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(54) Manufacture of dertergent granules by dry neutralisation

(57) A process for the manufacture of detergent granules comprising anionic non-soap surfactant the process comprising the dry neutralisation of surfactant acid with habit modified Sodium Carbonate. A high active detergent granule comprising greater than 30 wt% anionic surfactant, the surfactant comprising a major part of non-soap anionic surfactant, habit modified Sodium Carbonate, and less than 10 wt% preferably zero, zeolite, is obtainable by the process.

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Description

[0001] This invention relates to the manufacture of detergent granules by dry neutralisation, in particular to a process for the dry neutralisation of surfactant acid with Sodium Carbonate to form detergent granules comprising anionic non-soap surfactant.

BACKGROUND

[0002] Detergent granules are normally manufactured as agglomerates of smaller particles. This agglomeration can be achieved by spray drying, mixing, or a combination of those processes. Many detergent granules comprise non-soap anionic surfactants, for example alkyl benzene sulphonate. Such granules have been prepared by *in-situ* neutralisation of the acid precursor of the non-soap anionic surfactant, referred to hereafter as "surfactant acid" with a solid alkali salt, usually Sodium Carbonate.

[0003] GB 1 369 269 discloses a process for the neutralisation of synthetic organic anionic detergent acids, such as straight chain alkyl benzene sulphonic acid, by mixing the acid with an excess of powdered Sodium Carbonate in a modified mixer with a cutting arrangement, for example a Lödige ploughshare mixer. A builder and/or filler salt is taught to be added with the Sodium Carbonate in order to make the product more free flowing. The choppers or cutters in the mixer are used during addition of the acid. Examples 1 and 2 include a sodium tripolyphosphates in the dry mix. The powders produced are free flowing. Example 3 uses no sodium tripolyphosphate but the product requires pulverisation and is not described as free flowing. A problem with this disclosure is that it is now desirable to exclude phosphate from the granule, but this document does not teach an effective process for its elimination.

[0004] GB 2 221 695 describes a dry neutralisation process for preparation of detergent powder of high bulk density in a high speed mixer granulator, with a stirring and a cutting action. In most of the examples, zeolite or Sodium Tripolyphosphate is used in addition to Sodium Carbonate.

In examples 26 to 29, very high levels of Sodium Carbonate are used and a special calcite flow aid is dosed at 4% to assist with the granulation. Despite this, the flow properties of example 26 are very poor and addition of Sodium Tripolyphosphate is taught as a remedy for this problem. A problem with this process is that the use of a flow aid is a major process complication and it is now desirable to exclude phosphate from the granule.

[0005] WO 2002/28454 describes a dry neutralisation process carried out in a horizontal thin-film evaporator drier. Use of small particle size Sodium Carbonate is taught to reduce the amount of unneutralised surfactant acid in the resulting product. Such unneutralised material is known to be undesirable as it continues to react with the Sodium Carbonate and causes powder caking. In the examples, zeolite is also added. This addition would reduce the level of anionic surfactant in the detergent granule.

Furthermore, it is now desirable to be able to eliminate use of zeolite from a detergent granule if it is not essential in the formulation.

[0006] US 7 053 038 describes a dry neutralisation process carried out in a gas fluidisation granulator using small particle size Sodium Carbonate and an inorganic acid, such as sulphuric acid. Both zeolite and sodium tripolyphosphate are included in all the examples.

[0007] EP 1 534 812 discloses dry neutralisation of preformed spray dried particles comprising a carbonate salt and polyacrylate. The process is carried out under low shear conditions in order to avoid agglomeration. In all of the examples, the carbonate salt is the Burkeite double salt formed when Sodium Carbonate and sodium sulphate are spray dried together. These particles are too strong to be used in the process of the present invention. As further explained later this process does not make habit modified Sodium Carbonate.

[0008] EP 0 221 776 describes a process to spray dry Sodium Carbonate and a crystal growth modifier to make, so called, habit modified carbonate granules. The crystal growth modifier is preferably polymeric polycarboxylate. The patent describes the manufacture of habit modified Burkeite in the majority of the examples. Only example 1 crystal habit modifies Sodium Carbonate itself.

[0009] Habit modified Sodium Carbonate is also spray dried for use as a carrier granule in WO 2006/081930. Polyaspartates are used in place of the polycarboxylates of EP 0 221 776.

[0010] Throughout this specification habit modified Sodium Carbonate is a term used to encompass such prior art materials. The term does not include habit modified Burkeite, although low concentrations of Burkeite could conceivably be included in admixture with the desired habit modified Sodium Carbonate provided that the resulting admixture remains characterised as described below.

[0011] There remains a need for a process to manufacture detergent granules by dry neutralisation, that does not require the use of additives such as zeolite, Sodium Tripolyphosphate, or flow aids to facilitate satisfactory granulation and at the same time provides the required conversion of surfactant acid to surfactant.

[0012] It is an object of the present invention to provide an improved process for the manufacture of detergent granules comprising non-soap anionic surfactant by dry neutralisation. It is also an object to provide detergent granules comprising

Sodium Carbonate and exceptionally high levels of non-soap anionic surfactant, which exhibit improved storage and handling properties.

SUMMARY OF THE INVENTION

[0013] According to the present invention there is provided a process for the manufacture of detergent granules comprising anionic non-soap surfactant, the process comprising the step of dry neutralisation of surfactant acid with habit modified Sodium Carbonate.

[0014] The invention also provides detergent granules comprising at least 30 wt% anionic surfactant comprising a major part of anionic non-soap surfactant and habit modified Sodium Carbonate, and with less than 10 wt%, preferably zero, zeolite, obtainable by the process.

DETAILED DESCRIPTION OF THE INVENTION

The habit modified Sodium Carbonate (HMC)

[0015] Habit modified Sodium Carbonate is a crystal growth modified Sodium Carbonate, which comprises a mixture of Sodium Carbonate and polymer. Its manufacture is, for example, described in EP 0 221 776 and WO 2006/081930. It is not the same thing as habit modified Burkeite; the double salt of Sodium Carbonate and Sodium Sulphate.

[0016] It is essential that the polymer used as crystal growth modifier is present when crystallisation of the habit modified Sodium Carbonate occurs, that is to say, it must be incorporated not later than the Sodium Carbonate.

[0017] Habit modified Sodium Carbonate is further characterised by its specific surface area, measured by nitrogen adsorption. The specific surface area ("SSA") of the Sodium Carbonate 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 Habit modified Sodium Carbonate is characterised by having 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.

[0018] The pore volume in pores less than 2 micron may further characterise the habit modified Sodium carbonate. This is measured by a conventional mercury porosimetry method. Pore volumes of 0.3 ml/g or greater are advantageous.

[0019] An alternative characterisation of the habit modified Sodium Carbonate, comprising polymer and Sodium Carbonate, is to use it in the process of claim 1 with sulphonic acid and to determine the maximum Sodium Sulphonate anionic non-soap surfactant levels achievable before over-granulation occurs. Over-granulation means that the discrete detergent granules begin to coalesce into a sticky mass and it is no longer possible to discharge them as a free flowing product without adding flow aid or other solid materials such as Zeolite or Sodium Tripolyphosphate. If the anionic Sodium Sulphonate surfactant level achieved is greater than 30 wt%, preferably greater than 35 wt%, more preferably greater than 45 wt%, then the Sodium Carbonate is habit modified for the purposes of this invention.

[0020] Habit modified Sodium Carbonate, herein also referred to as HMC, may be made by spray drying, as described in EP 0 221 776 and WO 2006/081930. Alternative drying methods, as described in those patent applications, may also be employed: for example, air drying, oven drying, drum drying, ring drying, freeze drying, solvent drying, or microwave drying.

[0021] HMC can also be made by precipitation of a saturated Sodium Carbonate solution, which further comprises a growth modifying polymer, in an evaporator, separating the precipitate; e.g. by filtration and drying the precipitate to habit modified Sodium Carbonate. The remaining solution is augmented with fresh Sodium Carbonate solution and polymer solution and returned to the evaporator. The advantage of a precipitation process over one that relies entirely on drying is that energy consumption is lower.

The polymer

[0022] An essential component of habit modified Sodium Carbonate is the polymer. Suitable crystal growth modifying polymers may be selected from polycarboxylates. Polyaspartates and polyaspartic acid are advantageously used due to their biodegradability.

[0023] Preferred polymeric polycarboxylate crystal growth modifiers used in the invention 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 60% 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 reasons other than crystal growth modification, for example, building, structuring or antiredeposition.

[0024] The polycarboxylate crystal growth modifier preferably has a molecular weight of at least 1000, advantageously from 1000 to 300 000, especially from 1000 to 250 000.

Polycarboxylate crystal growth modifiers having molecular weights in the 3000 to 100 000 range, especially 3500 to 70 000 and more especially 10 000 to 70 000 are preferred. All molecular weights quoted herein are those provided by the manufacturers.

[0025] Preferred crystal growth modifiers are homopolymers and copolymers of acrylic acid or maleic acid. Of especial interest are polyacrylates and acrylic acid/maleic acid copolymers.

[0026] Suitable polymers, which may be used alone or in combination, include the following:

[0027] Salts of polyacrylic acid such as sodium polyacrylate, for example Versicol (Trade Mark) E5 E7 and E9 ex Allied Colloids, average molecular weights 3500, 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.

[0028] A second group of polymeric crystal growth modifiers comprises polyaspartic acids and polyaspartates.

[0029] Preferred polymeric crystal growth modifiers in this second group have a molecular weight of at least 1000, advantageously from 3500 to 300000, especially from 4000 to 250000. HMC is preferably prepared using polyaspartate crystal growth modifiers having molecular weights in the 3500 to 100000 range, especially 4000 to 70000 and more especially 5000 to 70000. All molecular weights quoted herein are those provided by the manufacturers.

[0030] 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.

[0031] 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.

[0032] Amounts of from 0.1 to 20 wt% of the crystal growth modifier, preferably from 0.2 to 5 wt%, most preferably 1 to 5 wt%, based on the total amount of Sodium Carbonate are generally sufficient to produce suitable habit modified Sodium Carbonate.

[0033] Mixtures of any two or more polymeric crystal growth modifiers may, if desired, be used in the process and detergent granule compositions of the invention.

The Sodium Carbonate

[0034] The Sodium Carbonate used to make the habit modified 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 acid

[0035] The surfactant acid is an acid precursor of an anionic non-soap surfactant which, when reacted with habit modified Sodium Carbonate will be neutralised to form the sodium salt of the anionic surfactant. Surfactant acids in liquid, pumpable, form are preferred.

[0036] A preferred class of anionic surfactants is alkyl aryl sulphonates. The preferred surfactant acid is linear alkyl benzene sulphonic acid, also referred to as LAS acid and HLAS. This surfactant acid gives a 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.

[0037] A second preferred class of anionic surfactant is the 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.

[0038] Other suitable surfactant acids include alpha-olefin sulphonic acids, internal olefin sulphonic acids, fatty acid ester sulphonic acids and primary sulphonic acids.

[0039] It is also possible to use combinations of surfactant acids as will be apparent to the skilled person.

[0040] Soaps formed by the dry 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 surfactant acid.

[0041] The surfactant acid (or mixture of surfactant acids) may be used in a partially pre-neutralised form without 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.

Optional further ingredients present during the process

[0042] The HMC dry neutralisation process has all of the advantages and flexibility of prior art dry neutralisation processes.

[0043] The surfactant acid may be added in admixture with other liquid components. Among these, 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 acid is nonionic surfactant. This is typically added to the surfactant acid to reduce viscosity to enable it to be added at a lower temperature.

[0044] 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 do-cis 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 alkylpolyglycosides, 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 throughput of the reaction vessel/mixer.

[0045] Other liquid additives that may be added with the anionic surfactant acid, or added as separate liquid stream (s), include inorganic acids, such as sulphuric acid, and hydrotropes, such as para toluene sulphonic acid.

[0046] A small amount of water, sufficient to initiate the neutralisation reaction but not sufficient to cause substantial agglomeration, may be premixed with the surfactant acid before the latter is introduced into the mixer, but addition of water is not essential. If a coloured product is desired, dyestuff may conveniently be premixed with the surfactant acid and water before addition to the mixer. The amount of water to be added may up to about 2 wt% based on the total granule ingredients.

[0047] Additional solid may be admixed with the habit modified Sodium Carbonate. This can be done either before or during neutralisation of the surfactant acid. Unmodified Sodium Carbonate, i.e. soda ash, may be used in admixture with the habit modified Sodium Carbonate. Zeolite and/or other builder materials could be added, although they are not needed to gain the good granule properties ascribed to the use of HMC. It is preferred to avoid use of zeolite completely, except perhaps as a final whitening coating. A complete detergent system can nevertheless be formulated into a single simple dry neutralised granule especially when Calcium tolerant surfactant blends are used. Calcium tolerant surfactant blends are those single or mixed surfactants, which do not require builders to be present for effective detergency across a normal range of water hardness. We use the following method to test a surfactant blend for Calcium-tolerance. First 0.7 g/L of the surfactant blend are dissolved in water containing sufficient Calcium ions to give a French hardness of 40 (4×10^{-3} Molar Ca^{2+}). Other electrolytes such as Sodium Chloride, Sodium Sulphate, and Sodium hydroxide are then added as necessary to adjust the ionic strength to 0.05M and the pH to 10. The adsorption of light of wavelength 540 nm through 4 mm of sample is measured 15 minutes after sample preparation. Ten measurements are made and an average value is calculated. Calcium tolerant blends are those that give an average value of less than 0.08.

[0048] Calcium tolerant surfactant blends that may be dry neutralised include mixtures of LAS with nonionic high EO, SLES paste and/or AOS paste.

[0049] In addition to the essential habit modified Sodium Carbonate, conventional builders and non habit modified Sodium Carbonate may also be added to the mixer. Examples of such builders include crystalline and amorphous alkali metal aluminosilicates, alkali metal phosphates, and mixtures thereof. The total of habit modified Sodium Carbonate and Sodium Carbonate should always 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. This represents a molar excess of 3:1 or more.

[0050] The solids present in the mixer may also include other solid ingredients desired for inclusion in the detergent granule, for example, fluorescers; polycarboxylate polymers; antiredeposition agents, for example, sodium carboxymethyl cellulose; or fillers such as sodium sulphate, diatomaceous earth, calcite, kaolin or bentonite.

[0051] 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 dry neutralisation.

[0052] Other anionic surfactants that may be present in detergent granules prepared by the process of the invention include 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.

The dry neutralisation process

[0053] The surfactant acid is preferably used in liquid form and advantageously it is reacted while mixing with a molar excess of habit modified Sodium Carbonate to form a sodium salt of the anionic surfactant, while mixing. As an alternative to use of a molar excess of habit modified Sodium Carbonate the reaction may be done with a mixture of habit modified Sodium Carbonate and a smaller amount of other conventional Sodium Carbonate, such as light ash and/or Burkeite, with a corresponding reduction in the granulation benefits of the invention. Nevertheless, if large amounts of Sodium Carbonate are to be used this hybrid process reduces the amount of specially habit modified raw material needed.

[0054] A wider than normal range of ratios of liquid to solid ingredients may be used in the dry neutralisation reaction. Because the system is self structuring, no zeolite or similar structurant is needed and the process is easy to control.

[0055] The total amount of free water that can be tolerated in the process preferably should not amount to more than 8 wt% of the total composition, preferably not more than 4 wt%.

[0056] When habit modified Sodium Carbonate is used in the dry neutralisation process then the resulting granule will comprise neutralised anionic surfactant together with any excess habit modified Sodium Carbonate. The habit modified Sodium Carbonate is an excellent substrate for additional liquid components and it also functions in the same way as Sodium Carbonate as a buffer in a detergent composition.

The invention may thus advantageously be used to prepare detergent powders in which Sodium Carbonate is used without any other builder present - especially if a Calcium tolerant surfactant blend or mixture is used. To ensure the presence of significant quantities of Sodium Carbonate in the granule substantially more habit modified Sodium Carbonate than is required for neutralisation may be present.

[0057] A process feature known to the person skilled in the art of dry neutralisation is that the surfactant acid should be added to the mixer sufficiently gradually so that it will be consumed immediately and will not accumulate in the mixer in unreacted form. We have found that this applies equally to the process using habit modified Sodium Carbonate. The time required and preferred for addition of the surfactant acid is of course dependent on the amount to be added, but in general addition preferably takes place over a period of at least 1 minute, more preferably over a period of from 2 to 12 minutes, most preferably from 3 to 10 minutes.

The mixer

[0058] 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 is advantageous. The HMC starting material has a relatively low crush strength and the mixer should be selected so that it breaks up and rapidly provides fine, material with a consequent large total surface area for reaction and for regranulation.

Thus, a conventional fluid bed granulator would not be preferred for the dry neutralisation process using habit modified carbonate.

[0059] 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. The cutters would be off during the solids pre-mixing.

[0060] 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.

[0061] The stirrer and cutter may be operated independently of one another, and at separately variable speeds. The vessel can be cooled.

[0062] 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.

[0063] 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.

[0064] The temperature of the powder mass in the mixer should be maintained throughout at 55 °C or below, preferably below 50 °C, more preferably below 47 °C, and desirably below 40 °C. If the temperature is allowed to rise too much, agglomeration and lump formation may occur.

The detergent granule

[0065] The granular product of the process is a particulate solid with a bulk density in the range 450 to 720 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 1700 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.

[0066] The product generally has excellent flow properties, low compressibility and little tendency towards caking.

[0067] The particulate detergent granules that are the direct result of the dry neutralisation process may have an anionic surfactant content of 25 wt% to 45 wt%, or even higher. The absence of the need for a granulation aid such as zeolite, together with the ease that the reaction can be driven results in the potential to achieve exceptionally high levels of anionic surfactant in the granule. For example, greater than about 30 wt%, preferably greater than 35 wt%, even greater than 40 wt%, or over 45 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.

[0068] The detergent granules may also comprise water in an amount of 0 to 8% and preferably 0 to 4% by weight of the granules.

[0069] 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.

[0070] 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.

Further processing

[0071] If desired, further ingredients may be admixed to the detergent granules after they have been manufactured.

[0072] 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.

[0073] 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.

[0074] 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.

[0075] 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, antiredeposition 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.

[0076] The skilled detergent formulator can decide which ingredients are suitable for admixture in the mixer, and which are not.

[0077] The detergent granules may be mixed with another powder obtained from any conventional detergent production process including spray drying or non spray drying processes. For convenience, such other powder is hereinafter called a base powder. 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.

[0078] The total amount of surfactant present in the detergent composition is suitably from to 5 to 40 wt%, although amounts outside this range may be employed as desired.

[0079] The detergent granules may typically constitute 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 5 to 45 wt%, preferably 10 to 35 wt% of anionic surfactant, this anionic surfactant being derived wholly or in part from the granular product of the dry neutralisation reaction. The process of the invention is of especial interest for the production of detergent powders or components containing relatively high levels of anionic surfactant, for example, 15 to 30 wt%, more especially 20 to 30 wt%. In addition, the fully formulated detergent composition may comprise from 0 to 10 wt% of nonionic surfactant, and from 0 to 5 wt% of fatty acid soap.

[0080] Fully formulated detergent compositions, comprising other ingredients and the detergent granules produced by dry neutralisation of habit modified Sodium Carbonate; preferably have a bulk density of at least 400 g/l, more preferably at least 450 g/litre.

[0081] The invention will now be further described with reference to the following non limiting examples. In the examples, in addition to the SSA, pore volume and loading tests described above, the detergent granule properties are measured according to the following known test protocols.

Dynamic flow rate (DFR)

[0082] 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 35 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.

[0083] 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:

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

Unconfined Compression Test (UCT)

[0084] 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 freestanding 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.

[0085] The cohesiveness of a powder is classified by the weight (w) as follows:

$$w < 1.0 \text{ kg Good flowing}$$

$$1.0 \text{ kg} < w < 2.0 \text{ kg Moderate flowing.}$$

$$2.0 \text{ kg} < w < 5.0 \text{ kg Cohesive.}$$

$$5.0 \text{ kg} < w \text{ Very cohesive.}$$

Dissolution time (T90)

[0086] A 1-litre beaker is filled with 500mls of demineralised water at 20-25°C and stirred with a magnetic stirrer adjusted to give a vortex of about 4cm. A sample of powder is added to the water. The dissolution is measured according to solution conductivity. The 'T90' value is the time taken to achieve 90% of the final conductivity value.

Bulk density (BD)

[0087] This is measured by taking the increase in weight of a 1 litre container when it is filled with detergent granules and tapped lightly.

EXAMPLES

[0088] Sodium carbonate materials for use in dry neutralisation were obtained. Dense granulated sodium carbonate (reference carbonate A) and light soda ash (reference carbonate B) were sourced directly from Brunner Mond. Reference carbonate C and HMC 1 to 6 were manufactured as described below.

HMC 1 - Spray dried HMC (low moisture)

[0089] HMC was prepared according to WO 2006/081930 A1 by mixing together 29.8 kg of Sokalan CP5 solution (40% active material) with 1373.8kg of water in a stirred tank. Into this solution was then dissolved 596.4 kg of light Sodium Carbonate (ex Brunner Mond). The resultant solution was then spray dried in a 2.5 m diameter spray-drying tower to a final product moisture content of 1.8 % (by IR Balance).

HMC 2 - Spray dried HMC (high moisture)

[0090] The preparation was as for HMC 1 except that the HMC was spray dried to a final product moisture content of 12.9 % (by IR Balance).

HMC 3 - Oven dried HMC

[0091] 0.06kg of Sokalan CP5 solution (40% active material) was mixed with 2.74 kg of water in a stirred tank. Into this solution was then dissolved 1.2 kg of light Sodium Carbonate (ex Brunner Mond). The resultant solution was then dried in shallow trays (solution depth approximately 0.5cm) in an oven at 85°C.

HMC 4 - Drum dried HMC

[0092] A solution with composition by weight, 69.58% water, 0.6% Sokalan CP5 (100% active material) and 29.82% light Sodium Carbonate (ex Brunner Mond) was dried using a 0.391m diameter twin-drum dryer (drying time of 25.6 seconds, drum temperature 148°C).

HMC 5 - Microwave dried HMC

[0093] 1.5 g of Sokalan CP5 solution (40% active material) was mixed with 68.5 g of water in a beaker. Into this solution was then dissolved 30g of light Sodium Carbonate (ex Brunner Mond). The resultant solution was then dried in shallow trays (solution depth approximately 0.5cm) in a microwave oven (Samsung MX35 1000W).

HMC 6 - Precipitated HMC

[0094] 29.8 g of Sokalan CP5 solution was dissolved in 1400 g of demin. water in glass beaker. To this solution was added 590g of light Sodium Carbonate (ex Brunner Mond). The resultant solution was then heated to 70°C with constant stirring and left open to atmosphere to allow evaporation. Heating and stirring were continued until the solution volume had reduced to approximately half its initial volume. The resultant slurry was filtered to remove the crystals precipitated during evaporation. These crystals were then oven dried at 85°C to produce the final product.

Reference Carbonate C - Spray dried modified Burkeite

[0095] 425.2kg of water was added to a 1m^3 mixing vessel having agitation impellers. To the water were sequentially added 25.3kg of sodium polyacrylate solution (Sokalan PA40 ex BASF) followed by 330kg of Sodium Sulphate. The temperature of the mixture was then raised to 60°C and agitated for 8 minutes. 123.7 kg of Sodium Carbonate (Light ash ex Brunner Mond) was then added whilst maintaining agitation to form a slurry. The temperature of the resultant mixture was then raised to 82°C and agitated for a further 12 minutes. 54.9kg of alkaline silicate solution (Crystal 112 ex Ineos Silicas) was then added. The resultant 53 wt% slurry was spray-dried to form a Burkeite carrier material similar to that made in the examples of EP 1 534 812 (Kao).

[0096] The above prepared samples had their specific surface area (SSA) and porosity in small pores (<2 micron diameter) measured using the BET method already described. In addition, by dry neutralisation experiments the maximum amount of LAS acid (HLAS) surfactant acid that could be used with the different types of Sodium Carbonate was determined.

[0097] In Table 1 the SSA, porosity and HLAS capacity is summarised for carbonate materials used. It can be seen that there is a correlation between SSA and the amount of surfactant acid.

Table 1

Carbonate	**Example**	**pore vol ml/g (diameter <2 micron)**	**SSA (m^2/g)**	**LAS Capacity (gHLAS /100g carrier)**
Dense Ash	Ref A	0.07	0.46	9.4
Light Ash	Ref B	0.21	1.00	22.5*
Burkeite	Ref C	0.48	3.08	10.0
Spray Dried HMC	HMC 1	0.64	8.17	98.3
Drum Dried HMC	HMC 4	0.78	8.69	80.7
Microwave HMC	HMC 5	0.72	8.88	122.0
Oven Dried HMC	HMC 3	0.78	10.86	157.5
Precipitated HMC	HMC 6	0.77	12.36	135.0

*granulation was not possible. The product was a sticky mess, so the amount of surfactant acid noted here is not a true granule carrying capacity.

[0098] Throughout the examples the surfactant acid used is LAS acid: C9 to C11 Linear Alkyl Benzene Sulphonic Acid having a mean molecular weight of 320 a purity of 97% and containing 0.8% water.

Example 1 - Neutralisation of LAS acid in Fukae mixer

[0099] 4.0 kg of HMC 1 were charged to a Fukae FS30 high shear granulator/mixer, and mixed using an agitator speed of 200 rpm and a chopper speed of 1300 rpm. Whilst the powder was mixing 1.8 kg of LAS acid was added at a constant rate over a period of 4 minutes using a peristaltic pump. On completion of the addition of the LAS acid, mixing was continued for a further 30 seconds, after which time, the solid product was discharged from the mixer.

[0100] The granulated product was a readily soluble, free-flowing powder (flow-rate 130), having a bulk density of 705 kg/m^3, and a dissolution time (T90) of 34 seconds.

Example 2 - Neutralisation of LAS acid in Ploughshare mixer

[0101] 12 kg of HMC 1 were charged to a Morton (130 litre) Ploughshare granulator/mixer, and mixed using an agitator speed of 100 rpm and a chopper speed of 1000 rpm. Whilst the powder was mixing 5.09 kg of LAS acid was added at a constant rate over a period of 4.5 minutes using a peristaltic pump. On completion of the addition of the LAS acid, mixing was continued for a further 30 seconds, after which time, the solid product was discharged from the mixer.

[0102] The granulated product was a readily soluble, free-flowing powder (flow-rate 135), having a bulk density of 532 kg/m^3, and a dissolution time (T90) of 30 seconds.

Example 3 - Neutralisation of LAS acid in Z blade mixer

[0103] 0.3 kg of HMC 1 was charged to a Winkworth (Type 2Z) z-blade mixer. Whilst the powder was mixing 0.135 kg of LAS acid was poured in at a constant rate over a period of 4 minutes. On completion of the addition of the LAS acid, mixing was continued for a further 30 seconds, after which time, the solid product was discharged from the mixer.

[0104] The granulated product was a readily soluble, free-flowing powder (flow-rate 108), having a bulk density of 496 kg/m^3, and a dissolution time (T90) of 25 seconds.

Example 4 - Neutralisation of LAS acid in high shear mixer

[0105] 1.0 kg of HMC 1 were charged to a Zanchetta RotoJunior (10 litre) high shear granulator/mixer, and mixed using an agitator speed of 350 rpm and a chopper speed of 1350 rpm. Whilst the powder was mixing 0.45 kg of LAS acid was added at a constant rate over a period of 4 minutes using a peristaltic pump. On completion of the addition of the LAS acid, mixing was continued for a further 30 seconds, after which time, the solid product was discharged from the mixer.

[0106] The granulated product was a readily soluble, free-flowing powder (flow-rate 142), having a bulk density of 549 kg/m^3, and a dissolution time (T90) of 32 seconds.

Example 5 - Neutralisation of LAS acid by high moisture HMC

[0107] This is essentially a repeat of Example 1, but using 4.0 kg of higher moisture HMC 2 instead of HMC 1. The HMC was charged to a Fukae FS30 high shear granulator/mixer, and mixed using an agitator speed of 200 rpm and a chopper speed of 1300 rpm. Whilst the powder was mixing 1.54 kg of LAS acid was added at a constant rate over a period of 4 minutes using a peristaltic pump. On completion of the addition of the LAS acid, mixing was continued for a further 30 seconds, after which time, the solid product was discharged from the mixer.

[0108] The granulated product was a readily soluble, free-flowing powder (flow-rate 144), having a bulk density of 570 kg/m^3, and a dissolution time (T90) of 34 seconds.

Example 6 - Neutralisation of HMC with a LAS acid/NI blend

[0109] 400 g of LAS acid was thoroughly mixed with 100 g of ethoxylated alcohol nonionic surfactant (Neodol 25-7 ex Shell Chemicals) to form a liquid blend.

[0110] 1.0 kg of HMC 1 was charged to a Zanchetta RotoJunior (10 litre) high shear granulator/mixer, and mixed using an agitator speed of 350 rpm and a chopper speed of 1350 rpm. Whilst the powder was mixing 0.453 kg of the LAS acid/ nonionic surfactant liquid blend was added at a constant rate over a period of 4 minutes using a peristaltic pump. On completion of the addition of the liquid blend, mixing was continued for a further 30 seconds, after which time, the solid product was discharged from the mixer.

[0111] The granulated product was a readily soluble, free-flowing powder (flow-rate 129), having a bulk density of 655 kg/m^3, and a dissolution time (T90) of 40 seconds.

Example 7 - Neutralisation of HMC with a LAS acid/fatty acid blend

[0112] 400 g of LAS acid was thoroughly mixed with 100 g of fatty acid (Pristerine 4916) to form a liquid blend.

[0113] 1.0 kg of HMC 1 was charged to a Zanchetta RotoJunior (10 litre) high shear granulator/mixer, and mixed using an agitator speed of 350 rpm and a chopper speed of 1350 rpm. Whilst the powder was mixing 0.45 kg of the LAS acid/ fatty acid liquid blend was added at a constant rate over a period of 4 minutes using a peristaltic pump. On completion of the addition of the liquid blend, mixing was continued for a further 30 seconds, after which time, the solid product was discharged from the mixer.

[0114] The granulated product was a readily soluble, free-flowing powder (flow-rate 148), having a bulk density of 582 kg/m^3, and a dissolution time (T90) of 40 seconds.

Example 8 - Neutralisation of LAS acid in Z blade mixer

[0115] This is essentially a repeat of Example 3 using the oven dried material HMC 3 in place of the spray dried HMC 1. 0.3 kg of oven dried HMC 3 was charged to a Winkworth (model 2Z) z-blade mixer. Whilst the powder was mixing 0.135 kg of LAS acid was poured at a constant rate over a period of 4 minutes. On completion of the addition of the LAS acid, mixing was continued for a further 30 seconds, after which time, the solid product was discharged from the mixer.

[0116] The granulated product was a readily soluble, free-flowing powder (flow-rate 111), having a bulk density of 482 kg/m^3, and a dissolution time (T90) of 27 seconds.

Example 9 - Neutralisation of LAS acid in Z blade mixer

[0117] This is a repeat of Example 8 using more LAS acid. 0.3 kg of HMC 3 was charged to a Winkworth (model 2Z) z-blade mixer. Whilst the powder was mixing 0.215 kg of LAS acid was poured at a constant rate over a period of 4 minutes. On completion of the addition of the LAS acid, mixing was continued for a further 30 seconds, after which time, the solid product was discharged from the mixer.

[0118] The granulated product was a readily soluble, free-flowing powder (flow-rate 120), having a bulk density of 526 kg/m^3, and a dissolution time (T90) of 34 seconds.

Example 10 - Neutralisation of LAS acid in high shear mixer

[0119] This is modification of Example 9 using still more LAS acid and a different mixer. 1.0 kg of HMC 3 was charged to a Zanchetta RotoJunior (10 litre) high shear granulator/mixer, and mixed using an agitator speed of 350 rpm and a chopper speed of 1350 rpm. Whilst the powder was mixing 0.45 kg of LAS acid was added at a constant rate over a period of 4 minutes using a peristaltic pump. On completion of the addition of the LAS acid, mixing was continued for a further 30 seconds, after which time, the solid product was discharged from the mixer.

[0120] The granulated product was a readily soluble, free-flowing powder (flow-rate 110), having a bulk density of 557 kg/m^3, and a dissolution time (T90) of 33 seconds.

Example 11 - Neutralisation of LAS acid in high shear mixer

[0121] This is a repeat of Example 10 with even more LAS acid. 1.0 kg of HMC 3 was charged to a Zanchetta RotoJunior (10 litre) high shear granulator/mixer, and mixed using an agitator speed of 350 rpm and a chopper speed of 1350 rpm. Whilst the powder was mixing 0.721 kg of LAS acid was added at a constant rate over a period of 4 minutes using a peristaltic pump. On completion of the addition of the LAS acid, mixing was continued for a further 30 seconds, after which time, the solid product was discharged from the mixer.

[0122] The granulated product was a readily soluble, free-flowing powder (flow-rate 142), having a bulk density of 655 kg/m^3, and a dissolution time (T90) of 42 seconds.

Comparative Example A - Neutralisation of LAS acid with Sodium Carbonate in Fukae

[0123] This is a comparative example that substitutes the HMC neutralisation process according to Example 1 with an analogous process using unmodified Sodium Carbonate. 4.0 kg of commercial light soda ash (ex Brunner Mond) with mean particle size of 110 micron (Reference Carbonate B) were charged to a Fukae FS30 high shear granulator/ mixer, and mixed using an agitator speed of 200 rpm and a chopper speed of 1300 rpm. Whilst the powder was being mixed, 1.032 kg of LAS acid was added at a constant rate over a period of 4 minutes using a peristaltic pump. On completion of the addition of the LAS acid, mixing was continued for a further 30 seconds, after which time, the product was discharged from the mixer.

[0124] This over granulated product had very poor flow properties, having the appearance of wet sand, and was not suitable for use as detergent granules. Even use of lower amounts of surfactant acid did not give satisfactory granules using this process.

Examples 12 to 16 and B - Dry neutralisation of LAS acid using various carbonate materials

Example 12

[0125] 30 g of HMC 1 was placed in a laboratory scale granulator (Braun MR 500 CA) and reacted with LAS acid, which was added manually to the granulator, via a syringe, through a small hole drilled in the top of the granulator's lid until the onset of granulation. The weight of LAS acid added at that point was 18 g. Further LAS acid was then added until the granules started to stick together as dough (over-granulation). The maximum amount of LAS acid that could be added to form detergent granules was 29.5 g.

Example 13

[0126] 20 g of HMC 3 was placed in a laboratory scale granulator (Braun MR 500 CA) and reacted with LAS acid, which was added manually to the granulator, via a syringe, through a small hole drilled in the top of the granulator's lid until the onset of granulation. The weight of LAS acid added at that point was 15 g. Further LAS acid was then added until the granules started to stick together as dough. The maximum amount of LAS acid that could be added to form detergent granules (before over-granulation) was 31.5 g.

Example 14

[0127] 30 g of HMC 4 was placed in a laboratory scale granulator (Braun MR 500 CA) and reacted with LAS acid, which was added manually to the granulator, via a syringe, through a small hole drilled in the top of the granulator's lid until the onset of granulation. The weight of LAS acid added at that point was 13 g. Further LAS acid was then added until the granules started to stick together as dough. The maximum amount of LAS acid that could be added to form granules (before over-granulation) was 24.2 g.

Example 15

[0128] 20 g of HMC 5 was placed in a laboratory scale granulator (Braun MR 500 CA) and reacted with LAS acid, which was added manually to the granulator, via a syringe, through a small hole drilled in the top of the granulator's lid until the onset of granulation. The weight of LAS acid added at that point was 13 g. Further LAS acid was then added until the granules started to stick together as dough. The maximum amount of LAS acid that could be added to form granules (before over-granulation) was 24.4 g.

Example 16

[0129] This example was a repeat of Example 12 with 30 g of HMC 6 replacing the 30 g of HMC 1.

[0130] The amount of LAS acid that could be added to the point of "maximum granulation" (i.e.: maximum amount of LAS acid before over-granulation occurs) was determined to be 37.0 g

Comparative Example B

[0131] 40 g of commercial anhydrous Sodium Carbonate (Light Ash ex Brunner Mond) (Reference Carbonate B) was placed in a laboratory scale granulator (Braun MR 500 CA) and reacted with LAS acid which was added manually to the granulator, via a syringe, through a small hole drilled in the top of the granulator's lid until the onset of granulation. The weight of LAS acid added at that point was 9 g. Even at this low level of addition of LAS acid, the granules were of poor quality in terms of flow and stickiness. Addition of further LAS acid caused the granules started to form an even stickier mass.

Examples 17-22 showing granulation over a range of LAS/Carbonate ratios.

[0132] One of the advantages of the inventive process is the ability to granulate successfully over a wide range of HLAS carbonate ratios. This series of examples were prepared to demonstrate this benefit. The method and materials are the same as for Example 4.

[0133] The amount of LAS acid added, and key physical properties of the resulting detergent granules (BD - bulk density, DFR - Dynamic flow rate, d - Mean particle size, and T90 - dissolution rate) are shown in Table 2. All samples have good granulometry, flow-rate and dissolution properties.

Table 2

Example	**17**	**18**	**19**	**20**	**21**	**22**
LAS acid/HMC w/w	356g/kg	406g/kg	449g/kg	502g/kg	544g/kg	624g/kg
BD (kg/m^3)	594.45	592.425	619.65	635.625	663.75	743.625
DFR (ml/s)	98	118	120	125	87	85
D (micron)	365	331	362	392	311	460
T90 (s)	41.7	37.7	42	44	48.5	57.5

Comparative Example C: Preparation of Detergent Granules using Burkeite (Reference Carbonate C)

[0134] 1.5 kg of the spray-dried Reference Carbonate C were charged to a Zanchetta RotoJunior (10 litre) high shear granulator/ mixer, and mixed using an agitator speed of 350 rpm and a chopper speed of 1350 rpm. Whilst the powder was mixing 0.15 kg of LAS acid was added at a constant rate over a period of 2.5 minutes. On completion of the addition of the LAS acid, mixing was continued for a further 30 seconds, after which time, the solid product was discharged from the mixer. The granulated product was a free-flowing powder (flow-rate 115), having a bulk density of 715 kg/m^3.

Comparative Example D: Preparation of Detergent Granules using milled ash.

[0135] 1.5kg of Sodium Carbonate (light ash ex Brunner Mond) that had previously been milled to a mean particle size of 50 micron (Reference Carbonate D) were charged to a Zanchetta RotoJunior (10 litre) high shear granulator/mixer, and mixed using an agitator speed of 350 rpm and a chopper speed of 1350 rpm. Whilst the powder was mixing 0.364 kg of LAS acid was added at a constant rate over a period of 5.75 minutes. The amount added was just sufficient to prevent over-granulation. On completion of the addition of the LAS acid, mixing was continued for a further 30 seconds, after which time, the solid product was discharged from the mixer.
The granulated product was a free-flowing powder (flow-rate 90), having a bulk density of 705 kg/m^3.

Examples 23 and 24 - Perfume loading of detergent granules

Example 23

[0136] 200 g of the detergent granules from Example 2 was sprayed in a laboratory scale rotating pan with 6.0 g of perfume oil. The flow rate of the resultant powder was measured as 137 g/min.

Example 24

[0137] 200 g of the detergent powder from Example 2 was sprayed in a laboratory scale rotating pan with 10.0 g of perfume oil. The flow rate of the resultant powder was measured as 140 g/min.

Example 25 - Neutralisation of LAS acid in high shear mixer (no chopping action)

[0138] 1.0 kg of HMC 1 were charged to a Zanchetta RotoJunior (10 litre) high shear granulator/mixer, and mixed using an agitator speed of 350 rpm but with the choppers switched off. Whilst the powder was mixing 0.353 kg of LAS acid was added at a constant rate over a period of 4 minutes using a peristaltic pump. On completion of the addition of the LAS acid, mixing was continued for a further 30 seconds, after which time, the solid product was discharged from the mixer.

[0139] The granulated product was a readily soluble, free-flowing powder (flow-rate 146), having a bulk density of 549 kg/m^3, and a UCT value of 2.5 kg - this means it would cake easily, for example in silo-storage. Thus, this variant of the process is less preferred due to the lower loading of the anionic surfactant achievable and the caking problem indicated by the high UCT result.

[0140] Note that this example is essentially a repeat of Example 4 (which has the choppers/cutters operating) and achieves a higher surfactant content, similar DFR and same bulk density but has been measured to have a UCT of zero and would therefore not have a caking problem.

Example 26 and Comparative Example E - Storage stability

[0141] 398 g of the detergent granules of Example 2 was stored in an open, plain cardboard carton (dimensions 15.4 cm wide, 7.0 cm deep and 13.0 cm high) at a temperature of 28°C and relative humidity of 70%RH for a period of 6 weeks. On removal from storage, these detergent granules had not caked and were still free-flowing (flow rate-133).

[0142] For comparison, 388 g of the product of Comparative Example A was stored in the same type of cardboard carton under the same conditions for a period of less than 6 weeks. On removal from storage, this powder was heavily caked, in large lumps and did not flow freely from the carton.

[0143] The granules according to the invention made using habit modified Sodium Carbonate in the dry neutralisation process are non-caking at higher surfactant levels than those made with conventional Sodium Carbonate in the dry neutralisation process.

Claims

1. A process for the manufacture of detergent granules comprising anionic non-soap surfactant the process comprising the dry neutralisation of surfactant acid with habit modified Sodium Carbonate.

2. A process according to claim 1 in which the surfactant acid is used in liquid form.

3. A process according to any preceding claim in which the surfactant acid is reacted while mixing with a molar excess

of habit modified Sodium Carbonate to form a sodium salt of the anionic surfactant, while mixing.

4. A process according to claim 3 in which the mixing is carried out in a mixer with a chopping action and the chopping action is used during the dry neutralisation reaction.

5. A process according to claim 4 in which the mixing is carried out in a mixer, which has both a stirring action and a cutting action, and both actions are used during the dry neutralisation reaction.

6. A process according to any preceding claim in which the neutralising agent compasses a mixture of habit modified carbonate with a smaller amount of Sodium Carbonate and/or Burkeite.

7. A process according to any preceding claim in which the habit modified Sodium Carbonate 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.

8. A process according to claim 7 in which the habit modified Sodium Carbonate is **characterised by** having
a pore volume, in pores less than 2 micron diameter,
of 0.3 ml/g or greater.

9. A high active detergent granule comprising:

a) greater than 30 wt% anionic surfactant, said surfactant comprising a major part of non-soap anionic surfactant,
b) habit modified Sodium Carbonate, and
c) less than 10 wt%, preferably zero, zeolite,
obtainable by the process according to any preceding claim.

10. A detergent granule according to claim 9 **characterised in that** the non-soap anionic surfactant level in the granule is greater than 30 wt%, preferably greater than 35 wt%, even greater than 40 wt% and preferably even greater than 45 wt%.

11. A detergent granule according to claim 9 or claim 10, further comprising perfume.

12. A detergent granule according to any one of claims 9 to 11, further comprising nonionic surfactant.

13. A detergent granule according to any one of claims 9 to 12, further comprising soap.

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EUROPEAN SEARCH REPORT

Application Number
EP 08 15 6714

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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	23 October 2008	Richards, Michael

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