixture decreases to a volume less than that of the Borax alone initially, as illustrated in Figure 6. Depending on particle size and other factors, bulk-density increases of up to 50 percent have been obtained with additions of as little as 2 percent (by weight) of hydrophobic silica.

The combined lack of agglomeration and free-flowing characteristic of powders conditioned with hydrophobic silica is especially beneficial in preventing powder separation and the resultant air gaps in powder fills. We have successfully used 1 to 2 percent hydrophobic silica additive to pyrotechnic and composite explosive powders in the filling of 5 to 6 mm diameter tubes about 90 cm long. The hydrophobic silica additive not only allowed simple and rapid filling of the tubes but provided the compactness of filling and preclusion of air gap formation requisite for minimizing failure of reaction propagation over the length of the tube. Upon storing these tubes all powder settling, due to handling, etc., was evident at the top of the tube, thus allowing simple topping off of the tubes before use. Without

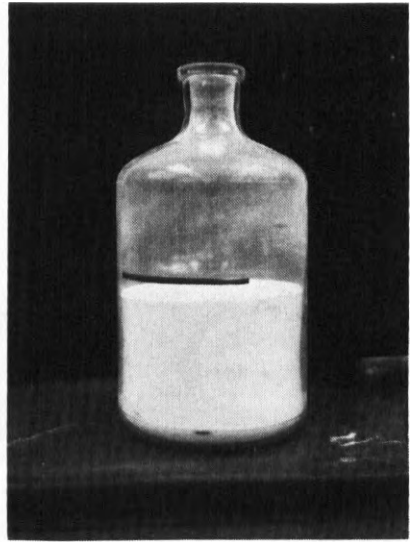


Fig. 5. Six liters BoraxTM powder in a jar with two liters of SilanoxTM poured on its surface.

Fig. 6. Six liters BoraxTM powder and two liters SilanoxTM reduced to less than six liters total after simple mixing.

the hydrophobic silica additive storage and handling caused a high degree of propagation failures due to powder separation within the tubes.

The fluidity of powder treated with hydrophobic silica is amazing. When agitated, it appears to be a liquid and gives the illusion that surface tension exists.

There is, however, one potential disadvantage, which is associated with the increased bulk density. The mechanism for this increase in bulk density is the fluidization of the individual particles--they flow and slip past each other readily so that they compact much better--hence, increased bulk density. If, however, this powder stands for an extended time, it acquires a thixotropic tendency--it is difficult to achieve instant motion. Once disturbed, the powder becomes "liquefied" as far as flowability is concerned, but the initial force required for movement is increased. This is no problem in the fluidization process, but for dispersal of powders that are initially tightly contained, this must be considered.

The question invariably arises: how much hydrophobic silica is required for optimum fluidity? This question cannot be readily answered as the optimum amount depends on many factors. The mechanism is a coating action in which the millimicron hydrophobic silica attempt to coat the much larger micron-sized particles. Incomplete coating will be effective, but not optimum. On the other hand, excess hydrophobic silica will not improve flowability appreciably and will in fact in many cases segregate from the coated particles, floating on the surface as a separate layer.

During milling, the hydrophobic silica will continuously coat fresh surfaces as long as excess hydrophobic silica is present. Once all hydrophobic silica has coated the particles, further milling will start to degrade the system. If the particles were initially waxy, the problem will recur and affect the milling action. Adding more hydrophobic silica will allow further milling and reestablish the flowability. Hence, the amount of hydrophobic silica required depends on the material to be fluidized and its particle size. If the particle size is reduced, either by milling, by deagglomeration, or by another particle reduction technique, additional hydrophobic silica will be required.

SUMMARY

In summary, we have described a flowability additive or conditioner that can be utilized with most pyrotechnic, propellant, explosive, and other powder formulations where problems of hygroscopicity, agglomeration, poor flowability, and perhaps even low bulk density are prevalent. The additive is a hydrophobic silica; it is not new, has been utilized in powder technology for many years, and is commercially available. It has a bulk density of about 0.05 g/cc, a particle size of about a millimicron, and should be treated with caution for health and safety reasons as it is readily respirable. Because of its low bulk density, a very small amount--from 1 to 3 weight

percent--is adequate in most cases. It can totally eliminate agglomeration problems, minimize hygroscopic problems, and improve the flowability of powders by many orders of magnitude. We have used it very effectively with explosive, propellant, and pyrotechnic powders to prepare homogeneous mixtures with a minimum of mixing, to mill difficult materials, and to obtain amazing flow properties in troublesome powders. It has proven effective in fluidization processes, particularly for the rapid dispersion of powders and powder elutriation.

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