

Description**FIELD OF THE INVENTION**

5 This invention relates to an anti-foaming agent granular product which is suited for compounding into powdered detergents for clothing and to a process for producing the same.

BACKGROUND OF THE INVENTION

10 In European countries, drum type washing machines are predominantly used. Detergents to be used in drum type washing machines generally contain an anti-foaming agent because a foam reduces washing efficiency.

In Japan, on the other hand, pulsator type washing machines have hitherto been popular, and foaming has not particularly given rise to a problem of washing efficiency. Detergents producing foam to a moderate
15 degree have been rather preferred from habit.

The recent spread of an automatic washing machine entailed a change in thinking about foam on washing. Besides, foam may run over a washing machine tub, and too much foam takes so much time for rinsing with water. From these and other reasons, a detergent which is inhibited from foaming has been demanded.

20 Silicone is a well-known anti-foaming agent which inhibits foaming on washing. Silicon effectively inhibits foaming immediately after being compounded into a powdered detergent but undergoes reduction in anti-foaming effect with time. While silicone is spread on the interface between air and water to exert its anti-foaming effect, when a detergent after storage is mixed with water, silicone is dispersed in an aqueous solution, and its anti-foaming effect cannot be fully manifested.

25 From this reason, silicone is generally compounded into a detergent after being granulated or treated with a coating so that it may not contact directly with detergent components. In general, silicone granules obtained by adsorbing silicone onto a builder of detergents, such as sodium sulfate, sodium carbonate, and sodium tripolyphosphate, as a carrier and mixing in the presence of a binder are used.

However, when these silicone granules using a builder as a carrier are stored in high temperatures,
30 oozing of silicone cannot be sufficiently inhibited.

JP-A-50-157403 (corresponding to British Patent 1492939) (the term "JP-A" as used herein means an "unexamined published Japanese patent application") proposes that water-insoluble starch can be used as the carrier for silicone, and JP-A-61-271007 (corresponding to European Patent 206522) and JP-A-62-57616 (corresponding to U.S. Patent 4,818,292) proposes anti-foaming agent granular product in which preliminar-
35 ily gelatinized and partially hydrated water-swelling and water-insoluble starch is used as a carrier. However, the granules are hardly dissolved in cold water-washing condition as in Japan because of water-insolubility of the starch carrier and liable to remain on laundry as an insoluble matter.

DE-A-23 38 468 discloses a mixture for a washing and purifying agent which includes an anti-foaming agent comprising a silicone compound applied to a carrier. A preferred silicone compound is represented
40 by polydimethylsiloxane. In a specific embodiment the silicone compounds may be adsorbed by a solid material like sodium carbonate, sodium tripolyphosphate, sodium silicate, clay, starch and silica. The carrier may be represented by gelatin, agar, gum arabic or polyethylene glycol. Furthermore, the anti-foaming agent and the carrier material may be combined to a granulated product.

Accordingly, it has been demanded to develop a silicone-containing anti-foaming agent granular product
45 whose anti-foaming effect is not reduced during storage due to oozing of silicone and which is easily dissolved even in cold water.

SUMMARY OF THE INVENTION

50 An object of this invention is to provide an silicone-containing anti-foaming agent granular product whose anti-foaming effect is not reduced during storage due to oozing of silicone and which is easily dissolved even in cold water.

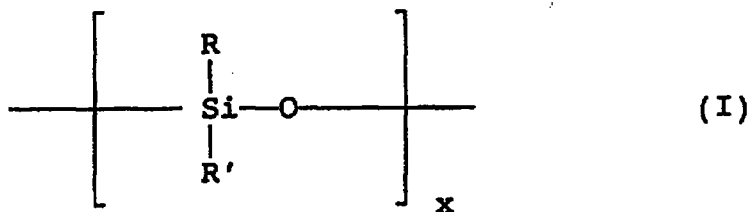
The inventors have conducted extensive investigations and, as a result, found that the above object is accomplished by using a water-soluble starch as a carrier of silicone, thus having reached the present
55 invention.

The present invention relates to an antifoaming agent granular product comprising (a) a silicone anti-foaming agent, (b) at least one compound selected from the group consisting of a water-soluble starch, a modified water-soluble starch or a derivative thereof, the (a)/(b) weight ratio being from 0.1 to 0.5 and the

total amount of (a) and (b) being from 30 to 80% by weight based on the total weight of the granular product, (c) from 0.5 to 40% by weight, based on the total weight of the granular product, of an inorganic builder or a clay mineral, and (d) from 10 to 40% by weight, based on the total weight of the granular product, of an organic binder having a melting point or a softening point of from 40 to 160 °C. The present invention further relate to a process for producing the anti-foaming agent granular product.

DETAILED DESCRIPTION OF THE INVENTION

The silicone anti-foaming agent which can be used as component (a) in the present invention is not particularly limited. Polysiloxanes represented by formula (I):



wherein R and R', which may be the same or different, each represents an alkyl group having from 1 to 6 carbon atoms or an aryl group; and x is an integer of from 20 to 2000, are most frequently employed. In particular, polydimethylsiloxane of the above formula wherein R and R' each represents a methyl group is suitable.

The water-soluble starch, the modified water-soluble starch or the derivative thereof which can be used as component (b) in the present invention includes an esterified starch (e.g., starch phosphate), an etherified starch (e.g., carboxymethylated starch), an enzyme-modified dextrin (e.g., maltodextrin), and a roasted dextrin, with the enzyme-modified dextrin (e.g., maltodextrin) and the roasted dextrin being preferred. Component (b) serves as a carrier for the silicone anti-foaming agent (a).

Components (a) and (b) are used at an (a)/(b) weight ratio of from 0.1 to 0.5, and preferably from 0.15 to 0.4. An (a)/(b) weight ratio less than 0.1 is economically disadvantageous. If it exceeds 0.5, silicone oozes out and cannot be stably supported by the carrier. The total content of components (a) and (b) in the granular product ranges from 30 to 80% by weight, preferably 50 to 80% by weight, more preferably 70 to 80% by weight, based on the total weight of the granular product. A total content less than 30% by weight is economically disadvantageous. If it exceeds 80% by weight, granulation becomes difficult.

The inorganic builder or clay mineral which can be used as component (c) in the present invention is used as a granulation aid. Examples of suitable inorganic builders or clay minerals are sulfates, carbonates, bicarbonates, sesquicarbonates, tripolyphosphates, zeolite, and bentonite. Preferred of them are water-soluble builders. Examples of the water-soluble builders include sodium sulfate, sodium carbonate, sodium bicarbonate, sodium sesquicarbonate, sodium tripolyphosphate. Among them, sodium saltate is preferred.

Component (c) is used in an amount of from 0.5 to 40% by weight, and preferably from 3.0 to 30% by weight, based on the total weight of the granular product. If the content of component (c) is less than 0.5% by weight, granulation of silicone-on-carrier becomes difficult.

In order to granulate the above-described components (a), (b), and (c), a binding aid is used as component (d). As a binding aid, an organic binder having a melting point or a softening point of from 40 to 160 °C, and preferably from 45 to 85 °C, is employed for maintaining storage stability of granules in high temperatures. The organic binder (d) is a nonionic substance. Specific examples of suitable organic binders (d) include polyethylene glycol having a molecular weight of from 1,500 to 20,000, polyethylene glycol alkyl ethers having from 8 to 22 carbon atoms in the alkyl moiety thereof, fatty acids containing alkyl group(s) having from 8 to 22 carbon atoms, and ethylene oxide-propylene oxide block copolymers. The most preferred of them is polyethylene glycol. Component (d) is used in an amount of from 10 to 40% by weight based on the total weight of the granular product. If the amount is less than 10% by weight, granulation is difficult. If it exceeds 40% by weight, the resulting granules has reduced solubility.

The anti-foaming agent granular product comprising components (a) to (d) according to the present invention does not undergo oozing of silicone while exhibiting satisfactory solubility.

The anti-foaming agent granular product is compounded into a detergent. From the viewpoint of environmental conservation, phosphorus-free detergents (zeolite-compounded detergents) are now mostly

used as powdered detergents for clothing. When the silicone-containing anti-foaming agent granular product are added to phosphorus-free detergents, the granules are coated with water-insoluble zeolite during storage, resulting in reduction in solubility of the granules. This being the case, it is preferable that the granules further contain an anionic surface active agent or a nonionic surface active agent having a melting point or softening point of less than 40 °C as component (e).

Examples of suitable anionic surface active agents as component (e) include sulfonate and sulfate type anionic surface active agents, such as straight chain alkylbenzenesulfonates, alkylsulfates, polyoxyethylene alkyl ether sulfates, α -olefinsulfonates, and alkanesulfonates (the salts include sodium salts, potassium salts and the like). Examples of suitable nonionic surface active agents as component (e) include polyoxyethylene alkyl or alkylphenyl ethers having a melting point or softening point of less than 40 °C. To improve solubility of granules, component (e) is used in an amount of from 0.1 to 20% by weight, preferably from 0.5 to 10% by weight, and more preferably from 0.5 to 5% by weight, based on the total weight of the granular product. If the amount is less than 0.1% by weight, no improvement on solubility can be obtained. If it exceeds 20% by weight, granulation becomes difficult. From the standpoint of granulation properties, anionic surface active agents are preferred as component (e). In using nonionic surface active agents, those having a melting point or softening point of 20 °C or higher are preferred from the standpoint of granulation properties.

The density of the anti-foaming agent granular product according to the present invention is preferably from 0.45 to 0.65 g/cc.

The anti-foaming agent granular product according to the present invention is desirably produced by a process comprising:

- (1) adding a silicone anti-foaming agent (a) to water-soluble starch, modified starch or a derivative thereof (b) while mixing to obtain a homogeneous mixture wherein the (a)/(b) weight ratio is from 0.1 to 0.5; and
- (2) mixing the resulting homogeneous mixture with an inorganic builder or clay mineral (c) and an organic binder (d) having a melting point or a softening point of from 40 to 160 °C with stirring under heating at a temperature not less than the melting point or a softening point of the organic binder (d), followed by granulation by extrusion granulation, tumbling granulation, wherein the total amount of (a) and (b) is selected from 30 to 80% by weight, the amount of (c) is selected from 0.5 to 40% by weight, and the amount of (d) is selected from 10 to 40% by weight, based on the total weight of the granular product.

Where component (e), i.e., an anionic surface active agent or a nonionic surface active agent having a softening point of less than 40 °C is used, it is mixed with the above-described homogeneous mixture obtained in the step (1) or admixed in the step (2), wherein the amount of (e) is selected from 0.1 to 20% by weight, based on the total weight of the granular product.

For granulation, if desired, anti-caking agents, e.g., silica, and other additives, such as dyestuffs, may be added in an amount up to 5% by weight based on the total weight of the granules.

Granulation is preferably performed so that the resulting granules have an average particle size of from 100 to 1,500 μm , preferably from 200 to 1,300 μm , and more preferably from 300 to 1,000 μm . It is also preferable that the resulting granules contain not more than 5% by weight, based on the total weight of the granular product, of particles smaller than 100 μm and/or not more than 5% by weight, based on the total weight of the granular product, of particles greater than 1,500 μm .

The thus obtained anti-foaming agent granular product of the present invention is mixed into a powdered detergent in a proportion of from 0.1 to 5% by weight based on the total weight of the detergent. The powdered detergent is not particularly limited, but it is a detergent containing an anionic surface active agent as a main detergent base that is required to be combined with an anti-foaming agent. Such a detergent generally comprises from 10 to 60% by weight, based on the total weight of the detergent, of anionic surface active agents, such as straight chain alkylbenzenesulfonates, alkylsulfates, polyoxyethylene alkyl ether sulfates, α -olefinsulfonates, and higher fatty acid salts (the salts include sodium salts and potassium salts); from 30 to 80% by weight, based on the total weight of the detergent, of builders, such as carbonates, silicates, sulfates, phosphates, and zeolite; up to 30% by weight, based on the total weight of the detergent, of nonionic surface active agents (e.g., polyoxyethylene alkyl ethers), cationic surface active agents, amphoteric surface active agents, or bleaching agents, such as percarbonates and perborates; and from 2 to 8% by weight, based on the total weight of the detergent, of other components, such as anti-redeposition agents (e.g., carboxymethyl cellulose and polyethylene glycol), enzymes (e.g., protease, cellulase and lipase), fluorescent brightening agents and perfumes.

The anti-foaming agent granular product of the present invention is also useful for detergents containing a nonionic surface active agent as a main detergent base since they are foamy under laundry conditions in European countries. The anti-foaming agent granular product of the invention is further useful as well for

other detergents required to have anti-foaming properties, such as detergents for dish washing.

The anti-foaming agent granular product according to the present invention, when compounded into a powdered detergent, does not cause oozing of silicone during storage and hence, undergoes no reduction in anti-foaming effect. Moreover, since the anti-foaming agent granular product employs water-soluble starch as a carrier for a silicone anti-foaming agent, it exhibits satisfactory solubility in water and leaves no insoluble matter on laundry.

The present invention is now illustrated in greater detail with reference to the following Examples, but it should be understood that the present invention is not deemed to be limited thereto. All the parts and percents are by weight unless otherwise indicated.

EXAMPLE 1

(1) Preparation of Anti-Foaming Agent Granular Product:

As the anti-foaming agent, 20 g of silicone (compound type, "FS Anti-Foam", trade name, produced by Dow Corning Co.) were mixed with 100 g of maltodextrin (enzyme-modified dextrin, produced by Nichiden Kagaku Co., Ltd.) to prepare a homogeneous mixture.

The resulting homogeneous mixture, polyethylene glycol, and neutral anhydrous sodium sulfate were mixed at a ratio shown below at a temperature of from 70 to 80°C and granulated by means of an extrusion granulator ("Model EXKS-1", trade name, manufactured by Fuji Powdal Co., Ltd.) to obtain granules.

Composition of Anti-Foaming Granules:

Homogeneous mixture	50%
Polyethylene glycol (PEG-6000; melting point: 58°C)	25%
Neutral anhydrous sodium sulfate	25%

The granules were classified using sieves of 1.00 and 0.50 mm (16 and 32 mesh) to adjust the particle size.

Particle Size Distribution:

Average particle size:	800 μ m
Particles having a particle size of 1000 μ m or greater:	5%
Particles having a particle size of 250 μ m or smaller:	5%

(2) Solubility of Granules:

The resulting granules had satisfactory water solubility. Water solubility was examined by adding 300 mg of the granules to 300 ml of water at 10°C placed in a 500 ml beaker while stirring by means of a stirrer bar (length: 5cm) at a rotation rate of about 500 to about 700 rpm. As a result, all the granules were dissolved within 2 minutes.

EXAMPLE 2

A powdered detergent having the following composition and a bulk density of 0.7 g/cm³ was prepared.

Composition of Powdered Detergent:

Sodium straight chain alkyl(C ₁₂ -C ₁₃)benzenesulfonate	26%
Sodium alkyl(C ₁₂ -C ₁₃)sulfate	8%
Tallow fatty acid sodium salt	5%
Polyoxyethylene($\bar{p}$ = 13) alkyl(C ₁₂ -C ₁₃) ether	5%
Zeolite	24%
Sodium carbonate	12%
No. 2 Sodium silicate	12%
Sodium sulfate	3%
Water	5%

Each of anti-foaming components shown in Table 1 below was added to the resulting powdered detergent in an amount shown, and retention of foam in repeated washing and anti-foaming effect after storage were evaluated according to the following test methods. The results obtained are shown in Table 1.

1) Retention of Foam:

Washing test was conducted using the powdered detergent containing the anti-foaming component under the following conditions. The height of foam was determined after each of first, second and third time washing. Washing test was conducted thrice and the results were expressed in the average value thereof.

Washing Conditions:

Washing machine:	"Ginga" produced by Toshiba Corp.; volume: 2.2 kg
Amount of Water:	30 l
Amount of Detergent:	25 g
Laundry:	600 g of cotton shirts and 400 g of T/C (Tetoron/cotton union yarn) shirts each having been worn for 3 days were washed three times.
Washing Time:	7 minutes each

2) Anti-Foaming Effect After Storage:

The powdered detergent containing the anti-foaming component was stored at 5°C, 30°C, or 40°C for 20 days and then subjected to washing test under the same washing conditions as in (1) above (washing was conducted only once). The height of foam was determined after washing. The test was conducted thrice and the results were expressed in the average value thereof.

TABLE 1

Sample No.	Comparison			Invention		
	1	2	3	4	5	6
Anti-Foaming Component (part) ¹⁾ :						
Silicone ²⁾	-	0.5	-	-	-	-
Homogeneous Mixture ³⁾	-	-	0.5	-	-	-
Anti-Foaming Agent Granules ⁴⁾	-	-	-	0.5	1	2
Foam Retention (cm):						
1st Washing	8	2	2	1-2	0-1	0
2nd Washing	8	2-3	2-3	2	1	0-1
3rd Washing	7-8	3	3	2-3	2	1
Anti-Foaming Effect after storage (cm):						
stored at 40 °C	8	8	6	2	1	0-1
stored at 30 °C	8	7	5-6	1-2	0-1	0
stored at 5 °C	8	6	5	0	0	0

Note:

1): Per 100 parts of the detergent

2): Silicone compound produced by Dow Corning Co.

3): Maltodextrin/silicone homogeneous mixture prepared in Example 1

4): Granules prepared in Example 1

EXAMPLE 3

(1) Preparation of Anti-Foaming Agent Granular Product:

As the anti-foaming agent, 20 g of silicone (compound type, "FS Anti-Foam", trade name, produced by Dow Corning Co.) were mixed with 100 g of maltodextrin (enzyme-modified dextrin, produced by Nichiden Kagaku Co., Ltd.) to prepare a homogeneous mixture. To the mixture was added 10 g of an alkyl ether sulfate ("Emal 10 Powder", trade name, an anionic surface active agent produced by Kao Corp.) to obtain a mixture.

The resulting mixture, polyethylene glycol (product of Sanyo Chemical Industries, Ltd.), and neutral anhydrous sodium sulfate (product of Shikoku Kasei Co., Ltd.) were mixed at a ratio shown below at a temperature of from 70 to 80 °C and granulated by means of an extrusion granulator ("Model EXKS-1", trade name, manufactured by Fuji Powdal Co., Ltd.) to obtain granules.

Composition of Anti-Foaming Agent Granular Product:

Homogeneous mixture/anionic surface active agent mixture	50%
Polyethylene glycol (PEG-6000, melting point: 58 °C)	25%
Neutral anhydrous sodium sulfate	25%

The granules were classified using sieves of 16 and 32 mesh to adjust the particle size.

Particle Size Distribution:

Average particle size:	800 μm
Particles having a particle size of 1000 μm or greater:	5%
Particles having a particle size of 250 μm or smaller:	5%

10 (2) Solubility of Granules:

Water solubility of the resulting granules was examined in the same manner as in Example 1. As a result, all the granules were dissolved within 2 minutes.

15 EXAMPLE 4

A powdered detergent having the following composition and a bulk density of 0.7 g/cm³ was prepared.

20 Composition of Powdered Detergent:

Sodium straight chain alkyl(C ₁₂ -C ₁₃)benzenesulfonate	26%
Sodium alkyl(C ₁₂ -C ₁₃)sulfate	8%
Tallow fatty acid sodium salt	5%
Polyoxyethylene($\bar{p}$ = 13) alkyl(C ₁₂ -C ₁₃) ether	5%
Zeolite	24%
Sodium carbonate	6%
Potassium carbonate	6%
No. 2 Sodium silicate	12%
Sodium sulfate	3%
Water	5%

Each of anti-foaming components shown in Table 2 below was added to the above-prepared powdered detergent, and retention of foam and anti-foam effect after storage were evaluated in the same manner as in Example 2. Further, solubility of the granular anti-foaming component after storage was evaluated according to the following test method. The results obtained are shown in Table 2.

3) Solubility of Granular Anti-Foaming Component After Storage:

The powdered detergent containing the anti-foaming component was stored at 5°C, 30°C, or 40°C for 20 days and then subjected to anti-foaming effect after storage as in (2) above under the same washing conditions as in (1) above (washing was conducted only once). At this time, solubility of granular anti-foaming component after storage was examined by fixing an open mesh bag for collecting flocks (product of Leck Co., Ltd.) was to the washing machine tub. Any insoluble matter collected in the bag was observed and rated as follows.

- A: No insoluble matter was collected.
- B: A slight amount of an insoluble matter was collected.
- C: A considerable amount of an insoluble matter was collected.

TABLE 2

Sample No.	Comparison			Invention			Comparison	
	1	2	3	4	5	6	7	8
Anti-Foaming Component (part) ¹⁾ :								
Silicone ²⁾	-	0.5	-	-	-	-	-	-
Homogeneous Mixture ³⁾	-	-	0.5	-	-	-	1	2
Anti-Foaming Agent Granules ⁴⁾	-	-	-	0.5	1	2	-	-
Foam Retention (cm):								
1st Washing	8	2	2	1-2	0-1	0	1	0-1
2nd Washing	8	2-3	2-3	2	1	0-1	1-2	1
3rd Washing	7-8	3	3	2-3	2	1	2	1-2
Anti-Foaming Effect After Storage (cm):								
stored at 40°C	8	8	6	2	1	0-1	3	2
stored at 30°C	8	7	5-6	1-2	0-1	0	2	1-2
stored at 5°C	8	6	5	0	0	0	1-2	1
Solubility After Storage:								
stored at 40°C	A	A	B	A	A	A	B to C	C
stored at 30°C	A	A	B	A	A	A	B to C	C
stored at 5°C	A	A	B	A	A	B	B to C	C

- Note:
- 1): Per 100 parts of the detergent
 - 2): Silicone compound produced by Dow Corning Co.
 - 3): Maltodextrin/silicone homogeneous mixture prepared in Example 3.
 - 4): Granules prepared in Example 3

EXAMPLE 5

(1) Preparation of Anti-Foaming Agent Granular Product:

As the anti-foaming agent, 35 g of silicone (compound type, "FS Anti-Foam", trade name, produced by Dow Corning Co.) were mixed with 100 g of maltodextrin (enzyme-modified dextrin, produced by Nichiden Kagaku Co., Ltd.) to prepare a homogeneous mixture. To the mixture was added 3 g of an alkyl ether sulfate ("Emal 10 Powder", trade name, an anionic surface active agent produced by Kao Corp.) to obtain a mixture.

The resulting mixture, polyethylene glycol (product of Sanyo Chemical Industries, Ltd.), and neutral anhydrous sodium sulfate (product of Shikoku Kasei Co., Ltd.) were mixed at a ratio shown below at a temperature of from 70 to 80 °C and granulated by means of an extrusion granulator ("Model EXKS-1", trade name, manufactured by Fuji Powder Co., Ltd.) to obtain granules.

Composition of Anti-Foaming Agent Granular Product:

Homogeneous mixture/anionic surface active agent mixture	75%
Polyethylene glycol (PEG-6000, melting point: 58 °C)	22%
Neutral anhydrous sodium sulfate	3%

The granules were classified using sieves of 16 and 32 mesh to adjust the particle size.

Particle Size Distribution:

Average particle size:	800 μm
Particles having a particle size of 1000 μm or greater:	5%
Particles having a particle size of 250 μm or smaller:	5%

EXAMPLE 6

A hundred parts of the powdered detergent obtained in Example 4 were mixed with 1.5 part of the anti-foaming agent granules obtained in Example 5, and the resulting detergent was evaluated for retention of foam, anti-foaming effect after storage, and solubility of the anti-foaming agent after storage in the same manner as in Example 4.

As a result, retention of foam after the 1st, 2nd, and 3rd washing was 0 cm, 0 cm, and 1 cm, respectively, and the anti-foaming effect after storage at 5 °C, 30 °C, or 40 °C was 0 cm, 0 cm, or 1 cm, respectively. Further no insoluble matter was collected in the mesh bag for collecting flocks.

While the invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the scope thereof.



Claims

1. An anti-foaming agent granular product comprising:
 - (a) a silicone anti-foaming agent;
 - 5 (b) at least one compound selected from the group consisting of a water-soluble starch, a modified water-soluble starch or a derivative thereof; wherein the (a)/(b) weight ratio is from 0.1 to 0.5 and the total amount of (a) and (b) is from 30 to 80% by weight based on the total weight of the granular product;
 - (c) from 0.5 to 40% by weight, based on the total weight of the granular product, of an inorganic builder or a clay mineral; and
 - 10 (d) from 10 to 40% by weight, based on the total weight of the granular product, of an organic binder having a melting point or softening point of from 40 to 160 °C.
2. An anti-foaming agent granular product as claimed in Claim 1, wherein said anti-foaming agent granular product further comprises (e) from 0.1 to 20% by weight, based on the total weight of the granular product, of an anionic surface active agent or a nonionic surface active agent having a melting point or softening point of less than 40 °C.
3. An anti-foaming agent granular product as claimed in Claim 1, wherein said silicone anti-foaming agent is at least one compound selected from among polysiloxanes.
4. An anti-foaming agent granular product as claimed in Claim 1, wherein said silicone anti-foaming agent is polydimethylsiloxane.
- 25 5. An anti-foaming agent granular product as claimed in Claim 1, wherein said water-soluble starch, said modified starch or said derivative thereof is at least one compound selected from among an esterified starch, an etherified starch, an enzyme-modified dextrin and roasted dextrin.
6. An anti-foaming agent granular product as claimed in Claim 1, wherein said water-soluble starch, said modified water-soluble starch or said derivative thereof is at least one compound selected from among an enzyme-modified dextrin and a roasted dextrin.
- 30 7. An anti-foaming agent granular product as claimed in Claim 1, wherein said inorganic builder or said clay mineral is at least one compound selected from among sulfates, carbonates, bicarbonates, sesquicarbonates, tripolyphosphates, zeolite and bentonite.
- 35 8. An anti-foaming agent granular product as claimed in Claim 1, wherein said inorganic builder or said clay mineral is sodium sulfate.
- 40 9. An anti-foaming agent granular product as claimed in Claim 1, wherein said organic binder is at least one compound selected from among polyethylene glycol having a alkyl ethers having from 8 to 22 carbon atoms in the alkyl moiety thereof, fatty acids containing alkyl group(s) having from 8 to 22 carbon atoms, and ethylene oxide-propylene oxide block copolymers having a melting point or softening point of from 40 to 160 °C is polyethylene glycol.
- 45 10. An anti-foaming agent granular product as claimed in Claim 1, wherein said organic binder is polyethylene glycol having a molecular weight of from 1,500 to 20,000.
11. An anti-foaming agent granular product as claimed in Claim 2, wherein the component (e) is at least one compound selected from among straight chain alkylbenzenesulfonates, alkylsulfates, polyoxyethylene alkyl ether sulfates, α -olefinsulfonates, and alkanesulfonates.
- 50 12. A process for producing an anti-foaming agent granular product comprising:
 - (1) adding a silicone anti-foaming agent (a) to a water-soluble starch, a modified water-soluble starch or a derivative thereof (b) while mixing to obtain a homogeneous mixture, wherein the (a)/(b) weight ratio is from 0.1 to 0.5; and
 - 55 (2) mixing the resulting homogeneous mixture with an inorganic builder or clay mineral (c) and an organic binder (d) having a melting point or softening point of from 40 to 160 °C with stirring under



heating at a temperature not less than the melting point or softening point of the organic binder (d), followed by granulation,

wherein the total amount of (a) and (b) is selected from 30 to 80% by weight, the amount of (c) is selected from 0.5 to 40% by weight, and the amount of (d) is selected from 10 to 40% by weight, based on the total weight of the granular product.

13. A process for producing an anti-foaming agent granular product as claimed in claim 12, wherein, as component (e), an anionic surface active agent or a nonionic surface active agent having a melting point or softening point of less than 40 °C is mixed with said homogeneous mixture, or admixed in said step (2), wherein the amount of (e) is selected from 0.1 to 20% by weight, based on the total weight of the granular product.

14. A powder detergent comprising an anionic surface active agent or a nonionic surface active agent, as a main detergent base, and an anti-foaming agent granular product as claimed in Claim 1.

15. A phosphorous-free powder detergent comprising an anionic surface active agent or a nonionic surface active agent, as a main detergent base, zeolite and an anti-foaming agent granular product as claimed in Claim 2.

20 Patentansprüche

1. Körniges Antischaummittelprodukt, umfassend:

(a) Ein silikonenthaltendes Antischaummittel;

(b) wenigstens eine Verbindung, ausgewählt aus der Gruppe, bestehend aus einer wasserlöslichen Stärke, einer modifizierten wasserlöslichen Stärke oder einem Derivat davon; worin das (a)/(b)-Gewichtsverhältnis 0,1 bis 0,5 beträgt und die Gesamtmenge von (a) und (b) 30 bis 80 Gew.-%, bezogen auf das Gesamtgewicht des körnigen Produktes beträgt;

(c) 0,5 bis 40 Gew.-%, bezogen auf das Gesamtgewicht des körnigen Produktes eines anorganischen Builders oder eines Tonmaterials und

(d) 10 bis 40 Gew.-%, bezogen auf das Gesamtgewicht des granularen Produktes eines organischen Bindemittels mit einem Schmelzpunkt oder einem Erweichungspunkt von 40 bis 160 °C.

2. Körniges Antischaummittel gemäß Anspruch 1, bei dem das körnige Antischaummittel weiterhin umfaßt:

(e) 0,1 bis 20 Gew.-%, bezogen auf das Gesamtgewicht des körnigen Produktes eines anionischen, oberflächenaktiven Mittels oder eines nichtionischen oberflächenaktiven Mittels mit einem Schmelzpunkt oder Erweichungspunkt von weniger als 40 °C.

3. Körniges Antischaummittelprodukt gemäß Anspruch 1, bei dem das Silikon-Antischaummittel wenigstens eine Verbindung, ausgewählt aus Polysiloxanen ist.

4. Körniges Antischaummittelprodukt gemäß Anspruch 1, bei dem das Silikon-Antischaummittel ein Polydimethylsiloxan ist.

5. Körniges Antischaummittelprodukt gemäß Anspruch 1, bei dem die wasserlösliche Stärke, die modifizierte wasserlösliche Stärke oder das Derivat davon, wenigstens eine Verbindung ist, ausgewählt aus einer veresterten Stärke, einer veretherten Stärke, einem Enzymmodifizierten Dextrin und einem gerösteten Dextrin.

6. Körniges Antischaummittelprodukt gemäß Anspruch 1, bei dem die wasserlösliche Stärke, die modifizierte wasserlösliche Stärke oder das Derivat davon wenigstens eine Verbindung ist, ausgewählt aus einem enzymmodifizierten Dextrin und einem gerösteten Dextrin.

7. Körniges Antischaummittelprodukt gemäß Anspruch 1, bei dem der anorganische Builder oder das Tonmaterial wenigstens eine Verbindung ist, ausgewählt aus Sulfaten, Carbonaten, Bicarbonaten, Sesquicarbonaten, Tripolyphosphaten, Zeolithen und Bentoniten.



8. Körniges Antischaummittelprodukt gemäß Anspruch 1, bei dem der anorganische Builder oder das Tonmaterial Natriumsulfat ist.
9. Körniges Antischaummittelprodukt gemäß Anspruch 1, bei dem das organische Bindemittel wenigstens eine Verbindung ist, ausgewählt aus Polyethylenglykolalkylether mit 8 bis 22 Kohlenstoffatomen in dessen Alkylrest Fettsäuren, enthaltend Alkylgruppe(n) mit 8 bis 22 Kohlenstoffatomen, Ethylenoxid-Propylenoxid-Blockcopolymeren mit einem Schmelzpunkt oder Erweichungspunkt von 40 bis 160 °C und Polyethylenglykol.
10. Körniges Antischaummittelprodukt gemäß Anspruch 1, bei dem das organische Bindemittel Polyethylenglykol mit einem Molekulargewicht von 1.500 bis 20.000 ist.
11. Körniges Antischaummittelprodukt gemäß Anspruch 2, bei dem die Komponente (e) wenigstens eine Verbindung ist, ausgewählt aus geradkettigen Alkylbenzolsulfonaten, Alkylsulfaten, Polyoxyethylenalkyl, Ethersulfaten, α -Olefin-sulfonaten und Alkansulfonaten.
12. Verfahren zur Herstellung eines körnigen Antischaummittelproduktes, umfassend:
 - (1) Zugabe eines Silikon-Antischaummittels (a) zu einer wasserlöslichen Stärke, einer modifizierten wasserlöslichen Stärke oder einem Derivat davon, (b) unter Vermischen und Erhalt einer homogenen Mischung, wobei das (a)/(b)-Gewichtsverhältnis 0,1 bis 0,5 beträgt und
 - (2) Mischen der erhaltenen homogenen Mischung mit einem anorganischen Builder oder Tonmaterial (c) und einem anorganischen Bindemittel (d) mit einem Schmelzpunkt oder Erweichungspunkt von 40 bis 160 °C unter Rühren und Erhitzen auf eine Temperatur von nicht weniger als dem Schmelzpunkt und Erweichungspunkt des organischen Binders (d) und anschließend Granulieren, wobei die Gesamtmenge (a) und (b) aus 30 bis 80 Gew.-%, ausgewählt ist, und die Menge (c) aus 0,5 bis 40 Gew.-% ausgewählt ist, und die Menge (d) aus 10 bis 40 Gew.-% ausgewählt ist, jeweils bezogen auf das Gesamtgewicht des körnigen Produktes.
13. Verfahren zur Herstellung eines körnigen Antischaummittelproduktes gemäß Anspruch 12, bei dem als Komponente (e) ein anionisches oberflächenaktives Mittel oder ein nichtionisches oberflächenaktives Mittel mit einem Schmelzpunkt und Erweichungspunkt von weniger als 40 °C mit der homogenen Mischung vermischt wird, oder in der Stufe (2) vermischt wird, wobei die Menge (e) von 0,1 bis 20 Gew.-%, bezogen auf das Gesamtgewicht des körnigen Produktes ausgewählt ist.
14. Pulverdetergens, umfassend ein anionisches oberflächenaktives Mittel oder ein nichtionisches oberflächenaktives Mittel als Hauptdetergenzien-Grundlage und ein körniges Antischaummittelprodukt gemäß Anspruch 1.
15. Phosphorfreies Pulverdetergens, umfassend ein anionisches oberflächenaktives Mittel oder ein nichtionisches oberflächenaktives Mittel als Hauptdetergenzien-Grundlage, Zeolith und ein pulverförmiges Antischaummittel gemäß Anspruch 2.

Revendications

1. Produit granulaire d'agent anti-mousse, comportant:
 - (a) un agent anti-mousse au silicone;
 - (b) au moins un composé choisi dans le groupe constitué d'un amidon soluble dans l'eau, d'un amidon modifié soluble dans l'eau ou d'un dérivé de ceux-ci; dans lequel le rapport pondéral (a)/(b) vaut de 0,1 à 0,5, et la quantité totale de (a) et de (b) est de 30 à 80% en poids, calculés sur le poids total du produit granulaire;
 - (c) de 0,5 à 40% en poids, calculés sur le poids total du produit granulaire, d'un adjuvant inorganique ou une argile minérale; et
 - (d) de 10 à 40% en poids, calculés sur le poids total du produit granulaire, d'un liant organique présentant un point de fusion ou un point de ramollissement de 40 à 160 °C.
2. Produit granulaire d'agent anti-mousse selon la revendication 1, dans lequel ledit produit granulaire d'agent anti-mousse comporte en outre (e) de 0,1 à 20% en poids, calculés sur le poids total du produit granulaire, d'un agent tensioactif anionique ou d'un agent tensioactif non ionique présentant un



point de fusion ou un point de ramollissement inférieur à 40 ° C.

3. Produit granulaire d'agent anti-mousse selon la revendication 1, dans lequel ledit agent anti-mousse au silicone est au moins un composé choisi parmi des polysiloxanes.
- 5 4. Produit granulaire d'agent anti-mousse selon la revendication 1, dans lequel ledit agent anti-mousse au silicone est le polydiméthylsiloxane.
- 10 5. Produit granulaire d'agent anti-mousse selon la revendication 1, dans lequel ledit amidon soluble dans l'eau, ledit amidon modifié ou ledit dérivé de ceux-ci est au moins un composé choisi parmi un amidon estérifié, un amidon étherifié, une dextrine modifiée par enzyme et une dextrine grillée.
- 15 6. Produit granulaire d'agent anti-mousse selon la revendication 1, dans lequel ledit amidon soluble dans l'eau, ledit amidon modifié soluble dans l'eau ou ledit dérivé de ceux-ci est au moins un composé choisi parmi une dextrine modifiée par enzyme et une dextrine grillée.
- 20 7. Produit granulaire d'agent anti-mousse selon la revendication 1, dans lequel ledit adjuvant inorganique ou ladite argile minérale sont au moins un composé choisi parmi des sulfates, carbonates, bicarbonates, sesquicarbonates, tripolyphosphates, zéolite et bentonite.
- 25 8. Produit granulaire d'agent anti-mousse selon la revendication 1, dans lequel ledit adjuvant inorganique ou ladite argile minérale est du sulfate de sodium.
- 30 9. Produit granulaire d'agent anti-mousse selon la revendication 1, dans lequel ledit liant inorganique est au moins un composé choisi parmi des alkyléthers de polyéthylèneglycol présentant de 8 à 22 atomes de carbone dans la fraction alkyle, des acides gras contenant un ou des groupes alkyles présentant de 8 à 22 atomes de carbone, et des copolymères-bloc d'oxyde d'éthylène et d'oxyde de propylène présentant un point de fusion ou un point de ramollissement de 40 à 160 ° C (polyéthylèneglycol).
- 35 10. Produit granulaire d'agent anti-mousse selon la revendication 1, dans lequel ledit liant organique est un polyéthylène glycol présentant un poids moléculaire de 1500 à 20000.
11. Produit granulaire d'agent anti-mousse selon la revendication 2, dans lequel le composant (e) est au moins un composé choisi parmi des sulfates d'alkyle, des alkyl-éther sulfates de polyoxyéthylène, des sulfonates d' α -oléfine, des sulfonates d'alcane, et des sulfonates d'alkyl-benzène à chaîne droite.
- 40 12. Procédé de production d'un produit granulaire d'agent anti-mousse, comportant les étapes consistant à:
(1) ajouter un agent anti-mousse au silicone (a) à un amidon soluble dans l'eau, à un amidon modifié soluble dans l'eau ou à un dérivé de ceux-ci (b), tout en mélangeant, pour obtenir un mélange homogène, le rapport pondéral (a)/(b) étant de 0,1 à 0,5; et
(2) mélanger le mélange homogène obtenu avec un adjuvant inorganique ou une argile minérale (c) et un liant organique (d) présentant un point de fusion ou un point de ramollissement de 40 à 160 ° C, tout en agitant avec chauffage à une température qui n'est pas inférieure au point de fusion ou au point de ramollissement du liant organique (d), avec ensuite granulation,
45 dans lequel la quantité totale de (a) et de (b) est choisie entre 30 et 80% en poids, la quantité de (c) est choisie entre 0,5 et 40% en poids et la quantité de (d) est choisie entre 10 et 40% en poids, calculés sur le poids total du produit granulaire.
- 50 13. Procédé pour la production d'un produit granulaire d'agent anti-mousse selon la revendication 12, dans lequel en tant que composant (e), un agent tensioactif anionique ou un agent tensioactif non-ionique présentant un point de fusion ou un point de ramollissement inférieur à 40 ° C, est mélangé ou mélange homogène ou ajouté dans ladite étape (2), et dans lequel la quantité de (e) est choisie de 0,1 à 20% en poids, calculés sur le poids total du produit granulaire.
- 55 14. Détergent en poudre comportant un agent tensioactif anionique ou un agent tensioactif non ionique comme base détergente principale, et un produit granulaire d'agent anti-mousse selon la revendication 1.



15. Détergent en poudre, exempt de phosphore, comportant un agent tensioactif anionique ou un agent tensioactif non-ionique comme base détergente principale, une zéolite et un produit granulaire d'agent anti-mousse selon la revendication 2.

5

10

15

20

25

30

35

40

45

50

55