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(54) Detergent compositions and process for preparing them.

(57) A batch process for the preparation of detergent powder of high bulk density comprises neutralising a detergent acid (anionic surfactant precursor), eg linear alkylbenzene sulphonic acid, with a particulate solid water-soluble alkaline inorganic material, for example, sodium carbonate (optionally plus other alkaline materials and/or detergency builders, for example, alkali metal aluminosilicate), in a high-speed mixer/granulator, eg Fukae mixer, and granulating the product in the mixer. The reaction mixture remains particulate throughout the process, without the need to keep the temperature during the neutralisation step to 55°C or below, and a high-quality high-bulk-density particulate product is obtained.

EP 0 438 320 A2

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DETERGENT COMPOSITIONS AND PROCESS FOR PREPARING THEM

TECHNICAL FIELD

The present invention relates to granular detergent compositions and components of high bulk density, and their preparation by a dry neutralisation process.

BACKGROUND AND PRIOR ART

Recently there has been considerable interest within the detergents industry in the production of detergent powders having relatively high bulk density, for example, 650 g/litre and above. It has been suggested that such powders containing anionic surfactants, for example alkyl benzene sulphonate, may be prepared by methods involving in-situ neutralisation of an acid precursor of the anionic surfactant with an alkali such as sodium hydroxide or sodium carbonate.

For example, JP 60 072 999A (Kao) and GB 2 166 452B (Kao) disclose a process in which detergent sulphonic acid, sodium carbonate and water are mixed in a strongly shearing apparatus ; the solid mass obtained is cooled to 40°C or below and pulverised ; and the fine powder thus obtained is granulated. This process is typical of those disclosed in the art in that the product of the neutralisation reaction is a doughy mass, and the reaction requires apparatus such as a kneader with a very high energy requirement ; and separate pulverisation and granulation steps in different apparatus are required in order to obtain an acceptable granular detergent product.

There has also been considerable recent interest in the use of high-speed mixer/granulators in the preparation of high-bulk-density detergent powders. For example, EP 158 419B (Hashimura) discloses a process in which nonionic surfactant and soda ash are mixed and granulated in a reactor having horizontal and vertical blades rotating at different speeds, to give a detergent powder built with sodium carbonate and containing a high level of nonionic surfactant.

GB 1 404 317 (Bell) discloses the preparation of a detergent powder of low or moderate bulk density by a dry neutralisation process. Detergent sulphonic acid is mixed with an excess of soda ash in the presence of sufficient water to initiate the neutralisation reaction but not enough to wet the resultant product, which is in the form of a free-flowing powder. The process is carried out in apparatus, for example a ribbon blender, planetary mixer or air transfer mixer, in which the reactants are "tossed and fluffed", and carbon dioxide liberated during the neutralisation is entrapped in the product particles. The process is thus directed towards the production of light, porous particles comparable to those obtained by spray-drying.

GB 1 369 269 (Colgate) discloses a process for the production of anionic detergent, by vigorously mixing detergent sulphonic acid with powdered sodium carbonate in a mixer with a cutting arrangement, for example a Lödige ploughshare mixer. In order to obtain a granular product rather than a doughy mass, it is necessary to blow the detergent sulphonic acid in by means of a gas stream, to ensure adequate fluidisation and mixing of the reactants : this requires quite complex modification of the mixer. The reaction apparently proceeds slowly and produces a relatively coarse product requiring an additional size reduction step.

US 4 690 785 (Witco) discloses a process for the production of alkylbenzene sulphonate powder by the neutralisation of alkylbenzene sulphonic acid with a base in solid or solution form. A substantial amount of water is present at the beginning of the process, and the heat generated by the exothermic reaction is used to drive off this, and the water generated by the reaction itself ; reaction temperatures of about 100°C are typical.

EP 352 135A (Unilever), published on 24 January 1990, relates to a process for the production of free-flowing detergent powders and detergent powder components of high bulk density and small particle size by dry neutralisation at relatively low temperatures using only a single piece of apparatus : a high-speed mixer/granulator having both a stirring action and a cutting action. Maintenance of a temperature not higher than 55°C throughout the neutralisation step is stated to be essential ; if necessary, cryogenic cooling may be employed.

The present inventors have now surprisingly discovered that, with improved control of other process parameters, this process can be carried out successfully - or even advantageously - without the need for cooling to temperatures not exceeding 55°C throughout the neutralisation step.

Our copending European Patent Application No. 90 202 429.8 filed on 13 September 1990 describes and claims a process for the continuous preparation of a granular detergent composition of high bulk density, involving the continuous dry neutralisation of a liquid anionic surfactant precursor such as linear alkylbenzene sulphonic acid in a high-speed mixer such as the Lödige CB 30 Recycler, which contains a central horizontal stirring axis but no separate cutting elements. Neutralisation and granulation take place completely during a very short residence period in the Recycler, and the reaction mixture then passes continuously to a moderate-speed mixer/granulator such as the Lödige KM 300 ploughshare mixer, where the residence time is longer, for densification.

DEFINITION OF THE INVENTION

The present invention provides a batch process for the preparation of a granular detergent composition or component having a bulk density of at least 650 g/litre, which process includes the step of neutralising a liquid acid precursor of an anionic surfactant with a solid water-soluble alkaline inorganic material, the process being characterised by the steps of :

(i) fluidising a particulate solid water-soluble alkaline inorganic material in an amount in excess of that required for neutralisation, optionally in admixture with one or more other particulate solids, in a high-speed mixer/granulator having both a stirring action and a cutting action ;

(ii) adding the acid precursor to the high-speed mixer/granulator, without maintaining a temperature of 55°C or below, whereby neutralisation of the acid precursor by the water-soluble alkaline inorganic material occurs while the mixture remains in particulate form ;

(iii) granulating the mixture in the high-speed mixer/granulator, in the presence of a liquid binder, whereby a granular detergent composition or component having a bulk density of at least 650 g/litre is formed.

The invention also provides a granular detergent composition or component prepared by this process.

DETAILED DESCRIPTION OF THE INVENTION

The process

The subject of the invention is the preparation of high-bulk-density detergent powder by a batch process involving the dry neutralisation of the acid precursor of an anionic surfactant with an alkaline solid. The process is carried out batchwise in a high-speed mixer/granulator and involves the previously defined process steps (i), (ii) and (iii).

A very important characteristic of the process of the invention is that the reaction mixture remains throughout in particulate or granular form. Caking, balling and dough formation are avoided, and the product at the end of the granulation step needs no further particle size reduction. The process of the invention generally produces a granular product containing at least 50 wt%, preferably at least 70 wt%, of particles smaller than 1700 µm. This is achieved by ensuring that liquid components, particularly the acid anionic surfactant precursor, do not have an opportunity to act as binders or agglomerating agents.

First, step (i) ensures that there is initially a large amount of particulate solids present, relative to the liquids to be added, in the mixer before the introduction of the liquids. Preferably the total solids present in step (i) amount to at least 60 wt%, more preferably at least 67 wt%, of the total composition present in step (ii). It is therefore advantageous to add as high a proportion as possible of the solid ingredients of the final product at this stage.

The solids must of course include a particulate water-soluble alkaline inorganic material (neutralising agent), in at least slight excess over the amount required for neutralisation. The terms "particulate solid water-soluble alkaline inorganic material" and "neutralising agent" used herein of course include combinations of two or more such materials. If the neutralising agent is a material that itself can play a useful role in the final composition, substantially larger amounts than this may be used.

According to a preferred embodiment of the invention the neutralising agent comprises sodium carbonate, either alone or in admixture with one or more other particulate water-soluble alkaline inorganic materials, for example, sodium bicarbonate and/or sodium silicate. Sodium carbonate is of course also useful as a detergency builder and provider of alkalinity in the final composition. This embodiment of the invention may thus advantageously be used to prepare detergent powders in which sodium carbonate is the sole or principal builder, and in that case substantially more sodium carbonate than is required for neutralisation may be present.

The sodium carbonate embodiment of the invention is also suitable, however, for the preparation of detergent compositions in which substantial amounts of other builders are present. Those other builders may also advantageously be present in the high-speed mixer/granulator in step (i). Examples of such builders include crystalline and amorphous alkali metal aluminosilicates, alkali metal phosphates, and mixtures thereof. Sodium carbonate may nevertheless be present in excess of the amount required for neutralisation, in order to provide alkalinity in the product : an excess of about 10 to 15 wt% is then suitable.

The solids present in step (i) may also include any other desired solid ingredients, for example, fluorescers;

polycarboxylate polymers ; antiredeposition agents, for example, sodium carboxymethyl cellulose ; or fatty acids for in-situ neutralisation to form soaps.

If desired, solid particulate surfactants, for example, alkylbenzene sulphonate and/or alkyl sulphate in powder form, may form part of the solids charge in step (i). Thus, for example, a detergent powder prepared by the process of the invention may contain alkylbenzene sulphonate in part introduced as a powder in step (i), and in part prepared in situ in step (ii).

Alternatively or additionally, a spray-dried detergent base powder may form part of the solids charge in step (i).

It is an important feature of the process of the invention that the solids be very efficiently mixed and fluidised before the introduction of any liquid ingredients : the term "fluidisation" as used herein means a state of mechanically induced vigorous agitation in which the mass of particles is to some extent aerated, but does not necessarily imply the blowing in of a gas. This state is achieved by the choice of apparatus : a high-speed mixer/granulator having both a stirring action and a cutting action. Preferably the high-speed mixer/granulator has rotatable stirrer and cutter elements that can be operated independently of one another, and at separately changeable or 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.

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. If necessary, the vessel can be fitted with a cooling jacket.

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

Yet 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. This configuration, however, has the disadvantage that mixing and fluidising in step (i) is less efficient, and may need to be supplemented by the blowing in of gas as described in the aforementioned GB 1 369 269 (Colgate).

Step (ii) of the process of the invention is the introduction of the acid surfactant precursor. The way in which this step is conducted is crucial to the success of the process. In particular, it is believed to be critical to ensure throughout the neutralisation step that any liquid components do not have the opportunity to cause substantial agglomeration.

Initial work on the present process, with control of the temperature during step (ii) to 55°C or below, indicated that the solids, efficiently fluidised by the action of the mixer, had to be wetted with just sufficient water to initiate and promote the neutralisation reaction before they encountered the acid precursor. The amount of free water present in step (ii) was therefore believed to be very important, the term "free water" being used to mean water not firmly bound as water of hydration or crystallisation to inorganic materials. It was believed that, if insufficient free water were present, the reaction would not proceed rapidly, and unreacted detergent acid precursor would accumulate in the mixer and act as a binder, causing substantial agglomeration, balling up and even dough formation. Addition of a carefully controlled amount of water at the neutralisation stage was therefore considered an important part of the process as then conceived. That combination of temperature control and process water control formed the basis of the above-mentioned EP352 135A (Unilever).

It has now been found, at least when a crystalline alkali metal aluminosilicate is present as part of the solids charge, that the process may advantageously be carried out without any addition of water at the neutralisation stage, and without control of the temperature throughout the neutralisation stage to $\leqq$55°C. When aluminosilicate is present, preferably no water is added earlier than to the granulation stage (iii).

Another important process parameter is the manner of addition of the acid precursor to the high-speed mixer/granulator in step (ii). It would appear that the rate and manner of addition should be such that the acid precursor will be consumed immediately and will not accumulate in the mixer in unreacted form. It is preferred that the acid precursor be introduced gradually, rather than in a single, substantially instantaneous addition, into the high-speed mixer/granulator.

The actual time required and preferred for addition of the acid precursor is of course dependent on the amount to be added. It was initially thought that very gradual addition over a period of at least 1 minute, and preferably longer, was necessary, but it has subsequently been found, following the optimisation of other process variables (moisture content, powder mixing efficiency, powder temperature), that rapid addition over a period of less than 1 minute is also possible and may even be preferred. Another measure that can be used to reduce the addition time is the use of more than one manifold, for example, two, for the introduction of the acid precursor, so that it is introduced simultaneously into two or more different locations within the high-speed mixer/granulator. Addition of the acid is thus still preferably "gradual" in the sense that it should be added in such a way that high local concentrations should be avoided, either by spreading addition out over time, or over space, or both.

The addition time may accordingly range, for example, from 0.5 to 12 minutes, and a time of from 1 to 10 minutes, more especially a time of from 1 to 3 minutes, is presently preferred.

The speed at which acid precursor is introduced into the mixer may also be expressed as a rate of addition. For a batch size of 750 kg, a rate of linear alkylbenzenesulphonic acid of from 80 to 200 kg/min, especially 100 to 140 kg/min, has been found to give good results.

Other liquid detergent ingredients may be introduced during step (ii). Examples of such ingredients include nonionic surfactants, and low-melting fatty acids which may be also be neutralised in situ, to form soaps.

The neutralisation step (ii) may typically take from 0.5 to 12 minutes, and, as indicated above, the addition of the acid precursor (optionally plus other liquid ingredients) may or may not be preceded by a separate step in which water (optionally plus other liquid ingredients) is added to the mixer.

As indicated previously, the temperature of the powder mass in the high-speed mixer/granulator need not be maintained throughout step (ii) at 55°C or below, as previously thought, in order to avoid agglomeration and lump formation. The neutralisation step can therefore be carried out successfully at temperatures above 55°C. Preferably, however, the temperature is not allowed to exceed 100°C, in order that excessive moisture loss may be avoided ; more preferably, the temperature does not exceed 75°C.

The temperature of the reaction mixture of course rises during the neutralisation step owing to the exothermicity of the reaction, the amount of the increase depending on the proportion of acid precursor in the mixture; for example, it has been found that in the preparation of a composition containing about 25 wt% alkylbenzene sulphonate, as described in the Example below, the temperature typically rises to about 35°C above ambient, ie about 55-65°C. There would appear to be no advantage in operating at a temperature above that occurring naturally. Generally, a temperature within the range of from above 55°C to 75°C, preferably from above 55°C to 70°C, appears to be suitable. If desired, a water-jacket may be used to provide temperature control.

A very important feature of the process of the invention is granulation in the high-speed mixer/granulator. This will generally take the form of a separate granulation step (iii) after addition of the acid precursor and neutralisation are complete. When operating at higher temperatures, however, granulation can sometimes start to occur before neutralisation is complete, and steps (ii) and (iii) of the process may then be regarded as having coalesced to form a single continuous step (ii)/(iii).

The granulation or densification process leads to a product of very high bulk density. When working at lower temperatures (the process of EP 352 135A) it was found that granulation required the presence of a liquid binder, but in an amount significantly lower than that used when granulating a powder in conventional apparatus such as a pan granulator. The binder, added prior to granulation but after neutralisation was complete, would generally comprise water and/or a liquid detergent ingredient, for example, an aqueous solution of a polycarboxylate polymer, or a nonionic surfactant, or a mixer of any of these. It has now been found that addition of binder for step (iii) is not essential, and that instead the temperature may be allowed to rise to effect granulation. It may still be convenient, however, to introduce liquid ingredients such as nonionic surfactant at this stage, and then a lower granulation temperature can be used.

During steps (i), (ii) and (iii) of the process of the invention, the stirrer and cutter elements of the high-speed mixer/granulator are preferably operated at high speed to provide the most efficient mixing possible and to maintain the reaction mixture in particulate form. The stirrer speed thoughout these steps may suitably lie within the range of from 60 to 150 rpm, preferably from 80 to 120 rpm, and the cutter speed within the range of from 1000 to 3000 rpm. The preferred stirrer and cutter speeds will, however, depend on the batch size and are also subject to machine limitations : for example, the Fukae FS-1200 mixer, which is suitable for processing a 750 kg batch, has a maximum stirrer speed of 100 rpm and a maximum cutter speed of 2000 rpm, so that the preferred stirrer speed range is cut down to 60-100 rpm, and the preferred cutter speed range to 1000-2000 rpm. Smaller machines, such as the FS-30, suitable for processing a 15 kg batch, can provide higher maximum speeds.

The product of the granulation step (iii) is a particulate solid of high bulk density : at least 650 g/litre, preferably at least 750 g/litre, and more preferably at least 800 g/litre. As previously indicated, the particle size distribution is generally such that at least 50 wt%, preferably at least 70 wt% and more preferably at least 85 wt%, of particles are smaller than 1700 µm, and the level of fines (particles <180 µm) is low. No further treatment has generally been found to be necessary to remove either oversize particles or fines.

Although the product generally has good flow properties, low compressibility and little tendency towards caking, those powder properties may be improved further and bulk density further increased by the admixture of a finely divided particulate flow aid after granulation is complete. Depending on the flow aid chosen, it may suitably be added in an amount of from 0.2 to 12.0 wt%, based on the total product.

During addition of the flow aid, the stirrer speed may advantageously be reduced, for example, to 60-80 rpm, and the cutter is preferably not employed. Comminution of the particles is to be avoided if possible at this stage.

Suitable flow aids include crystalline and amorphous alkali metal aluminosilicates having an average particle size within the range of from 0.1 to 20 μm, preferably from 1 to 10 μm. The crystalline material (zeolite) is preferably added in an amount of from 3.0 to 12.0 wt%, more preferably from 4.0 to 10.0 wt%, based on the total product. The amorphous material, which is more weight-effective, is preferably added in an amount of from 0.2 to 5.0 wt%, more preferably from 0.5 to 3.0 wt%, based on the total product. A suitable amorphous material is available commercially from Crosfield Chemicals Ltd, Warrington, Cheshire, England, under the trade mark Alusil. If desired, both crystalline and amorphous aluminosilicates may be used, together or sequentially, as flow aids.

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.

A process which comprises admixing finely divided amorphous sodium aluminosilicate to a dense granular detergent composition containing surfactant and builder and prepared and/or densified in a high speed mixer/granulator is described and claimed in EP 339 996A (Unilever).

The product

As already indicated, the process of the invention produces a granular high-bulk-density solid, containing surfactant and builder, and having a bulk density of at least 650 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.

This 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. The densified granulate may typically constitute from 40 to 100 wt% of a final product.

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.

The process may with advantage be used to prepare detergent compositions containing from 5 to 35 wt%, or more, of anionic surfactant, this anionic surfactant being derived wholly or in part from the in-situ neutralisation reaction of step (ii).

The anionic surfactant prepared at least in part by in-situ neutralisation may, for example, be selected from linear alkylbenzene sulphonates, alpha-olefin sulphonates, internal olefin sulphonates, fatty acid ester sulphonates and combinations thereof. The process of the invention is especially useful for producing compositions containing alkylbenzene sulphonates, by in-situ neutralisation of the corresponding alkylbenzene sulphonic acid.

Other anionic surfactants that may be present in compositions prepared by the process of the invention include primary and secondary alkyl sulphates, alkyl ether sulphates, and dialkyl sulphosuccinates. Anionic surfactants are of course well known and the skilled reader will be able to add to this list by reference to the standard textbooks on this subject.

As previously indicated, nonionic surfactants may also be present. These too are well known to those skilled in the art, and include primary and secondary alcohol ethoxylates.

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.

If desired, soap may also be present, to provide foam control and additional detergency and builder power.

Typically, detergent compositions produced by the process of the invention may comprise form 10 to 35 wt% of anionic surfactant, from 0 to 10 wt% of nonionic surfactant, and from 0 to 5 wt% of fatty acid soap.

Typical products of the invention

The following are general, non-limiting examples of formulation types that may readily be prepared by the process of the invention.

(1) Compositions containing crystalline or amorphous alkali metal aluminosilicate, especially crystalline zeolite and more especially zeolite 4A, as a detergency builder :

(a) from 5 to 35 wt% of non-soap detergent-active material consisting at least partially of anionic surfactant,

(b) from 15 to 45 wt% (anhydrous basis) of crystalline or amorphous alkali metal aluminosilicate,

and optionally other detergent ingredients, including any excess of the neutralising agent for the anionic surfactant, to 100 wt%. The weight ratio of (b) to (a) is preferably at least 0.9 :1.

An especially preferred class of detergent compositions that may be prepared by the process of the invention is described and claimed in EP 340 013A (Unilever). These compositions comprise :

(a) from 17 to 35 wt% of non-soap detergent-active material consisting at least partially of anionic surfactant, and

(b) from 28 to 45 wt% of crystalline or amorphous alkali metal aluminosilicate,

the weight ratio of (b) to (a) being from 0.9 :1 to 2.6 :1, preferably from 1.2 :1 to 1.8 :1, and optionally other detergent ingredients to 100 wt%.

(2) Compositions as described in EP 351 937A (Unilever) :

(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, preferably from 0.4 :1 to 9 :1 and more preferably from 0.4 :1 to 5 :1, and optionally other detergent components to 100 wt%.

These compositions preferably contain a total of from 15 to 70 wt% of water-soluble crystalline inorganic salts, which may comprise, for example, sodium sulphate, sodium ortho- or pyrophosphate, or sodium meta- or orthosilicate. Especially preferred compositions contain from 15 to 50 wt%, more preferably from 20 to 40 wt%, of sodium tripolyphosphate.

As previously indicated, all these preferred classes of detergent composition that may be prepared by the process of the invention may contain conventional amounts of other conventional ingredients, for example, bleaches, enzymes, lather boosters or lather controllers as appropriate, antiredeposition and antiincrustation agents, perfumes, dyes and fluorescers. These may be incorporated in the product at any suitable stage, and the skilled detergent formulator will have no difficulty in deciding which ingredients are suitable for admixture in the high-speed mixer/granulator, and which are not.

The process of the invention has the advantage over conventional spray-drying processes that the very high temperatures encountered in spray-drying towers are not involved, so fewer restrictions are imposed on the way in which heat-sensitive ingredients such as bleaches and enzymes are incorporated into the product.

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

EXAMPLES

Example 1

A 750 kg batch of high-bulk-density detergent powder having the following nominal formulation was prepared using a Fukae (Trade Mark) FS-1200 high-speed mixer/granulator :

	wt%
Linear alkylbenzene sulphonate	25.0
Nonionic surfactant	2.0
Soap	1.0
Zeolite 4A (anhydrous))	(35.0
Water with zeolite)	(9.99
Sodium silicate	4.0
Acrylate/maleate copolymer	1.0
Fluorescer	0.18
Sodium carboxymethyl cellulose	0.9
Sodium carbonate	15.51
Total added water	2.0
Speckles	0.8
Enzyme	0.6
Perfume	0.25

	100.00

The ratio of zeolite (anhydrous) to total non-soap surfactant in this composition was 1. 29 : 1.

The process was carried out as follows :

(i) Solid ingredients as specified below were dry-mixed in the Fukae mixer for 1 minute, using a stirrer speed of 100 rpm and a cutter speed of 2000 rpm.

	parts
Zeolite 4A (hydrated)	40.0
Sodium carbonate	19.53*
Sodium carboxymethylcellulose	0.9
Sodium silicate	4.0
Acrylic/maleic copolymer	1.0
Fluorescer	0.18
Fatty acid	0.92

Total solids	66.53

*This amount of sodium carbonate represented a 5-fold excess over that required for neutralisation of the alkylbenzene sulphonic acid (see paragraph (ii) below).

(ii) Linear alkylbenzene sulphonic acid (23.5 parts) was added over a period of 2-3 minutes while the mixer was operated at a stirrer speed of 100 rpm and a cutter speed of 2000 rpm. The mixer was then operated for a further 1 minute at the same stirrer and cutter speeds. The temperature was maintained below 60°C by means of a cooling jacket filled with water. Throughout this step, the reaction mixture remained in particulate form. No water was added before or during this step.

Total liquids 23.5

Solids as % of total	73.9

(iii) Nonionic surfactant (2.0 parts) was added over a period of 1 minute, while the mixer was operated at a stirrer speed of 80 rpm and a cutter speed of 2000 rpm. Water (1.6 parts) was then added over a period of a further 1 minute while the mixer continued to operate at the same stirrer and cutter speeds. The mixer was then operated at the same stirrer and cutter speeds for a further 18 minutes to effect granulation, while the temperature was maintained at about 60°C by means of a cooling jacket filled with water. The product of this step was a granular solid.

Total liquids	27.1
Solids as % of total	71.1

(iv) Zeolite (a further 5 parts) was then added as a flow aid, while the mixer was operated for 1 minute at a stirrer speed of 80 rpm without the cutter.

The resulting powder was free-flowing, had a bulk density of 878 g/litre, and contained 96 wt% of particles <1700 µm. The particle porosity was 0.1.

Coloured speckles of the same powder (0.8 parts) and enzyme granules (0.6 parts) were mixed with the powder using a rolling drum, and perfume (0.25 parts) were sprayed on, to give a fully formulated high-bulk-density detergent powder having excellent powder properties.

Examples 2 to 4, Comparative Example A

Further 750 kg batches of the nominal formulation given in Example 1, minus the postdosed ingredients (speckles, enzyme, perfume) were prepared using the Fukae FS-1200 mixer.

Examples 2 to 4 were in accordance with the present invention, without temperature control during the neutralisation step : while Comparative Example A employed temperature control (a water jacket containing water cooled to 9°C) during the neutralisation step and was in accordance with EP 352 135A (Unilever) published on 24 January 1990.

Processing was as follows :

(i) The solid ingredients were dry-mixed in the Fukae mixer for 1 minute, using the stirrer and cutter speeds specified in Table 1 below.

(ii) Linear alkylbenzene sulphonic acid was added, over the period shown in Table 1, below, while the mixer was operated at the same stirrer and cutter speeds. The acid addition times varied from 1 min 30 sec to 2 min 50 sec depending on whether a single manifold or two manifolds were used ; the acid flow rate was 60 kg/min (single manifold) or 90 kg/min (double manifold). A short "pulverisation" stage of 1 minute at the same stirrer and cutter speeds followed to allow for any temperature/reaction lag. Throughout step (ii), the reaction mixture remained in particulate form. No water was added before or during this step.

(iii) Nonionic surfactant was poured onto the powder bed over a period of 1 minute, while the mixer continued to operate at the same stirrer and cutter speeds. Water, if required, was then sprayed onto the powder bed over a period of a further 2 to 3 minutes while the mixer continued to operate at the same stirrer and cutter speeds.

The mixer was then operated at the same stirrer and cutter speeds to effect granulation, the endpoint being detected by means of the amperage of the stirrer motor. The products of this step were all granular solids.

(iv) As in Example 1, further zeolite was then added as a flow aid, while the mixer was operated at a lower stirrer speed without the cutter.

Total batch times were in the range of from 8 to 21 minutes.

The properties of the resulting products are shown in Table 2 below.

TABLE 1

Examples 2 - 4 and A: processing conditions

Neutralisation step

	Manifolds	Acid Addition Time (min:sec)	Stirrer/cutter speeds (rpm)
2	1	2:50	80/2000
3	1	2:50	80/2000
4	2	2:00	80/2000
A	2	2:30	80/2000

Granulation step

Ex.	Water added (kg)	Granulation time (min:sec)	Process time (min:sec)
2	6	4:10	12:40
3	4	5:45	14:30
4	4	6:00	14:10
A	5	7:00	19:00

Stirrer/cutter speeds were as in the neutralisation step.

TABLE 2

Examples 2 - 4 and A: properties of products

	Yield <1700 µm (wt%)	Bulk density (g/l)
2	88	819
3	89	827
4	93	836
A	91	831

The powders of all four Examples were free-flowing and there was no significant difference between them.

Examples 5 and 6, Comparative Example B

Further 750 kg batches of the nominal formulation given in Example 1, minus the postdosed ingredients (speckles, enzyme, perfume) were prepared using the Fukae FS-1200 mixer, using higher controlled process temperatures in order to simulate operation at high ambient temperatures. Two manifolds were used for acid addition in each case. The powder temperature at the end of the neutralisation step was measured, showing Examples 5 and 6 to be within the present invention and Comparative Example B to be in accordance with EP 352 135A (Unilever).

Process details are shown in Table 3 and product properties in Table 4.

TABLE 3

Examples 5, 6 and B: processing conditions

Neutralisation step

	Acid Addition Time (min:sec)	Water jacket temp. (°C)	Powder temp. ex neutr. (°C)	Stirrer/cutter speeds (rpm)
B	1.40	warming	46°C	106/1250
5	1:29	35°C	57°C	80/2000
6	1:40	49°C	56°C	80/2000

Granulation step

	Water added (kg)	Granulation time (min:sec)	Process time (min:sec)
B	nil	4:15	8:50
5	nil	16:00	21:10
6	nil	4:00	10:50

TABLE 4

Examples 5, 6 and B: properties of products

	Yield <1700 um (wt%)	Bulk density (g/l)
B	81	777
5	79	860
6	80	797

All powders were free-flowing and did not differ significantly from one another.

Example 7

A high-bulk-density powder having a higher content of anionic surfactant was prepared by the process described above under Examples 2 to 4. The formulation was as follows :

		parts
Linear alkylbenzene sulphonate		30.0
Nonionic surfactant		2.0
Soap		1.0
Zeolite 4A (anhydrous))	(	35.0
Water with zeolite)	(	9.99
Sodium silicate		4.0
Acrylate/maleate copolymer		1.0
Fluorescer		0.18
Sodium carboxymethyl cellulose		0.9
Sodium carbonate		15.51

The stirrer and cutter speeds were 80 rpm and 2000 rpm respectively. The acid addition time was 1 min 40 sec, two manifolds being used. Cooling water (9°C) was used during the neutralisation step but the temperature nevertheless rose to 61 °C at the end of acid addition. No water was added at the neutralisation stage. The granulation time was 5 minutes and the total batch time 10 minutes.

The product obtained had exceptionally good powder properties :

Bulk density	791 g/l
Yield <1700μm	70 wt%
Fines content (<180 μm)	14 wt%
Dynamic flow rate	118 ml/s
Compressibility	8.8% v/v

Examples 8 and 9

Two powders containing sodium tripolyphosphate were prepared by the process of the invention, using the Fukae FS-1200 mixer. The batch size in each case was 670 kg. The formulations of the final products were as follows :

	%	
	8	9
Linear alkylbenzene sulphonate	31.3	25.6
Sodium tripolyphosphate	37.2	36.9
Sodium alkaline silicate	9.0	9.0
Sodium carbonate	12.0	12.8
Zeolite 4A (anhydrous)	4.4	8.7
Fluorescer	0.2	0.2
Sodium carboxymethylcellulose	1.4	1.4
Alusil	2.3	2.2
Moisture	2.2	3.3
	----	----
	100.00	100.00

The process was carried out substantially as described above under Examples 2 to 4. In each case the zeolite was introduced wholly as part of the initial solids charge, and the Alusil was added as a flow aid in the final stage of the process. The powder temperature in the neutralisation stage was above 55°C in both cases.

Process details and powder properties were as follows :

	8	9
Maximum powder temperature (°C) (during neutralisation step)	67	56
Total process time (min)	7	10
Yield $\leq$1700 μm (wt%)	50	96.3
Bulk density (g/l)	727	947

The powder of Example 8 had exceptionally good flow properties, the dynamic flow rate being 139 ml/s.

Claims

1. A batch process for the preparation of a granular detergent composition or component having a bulk density of at least 650 g/litre, which process includes the step of neutralising a liquid acid precursor of an anionic surfactant with a solid water-soluble alkaline inorganic material, the process being characterised by the steps of :

   (i) fluidising a particulate solid water-soluble alkaline inorganic material in an amount in excess of that required for neutralisation, optionally in admixture with one or more other particulate solids, in a high-speed mixer/granulator having both a stirring action and a cutting action ;

   (ii) adding the acid precursor to the high-speed mixer/granulator without maintaining a temperature of 55°C or below, whereby neutralisation of the acid precursor by the water-soluble alkaline inorganic material occurs while the mixture remains in particulate form ;

(iii) granulating the mixture in the high-speed mixer/granulator, in the presence of a liquid binder, whereby a granular detergent composition or component having a bulk density of at least 650 g/litre is formed.

2. A process as claimed in claim 1, characterised in that in step (ii) the acid precursor is added gradually to the high-speed mixer/granulator.

3. A process as claimed in claim 2, characterised in that in step (ii) the acid precursor is added to the high-speed mixer/granulator over a period of at least 0.5 minute.

4. A process as claimed in claim 3, characterised in that in step (ii) the acid precursor is added to the high-speed mixer/granulator over a period of from 0.5 to 12 minutes.

5. A process as claimed in any preceding claim, characterised in that the temperature in the high-speed mixer/granulator during step (ii) does not exceed 100°C.

6. A process as claimed in any preceding claim, characterised in that the particulate water-soluble alkaline inorganic material comprises sodium carbonate.

7. A process as claimed in any preceding claim, characterised in that the acid precursor is a linear alkylbenzene sulphonic acid.

8. A process as claimed in any preceding claim, characterised in that the solids present in step (i) comprise the water-soluble alkaline inorganic material in admixture with crystalline or amorphous alkali metal aluminosilicate.

9. A process as claimed in claim 8, characterised in that no water is added prior to step (iii).

10. A process as claimed in any preceding claim, characterised in that the total solids present in step (i) amount to at least 60 wt% of the total composition present in step (ii).

11. A process as claimed in any preceding claim, characterised in that the high-speed mixer/granulator is bowl-shaped and has a substantially vertical stirrer axis.

12. A process as claimed in any preceding claim, characterised in that the high-speed mixer/granulator is operated at a stirrer speed within the range of from 60 to 150 rpm and a cutter speed within the range of from 1000 to 3000 rpm throughout steps (i), (ii) and (iii).

13. A process as claimed in any preceding claim, which further comprises the step of admixing a finely divided particulate flow aid to the granular detergent composition or component after the granulation step (iii) is complete.

14. A process as claimed in claim 13, characterised in that the high-speed mixer/granulator is operated at a stirrer speed within the range of from 60 to 80 rpm and a cutter speed of 0 rpm during addition of the flow aid.

15. A granular detergent composition or component therefor, characterised by a bulk density of at least 650 g/litre, prepared by a process as claimed in any preceding claim.

16. A detergent composition or component as claimed in claim 15, characterised in that it contains at least 50 wt% of particles smaller than 1700 μm.

17. A detergent composition or component as claimed in claim 15 or claim 16, characterised in that it comprises from 5 to 35 wt% of anionic surfactant.