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(54) **Detergent compositions and process for preparing them**

Waschmittelzusammensetzungen und Verfahren zu deren Herstellung

Compositions détergentes et procédé pour leur préparation

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- **DATABASE WPIL, No. 86-133904, 1986, Derwent Publications Ltd.; & JP-A- 61069897**
- **PATENT ABSTRACTS OF JAPAN, vol. 2, no. 59, 27 April 1978; & JP-A- 5316713**
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Description

TECHNICAL FIELD

[0001] The present invention relates to granular detergent compositions of high bulk density having good washing performance and good powder properties, and a process for preparing them.

BACKGROUND AND PRIOR ART

[0002] Recently there has been considerable interest within the detergents industry in the production of detergent powders having relatively high bulk density, for example, 600 g/litre and above. Particular attention has been paid to the densification of spray-dried powders by post-treatment. EP 219 328A (Unilever) discloses a granular low-phosphate detergent composition prepared by spray-drying a slurry to give a base powder containing a low to moderate level of sodium tripolyphosphate builder and low levels of inorganic salts, and then postdosing solid material including sodium sulphate of high bulk density and of smaller particle size than the base powder, thus filling the voids between base powder particles and producing a product of high bulk density.

[0003] JP 61 069897A (Kao) discloses a process in which a spray-dried detergent powder containing a high level of anionic surfactant and a low level of builder (zeolite) is subjected successively to pulverising and granulating treatments in a high-speed mixer/granulator, the granulation being carried out in the presence of an "agent for improving surface properties" having an average particle size up to 10μm and optionally a binder. It would appear that in the high-speed mixer/granulator, the spray-dried powder is initially broken down to a fine state of division; the surface-improving agent and optional binder are then added and the pulverised material granulated to form a final product of high bulk density. The surface-improving agent, which is a finely divided particulate solid such as fine sodium aluminosilicate, is apparently required in order to prevent the composition from forming into large balls or cakes.

[0004] EP 229 671A (Kao) discloses postdosing a crystalline alkaline inorganic salt, for example, sodium carbonate, to a spray-dried base powder prepared as in the above-mentioned JP 61 069897A (Kao) and containing a restricted level of water-soluble crystalline inorganic salts, to produce a high bulk density product.

[0005] GB 1 517 713 (Unilever) discloses a process in which spray-dried or granulated detergent powders containing sodium tripolyphbsphate and sodium sulphate are densified and spheronised in a "marumerizer" (Trade Mark). GB 1 453 697 (Unilever) discloses the use of the same apparatus to granulate together detergent powder components in the presence of a liquid binder to form a granular detergent composition. The "marumerizer" comprises a substantially horizontal roughened rotatable table positioned within and at the base of a substantially vertical smooth-walled cylinder. The disadvantage associated with this apparatus is that it produces powders or granules having a rather wide particle size distribution, and in particular containing a relatively high proportion of oversize particles. Such products exhibit poor dissolution and dispersion characteristics, particularly in low-temperature short duration machine washes as used in Japanese and other far-eastern washing machines. This can be apparent to the consumer as deposits on washed fabrics, and in machine washing leads to a high level of wastage.

[0006] EP 220 024A (Procter & Gamble) discloses a process in which a spray-dried detergent powder containing a high level (30-85 wt%) of anionic surfactant is mixed with an inorganic builder (sodium tripolyphosphate, or sodium aluminosilicate and sodium carbonate) and compacted under high pressure using a roll compactor ("chilsonator"); the compacted material, after removal of oversize material and fines, is then granulated using conventional apparatus, for example, a fluidised bed, tumble mixer, or rotating drum or pan.

[0007] EP 158 419A (Hashimura) discloses the preparation of a detergent powder by mixing a major proportion of soda ash (preferably 70 to 85 wt% of the mixture) and a minor proportion of surfactant (wholly or predominantly nonionic) in a high-speed mixer/granulator.

DE-A-3617756 describes a process in which constituents of a composition are mixed in a kneader, then comminuted in a mill and coated with finely divided zeolite before being granulated in a Marumerizer.

[0008] Seifen- Öle-Fette-Wachse 114 Jg - No 8/1988 page 315 describes the utilisation of a Patterson - Kelly agglomerator to treat a spray-dried powder and increase its bulk density.

[0009] EP-A-339996 which is a publication under Article 54(3) EPC includes an example 1 in which a spray -dried composition containing:-

	% by weight
Linear alkylbenzene sulphonate	20.0
Nonionic surfactant	2.0
Soap	1.0

(continued)

	% by weight
Zeolite (anhydr.)	35.0
Water with zeolite	10.0
Sodium silicate	4 0
Sodium succinate	2.0
Acrylate/maleate copolymer	2.0
Sodium sulphate	10.45
Sodium carbonate	10.0
Minor ingredients	1.55
Free moisture	2.0
	100.0

is treated in a Fukae (Trade Mark) FS-G series high speed mixer/granulator.

[0010] It has now been found that spray-dried powders containing moderate or high levels of water-soluble crystalline inorganic salts, including sodium tripolyphosphate and/or sodium carbonate, can be granulated and densified in a high-speed mixer/granulator, if necessary after pulverisation, without the need for an "agent for improving surface properties" or similar pulverulent material, even when high levels of anionic surfactant are present.

DEFINITION OF THE INVENTION

[0011] The present invention provides a process for the preparation of a granular detergent composition or component as defined in claim 1

DETAILED DESCRIPTION OF THE INVENTION

[0012] The invention is concerned with a process for the preparation of a detergent powder combining high bulk density, good powder properties and excellent washing and cleaning performance.

[0013] The present inventors have found that a detergent base powder prepared by any suitable method and containing substantial levels of water-soluble crystalline inorganic salts may be processed in a high-speed mixer/granulator, without the need for the use of an "agent for improving surface properties" during the granulation step as prescribed by JP 61 069897A (Kao), to give a dense granulate having good flow properties, even if relatively high levels of anionic surfactant are present. The product is characterised by an especially narrow particle size distribution, and in particular by a very small proportion or oversize material, giving good and rapid cold water dispersability and low insolubles.

The starting powder

[0014] A preferred starting powder has a ratio of total water-soluble crystalline inorganic salts (b) to total non-soap surfactant (a) within the range of from 0.4:1 to 9:1, more preferably from 0.4:1 to 5:1. An especially preferred range for the ratio of (b) to (a) is from 1:1 to 5:1.

[0015] Preferably the starting powder contains a total of from 15 to 70 wt% of water-soluble crystalline inorganic salts. As well as sodium tripolyphosphate and sodium carbonate, examples of such salts include sodium sulphate, sodium ortho- and pyrophosphates, and crystalline sodium silicates, that is to say, sodium silicates having a ratio (SiO_2 to Na_2O) $\leqq$ 1, such as sodium orthosilicate and sodium metasilicate. The alkaline and neutral silicates of higher ratio commonly used in detergent compositions are not to be regarded as crystalline.

[0016] According to a preferred embodiment of the invention, the starting powder contains from 15 to 50 wt%, more preferably from 20 to 40 wt%, of sodium tripolyphosphate.

[0017] The non-soap'surfactant present in the starting powder preferably consists at least partially of anionic surfactant. Suitable anionic surfactants will be well known to those skilled in the art, and include linear alkylbenzene sulphonates, particularly sodium linear alkylbenzenesulphonates having an alkyl chain length of C_8-C_{15}; primary and secondary alkyl sulphates, particularly sodium C_{12}-C_{15} primary alcohol sulphates; alkyl ether sulphates; alpha-olefin and internal olefin sulphonates; alkane sulphonates; dialkyl sulphosuccinates; fatty acid ester sulphonates; and combinations thereof.

[0018] If desired, the starting powder may contain nonionic surfactant. Nonionic surfactants too will be well known to those skilled in the art, and include primary and secondary alcohol ethoxylates, especially the C_{12}-C_{15} primary and

secondary alcohols ethoxylated with an average of from 3 to 20 moles of ethylene oxide per mole of alcohol.

[0019] Suitably the surfactant component of the starting powder may be constituted by from 0 to 70%, preferably from 8 to 60 wt%, of anionic surfactant, and from 0 to 20%, preferably from 0 to 10%, by weight of nonionic surfactant.

[0020] Other types of non-soap surfactant, for example, cationic, zwitterionic, amphoteric or semipolar surfactants, may also be present if desired. Many suitable detergent-active compounds are available and are fully described in the literature, for example, in "Surface-Active Agents and Detergents", Volumes I and II, by Schwartz, Perry and Berch.

[0021] If desired, soap may also be present, to provide foam control and additional detergency and builder power; soap is not included in the 12 to 70% figure for the surfactant content quoted previously.

[0022] The starting powder may be prepared by any suitable tower or non-tower method, for example, spray-drying or dry mixing. The invention is especially useful for the densification of a spray-dried powder.

[0023] If desired, at least part of the water-soluble crystalline inorganic salt to be included in the final product may be admixed to the remainder of the starting powder in the high-speed mixer/granulator itself. In this embodiment of the invention, the percentages and ratios specified above should be based on the total material introduced into the high-speed mixer/granulator, including the added salt.

[0024] Thus it is within the scope of the present invention to introduce into the high-speed mixer/granulator a starting powder, prepared for example by spray-drying, containing less than the amount of water-soluble crystalline inorganic salt specified above, and then to admix with that powder, in the high-speed mixer/granulator, sufficient water-soluble crystalline inorganic salt to bring the salt percentage (b) and the ratio (b) to (a) up to the specified level.

[0025] Similarly, it is within the scope of the invention to add surfactant, or indeed any other component, in the high-speed mixer/granulator provided that the final composition is as specified above, and provided that the component so added is not a finely divided "agent for improving surface properties" as described in JP 61 069897A (Kao) discussed previously. Thus, in the process of the invention, any component other than a finely divided particulate solid having a particle size up to 10μm may be added to the high-speed mixer/granulator prior to granulation.

[0026] One procedure according to the invention includes the step of admixing at least one inorganic or organic salt having a particle size of at least 100 μm with the remainder of the starting powder in the high-speed mixer/granulator. If the salt is water-soluble, inorganic and crystalline, it should be included within the percentages and ratios specified above which relate to the total amount of such salts in the material subjected to granulation in the high-speed mixer/granulator.

[0027] Salts that may conveniently be incorporated by this method include borax, sodium bicarbonate, sodium silicate, sodium tripolyphosphate, sodium carbonate, sodium perborate, sodium percarbonate, sodium citrate, sodium nitrilotriacetate, sodium succinate, sodium sulphate and combinations of these. These salts can give various benefits: for example, borax and sodium bicarbonate are buffers giving mild products of low in-wash pH.

The process

[0028] In the process of the invention, granulation is effected by means of a high-speed mixer/granulator having both a stirring action and a cutting action. Preferably the stirrer and the cutter may be operated independently of one another, and at separately variable speeds. Such a mixer is capable of combining a high energy stirring input with a cutting action, but can also be used to provide other, gentler stirring regimes with or without the cutter in operation. It is thus a highly versatile and flexible piece of apparatus.

[0029] A preferred type of high-speed mixer/granulator for use in the process of the invention is bowl-shaped and preferably has a substantially vertical stirrer axis. Especially preferred are mixers of the Fukae (Trade Mark) FS-G series manufactured by Fukae Powtech Kogyo Co., Japan; this apparatus is essentially in the form of a bowl-shaped vessel accessible via a top port, provided near its base with a stirrer having a substantially vertical axis, and a cutter positioned on a side wall. The stirrer and cutter may be operated independently of one another, and at separately variable speeds.

[0030] Other similar mixers found to be suitable for use in the process of the invention are the Diosna (Trade Mark) V series ex Dierks & Söhne, Germany; and the Pharma Matrix (Trade Mark) ex T K Fielder Ltd., England. Other similar mixers believed to be suitable for use in the process of the invention include the Fuji (Trade Mark) VG-C series ex Fuji Sangyo Co., Japan; and the Roto (Trade Mark) ex Zanchetta & Co srl, Italy.

[0031] Another mixer found to be suitable for use in the process of the invention is the Lödige (Trade Mark) FM series batch mixer ex Morton Machine Co. Ltd., Scotland. This differs from the mixers mentioned above in that its stirrer has a horizontal axis.

[0032] As indicated above, the use of a high-speed mixer/granulator is essential in the process of the invention to effect granulation and densification. If desired, the mixer may also be used for a pretreatment step before granulation is carried out.

[0033] For example, it is within the scope of the invention, as previously indicated, for one or more further ingredients to be admixed with an otherwise premixed powder prepared elsewhere (for example, by spray-drying). A suitable

stirring/cutting regime and residence time may be chosen in accordance with the materials to be mixed.

[0034] Another possible pretreatment that may be carried out in the high-speed mixer/granulator is pulverisation; whether or not this is necessary depends, among other things, on the method of preparation of the starting powder and its free moisture content. Powders prepared by spray-drying, for example, are more likely to require pulverisation than powders prepared by dry-mixing. Again, the flexibility of the apparatus allows a suitable stirring/cutting regime to be chosen: generally relatively high speeds for both stirrer and cutter. A relatively short residence time (for example, 2-4 minutes for a 35 kg batch) is generally sufficient.

[0035] The essential feature of the process of the invention is the granulation step, during which densification to the very high values of at least 673 g/litre, preferably at least 700 g/litre occurs, giving a dense, granular product of very uniform particle size and generally spherical particle shape.

[0036] Granulation is effected by running the mixer at a relatively high speed using both stirrer and cutter; a relatively short residence time (for example, 5-8 minutes for a 35 kg batch) is generally sufficient. The final bulk density can be controlled by choice of residence time, and it has been found that the powder properties of the resulting granulate are not optimum unless the bulk density has been allowed to rise to at least 673 g/litre.

[0037] The presence of a liquid binder is necessary for successful granulation. The amount of binder added preferably does not exceed that needed to bring the free moisture content of the composition above about 6 wt%, since higher levels may lead to a deterioration in the flow properties of the final granulate. If necessary, binder, preferably water, may be added before or during granulation, but some starting powders will inherently contain sufficient moisture. If a liquid binder is to be added, it may be sprayed in while the mixer is running. In one preferred mode of operation, the mixer is first operated at a relatively slow speed while binder is added, before increasing the speed of the mixer to effect granulation.

[0038] If the starting powder has a sufficient free moisture content to render the addition of a binder unnecessary, pulverisation (if required) and granulation need not be regarded as separate process steps but as one single operation. Indeed, it is not, in that case, necessary to decide in advance whether or not pulverisation is required: the mixer may simply be allowed to do what is necessary, since the mixer conditions required are generally substantially the same for pulverisation and for granulation.

[0039] According to a preferred embodiment of the invention, granulation is carried out at a controlled temperature somewhat above ambient, preferably above 30°C. The optimum temperature is apparently formulation-dependent, but appears generally to lie within the range of from 30 to 45°C, preferably about 35°C.

[0040] It is an essential feature of the present invention that during granulation no "agent for improving surface properties" as defined in the above-mentioned JP 61 069897A (Kao) be present. When processing a formulation having a relatively high ratio of aluminosilicate builder to surfactant, in accordance with the present invention, the use of a finely divided particulate material such as fine sodium aluminosilicate during the granulation step is not only unnecessary but can with some formulations make granulation more difficult, or even impossible.

The optional flow aid

[0041] In accordance with a preferred embodiment of the invention, a finely divided particulate flow aid may be admixed with the granular material after granulation is complete. Advantageously, flow aid is added while the granulate is still in the high-speed mixer/granulator, and the mixer is operated at a slow speed for a further short period. No further granulation occurs at this stage. It is also within the scope of the invention to add the flow aid to the granulate after removing the latter to different apparatus.

[0042] This embodiment of the invention should be distinguished from the prior art process of JP 61 069897A (Kao), mentioned above, in which an "agent for improving surface properties", which can be fine sodium aluminosilicate, is present during the granulation stage itself. It is within the scope of the present invention to add a particulate flow aid after granulation is complete, but, as explained above, it is essential to the invention that no finely divided particulate "agent for improving surface properties" be present during granulation. The addition of a flow aid after granulation is complete can have an additional beneficial effect on the properties of the granulate, regardless of the formulation, whereas the presence of this type of material during the granulation step in the process of the invention makes processing more difficult.

[0043] The preferred granulation temperature of from 30 to 45°C, preferably about 35°C, may also be maintained during the subsequent admixture of a flow aid.

[0044] The flow aid is a finely divided particulate material. The preferred average particle size is 0.1 to 20 μm, more preferably 1 to 10 μm.

[0045] According to one preferred embodiment of the invention, the flow aid is finely divided amorphous sodium aluminosilicate, as described and claimed in our copending application of even date, now EP-A-339996. A suitable material is available commercially from Crosfield Chemicals Ltd, Warrington, Cheshire, England, under the trade mark Alusil. This material is effective in improving flow properties even at very low levels, and also has the effect of increasing

bulk density. It is therefore possible to adjust bulk density by appropriate choice of the level of amorphous sodium aluminosilicate added after granulation.

[0046] Amorphous sodium aluminosilicate is advantageously used in an amount of from 0.2 to 5.0 wt%, based on the starting powder, more preferably from 0.5 to 3.0 wt%.

[0047] Another preferred flow aid is finely divided crystalline sodium aluminosilicate. The crystalline aluminosilicates discussed previously in the context of builders are also suitable for use as flow aids. They are, however, less weight-effective than the amorphous material and are suitably used in an amount of from 3.0 to 12.0 wt%, more preferably from 4.0 to 10.0 wt%.

[0048] If desired, both crystalline and amorphous sodium aluminosilicates may be used, together or sequentially, as flow aids.

[0049] Other flow aids suitable for use in the process of the invention include precipitated silica, for example, Neosyl (Trade Mark), and precipitated calcium silicate, for example, Microcal (Trade Mark), both commercially available from Crosfield Chemicals Ltd, Warrington, Cheshire, England.

The final granulate

[0050] The final granulate has a bulk density of at least 673 g/litre and preferably at least 700 g/litre. It is also characterised by an especially low particle porosity, preferably not exceeding 0.25 and more preferably not exceeding 0.20, which distinguishes it from even the densest powders prepared by spray-drying alone.

[0051] The final granulate may be used as a complete detergent composition in'its own right. Alternatively, it may be admixed with other components or mixtures prepared separately, and may form a major or minor part of a final product. Generally, any additional ingredients such as enzymes, bleach and perfume that are not suitable for undergoing the granulation process and the steps that precede it may be admixed to the granulate to make a final product.

[0052] In one preferred embodiment of the invention, for example, a detergent base powder is prepared by spray-drying an aqueous slurry of heat-insensitive and compatible ingredients; if desired, other ingredients may then be admixed as discussed above; and the resulting powder is densified and granulated in accordance with the process of the invention. Yet further ingredients may if desired be admixed after granulation; the densified granulate may typically constitute from 40 to 100 wt% of a final product.

[0053] In another embodiment of the invention, the densified granulate prepared in accordance with the present invention is an "adjunct" comprising a relatively high level of detergent-active material on an inorganic carrier; and this may be admixed in a minor amount with other ingredients to form a final product.

[0054] The invention is further illustrated by the following non-limiting Examples, in which parts and percentages are by weight unless otherwise stated.

EXAMPLES

[0055] In the Examples which follow, the following abbreviations are used.

LAS	sodium linear alkylbenzene sulphonate
NI	nonionic surfactant (ethoxylated alcohol)
NSD	total non-soap detergent
STP	sodium tripolyphosphate
Carbonate	sodium carbonate
Sulphate	sodium sulphate
Silicate	sodium alkaline silicate
g	good
Alu	Alusil (Trade Mark) N, finely divided amorphous sodium aluminosilicate
Zeo	Zeolite 4A (Wessalith (Trade Mark) ex Degussa)

Examples 1 & 2

[0056] Powders containing sodium tripolyphosphate and sodium sulphate were prepared by spray-drying aqueous slurries to the formulations (weight %) shown in Table 1.

Table 1

Example	1	2
LAS	12.2	9.7
NI	8.1	2.8
NSD (a)	20.3	12.5
STP	42.7	42.5
Sulphate	10.2	14.8
Salts (b)	52.9	57.3
Soap	-	4.9
Silicate	10.2	10.0
Minors	2.4	2.8
Water	14.2	12.5
(b):(a)	2.6	4.6

[0057] 20 kg batches of each powder were densified in a Fukae (Trade Mark) high-speed mixer/granulator, process conditions and resulting powder properties being shown in Table 2. In Example 1, the powder was initially subjected to a 2-3 minute warming up period, at a low stirrer speed (50 rev/min) and without the cutter running, until the temperature had reached about 30-35°C. This was followed by pulverisation (optional), then binder addition (also optional), then granulation, followed finally by addition of flow aid.

Table 2

	1	2(a)	2(b)
Pulverisation:			
Time (min)	4	0.5	0.5
Stirrer speed (rev/min)	180	180	180
Cutter speed (rev/min)	3000	1000	1000
Binder (water):			
Amount (wt %)	4	0.5	0.5
Addition time (min)	1	0.5	0.5
Stirrer speed (rev/min)	100	100	100
Cutter speed (rev/min)	3000	3000	3000
Granulation:			
Time (min)	15	7	6
Stirrer speed (rev/min)	140	140	140
Cutter speed (rev/min)	2700	3000	3000
Flow aid:			
Zeo or Alu	Alu	Alu	Zeo
Amount (wt %)	2	1.5	5
Addition time (min)	1	1	1
Stirrer speed (rev/min)	90	90	90
Cutter speed (rev/min)	300	300	300
Yield <1700 μm (wt %)	95	93	97
Average particle size (μm)	689	555	480
Bulk density (g/litre)	854	840	780
Dynamic flow rate (ml/s)	109	92	61
Compressibility (%v/v)	7.6	7	12
Particle porosity	<0.20	<0.20	<0.20

Comparison of Examples 2(a) and 2(b) shows the greater weight-effectiveness of Alusil as flow aid.

Examples 3 to 5

[0058] Powders containing sodium tripolyphosphate as the sole water-soluble crystalline inorganic salt were prepared by spray-drying aqueous slurries to the formulations (weight %) shown in Table 3.

Table 3

Example	3	4	5
LAS	48.6	25.3	26.4
NI	-	2.4	2.6
NSD (a)	48.6	27.7	29.0
STP	26.7	42.5	45.9
Salts (b)	26.7	42.5	45.9
Silicate	15.5	11.0	10.0
Minors	1.5	2.9	2.9
Water	7.7	15.9	12.2
(b):(a)	0.55	1.5	1.6

[0059] 20 kg batches of each powder were densified in a Fukae (Trade Mark) high-speed mixer/granulator as described in Examples 1 and 2, process conditions and resulting powder properties being shown in Tables 4 and 5.

Table 4

	3	5(a)	5(b)
Pulverisation:			
Time (min)	3	0.5	0.5
Stirrer speed (rev/min)	300	180	180
Cutter speed (rev/min)	3000	3000	3000
Binder (water):			
Amount (wt %)	2	none	none
Addition time (min)	1	-	-
Stirrer speed (rev/min)	100	-	-
Cutter speed (rev/min)	3000	-	-
Granulation:			
Time (min)	5	5	6
Stirrer speed (rev/min)	275	140	140
Cutter speed (rev/min)	3000	2700	2700
Flow aid:			
Zeo. or Alu.	Alu	Alu	Zeo
Amount (wt %)	1	1.5	5
Addition time (min)	1	1	1
Stirrer speed (rev/min)	90	90	90
Cutter speed (rev/min)	0	300	300
Yield <1700 μm (wt %)	80	94	93
Average particle size (μm)	693	528	389
Bulk density (g/litre)	673	720	820
Dynamic flow rate (ml/s)	134	83	96
Compressibility (%v/v)	3.5	14	11
Particle porosity	<0.20	<0.20	<0.20

Table 5

	4(a)	4(b)
Pulverisation:		
Time (min)	0.5	0.5
Stirrer speed (re.v/min)	180	180
Cutter speed (rev/min)	3000	3000
Binder (water):		
Amount (wt %)	1	0.5
Addition time (min)	0.5	0.5
Stirrer speed (rev/min)	100	100
Cutter speed (rev/min)	3000	3000
Granulation:		
Time (min)	4	4
Stirrer speed (rev/min)	140	140
Cutter speed (rev/min)	2700	2700
Flow aid:		
Zeo. or Alu.	Alu	Alu
Amount (wt %)	2.5	2.5
Addition time (min)	1	1
Stirrer speed (rev/min)	90	90
Cutter speed (rev/min)	300	300
Yield <1700 μm (wt %)	95	96
Average particle size (μm)	501	608
Bulk density (g/litre)	830	770
Dynamic flow rate (ml/s)	86	89
Compressibility (%v/v)	9	11
Particle porosity	<0.20	<0.20

Examples 6 to 8

[0060] Powders containing sodium tripolyphosphate, sodium carbonate and sodium sulphate were prepared to the formulations (weight %) shown in Table 6.

Table 6

Example	6	7	8
LAS	28.0	15.0	15.5
NI	-	3.0	1.5
NSD (a)	28.0	18.0	17.0
STP	27.0	30.0	26.0
Carbonate	5.0	10.0	18.9
Sulphate	15.0	15.0	17.2
Salts (b)	47.0	55.0	62.1
Soap	-	6.0	-
Silicate	8.0	9.0	9.0
Calcite	5.0	-	-
Minors	1.0	1.0	1.4
Water	11.0	11.0	9.8
(b):(a)	1.7	3.0	3.7

[0061] The powders were prepared by spray-drying aqueous slurries. However, the sodium carbonate in the powder of Example 6 was not incorporated via the slurry but postdosed in the Fukae mixer.

[0062] 20 kg batches of each powder were densified in a Fukae (Trade Mark) high-speed mixer/granulator as described in Examples 1 and 2, process conditions and resulting powder properties being shown in Table 7.

Table 7

	6	7
Pulverisation:		
Time (min)	1	1
Stirrer speed (rev/min)	300	300
Cutter speed (rev/min)	3000	3000
Binder (water):		
Amount (wt %)	0.5	1
Addition time (min)	2	1
Stirrer speed (rev/min)	100	100
Cutter speed (rev/min)	3000	3000
Granulation:		
Time (min)	4	4
Stirrer speed (rev/min)	225	200
Cutter speed (rev/min)	3000	3000
Flow aid:		
Zeo. or Alu.	Alu	Alu
Amount (wt %)	1	1
Addition time (min)	1	1
Stirrer speed (rev/min)	90	90
Cutter speed (rev/min)	0	0
Yield <1700 μm (wt %)	g	g
Average particle size (μm)	743	582
Bulk density (g/litre)	906	800
Dynamic flow rate (ml/s)	133	120
Compressibility (%v/v)	3.5	7.0
Particle porosity	<0.20	<0.20

Table 8

	8(a)	8(b)	8(c)
Pulverisation:	none	none	none
Time (min)	-	-	-
Stirrer speed (rev/min)	-	-	-
Cutter speed (rev/min)	-	-	-
Binder (water):			
Amount (wt %)	1.5	1.5	1
Addition time (min)	0.5	0.5	0.5
Stirrer speed (rev/min)	100	100	100
Cutter speed (rev/min)	3000	3000	3000
Granulation:			
Time (min)	10	7	7
Stirrer speed (rev/min)	140	140	140

Table 8 (continued)

	8(a)	8(b)	8(c)
Granulation:			
Cutter speed (rev/min)	2700	2700	2700
Flow aid:			
Zeo or Alu	Alu	Alu	Alu
Amount (wt %)	1.5	1.5	1
Addition time (min)	0.5	0.5	1
Stirrer speed (rev/min)	90	90	90
Cutter speed (rev/min)	300	300	300
Yield <1700 μm (wt %)	94.5	96	96
Bulk density (g/litre)	920	870	760
Dynamic flow rate (ml/s)	g	g	g
Compressibility (%v/v)	g	g	g
Particle porosity	<0.20	<0.20	<0.20

Examples 9 and 10

[0063] Powders containing sodium tripolyphosphate and sodium carbonate were prepared, by spray-drying aqueous slurries, to the formulations (weight %) shown in Table 9, and densified in the Fukae mixer as in previous Examples, as shown in Table 10.

Table 9

Example	9	10
LAS	38.0	22.7
NI	-	2.1
NSD (a)	38.0	24.8
STP	21.0	37.1
Carbonate	22.0	17.5
Salts (b)	43.0	54.6
Silicate	12.0	9.3
Minors	1.0	1.0
Water	6.0	10.3
(b):(a)	1.1	2.2

Table 10

	9	10
Pulverisation:		
Time (min)	3	3
Stirrer speed (rev/min)	300	300
Cutter speed (rev/min)	3000	3000
Binder (water):		
Amount (wt %)	2	1
Addition time (min)	1	1
Stirrer speed (rev/min)	100	100
Cutter speed (rev/min)	3000	3000
Granulation:		
Time (min)	5	5
Stirrer speed (rev/min)	275	275
Cutter speed (rev/min)	3000	3000
Flow aid:		
Zeo or Alu	Alu	Alu
Amount (wt %)	1	1
Addition time (min)	1	1
Stirrer speed (rev/min)	90	90
Cutter speed (rev/min)	0	0
Yield <1700 μm (wt %)	80	90
Average particle size (μm)	810	566
Bulk density (g/litre)	746	801
Dynamic flow rate (ml/s)	137	122
Compressibility (%v/v)	3.0	10
Particle porosity	<0.20	<0.20

Example 11

[0064] A powder containing sodium tripolyphosphate, sodium sulphate and borax was prepared to the formulation (weight %) shown in Table 11.

Table 11

LAS	28.0
NSD (a)	28.0
STP	27.0
Sulphate	19.7
Borax	10.0
Salts (b)	56.7
Polyacrylate polymer	4.5
Minors	0.8
Water	10.0
(b):(a)	2.03

[0065] The powder was prepared by spray-drying an aqueous slurry of all the ingredients except the borax. 9.0 kg of spray-dried base powder and 1.0 kg of borax were mixed and granulated/densified in the Fukae mixer, process conditions and resulting powder properties being shown in Table 12.

Table 12

	11
Mixing:	
Time (min)	5
Stirrer speed (rev/min)	200
Cutter speed (rev/min)	0
Binder (water):	
Amount (wt %)	1
Addition time (min)	1
Stirrer speed (rev/min)	300
Cutter speed (rev/min)	3000
Granulation:	
Time (min)	9
Stirrer speed (rev/min)	300
Cutter speed (rev/min)	3000
Breakdown of oversize:	
Time (min)	1.5
Stirrer speed (rev/min)	75
Cutter speed (rev/min)	3000
Flow aid:	
Zeo or Alu	Alu
Amount (wt %)	1
Addition time (min)	0.5
Stirrer speed (rev/min)	75
Cutter speed (rev/min)	0
Discharge:	
Time (min)	0.5
Stirrer speed (rev/min)	75
Cutter speed (rev/min)	0

[0066] During granulation the temperature rose from an initial 20°C to about 40-45 °C. It was not necessary to cool the mixer.

[0067] The properties of the densified granulate were as follows:

Yield <1700 μm (wt %)	82.1
Average particle size (μm)	583
Bulk density (g/litre)	887
Dynamic flow rate (ml/s)	140
Compressibility (%v/v)	4.7
Particle porosity	<0.20

[0068] The product was a mild detergent powder giving a pH (1 wt% aqueous solution) of 9.2.

Claims

1. A process for the preparation of a granular detergent composition or component having a bulk density of at least 673 g/litre, **characterised by** the step of treating a particulate starting material comprising:

(a) from 12 to 70 wt% of non-soap detergent-active material, and
(b) at least 15 wt% of water-soluble crystalline inorganic salts, including sodium tripolyphosphate and/or sodium carbonate,

the weight ratio of (b) to (a) being at least 0.4:1, and optionally other detergent components to 100 wt%, in a high-speed mixer/granulator having independently controllable stirrer and cutter elements, in the absence of a finely divided particulate agent for improving surface properties having an average particle size not greater than 10μm, whereby granulation and densification to a bulk density of at least 673 g/litre are effected,

with the proviso that the said starting material does not contain:

	% by weight
Linear alkylbenzene sulphonate	20.0
Nonionic surfactant	2.0
Soap	1.0
Zeolite (anhydr.)	35.0
Water with zeolite	10.0
Sodium silicate	4.0
Sodium succinate	2.0
Acrylate/maleate copolymer	2.0
Sodium sulphate	10.45
Sodium carbonate	10.0
Minor ingredients	1.55
Free moisture	2.0
	100.0

2. A process as claimed in claim 1, **characterised in that** granulation is carried out in a bowl-type high-speed mixer/granulator having a substantially vertical stirrer axis.

3. A process as claimed in claim 1 or claim 2, **characterised in that** the particulate starting material consists at least partially of a spray-dried powder.

4. A process as claimed in any preceding claim, **characterised in that** the particulate starting material has a ratio of (b) to (a) within the range of from 0.4:1 to 5:1.

5. A process as claimed in claim 4, **characterised in that** the particulate starting material has a ratio of (b) to (a) within the range of from 1:1 to 5:1.

6. A process as claimed in any preceding claim, **characterised in that** the particulate starting material comprises from 15 to 70 wt% of water-soluble crystalline inorganic salts including sodium tripolyphosphate and/or sodium carbonate.

7. A process as claimed in claim 6, **characterised in that** the particulate starting material comprises from 15 to 50 wt% of sodium tripolyphosphate.

8. A process as claimed in any preceding claim, **characterised in that** the non-soap detergent-active material of the particulate starting material consists at least partially of anionic detergent-active material.

9. A process as claimed in any preceding claim, **characterised in that** the particulate starting material is prepared by a process including the step of admixing at least one inorganic or organic salt having a particle size of at least 100 μm with the remainder of the particulate starting material in the high-speed mixer/granulator.

10. A process as claimed in claim 9, **characterised in that** the salt is selected from borax, sodium bicarbonate, sodium silicate, sodium tripolyphosphate, sodium carbonate, sodium perborate, sodium percarbonate, sodium citrate, sodium nitrilotriacetate, sodium succinate, sodium sulphate and combinations thereof.

11. A process as claimed in any preceding claim, which further comprises the step of admixing a finely divided particulate flow aid to the granular material after granulation is complete.

12. A process as claimed in claim 11, **characterised in that** the flow aid is amorphous sodium aluminosilicate and is added in an amount of from 0.2 to 5.0 wt%, based on the total composition.

13. A process as claimed in claim 11, **characterised in that** the flow aid is finely divided crystalline sodium aluminosilicate and is added in an amount of from 3.0 to 12.0 wt% based on the total composition.

14. A process according to any preceding claim wherein the detergent composition or component prepared by the process has a particle porosity of less than 0.25.

15. A process according to claim 14 wherein the detergent composition or component has a particle porosity of less than 0.20.

Patentansprüche

1. Verfahren zur Herstellung einer körnchenförmigen Waschmittelzusammensetzung oder -komponente mit einer Schüttdichte von mindestens 673 g/l, **gekennzeichnet durch** den Schritt der Behandlung eines teilchenförmigen Ausgangsmaterials umfassend:

(a) 12 bis 70 Gew.-% eines nichtseifenartigen waschaktiven Materials und
(b) mindestens 15 Gew.-% wasserlöslicher kristalliner anorganischer Salze, einschließlich Natriumtripolyphosphat und/oder Natriumcarbonat,

wobei das Gewichtsverhältnis von (b) zu (a) mindestens 0,4:1 beträgt, und gegebenenfalls andere Waschmittelbestandteile bis zu 100 Gew.-%,

in einem Hochgeschwindigkeitsmischer/Granulator mit unabhängig voneinander regelbaren Rühr- und Schneidelementen in Abwesenheit eines feinverteilten teilchenförmigen Mittels zur Verbesserung der Oberflächeneigenschaften mit einer durchschnittlichen Teilchengröße nicht größer als 10 µm, wo**durch** Granulierung und Verdichtung zu einer Schüttdichte von mindestens 673 g/l bewirkt wird, mit der Maßgabe, daß das Ausgangsmaterial nicht enthält:

	Gew.-%
Lineares Alkylbenzolsulfonat	20.0
Nichtionisches oberflächenaktives Mittel	2.0
Seife	1.0
zeolith (wasserfrei)	35.0
Wasser mit Zeolith	10.0
Natriumsilicat	4.0
Natriumsuccinat	2.0
Acrylat/Maleat-Copolymer	2.0
Natriumsulfat	10.45
Natriumcarbonat	10.0
Nebenbestandteile	1.55
Freier Wassergehalt	2.0
	100.0

2. Verfahren nach Anspruch 1, **dadurch gekennzeichnet, daß** die Granulierung in einem schalenförmigen Hochgeschwindigkeitsmischer/Granulator mit einer im wesentlichen vertikalen Rührerachse ausgeführt wird.

3. Verfahren nach Anspruch 1 oder 2, **dadurch gekennzeichnet, daß** das teilchenförmige Ausgangsmaterial zumindest teilweise aus einem sprühgetrockneten Pulver besteht.

4. Verfahren nach einem vorangehenden Anspruch, **dadurch gekennzeichnet, daß** das teilchenförmige Ausgangs-

material ein Verhältnis von (b):(a) innerhalb des Bereiches von 0,4:1 bis 5:1 aufweist.

5. Verfahren nach Anspruch 4, **dadurch gekennzeichnet, daß** das teilchenförmige Ausgangsmaterial ein Verhältnis von (b):(a) innerhalb des Bereiches von 1:1 bis 5:1 aufweist.

6. Verfahren nach einem vorangehenden Anspruch, **dadurch gekennzeichnet, daß** das teilchenförmige Ausgangsmaterial 15 bis 70 Gew.-% wasserlöslicher kristalliner anorganischer Salze, einschließlich Natriumtripolyphosphat und/oder Natriumcarbonat, umfaßt.

7. Verfahren nach Anspruch 6, **dadurch gekennzeichnet, daß** das teilchenförmige Ausgangsmaterial 15 bis 50 Gew.-% Natriumtripolyphosphat umfaßt.

8. Verfahren nach einem vorangehenden Anspruch, **dadurch gekennzeichnet, daß** das nichtseifenartige waschaktive Material des teilchenförmigen Ausgangsmaterials zumindest teilweise aus anionischem waschaktivem Material besteht.

9. Verfahren nach einem vorangehenden Anspruch, **dadurch gekennzeichnet, daß** das teilchenförmige Ausgangsmaterial durch ein Verfahren, einschließlich des Schrittes der Anmischung mindestens eines anorganischen oder organischen Salzes mit einer Teilchengröße von mindestens 100 µm mit dem Rest des teilchenförmigen Ausgangsmaterials in dem Hochgeschwindigkeitsmischer/Granulator hergestellt wird.

10. Verfahren nach Anspruch 9, **dadurch gekennzeichnet, daß** das Salz ausgewählt ist aus Borax, Natriumbicarbonat, Natriumsilicat, Natriumtripolyphosphat, Natriumcarbonat, Natriumperborat, Natriumpercarbonat, Natriumcitrat, Natriumnitrilotriacetat, Natriumsuccinat, Natriumsulfat und Kombinationen davon.

11. Verfahren nach einem vorangehenden Anspruch, zusätzlich umfassend den Schritt des Anmischens einer feinverteilten teilchenförmigen Fließhilfe zu dem körnchenförmigen Material, nachdem die Granulierung vollständig ist.

12. Verfahren nach Anspruch 11, **dadurch gekennzeichnet, daß** die Fließhilfe ein amorphes Natriumaluminosilicat darstellt und in einer Menge von 0,2 bis 5,0 Gew.-%, bezogen auf die Gesamtzusammensetzung, zugegeben wird.

13. Verfahren nach Anspruch 11, **dadurch gekennzeichnet, daß** die Fließhilfe ein feinverteiltes kristallines Natriumaluminosilicat darstellt und in einer Menge von 3,0 bis 12,0 Gew.-%, bezogen auf die Gesamtzusammensetzung, zugegeben wird.

14. Verfahren nach einem vorangehenden Anspruch, wobei die durch das Verfahren hergestellte Waschmittelzusammensetzung oder -komponente eine Teilchenporosität von weniger als 0,25 aufweist.

15. Verfahren nach Anspruch 14, wobei die Waschmittelzusammensetzung oder -komponente eine Teilchenporosität von weniger als 0,20 aufweist.

Revendications

1. Procédé de préparation d'une composition ou composant détergent granulaire ayant une densité apparente d'au moins 673 g/l, **caractérisé en ce qu'**il consiste à traiter une matière particulaire de départ comprenant :

   (a) de 12 à 70 % en poids d'un détergent actif non savonneux, et
   (b) au moins 15 % en poids de sels minéraux cristallins hydrosolubles, notamment le tripolyphosphate de sodium et/ou le carbonate de sodium,

   le rapport pondéral (b) : (a) étant d'au moins 0,4 : 1 et, facultativement, d'autres composants détergents q.s.p. 100 % en poids,
   dans un mélangeur/granulateur à grande vitesse comportant des éléments d'agitateur et de cisaille indépendamment réglables, en l'absence d'un agent particulaire finement divisé pour améliorer les propriétés superficielles, présentant une granulométrie moyenne qui ne dépasse pas 10 µm, de sorte qu'on effectue la granulation et la densification jusqu'à une densité apparente d'au moins 673 g/l,
   à la condition que ledit matériau de départ ne contiennent pas :

	% en poids
Alkylbenzène sulfonate linéaire	20,0
Tensioactif non ionique	2,0
Savon	1,0
Zéolite (anhydre)	35,0
Eau avec la zéolite	10,0
Silicate de sodium	4,0
Succinate de sodium	2,0
Copolymère acrylate/maléate	2,0
Sulfate de sodium	10,45
Carbonate de sodium	10,0
Ingrédients mineurs	1,55
Humidité libre	2,0

2. Procédé selon la revendication 1, **caractérisé en ce qu'**on effectue la granulation dans un mélangeur/granulateur à grande vitesse du type à cuvette présentant un axe d'agitateur substantiellement vertical.

3. Procédé selon la revendication 1 ou 2, **caractérisé en ce que** la matière particulaire de départ consiste en poudre au moins partiellement séchée par pulvérisation.

4. Procédé selon l'une quelconque des revendications précédentes, **caractérisé en ce que**, dans la matière particulaire de départ, le rapport (b) : (a) est compris entre 0,4 : 1 et 5 : 1.

5. Procédé selon la revendication 4, **caractérisé en ce que** le rapport (b) (a) dans la matière particulaire de départ est compris entre 1 : 1 et 5 : 1.

6. Procédé selon l'une quelconque des revendications précédentes, **caractérisé en ce que** la matière de départ comprend de 15 à 70 % en poids de sels minéraux cristallins hydrosolubles, notamment du tripolyphosphate de sodium et/ou du carbonate de sodium.

7. Procédé selon la revendication 6, **caractérisé en ce que** la matière particulaire de départ comprend de 15 à 50 % en poids de tripolyphosphate de sodium.

8. Procédé selon l'une quelconque des revendications précédentes, **caractérisé en ce que** le détergent actif savonneux dans la matière particulaire de départ consiste au moins partiellement en détergent actif anionique.

9. Procédé selon l'une quelconque des revendications précédentes, **caractérisé en ce qu'**on prépare la matière particulaire de départ par un procédé consistant à mélanger au moins un sel minéral ou organique d'une granulométrie d'au moins 100 µm avec le complément de la matière particulaire de départ dans le mélangeur/granulateur à grande vitesse.

10. Procédé selon la revendication 9, **caractérisé en ce que** le sel est choisi parmi le borax, le bicarbonate de sodium, le silicate de sodium, le tripolyphosphate de sodium, le carbonate de sodium, le perborate de sodium, le percarbonate de sodium, le citrate de sodium, le nitrilotriacétate de sodium, le succinate de sodium, le sulfate de sodium et des combinaisons de ceux-ci.

11. Procédé selon l'une quelconque des revendications précédentes, qui consiste à incorporer dans la matière granulaire après achèvement de la granulation, un agent particulaire finement divisé d'assistance à l'écoulement.

12. Procédé selon la revendication 11, **caractérisé en ce que** l'agent d'assistance à l'écoulement est l'aluminosilicate amorphe de sodium et on l'ajoute à raison de 0,2 à 5,0 % en poids par rapport à la composition totale.

13. Procédé selon la revendication 11, **caractérisé en ce que** l'agent d'assistance à l'écoulement est un aluminosilicate de sodium cristallin finement divisé et on l'ajoute à raison de 3,0 à 12,0 % par rapport au poids de la composition totale.

14. Procédé selon l'une quelconque des revendications précédentes, dans lequel la composition ou composant détergent préparé par le procédé présente une porosité de particules inférieure à 0,25.

15. Procédé selon la revendication 14, dans lequel la porosité des particules de la composition ou composant détergent est inférieure à 0,20.