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(54) Agglomerates for addition to detergent powders.

(57) An agglomerate comprising whitening particulate material of average particle size less than 20 microns, a bulk density less than 400 grams per litre and a reflectance value (R infinity 460) of greater than 85. Such agglomerates are often especially white, bright and unnoticeable when added to a detergent base washing powder.

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AGGLOMERATES FOR ADDITION TO DETERGENT POWDERS

This invention relates to an agglomerated composition of improved colour and in particular to white agglomerates of clay fabric softener for addition to white or differently coloured detergent base powders.

Detergent powders without added colour are generally white or near-white in colour, but some ingredients especially certain classes of fabric softening clay, enzyme granules or bleach precursors may be brown, yellow or grey. The incidence of such discoloured particles in a finished detergent powder can give the whole product an off-white unattractive appearance.

GB 2 199 338 (Unilever Plc) proposes the use of large vividly coloured particles ("speckles") in detergent powder to render the presence of slightly discoloured particles unnoticeable.

GB 2 121 843 (Colgate-Palmolive Co) proposes incorporating dyes or pigments in a liquid agglomerating spray used in the manufacture of bentonite clay agglomerates to form clay speckles.

In some powders however the use of speckles may not be desirable or may be ineffective in camouflaging the discoloured particles.

We have surprisingly found that agglomerates coated or granulated with a whitening particulate material of a certain average particle size, bulk density and reflectance value (measured as R infinity at 460 nm which represents the reflectance value of a layer so thick that a further increase in thickness of the layer fails to change the reflectance) are often especially white, bright and unnoticeable when added to a detergent base washing powder.

A first aspect of the present invention accordingly provides agglomerates comprising whitening particulate material of average particle size less than 20 microns, a bulk density of less than 400 grams per litre and a reflectance value (R infinity 460) of greater than 85.

A second aspect of the invention provides a fabric softener comprising clay agglomerates, said agglomerates comprising whitening particulate material of average particle size less than 20 microns, a bulk density of less than 400 grams per litre and a reflectance value (R infinity 460) of greater than 85.

A third aspect of the invention provides agglomerates comprising sufficient whitening particulate material to give the agglomerate an R infinity 460 value greater than 75.

The agglomerates of improved colour can be formed either as a cogranulate with the whitening particulate material or as agglomerates coated with the whitening particulate material.

The cogranulated agglomerates preferably comprise from 30% to 60% by weight of the particulate material, more preferably from 40% to 50% by weight.

The average particle size of the particulate material is preferably less than 15 microns, more preferably less than 10 microns.

The bulk density of the particulate material is preferably less than 250 grams per litre.

The reflectance value measured as R infinity 460 is preferably greater than 95.

When the particulate material is present as a coating on the agglomerates it preferably comprises from 10 to 40% by weight of the total agglomerate composition. More preferably the particulate material comprises from 15 to 25% by weight of the total agglomerate composition.

The particulate material is preferably a precipitated calcium carbonate or a silica. The precipitated calcium carbonate employed can be in the form of particles of average particle size of the order of 4 microns, built up from trigonal or aragonite crystals.

The silica employed is in the form of a precipitated amorphous powder of particle size of the order of 10 microns.

A type of precipitated calcium carbonate which is most useful in whitening the agglomerates is that which is known as SOCAL U3 (ex Solvay). A type of silica which is most useful in whitening the agglomerates is that which is known as Microsil (ex Crosfields).

Clay softeners are well-known in the detergent patent literature. Included among such clay softeners are various heat-treated kaolins and various multi-layer smectites. GB 1 400 898 (Procter and Gamble) suggests the use of smectite clays having a relatively high exchange capacity. There is a desire to boost the performance of fabric softening clays in the wash and according to our copending patent application EP 287 344 it has been found that if certain nonionic surfactant materials are carried on the clay, at a specified level relative thereto, and the moisture content of the composition is controlled, the fabric softening performance is enhanced. The examples of the invention included herein are directed towards clay carrying a nonionic surfactant but it should be understood that the invention is not limited to clays.

It has been found that the moisture content of clay agglomerates must be between 7.5% and 12% by weight, preferably from 8% to 10%. The term "moisture" in this context is not necessarily the total water content, but rather it is the water which is lost from the composition by drying in a static environment at

135 °C to a constant weight. Usually, when freshly prepared, the clay/nonionic agglomerates will have a higher moisture content, such as, for example from 10% to 16% moisture, and will therefore be too sticky for use, so that some post drying is necessary. When post-drying high moisture content clay/nonionic agglomerates, a drying air temperature of 85-90 °C has been found to be suitable. Where the agglomerates are to be coated with precipitated calcium carbonate it may be desirable to "over-dry" the agglomerates so that moisture accommodated by the agglomerates as a result of the coating process leaves the agglomerates with a final moisture content in the desired range.

The nonionic surfactant system exists as a cloudy phase in the temperature range of 0 °C to 80 °C, preferably 0 °C to 15 °C in distilled water at 1% concentration. In practise this means that the system has a cloud point of not more than 80 °C, preferably not more than 15 °C. The cloud point correlates approximately to the hydrophilic-lipophilic balance (HLB) of the surfactant system and it is therefore preferred that the HLB should be less than 13.5, such as not more than 12.0, ideally less than 9.5. The HLB should be above 6.0, preferably above 8.0 to provide sufficient detergency.

Specific nonionic surfactants are alkyl (C_6-C_{22}) phenols-ethylene oxide condensates, the condensation products of aliphatic (C_8-C_{18}) primary or secondary linear or branched alcohols with ethylene oxides, and products made by condensation of ethylene oxide with the reaction products of propylene oxide and ethylenediamine.

The clay softener may be any such material capable of providing a softening benefit. The effectiveness of a clay material as a fabric softener will depend on the level of smectite clay. It is preferred that the ratio of the clay to the nonionic surfactant in the agglomerate is from 3:1 to 20:1, most preferably 4:1 to 10:1.

Where the agglomerates are to be handled by conveyors, feeders, mixers, filling machinery or are to be subjected to shipping shocks it may be necessary to employ a binder, in addition to the nonionic if present, in the granulation process to improve the structural stability of the agglomerate. Suitable binders include copolymers of polyacrylate and maleic anhydride, polyacrylates, sugars, nonionic surfactants, polyethylene glycol, polyoxyethylene alkyl ether, fatty acid monoethanolamide, carboxymethyl cellulose, soap and latex.

The agglomerates can be made by known granulation processes typically by those described in GB 2 121 843B. The cogranulated agglomerates can be made in any granulater where the binding material can be contacted with materials to be agglomerated; preferably a high shear, short residence time granulator, such as a Schugi Flexomix or a L ödige Recycler, or a longer residence time, low shear granulater, such as a continuous drum granulater, Eirich pan granulater or a drum or cement mixer. The coated agglomerates can be made in any suitable device such as a rotary drum, pan or marumeriser mixer using agglomerates made by a known granulation process.

Where the agglomerates are to be coated with the particulate material, it may be desirable to include a binder in the coating solution (usually water) to aid adherence of the particulate material to the agglomerate and to form durable bonds within the coating layer.

A preferred process for forming coated agglomerates comprises granulating the agglomerates with an excess of nonionic surfactant in a drum mixer to form "sticky" granules followed by coating with the particulate material. The advantages of this process are that an improved coating adherence and colour is obtained. The especially improved colour is thought to be due to the fact that no binder is present at the light scattering surface of the agglomerate.

A particularly preferred binder is Sokalan CP5 (ex BASF) a copolymer of maleic anhydride and polyacrylate supplied as a 40% aqueous solution.

In addition to the binder it may be necessary to employ a plasticiser to improve the friability resistance of the coating. For example the addition of 2% by weight sorbitol or glycerol to the binder spray greatly decreases the friability of the agglomerate, especially if the agglomerate is air dried.

When the agglomerates of the invention or the washing products containing them, contain a detergent active material, this may be selected from nonionic detergent active materials, anionic detergent active materials, zwitterionic or amphoteric detergent active materials or mixtures thereof.

The anionic detergent active materials are usually water-soluble alkali metal salts of organic sulphates and sulphonates having alkyl radicals containing from about 8 to about 22 carbon atoms, the term alkyl being used to include the alkyl portion of higher acyl radicals. Examples of suitable synthetic anionic detergent compounds are sodium and potassium alkyl sulphates, especially those obtained by sulphating higher (C_8-C_{18}) alcohols produced for example from tallow or coconut oil, sodium and potassium alkyl (C_9-C_{20}) benzene sulphonates, particularly sodium linear secondary alkyl (C_{10}-C_{15}) benzene sulphonates; sodium alkyl glyceryl ether sulphates, especially those ethers of the higher alcohols derived from tallow or coconut oil and synthetic alcohols derived from petroleum; sodium coconut oil fatty monoglyceride sulphates and sulphonates; sodium and potassium salts of sulphuric acid esters of higher (C_8-C_{18}) fatty alcohol-alkylene oxide, particularly ethylene oxide, reaction products; the reaction products of fatty acids

such as coconut fatty acids esterified with isethionic acid and neutralised with sodium hydroxide; sodium and potassium salts of fatty acid amides of methyl taurine; alkane monosulphonates such as those derived by reacting alpha-olefins (C_8-C_{20}) with sodium bisulphite and those derived from reacting paraffins with SO_2 and Cl_2 and then hydrolysing with a base to produce a random sulphonate; and olefin sulphonates, which term is used to describe the material made by reacting olefins, particularly C_{10}-C_{20} alpha-olefins, with SO_3 and then neutralising and hydrolysing the reaction product. The preferred anionic detergent compounds are sodium (C_{11}-C_{15}) alkyl benzene sulphonates and sodium (C_{16}-C_{18}) alkyl sulphates.

When the fabric washing products contain a detergency builder material this may be any material capable of reducing the level of free calcium ions in the wash liquor and will preferably provide the composition with other beneficial properties such as the generation of an alkaline pH, the suspension of soil removed from the fabric and the dispersion of the fabric softening clay material.

Examples of phosphorus-containing inorganic detergency builders, when present, include the water-soluble salts, especially alkaline metal pyrophosphate, orthophosphates, polyphosphates and phosphonates. Specific examples of inorganic phosphate builders include sodium and potassium tripolyphosphates, phosphates and hexametaphosphates.

Examples of non-phosphorus-containing inorganic detergency builders, when present, include water-soluble alkali metal carbonates, bicarbonates, silicates and crystalline and amorphous alumino silicates. Specific examples include sodium carbonate (with or without calicte seeds), potassium carbonate, sodium and potassium bicarbonates and silicates.

Examples of organic detergency builders, when present, include the alkaline metal, ammonium and substituted ammonium polyacetates, carboxylates, polycarboxylates, polyacetyl carboxylates and poly-hydroxsulphonates. Specific examples include sodium, potassium lithium, ammonium and substituted ammonium salts of ethylenediaminetetraacetic acid, nitrilotriacetic acid, oxydisuccinic acid, melitic acid, benzene polycarboxylic acids and citric acid.

Apart from the ingredients already mentioned, a number of optional ingredients may also be present, either as part of the clay containing compositions or as part of the overall fabric washing product.

Examples of other ingredients which may be present in the composition include the lather boosters, lather depressants, oxygen-releasing bleaching agents such as sodium perborate and sodium percarbonate, peracid bleach percursors, chlorine-releasing bleaching agents such as tricloroisocyanuric acid, inorganic salts such as sodium sulphate, and, usually present in very minor amounts, fluorescent agents, perfumes, enzymes such as proteases, lipalases, cellulases and amylases, germicides and colourants.

When the agglomerates are included in a detergent base powder they are typically present at a level from 5 to 20% by weight.

A typical formulation is as follows:

	Parts by weight
Lauryl alkyl sulphonate	6
Nonionic detergent active	3
Soap	1.5
Zeolite	22
Sokalan CP5	3
Alkaline silicate	0.5
Perborate Monohydrate	7.5
TAED	1.8
Savinase	0.35
Carbonate	10.00
EDTA	0.15
Sulphate	24.39
SCMC	0.50
Clay agglomerates	10.00
Water, perfume, minors	9.31

Examples

The invention will now be illustrated by the following non-limiting examples.

Example 1A

Clay nonionic agglomerates were prepared by spraying 83 parts by weight of clay (KBU, clay of cec <50 meq/100g ex Colin Stewart Minerals) with 17 parts of Synperonic A3 (a nonionic surfactant ex ICI which is a C_{13}-C_{15} alcohol ethoxylated with approximately 3 moles of ethylene oxide per molecule and having a cloud point below 0 ° C) in a drum mixer.

The agglomerates were tumbled in a drum coater with 20% by weight of Socal U3 (precipitated calcium carbonate ex SOLVAY having a bulk density of 230 g/l a particle size of 4 microns, and an R infinity 460 of 96) and 20% by weight of a 25% solution of Sokalan CP5. The moisture content of the agglomerates as made was 18%, these were dried to a moisture content of 8%.

Example 1B

Example 1A was repeated excepting that the agglomerates were coated with 10% by weight Microsil a silica (ex Crosfields) having a particle size of 10-15 microns, a bulk density of 130 g/l and a reflectance value (R infinity 460) of 98.4.

Example 2

Example 1 was repeated excepting that the agglomerates were coated with 20% by weight Durcal, a calcite (ex Omya) having a bulk density of 670 g/l a particle size of 4 microns and a reflectance value (R infinity 460) of 93.

Example 3

Example 1 was repeated excepting that the agglomerates were coated with 20% by weight Speswhite, a kaolinite ex English China Clays Ltd (ECC).

Speswhite has a bulk density of 425 g/l, a particle size of 80% less than 2 microns and a reflectance value R infinity 460 of 85.

Example 4

Clay/nonionic/precipitated calcium carbonate agglomerates were prepared by co-granulating 83 parts by weight of clay ('KBU) with 83 parts by weight Socal U3 using 24 parts by weight of Synperonic A3 and 62 parts by weight of a 2% solution of Sokalan CP_5 as a granulating spray.

The agglomerates were then dried to a moisture content of approximately 8% on a fluidised bed dryer using drying air having a temperature of 80 ° C.

Example 5

Example 4 was repeated excepting that the agglomerates were cogranulated with 83 parts by weight Speswhite a kaolin ex ECC in place of the Socal U3.

The reflectance of the agglomerates was then determined and is quoted in Table I as an R460° (infinity) value which denotes, on a scale of 1 to 100 the amount of light reflected back from a sample. The higher the reflectance value the whiter the sample. R460° values presented here are an average of 5 with a least significant difference of 0.5.

Table I

Example	R460*
1A	80
1B	80
2	58
3	66
4	80
5	62

Claims

1. An agglomerate comprising whitening particulate material of average particle size less than 20 microns, a bulk density less than 400 grams per litre and a reflectance value (R infinity 460) of greater than 85.

2. An agglomerate comprising sufficient whitening particulate material to give the agglomerate an R infinity 460 value greater than 75.

3. An agglomerate as claimed in claim 1 or claim 2, wherein the whitening particulate material is present as a coating on the agglomerate.

4. An agglomerate as claimed in claim 1 or claim 2 wherein the whitening particulate material is present throughout the agglomerate as a cogranulate.

5. An agglomerate as claimed in any preceding claim wherein the bulk density of the whitening particulate material is less than 250 grams per litre.

6. An agglomerate as claimed in any preceding claims wherein the average particle size of the particulate material is less than 15 microns.

7. An agglomerate as claimed in any preceding claim wherein the average particle size of the particulate material is less than 10 microns.

8. An agglomerate as claimed in claim 3 wherein the particulate material comprises from 10 to 40% by weight of the total agglomerate composition.

9. A fabric softener comprising clay agglomerates, said agglomerates comprising whitening particulate material of average particle size less than 20 microns, a bulk density of less than 400 grams per litre and a reflectance value (R infinity 460) of greater than 85.

10. A detergent composition comprising from 5% to 20% by weight of agglomerates as claimed in claim 1.