ABSTRACT: Process for protecting ground finely divided powdered substances against agglomeration or reagglomeration wherein the substance to be protected is finely ground together with a finely divided hydrophobic silica or wherein a mixture of finely divided hydrophobic silica and finely divided hydrophilic silica is added to the substance to be protected already in finely ground state and intensively mixed therewith in a mill having a grinding action.
PROCESS FOR HINDERING THE AGGLOMERATION OR REAGGLOMERATION OF GROUND FINELY DIVIDED POWDERED SUBSTANCES

BACKGROUND OF THE INVENTION

Hydrophilic powders tend to agglomerate under the influence of atmospheric moisture and the pressures of packaging and storage. They, thereby, lose the valuable properties of their original finely divided state. For instance, they no longer can be dusted without difficulties as clusters of agglomerated particles are formed. The agglomeration in practice leads to particle sizes which are much coarser than the sizes obtained in their original state. It is known that the dispersibility of powered or fine crystalline substances which are sensitive to moisture can be maintained by the addition of finely divided synthetically produced silica or silicates or natural finely divided silica containing substances so as to prevent their caking upon storage and thereby facilitate automatic filling procedures and improve the accuracy of their dosage. These known procedures, however, only serve to prevent the caking together of already agglomerated particles which goes far beyond the original agglomeration so that to achieve the required stability more or less relatively large quantities, depending upon the nature of the substance to be stabilized, for example, finely divided silica must be added thereto. The agglomeration which already has taken place cannot be rendered retrogressive with such procedures.

Such agglomeration also occurs during the process of preparation of the finely divided substances such as, for example, during grinding. Grinding of products of all types often leads to disturbances with regard to the stability of the original fineness of the particles reached in the grinding and their dispersibility. Also, insufficient grinding properties, especially with substances not having sufficient grinding hardness, often leads to difficulties. A blatant example is in the grinding of spices during which the comminution, which originally occurs, is immediately followed by agglutination of the ground particles which leads to clogging of the mill. Sulfur behaves similarly on grinding and causes clogging of the mill. Attempts to hinder the agglomeration occurring during such grinding process by the addition of finely divided pyrogenic silica have not been lacking. However, the amounts required are comparatively high and in particular are undesirably high in pharmaceutical and food products and in some instances they undesirably affect the activity of the materials.

Other finely divided substances such as metal salts and oxides and especially magnesium oxide tend to reagglomerate when they are sprayed or blown as dusts and in addition are subject to a great extent to accumulation of electrostatic charges. Magnesium oxide, for example, in the case of its use to combat corrosion of oil heated boiler installations in the low temperature range is blown into such boiler installation and mainly acts to neutralize the SO$_2$ produced by the combustion of the oil to produce noncorrosive compounds. A substantial disadvantage in the use of MgO, however, is that in view of its tendency to reagglomerate its original particle fineness is not retained and that thereby its dustibility and accuracy of dosage is impaired.

DESCRIPTION OF THE INVENTION INCLUDING PREFERRED EMBODIMENTS

It is an object of the invention to provide a method for hindering the agglomeration or reagglomeration of finely divided powdered substances having a tendency to agglomerate or reagglomerate by the addition of finely divided silica which avoids the disadvantages mentioned above.

According to the invention it was found that this object could be achieved with the aid of hydrophobic (hydropihobized) finely divided active synthetically produced silicas either alone or in admixture with hydrophilic finely divided active synthetically produced silicas.

The hydrophobic silicas employed according to the invention can be finely divided wet precipitated silicas, pyrogenic silicas produced by pyrogenic decomposition of volatile silicic halides or electric arc silicas which have been hydrophobized in a known manner with organohalosilanes, such as, dimethyl dichlorosilane.

Wet precipitated hydrophobized silicas can, for instance, have a BET surface area of about 200 m$^2$/g, preferably about 100–150 m$^2$/g, such as, for example, in a hydrophobized precipitated silica containing 89–99.0 percent of silica and about 0.9 to 2.8 percent of carbon derived from chemically bound methyl groups which cause the hydrophobicity, and having a primary particle size of 20–300 nm, a secondary particle size of 0.7–9 μm, a BET surface area of 100 m$^2$/g, and a pH of 3.4–4.9 (4 percent in water), and for instance, DEGUSSA hydrophobized silicas D 17 and D 500.

Pyrogenic silicas, for instance, have a surface area between about 100 to 200 m$^2$/g, and an average primary particle size of about 10 to 50 μm, and a carbon content of about 112 to 116 percent, corresponding to about 0.6–0.8 m mol (CH$_3$) per 100 m$^2$, such as, for example, in the hydrophobized pyrogenic silica Aerosil R 972 (produced as described in Chemische Zeitschrift 89, 1965, pages 437–440) which is a pure pyrogenic silica which has hydrophobic properties by virtue of chemically bound methyl groups and has a SiO$_2$–CH$_3$ content >99.8 percent, a carbon content 1%±2 percent (corresponding to about 0.6 millimol of (CH$_3$) per square meter), a BET surface area of 200±30 m$^2$/g, an average primary particle size of about 20 μm and a pH of 3.6–4.04 percent dispersion in 1:1 methanol:water.

The hydrophilic silicas which can be used in combination with the hydrophobic silicas according to each embodiment of the invention can either be wet precipitated or pyrogenic silicas which have not been hydrophobized.

According to the invention the hydrophilic silica or mixture of hydrophobic and hydrophilic silica employed must be incorporated and intimately mixed with the substance to be protected against agglomeration or reagglomeration by a grinding operation either in that the hydrophilic silica is added to the substance before it is finely ground and such substance is finely ground in contact with such added hydrophobic silica or in that a mixture of hydrophobic and hydrophilic silica is added to the substance after it already is in the finely ground state and intimately mixed therewith in a mill having a grinding action. In both instances the addition of the silicas can be before or during the grinding operation.

The finely divided products which have been treated according to the invention in practice have the advantages of improved dustibility, improved stability of their finely divided nature or dispersibility against agglomeration and caking, improved dosibility in automatic weighings and improved behavior when conveyed pneumatically. In addition the accumulation of electrostatic charges which also is a cause of undesired agglomeration is avoided in powders normally having a tendency to accumulate such charges.

The following examples will serve to illustrate the process according to the invention.

EXAMPLE 1

A raw chromium phosphate was finely ground in a mill after addition of 3 wt. percent of hydrophobic precipitated finely divided silica (D 17) having a BET surface area of about 110 m$^2$/g containing 89.20 wt. percent of silica and about 2.80 wt. percent of carbon derived from methyl groups. A finely divided powder was obtained in which the original particle fineness was stabilized against reagglomeration for a long period after the grinding.

Analogous results were obtained when the hydrophobic precipitated finely divided silica was replaced by hydrophobized pyrogenic silica Aerosil R 972.

The use of hydrophilic silicas is considerably more effective at considerably lower quantities than the sole addition of hydrophilic silica as a so-called grinding assistant. The wind-
sifting operations which may follow the grinding operation proceed more rapidly and more effectively with regard to particle size separation the less the particles are agglomerated with each other.

When the grinding was carried out without addition of the hydrophobic silica, agglomeration of the ground particles did already initiate during the grinding operation because of the impact pressure of the grinding aggregates. When substances of insufficient grinding hardness are concerned agglomerations occur during the grinding operation which partially render the actual comminution efficiency of the grinding machine ineffective. As a consequence, in the past costly measurements were required to effect subsequent loosening of the agglomerates already formed in the grinding machine, such as, for example, the provision of a highly turbulent air stream or subsequent fine sieving arrangements. These extra measures are avoided by the addition of the hydrophobic silica as they already prevent the agglomeration which normally occurs in the mill.

The effectiveness of the grinding in the presence of the hydrophobic silica is easily seen by comparison of electron microphotographs (at an enlargement of 5000 x) of the ground products obtained with the addition of hydrophobic silica and of the ground product obtained without such addition. In the latter instance the incidence of layer agglomerations of the finely ground chromium phosphates particles is many times greater than when the grinding was carried out in the presence of the hydrophobic silicas.

**EXAMPLE 2**

A magnesium oxide in very finely ground state was intimately mixed in a mill having grinding action with a mixture of finely divided hydrosolubilized precipitated silica (D 17) and a finely divided hydrosolubilized precipitated silica (Ultrasil VN 3) having a surface area of about 240 m²/g and containing about 87 percent of silica and having a 12 percent loss on calcination and a particle size of about 16 μm once in a wt. ratio of 1:9 (b) and once in a wt. ratio of 5:5. The quantity of the mixture of the silicas was such that it was 10 wt. percent of the total mixture with the magnesium oxide.

A product was obtained whose original fine-particle nature after the grinding was stable against the influences of atmospheric moisture and the agglomerating influences of storage and packaging. The same effects were obtained whether the addition of the silica mixture and mixture thereof under grinding conditions was effected immediately after the magnesium oxide had been finely ground and before it had reagglomerated or whether it was effected after reagglomeration had taken place.

The effects of the incorporation of the silica mixture in the finely ground magnesium oxide can easily be seen from electron microphotographs at an enlargement of 30,000 taken of the untreated finely ground magnesium oxide (which had reagglomerated) and that of the mixture of the silica mixture with the magnesium oxide prepared as described above using the finely ground magnesium in its reagglomerated state as starting material. The silica magnesium oxide mixtures exhibit a considerably lower agglomeration and a more uniform average secondary structure. The average secondary structure of the mixture is about 5—10 times smaller than that of the original magnesium oxide, this effect being raised with increase in the proportion of the hydrophobic silica.

Further mixtures were prepared from the finely ground magnesium and the hydrophobic silica Ultrasil VN 3 and various proportions thereof were compared with those of the original magnesium oxide (without addition of silica). Material tested:

a. Original magnesium oxide
b. Magnesium oxide mixtures with 8 wt. percent silica mixture *5 to 9 wt. parts Ultrasil VN 3+5 to 1 wt. parts D 17.

I. Flow behavior:
   a. Insufficient, very hesitating
   b. Flows smoothly through measuring vessel

II. Spray behavior (spray pistol 2.5 mm. nozzle, quantity of air required to obtain uniform spraying)
   a. 26 ± 2 liters/minute
   b. 15 ± 1 liters/minute

III. Suspension behavior in flowing air

The materials tested were placed in a conical tube supplied with air at the bottom at an inlet speed of 8—10 m/sec., the outlet speed at the top being 0.05—0.1 m/sec. The quantity of the powder retained with the outlet speed of 0.1 m/sec. after 5 minutes' treatment was measured

a. 45 percent (55 percent carried out)
b. 30 percent (70 percent carried out)

IV. Pressure test

20 g. samples of the powders tested were subjected to a load of 3.2 kg. (corresponding to 0.17 kg/cm²) for 14 hours

a. loosely caked, did not disintegrate to original state with finger test
b. loosely shaped, disintegrated substantially to original state under light finger pressure

V. Adherence to polyvinyl chloride or glass tubes because of accumulation of static charge

The untreated magnesium powder had a substantially greater tendency to adhere to the tubes than the silica treated powders.

The mixture of magnesium oxide with hydrophobic plus hydrophilic silicas prepared as described above are especially advantageous when used to decrease the low temperature corrosion in large boiler installations as the disadvantages of untreated technical magnesium oxide powders, such as insufficient spray behavior, premature settling in the combustion chamber, deficient stability of the magnesium oxide during storage and distant transportation are avoided. The presence of, for example 8 to 10 percent of the mixture of 5—9 parts of hydrophobic silica and 1—5 parts of hydrophobic silica (the silica mixture as a whole being hydrophobized by the presence of the hydrophobic silica) produces a substantial improvement in the spray behavior and the stability of the magnesium oxide.

A further substantial advantage is that in view of the lowering of the tendency to reagglomerate caused by the presence of the silicas, the treated magnesium oxide can be metered without difficulty and can be blown with greater effectiveness over greater distances. Even portions of the boiler having unfavorable flow conditions can be well dusted with the finely divided stabilized MgO-SiO₂ mixture according to the invention. It is possible thereby to reduce the quantity of MgO previously necessary by about 40 percent.

The quantities of finely divided hydrophobic silica or mixtures of hydrophobic silica with hydrophilic silica which can be incorporated according to the invention in finely divided products having a tendency to agglomerate or reagglomerate can, depending upon the substance to be protected, be about 0.1 to 20 wt. percent, preferably, about 0.1 to 10 percent in the case of inorganic powders and about 0.1 to 0.5 percent in the case of organic powders, such as spices, based upon the total mixture.

We claim:

1. A method of protecting finely divided powdered substances against agglomeration or reagglomeration during grinding and subsequent thereto which comprises adding a finely divided synthetically produced hydrophobized active silica together with a finely divided synthetically produced hydrophobic silica to the substance to be protected and grinding the mixture whereby a finely divided powder which is free of agglomeration and substantially protected against subsequent agglomeration is obtained.

2. The method of claim 1 in which said hydrophobized silica is a silica which has been hydrophobized by treatment with an organic halogen silane and has a carbon content of 0.9 to 2.8 percent, a BET surface area of about 100—150 m²/g.

3. The method of claim 1 in which the finely divided powdery substance to be protected is magnesium oxide and such magnesium oxide is admixed in finely divided powdered state with about 8—10 wt. percent of a mixture of 5—9 wt. parts of the hydrophobized silica and 5—1 wt. parts of the hydrophilic silica and such admixture is intimately mixed in a mill having a grinding action.