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(54) Title: PROCESS FOR THE PRODUCTION OF A DETERGENT GRANULE, DETERGENT GRANULE AND DETERGENT COMPOSITION COMPRISING SAID GRANULE

(57) Abstract: There is provided a process for the production of a detergent granule comprising at least 40% by weight of an anionic surfactant and suitable for use as a granular detergent composition or a component thereof, which comprises the steps of (i) neutralising an anionic surfactant precursor with a source of alkali, (ii) adding Na_2SO_4 and Na_2CO_3 to form a slurry and (iii) spray-drying the obtained slurry to form a granule, whereby the molar ratio of Na_2SO_4 to Na_2CO_3 is in range of 1 : 0.9 to 1 : 1.3, and whereby the double salt $Na_2SO_4.Na_2CO_3$ is formed and whereby the slurry comprises a polycarboxylate polymer. There is also provided a spray-dried detergent carrier granule comprising at least 40% by weight of an anionic surfactant and suitable for use as a granular detergent composition or a component thereof, comprising (i) linear alkylbenzene sulphonate (LAS), soap and mixtures thereof, and (ii) the double salt $Na_2SO_4.Na_2CO_3$ obtainable by the process of the present invention. A third aspect is a detergent composition comprising such granules.

PROCESS FOR THE PRODUCTION OF A DETERGENT GRANULE, DETERGENT GRANULE AND DETERGENT COMPOSITION COMPRISING SAID GRANULE

TECHNICAL FIELD OF INVENTION

The present invention relates to the field of detergent powders, especially laundry detergent powders, and their production. More in particular, it relates in a first aspect to a process for the production of a detergent granule comprising at least 40% by weight of an anionic surfactant and suitable for use as a granular detergent composition or a component thereof. In a second aspect the invention relates to a detergent granule comprising at least 40% by weight of an anionic surfactant and which is obtainable by said process. In a third aspect the invention to relates detergent compositions comprising such granules.

BACKGROUND

This invention relates to the production of detergent granules comprising a surfactant system that gives effective washing. In particular, the invention relates to a process to produce such granules by spray-drying an aqueous slurry.

It is well known to prepare granular detergent products or powders by spray-drying of aqueous slurries. Such processes comprise the steps of preparing aqueous slurry comprising from 20 to 60% by weight water, followed by atomising slurry under high pressure to form droplets and then drying these in a counter-current spray-drying tower. Typical tower inlet and outlet temperatures are from 250-400ºC and 80-120ºC, respectively.

For example, EP-A-1 914 297 discloses a process for the preparation of a spray-dried detergent powder having a bulk density of 426g/l or less, wherein the spray-dried detergent powder comprises an anionic detersive surfactant and from 0% to 10% by weight zeolite builder and from 0% to 10% by weight phosphate builder, and wherein the process comprises the step of:
(a) preparing an aqueous slurry suitable for spray-drying comprising from 30% to 60% by weight water and from 40% to 70% by weight non-aqueous material, wherein the non-aqueous material comprises an inorganic component and an organic component wherein the weight ratio of the inorganic component to organic component is in the range of from 0.3:1 to 5:1; and
(b) spraying the slurry into a spray-drying tower, wherein the temperature of the slurry as it enters the spray-drying tower is in the range of from 65ºC to 140ºC, and wherein the outlet air temperature of the spray-drying tower is in the range of from 70ºC to 120ºC and wherein the non-aqueous material comprises anionic surfactant, polymeric carboxylate and carbonate salt.

EP-A-221 776 describes a process for the production of a porous, zero-phosphate powder suitable for use as a base for a granular detergent composition or a component thereof and capable of absorbing and retaining substantial quantities of liquid or liquefiable detergent components in liquid form, which process comprises the steps of (i) preparing an aqueous slurry comprising sodium carbonate, and optionally also comprising sodium sulphate, (ii) drying the slurry to form a powder, the process being characterised in that the total amount of sodium carbonate and (if present) sodium sulphate is at least 20 percent by weight based on the dried powder, the weight ratio of sodium carbonate to sodium sulphate (when present) in the slurry is at least 0.37:1, and from 0.1 to 60 percent by weight, based on the total amount of sodium carbonate and (if present) sodium sulphate in the dried powder, of a crystal growth modifier which is a polymeric polycarboxylate is incorporated in the slurry not later than the sodium carbonate, whereby crystal-growth-modified sodium carbonate monohydrate and/or crystal-growth modified Burkeite is or are formed in the slurry.

These processes can advantageously be used to prepare spray-dried detergent powders having a low bulk density a low content of anionic surfactants. It is difficult, however, to prepare detergent powders having an anionic detergent content of 40 wt% or higher. A further increase in anionic detergent content leads to poor drying rate due to high slurry moisture content of around 40-50% by weight. The high drying temperatures needed for drying off the excess water cost extra energy and may lead to incidences of fire in the tower and/or the dry cyclones. High anionic detergent slurries may also cause overflow and have transportation problems because of aeration and the very high viscosity.

The resulting high anionic detergent powders usually have a low bulk density and are difficult to handle and store and have higher packaging costs.

Moreover, spray-drying is an energy intensive process and it would be interesting from an environmental point of view to improve the current detergent manufacturing technology in this respect. Environmental aspects of detergent manufacturing processes are considered to be important, not only by the manufacturers but also by the consumers who are increasingly interested in the sustainability of our economic activities.

It is therefore a first object of the present invention to provide a more energy efficient process to prepare spray-dried detergent granules having an anionic detergent content above 40 wt% or higher that do not have the above-mentioned draw-backs. It particular, the detergent granules should have good powder properties.

It is a further object of the present invention to provide a more energy efficient process to prepare spray-dried (laundry) detergent powders having an anionic detergent content above 40 wt% or higher that do not have the above-mentioned draw-backs.

We have now surprisingly found that spray-dried detergent granules having an anionic detergent contents above 40 wt% or higher may be prepared from a slurry comprising Na_2SO_4 and Na_2CO_3 wherein the molar ratio of Na_2SO_4 to Na_2CO_3 is in range of 1 : 0.9 to 1 : 1.3, and whereby the double salt $Na_2SO_4.Na_2CO_3$ is formed.

Thus, these and other objects may be achieved by the process according to the invention, which comprises the steps of (i) neutralising an anionic surfactant precursor with a source of alkali, (ii) adding Na_2CO_3 and Na_2SO_4 to form a slurry and (iii) spray-drying the obtained slurry to form a granule, whereby the molar ratio of Na_2SO_4 to Na_2CO_3 is in range of 1 : 0.9 to 1 : 1.3, and whereby the double salt $Na_2SO_4.Na_2CO_3$ is formed and whereby the slurry comprises a polycarboxylate polymer.

DEFINTION OF THE INVENTION

According to a first aspect of the present invention there is provided a process for the production of a detergent granule comprising at least 40% by weight of an anionic surfactant and suitable for use as a granular detergent composition or a component thereof, which comprises the steps of (i) neutralising an anionic surfactant precursor with a source of alkali, (ii) adding adding Na_2SO_4 and Na_2CO_3 to form a slurry and and (iii) spray-drying the obtained slurry to form a granule, whereby the molar ratio of Na_2SO_4 to Na_2CO_3 is in range of 1 : 0.9 to 1 : 1.3, and whereby the double salt $Na_2SO_4.Na_2CO_3$ is formed and whereby the slurry comprises a polycarboxylate polymer.

According to a second aspect of the present invention there is provided a spray-dried detergent granule comprising at least 40% by weight of an anionic surfactant and suitable for use as a granular detergent composition or a component thereof, comprising
(i) linear alkylbenzene sulphonate (LAS), soap and mixtures thereof, and
(ii) the double salt $Na_2SO_4.Na_2CO_3$
obtainable by the process of the present invention.

According to a third aspect of the present invention there is provided a detergent composition comprising the granules according to the present invention.

DETAILED DESCRIPTION OF THE INVENTION

The first aspect of the present invention is a process for the production of a detergent granule comprising at least 40% by weight of an anionic surfactant and suitable for use as a granular detergent composition or a component thereof. In a first step of this process, an anionic surfactant precursor is neutralised with a source of alkali to form a surfactant paste. The anionic surfactant precursor is an acid precursor of an anionic non-soap surfactant which, when reacted with a source of alkali, will be neutralised to form a salt of the anionic surfactant.

Anionic surfactant precursors in liquid, pumpable, form are preferred. The anionic surfactant precursor is preferably selected from linear alkyl benzene sulphonic acid, fatty acid and mixtures thereof. Linear alkyl benzene sulphonic acid is also referred to as LAS acid and HLAS. LAS acid yields the corresponding linear alkyl benzene sulphonate (LAS) upon neutralisation. Preferably, the LAS non-soap anionic surfactant has an alkyl chain length of C8-18, more preferably C10-16 and most preferably C12-14.

Soaps formed by the neutralisation of carboxylic or fatty acids may be used as secondary anionic surfactants in admixture with the non-soap anionic surfactants. Preferred carboxylic acids are fatty acids with 12-18 carbon atoms, such as for example fatty acids of coconut oil, palm oil, palm kernel and tallow. The fatty acids may be saturated or unsaturated, branched or straight chain. Mixtures of fatty acids may be used. Fatty acids may be used at levels of up to 30 wt% based on the anionic surfactant precursor.

The anionic surfactant precursors (or mixture of surfactant precursors) may be used in a partially pre-neutralised form without complete loss of the advantageous effects of the invention. In effect, the surfactant acid is then a mixture of the surfactant acid with neutralised anionic non-soap surfactant.

The anionic surfactant precursors may be added in admixture with other components. Suitable components are neutralised anionic surfactants, for instance the salts of alkyl and/or alkenyl sulphuric acid half-esters (i.e. the sulphation products of primary alcohols) which give alkyl and/or alkenyl sulphates upon neutralisation. Among such non-soap anionic surfactants is primary alcohol sulphate (PAS), especially PAS having a chain length of C10-22, preferably C12-14. Coco PAS is particularly desirable.

Other suitable surfactant acids include alpha-olefin sulphonic acids, internal olefin sulphonic acids, fatty acid ester sulphonic acids and primary sulphonic acids. It is also possible to use combinations of surfactant acids as will be apparent to the skilled person.

Among the other components, in addition to the fatty acids and neutralised anionic surfactant already discussed, the most important additional component that may be added as liquids with the surfactant precursor is nonionic surfactant. This is typically added to the surfactant acid to reduce viscosity to enable it to be added at a lower temperature.

Suitable nonionic surfactants that may be used include the primary and secondary alcohol ethoxylates, especially the C8-C20 aliphatic alcohols ethoxylated with an average of from 1 to 50, preferably 1 to 20, moles ethylene oxide per mole of alcohol, and more especially the primary and secondary aliphatic alcohols ethoxylated with an average of from 1 to 10 moles of ethylene oxide per mole of alcohol. Non-ethoxylated nonionic surfactants include alkyl-polyglycosides, glycerol monoethers, and polyhydroxyamides (glucamide). As discussed already neutralised anionic surfactant may be mixed with the surfactant acid. This can have the advantage of increasing the throughput of the overall process.

Other liquid additives that may be added with the anionic surfactant precursor, or added as separate liquid stream(s), include inorganic acids, such as sulphuric acid, and hydrotropes, such as para toluene sulphonic acid.

The source of alkali which is reacted with the anionic surfactant precursor can be any suitable source of alkali, in liquid or solid form. Examples are aqueous alkali metal hydroxide solutions, preferably sodium hydroxide solutions, or sodium carbonate. Especially preferred are about 50% by weight concentrated aqueous sodium hydroxide solutions. The amount of water should be kept to a minimum, because the water will have to be dried off in the subsequent spray-drying step. On the other hand, it should not be so low that the neutralised surfactant paste is too viscous to handle.

The sodium carbonate may be of any type. Synthetic light soda ash has been found to be especially preferred; natural heavy soda ash is intermediate, while synthetic granular soda ash is the least preferred raw material.

The surfactant paste is preferably prepared in an agitated mixer provided with an open steam coil to heat the mass to a temperature of about 35-40ºC. The neutralisation reaction between the anionic surfactant precursor and the source of alkali yields a concentrated surfactant paste, which preferably has a solid content of between 60 to 80% by weight. The heat of neutralisation causes the temperature to rise from about 35-40ºC to about 75-80ºC, where it is maintained. It is beneficial to allow a few minutes additional time to ensure full neutralization.

In a second step of the process, sodium sulphate (Na_2SO_4) and sodium carbonate (Na_2CO_3) are added to the surfactant paste to form a slurry. The order of addition is not believed to be essential.

The slurry furthermore comprises a polycarboxylate polymer. For example, alkaline silicate and polycarboxylate copolymer may be pumped into the mixer with increased agitation speed improve the fluidity of total mass. Alkali metal silicates having a SiO2/M2O ratio, wherein M is sodium ion, of from 1.5 to 3.3, preferably from 1.8 to 2.6, are favourably used.

Among the polycarboxylate polymers, polyaspartates and polyaspartic acid are advantageously used due to their biodegradability. The polymeric polycarboxylates are used in amounts of from 0.1 to 20 wt%, preferably from 0.2 to 5 wt%, most preferably 1 to 5 wt%, based on the total amount of sodium carbonate. However, higher levels of polymer, for example, up to 30% by weight based on sodium carbonate, may be present in detergent granules of the invention, or full compositions comprising the detergent granules of the invention, for other reasons, for example, building, structuring or anti-redeposition.

The polycarboxylate polymer preferably has a molecular weight of at least 1,000, advantageously from 1,000 to 300,000, in particular from 1,000 to 250,000. Polycarboxylates having a molecular weight from 10,000 to 70,000 are especially preferred. All molecular weights quoted herein are those provided by the manufacturers.

Preferred polycarboxylates are homopolymers and copolymers of acrylic acid or maleic acid. Of special interest are polyacrylates and acrylic acid/maleic acid copolymers. Suitable polymers, which may be used alone or in combination, include the following:

Salts of polyacrylic acid such as sodium polyacrylate, for example Versicol (Trade Mark) E5 E7 and E9 ex Allied Colloids, average molecular weights 4000, 27 000 and 70 000; Narlex (Trade Mark) LD 30 and 34 ex National Adhesives and Resins Ltd, average molecular weights 5000 and 25 000 respectively; and Sokalan (Trade Mark) PA range ex BASF, average molecular weight 250 000; ethylene/maleic acid copolymers, for example, the EMA (Trade Mark) series ex Monsanto; methyl vinyl ether/maleic acid copolymers, for example Gantrez (Trade Mark) AN119 ex GAF Corporation; acrylic acid/maleic acid copolymers, for example, Sokalan (Trade Mark) CP5 ex BASF.

A second group of polycarboxylate polymers comprises polyaspartic acids and polyaspartates. Polyaspartate is a biopolymer synthesised from L-aspartic acid, a natural amino acid. Due in part to the carboxylate groups, polyaspartate has similar properties to polyacrylate. One preferred type of polyaspartate is thermal polyaspartate or TPA. This has the benefit of being biodegradable to environmentally benign products, such as carbon dioxide and water, which avoids the need for removal of TPA during sewage treatment, and its disposal to landfill. TPA may be made by first heating aspartic acid to temperatures above 180°C to produce polysuccinimide. Then the polysuccinimide is ring opened to form polyaspartate. Because the ring can open in two possible ways, two polymer linkages are observed, an [alpha]-linkage and a [beta]-linkage.

Mixtures of any two or more polymers, if desired, may be used in the process and detergent granule compositions of the invention.

In a third next step of the process of the invention, the obtained slurry is spray-dried to form a granule, whereby the molar ratio of Na_2SO_4 to sodium Na_2CO_3 is in range of 1 : 0.9 to 1 : 1.3, and whereby the double salt $Na_2SO_4.Na_2CO_3$ is formed. It is believed that the double salt $Na_2SO_4.Na_2CO_3$ contributes is a favourable manner to the high specific surface area ("SSA") of the granules, which in turn enables them to carry liquid components such as fatty acid/nonionic blends.

Typical tower inlet and outlet temperatures of the spray-drying process are from 250-400ºC and 80-120ºC, respectively.

The detergent granule

A second aspect of the present invention is a spray-dried detergent granule comprising at least 40% by weight of an anionic surfactant and suitable for use as a granular detergent composition or a component thereof. The granules has a relatively high specific surface area which makes them suitable as carrier for absorbing liquid components such as nonionic surfactants or nonionic surfactant/ fatty acid blends.

The granule according to the invention comprises:
(i) an alkali metal salt of a non-soap detergent, soap and mixtures thereof, and
(ii) the double salt $Na_2SO_4.Na_2CO_3$
and is obtainable by the process according to the invention. Preferably, the alkali metal salt of a non-soap detergent is linear alkylbenzene sulphonate (LAS).

The spray-dried detergent granule of the invention is a particulate solid with a bulk density in the range 350 to 800 g/litre. 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 1,700 microns, and the level of fines is low. No further treatment has generally been found to be necessary to remove either oversize particles or fines.

The spray-dried detergent granule is further characterised by its specific surface area, measured by nitrogen adsorption. The specific surface area (“SSA”) of the granules is measured by nitrogen absorption according to ASTM D 3663-78 standard based upon the Brunauer, Emmett, and Teller (BET) method described in J. Am. Chem. Soc. 60, 309 (1938). We used a Gemini Model 2360 surface area analyzer (available from Micromeritics Instrument Corp. of Norcross, Ga.). The spray-dried detergent granule has a specific surface area (SSA) of 5 m^2/g or greater, preferably 8 m^2/g or greater, even more preferably 10 m^2/g or greater.

The obtained granule generally has excellent flow properties, low compressibility and little tendency towards caking. The particulate detergent granules that are the direct result of the spray-drying process have an anionic surfactant content of at least 40 wt%. There is no need for a granulation aid such as zeolite, although it is possible to use them. It is possible to achieve exceptionally high levels of anionic surfactant in the granule. For example, greater than about 45 wt%, preferably greater than 50 wt%, or over 50 wt% anionic surfactant may be incorporated into the detergent granule. It is preferred for the anionic surfactant to comprise less than 10 wt% soap, based on the total anionic surfactant in the detergent granule.

The detergent granules may also comprise water in an amount of 0 to 8% and preferably 0 to 4% by weight of the granules. The detergent granules obtained from the process are storage stable at high levels of humidity. Thus, they can be used in a wide range of detergent products.

Desirably the detergent granules have an aspect ratio not in excess of two and more preferably are generally spherical in order to reduce segregation from other particles in a formulated powder detergent composition and to enhance the visual appearance of the powder.

The presence of the double salt $Na_2SO_4.Na_2CO_3$ can be detected using X-ray diffraction techniques that are known in the art. X-ray diffraction (XRD) is a non destructive analytical method for measuring characteristic diffraction angles and intensities from periodically ordered matter (crystalline material). Intensity and spatial distributions of the scattered X-rays form a specific diffraction pattern, which is the “fingerprint” of the sample and can be used for qualitative and quantitative evaluation, d-value calculation, the determination of crystallite size and defects by the peak shape and polymorphism.

The detergent composition

A third aspect of the present invention is a detergent composition, especially a laundry detergent composition, comprising the granules according to the present invention.

The spray-dried detergent granules of the present invention may be used as such, but they may also be supplemented with other detergent ingredients, components or additives to form a complete detergent composition. The detergent granules may be admixed with anything normally used in detergent formulations. They may be dry blended with solid materials and they may advantageously have further liquids added into them, using their spare liquid carrying capacity. It is especially advantageous to add conventional, or even higher than conventional, levels of perfume this way.

Other types of non-soap surfactant, for example, cationic, zwitterionic, amphoteric or semipolar surfactants, may also be used with the granules 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.

Soap may also be present, to provide foam control and additional detergency and builder power. The fully formulated composition may comprise up to 8 wt% soap.

The fully formulated detergent compositions including the detergent granules prepared by the process of the invention may contain conventional amounts of other detergent ingredients, for example, bleaches, enzymes, lather boosters or lather controllers as appropriate, anti-redeposition agents such as cellulosic polymers; anti incrustation agents, perfumes, dyes, shading dyes, fluorescers, sodium silicate; corrosion inhibitors including silicates; inorganic salts such as sodium sulphate, enzymes; coloured speckles; foam controllers; and fabric softening compounds. The detergent granule may if desired be mixed with other organic or inorganic builders, typically supplied in the form of granules of either pure builder or mixtures of builder and other ingredients. Especially preferred organic builders are acrylic polymers, more especially acrylic/maleic copolymers, suitably used in amounts of from 0.5 to 15 wt%, preferably from 1 to 10wt%. Such polymers may also fulfil the function of the habit modifying polymer.

The detergent granules of the present invention are hereinafter called a base powder. They may be mixed with another powder obtained from any conventional detergent production process including spray drying or non spray drying processes. As the detergent granules produced by the present invention may be admixed with such other powders, a significant degree of formulation flexibility is obtained and the level of active material in the fully formulated composition may be very high without an unnecessary increase in builder levels.

The total amount of surfactant present in the fully formulated detergent composition is suitably from to 15 to 70 wt%, although amounts outside this range may be employed as desired.

The detergent granules may typically form from 30 to 100 wt% of a final fully formulated detergent composition. Typically, the fully formulated detergent composition incorporating the detergent granules produced by the process of the invention may comprise from 15 to 60 wt%, preferably 20 to 50 wt% of anionic surfactant, this anionic surfactant being derived wholly or in part from the granular product of the spray-drying process. In addition, the fully formulated detergent composition may comprise from 0 to 35 wt% of nonionic surfactant, and from 0 to 5 wt% of fatty acid soap.

Fully formulated detergent compositions, comprising other ingredients and the detergent granules produced according to the invention preferably have a bulk density of about 350 to 750 g/litre, more preferably at least 450 g/litre.

Fully formulated detergent compositions may also include other solid ingredients desired for inclusion in the detergent powder, for example, fluorescers; polycarboxylate polymers; antiredeposition agents, for example, sodium carboxymethyl cellulose; or fillers such as sodium sulphate, diatomaceous earth, calcite, kaolin or bentonite.

If desired, solid particulate surfactants, for example, alkylbenzene sulphonate and/or alkyl sulphate in powder form, may form part of the solids charge to the mixer to further increase the activity level of surfactant in the granule, however it is preferred to produce all the anionic surfactant by spray-drying.

The process is generally not sensitive to the type of mixer used, provided intensive mixing is applied. We have found that to obtain the full advantages of the invention the use of a mixer with a chopping action may be advantageous.

Preferably, the mixing is carried out in a mixer having and using both a stirring action and a cutting action, most preferably these actions will be separately usable, as described below. The cutting action is the preferred chopping action. This may be advantageously achieved by the choice of mixer to be 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 Lödige mixer is preferred, vertical or horizontal axis cutters are desirable for high anionic loading. Also preferred are mixers of the Fukae FS-G type manufactured by Fukae Powtech Co Ltd., 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. The vessel can be cooled.

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. Z blade and sigma mixers (Winkworth machinery limited) are suitable mixers having a chopping action.

The invention will now be further described with reference to the following non-limiting examples. In the examples, the Bulk Density (BD), Dynamic Flow Rate (DFR) and Unconfined Compression Test (UCT) are measured according to the following known test protocol.

Bulk density (BD)

The bulk density properties in the present specification are measured by a method according to JIS K 3362.

Dynamic flow rate (DFR)

This is also called flow-rate. Powder flow may be quantified by means of the dynamic flow rate (DFR), in ml/s, measured by means of the following procedure. The apparatus used consists of a cylindrical glass tube having an internal diameter of 40 mm and a length of 600 mm. The tube is securely clamped in a position such that its longitudinal axis is vertical. Its lower end is terminated by means of a smooth cone of polyvinyl chloride having an internal angle of 15° and a lower outlet orifice of diameter 22.5 mm. A first beam sensor is positioned 150 mm above the outlet, and a second beam sensor is positioned 250 mm above the first sensor.

To determine the dynamic flow rate of a powder sample, the outlet orifice is temporarily closed, for example, by covering with a piece of card, and powder is poured through a funnel into the top of the cylinder until the powder level is about 10 cm higher than the upper sensor; a spacer between the funnel and the tube ensures that filling is uniform. The outlet is then opened and the time t (seconds) taken for the powder level to fall from the upper sensor to the lower sensor is measured electronically. The measurement is normally repeated two or three times and an average value taken. If V is the volume (ml) of the tube between the upper and lower sensors, the dynamic flow rate DFR (ml/s) is given by the following equation:

$$DFR = \frac{V}{t} \quad ml/s$$

Unconfined Compression Test (UCT)

In this test, freshly produced powder is compressed into a compact and the force required to break the compact is measured. The powder is loaded into a cylinder and the surface levelled. A 50 g plastic disc is placed on top of the powder and a 10 kg weighted plunger is placed slowly on top of the disc and allowed to remain in position for 2 minutes. The weight and plunger are then removed and the cylinder removed carefully from the powder to leave a free-standing cylinder of powder with the 50g plastic disc on top of it. If the compact is unbroken, a second 50 g plastic disc is placed on top of the first and left for approximately ten seconds. Then if the compact is still unbroken a 100 g disc is added to the plastic discs and left for ten seconds. The weight is then increased in 0.25 kg increments at 10 second intervals until the compact collapses. The total weight (w) needed to effect collapse is noted.

The cohesiveness of a powder is classified by the weight (w) as follows:
$w < 1.0$ kg Good flowing
$1.0 \text{ kg} < w < 2.0$ kg Moderate flowing.
$2.0 \text{ kg} < w < 5.0$ kg Cohesive.
$5.0 \text{ kg} < w$ Very cohesive.

EXAMPLES

Example 1

An aqueous slurry was prepared in an agitated mixer provided with an open steam coil to heat the mass. 2,500 kg of a slurry was prepared involving the following steps.

A charge made of clean water (523kg) and caustic soda solution (192kg) of 50% purity was dosed to the mixer and heated to a temperature of 40-40ºC. Following this step, a pre-weighed quantity (732kg) of commercial grade of sulphonic acid was dosed gradually over a period of 3-4 minutes with continuous agitation to form a neutralized paste. An additional time of 2 minutes was allowed to ensure that the neutralization reaction is complete. Preheated alkaline silicate (169kg) and copolymer (114kg) were pumped into the mixer with increased agitation speed so as to improve the fluidity of the total mass. At this stage, it may be preferred to maintain temperature at 75-80ºC by use of steam in open coil. Following this step, the steam valve was shut off and sodium sulphate (326kg)/ sodium carbonate (228kg) along with minors (fluorescer 0.91kg and Sodium Carboxy Methyl Cellulose (SCMC) 16.3kg) were dosed via screw conveyor adjusted to dose over a period of 2-3 minutes and the agitator speed was raised to 70-75rpm. When dosing solids, they fell close to the agitator blades to prevent build up on the wall or lump formation. In different examples, the solids were dosed in different sequences to promote formation of crystalline phases after due care was taken to ensure good dispersion/dissolution achieved. A final mixing step was allowed for another 2 minutes and then the mixed mass was discharged to the holding tank for subsequent operation in the spray drying tower.

In all examples, the above charge sheet was calculated for various formulations and used for making slurries. The slurries were transported by a low pressure pump, Reitz mill/magnetic separator and then to the HP pump. The slurry was sprayed in a 2.5 diameter spray drier by use of two spraying system nozzles to achieve desired throughput rate of 1100-1200 kg/hr of slurry at pressures of 25 bars. The tower was heated by hot air maintained at temperatures of 270-290ºC in counter current mode and dried powder was collected at the bottom of tower. Powder moisture content was controlled in the range of 2-3% and minor variations in air inlet temperature were required to maintain steady state conditions.

SD Base powder composition					
Spray dried base		**40%**	**45%**	**50%**	**55%**
				Modified	
Ingredients		%	%	%	%
Na-LAS		40.00	45.00	50.00	55.00
Silicate		8.00	8.00	5.00	3.50
Sokalan CP5 copolymer		3.00	3.00	3.00	4.00
Soda ash		15.00	15.00	15.00	15.00
sodium sulphate		29.23	24.11	22.00	17.35
SCMC		0.75	0.75	0.75	0.75
CBSX		0.06	0.06	0.06	0.06
moisture		3.00	3.00	3.00	3.00
Impurities		0.96	1.08	1.19	1.34
total		100.0	100.0	100.0	100.0

active/silicate ratio	5.00	5.63	10.00	15.71
Active/polymer ratio	13.3	15.0	16.7	13.8
organic/inorganic ratio	0.84	1.03	1.28	1.67
evaporative load/ AD	1.25	1.12	1.06	0.96
water added /ton base	3.60	3.54	3.82	3.77
Sulphate to carbonate molar ratio	1.45	1.2	1.09	0.84

The powder properties were examined as given below and additional nonionic / fatty acid blend was sprayed onto the tower base powder (indicated by% Active loaded) to give a detergent product having excellent powder properties.

	40%AD base powder 600 kg/hr				
	NI/FA Flow rate			without NI/FA	
Flow rate	**36 Kg/hr**	**45 Kg/hr**	**50 Kg/hr**	**0**	**0**
BD (g/l)	379	382	360	385	384
DFR (ml/sec)	109	110	113	98	102
UCT (gm)	1050	1300	1800	700	700
VCT (%)	20	19	20	20	20
PMC (%)	1.53	1.38	1.56	2.43	2.62

% Active loaded: 7.6% max

	45%AD base powder 600 kg/hr				
	with NI/FA spray on		ex-tower	without NI/FA	
Flow rate	**36 Kg/hr**	**45 Kg/hr**		**0**	**0**
BD (g/l)	357	343	296	377	384
DFR (ml/sec)	112	116	103	103	102
UCT (gm)	1250	2200	3450	700	700
VCT (%)	32	36	54	22	20
PMC (%)	2.16	2.87	3.34	2.29	2.62

% Active loaded: 7.0% max

	50%AD base powder				
	NI/FA Flow rate			without NI/FA	
Flow rate	**36 Kg/hr**	**45 Kg/hr**		**0**	**0**
BD (g/l)	333	313		377	384
DFR (ml/sec)	109	116		91	83
UCT (gm)	450	1250		200	200
VCT (%)	28	38		13	16
PMC (%)	3.33	3.66		1.43	2.43

% Active loaded: 7.0% max

	55% AD base powder		
	without NI/FA		NI/FA spray on
Flow rate	**0**	**0**	**36 Kg/hr**
BD (g/l)	328	316	322
DFR (ml/sec)	95	98	113
UCT (gm)	700	450	1500
VCT (%)	26	25	40
PMC (%)	3.45	2.57	4.29

% Active loaded: 5.6% max

Example 2

These base powders of Example 1 were also examined for presence of crystalline phases. Using the D8 Discover ex Bruker-AXS machine, the d-values of the diffraction lines of the samples were obtained and from them the crystalline compounds were identified.

Materials and methods:

	2θ (5 – 55°)
Theta 1	4.500
Theta 2	10.000/25.000/40.000
Phi (only transmission)	-
Detector Bias (kV / mA)	40 / 40
Time (sec)	150
Collimator (mm)	0.3 (monocap)
Detector distance (cm)	25
Tube Anode	Cu
Used SLM file	Detergent.slm

The results are given in the table below:

The presence of crystalline compounds in base powders

Sample	Burkeite	Sodium carbonate sulphate (equimolar)	Sodium sulphate	Sodium carbonate	Zeolite 4A
40%AD	+	-	+	-	+
45%AD	+	-	+	-	+
50%AD	-	+	+	-	+
55%AD	-	+	+	-	+
25%AD	+	-	+	-	+

“+” indicates the presence of a crystalline compound

“-“ indicates that a crystalline compound, if present, is below the detection limit of the used XRD method.

CLAIMS

1. Process for the production of a detergent granule comprising at least 40% by weight of an anionic surfactant and suitable for use as a granular detergent composition or a component thereof, which comprises the steps of (i) neutralising an anionic surfactant precursor with a source of alkali, (ii) adding Na_2SO_4 and Na_2CO_3 to form a slurry and (iii) spray-drying the obtained slurry to form a granule, whereby the molar ratio of Na_2SO_4 to Na_2CO_3 is in range of 1 : 0.9 to 1 : 1.3, and whereby the double salt $Na_2SO_4.Na_2CO_3$ is formed and whereby the slurry comprises a polycarboxylate polymer.

2. Process according to claim 1, wherein the anionic surfactant precursor is selected from Linear Alkyl Sulphate (LAS) acid, fatty acid and mixtures thereof.

3. Process according to any preceding claim in which anionic surfactant precursor is LAS acid.

4. Process according to any preceding claim in which the slurry comprises amorphous silicate.

5. Process according to claim 1, in which the polymer is selected from acrylic acid homopolymers, acrylic acid/maleic acid copolymers, and acrylic phosphinates.

6. Process according to claim 5, characterised in that the polymer is sodium polyacrylate.

7. Process according to claim 6, characterised in that the polymeric polycarboxylate has a molecular weight within the range of from 1,000 to 250,000, preferably within the range of from 3,000 to 100,000.

8. Process according to any preceding claim in which the granule is characterised by having a specific surface area of 5 m^2/g or greater, preferably 8 m^2/g or greater, even more preferably 10 m^2/g or greater.

9. A spray-dried detergent granule comprising at least 40% by weight of an anionic surfactant and suitable for use as a granular detergent composition or a component thereof, comprising
(i) an alkali metal salt of a non-soap detergent, soap and mixtures thereof, and
(ii) the double salt $Na_2SO_4.Na_2CO_3$
obtainable by the process according to any preceding claim.

10. Detergent granule according to claim 9, wherein the non-soap detergent is linear alkylbenzene sulphonate (LAS).

11. Detergent granule according to any one of claims 9-10, characterised by having a specific surface area of 5 m^2/g or greater, preferably 8 m^2/g or greater, even more preferably 10 m^2/g or greater.

12. Detergent granule according to any one of claims 9-11, characterised in that the anionic surfactant level in the granule is greater than 45 wt%, even greater than 50 wt% and preferably even greater than 60 wt%.

13. Detergent composition comprising the granules according to any one of claims 9-12.

14. Detergent composition according to claim 13, further comprising soap and/or nonionic surfactant.

15. Detergent composition according to any one of claims 13-14, further comprising a bleach system.

16. Detergent composition according to claim 15, wherein the bleach system is TAED/percarbonate.

17. Detergent composition according to any one of claims 13-16, further comprising fluorescer, preferably at a level of 0.05 to 0.5 wt%.

18. Detergent composition according to any one of claims 13-17, further comprising perfume.

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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2013/057340

A. CLASSIFICATION OF SUBJECT MATTER
INV. C11D11/02 C11D1/04 C11D1/22 C11D3/04 C11D3/10
C11D17/06 C11D3/37
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, PAJ, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2 298 650 A (SAMARAS NICHOLAS N T ET AL) 13 October 1942 (1942-10-13) claims 1,7 examples II,V page 1, line 74 - line 86 page 1, line 23 - line 39 page 1, line 110 - page 2, line 13 -----	1-18
Y	GB 523 479 A (MONSANTO CHEMICALS) 16 July 1940 (1940-07-16) pages - example IV ----- -/--	1-18

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search 12 June 2013	Date of mailing of the international search report 19/06/2013
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Neys, Patricia

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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2013/057340

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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Y	US 2011/257066 A1 (SOMERVILLE ROBERTS NIGEL PATRICK [GB] ET AL) 20 October 2011 (2011-10-20) claims examples -----	1-18

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