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(54) **Coating clay agglomerates with finely divided particulate material.**

(57) Granular detergent components or compositions having a bulk density of at least 600 g/l comprise:
i) a granular component which comprises smectite clay; and
ii) a finely divided particulate material wherein the finely divided particulate material is present at a level of from 0.5% to 15% by weight of the detergent component or composition and that the finely divided particulate material comprises sodium aluminosilicate and hydrophobic silica wherein the ratio of the sodium aluminosilicate to hydrophobic silica in component ii) is from 100:1 to 5:1.

A process for making suitable granular detergent components and compositions is also described.

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Background of the Invention

The present invention relates to the use of finely divided particulate materials to improve the colour of granular products which comprise clay. The finely divided particulate material comprises a mixture of sodium aluminosilicate and silica in a defined ratio. The silica used is hydrophobic silica, preferably fumed hydrophobic silica. The ratio of sodium aluminosilicate to silica is from about 100:1 to about 5:1, preferably from 20:1 to 4:1, and most preferably around 10:1.

It is known that clay particles are useful components in detergent compositions, largely due to the effect of softening fabrics during the laundering process. In particular clay particles have been incorporated into detergent products which are added during the wash cycle (rather than being added later during the rinse cycle) for the purposes of softening through the wash.

However, one of the disadvantages of clay is that it tends to give an off-white colour to the particles into which it is incorporated. This means that when a finished composition is made by blending its various components together, the particles which contain the clay are easily distinguished from particles which do not contain clay due to the difference in whiteness. This is readily apparent to the consumer who will generally find such product properties undesirable or even unacceptable. Furthermore, the problem becomes increasingly evident when particles are used which comprise high levels of clay.

Various ways of addressing this problem have been proposed in the prior art:
GB 2 120 293, published 30th November 1983, and GB 2 121 843, published on 4th January, 1984, both describe the addition of dyes or pigments to the liquid binder which is used to agglomerate the clay particles. This results in coloured clay "speckles", thereby masking the poor whiteness of the clay particles. The use of flow aids is also mentioned, but no indication is given of how suitable flow aids may be chosen.

EP A 353 994, published 7th February, 1990, discloses base granules of smectite clay coated with white inorganic material. Suitable inorganic materials are kaolin clay, calcium carbonate or titanium dioxide.

EP A 385 748, published 5th September, 1990, discloses the use of whitening particulates (e.g. silica, calcite) to coat the surface of the clay particles.

However, where whitening particulates have been suggested in the prior art, they are generally not active in the laundry process, and they need to be present at relatively high levels (e.g. at least 10% by weight) of the clay particle in order to be effective. Consequently such whitening particulates are expensive components which do not make any contribution to the laundry process itself.

It has now been found that clay particles which have excellent colour (i.e. whiteness), and which are very difficult to distinguish from the remainder of the white granules which are typically used in today's granular laundry detergents, can be made by coating the clay particles with a finely divided particulate material which is predominantly sodium aluminosilicate.

According to the present invention the most satisfactory results are achieved by premixing the sodium aluminosilicate with silica, preferably hydrophobic, fumed silica. The advantage of this mixture of finely divided particulate materials compared to the prior art is that it predominantly comprises materials which are active in the washing process (namely the aluminosilicate which performs as a builder), and is therefore a highly economic and efficient technique to solve the problem of providing white clay agglomerates for use in granular detergent compositions.

The present invention also addresses the problem of achieving more control over particle size distribution of the finished product. One of the factors influencing particle size distribution is the effectiveness of the finely divided particulate material which is introduced near to the end of the manufacturing process. The mixture of finely divided particulate materials of the present invention have been found to be more efficient in this regard.

Summary of the Invention

The present invention relates to granular detergent components or compositions having a bulk density of at least 600 g/l which comprise:

i) a granular component which comprises smectite clay; and

ii) a finely divided particulate material

wherein the finely divided particulate material is present at a level of from 0.5% to 15% by weight of the detergent component or composition and that the finely divided particulate material comprises sodium aluminosilicate and hydrophobic silica wherein the ratio of the sodium aluminosilicate to hydrophobic silica in component ii) is from 100:1 to 5:1.
A process for making suitable granular detergent components and compositions is also described.

Description of the Invention

The present invention comprises two essential components; a granular detergent component which comprises clay, and a finely divided particulate material which is a premixed powder comprising sodium aluminosilicate and silica. Both of these components will now be described in more detail

Granular Detergent Comprising Smectite-type Clay

The first essential feature of the compositions of the present invention is smectite-type clay, which is selected from the group comprising sodium hectorite, potassium hectorite, lithium hectorite, magnesium hectorite, calcium hectorite, sodium montmorillonite, potassium montmorillonite, magnesium montmorillonite, calcium montmorillonite, sodium saponite, potassium saponite, lithium saponite, magnesium saponite, calcium saponite, and mixtures thereof. All of these may be organically modified. The hectorites may be natural or synthetic. Preferred smectite-type clays are sodium montmorillonite and potassium montmorillonite.

The clays used herein have a particle size range of up to about 1 micron.

The clay minerals which are not organically modified can be described as expandable, three-layered clays, i.e., aluminosilicates and magnesium silicates, having an ion exchange capacity of at least 50 meq/100g. of clay and preferably at least 60 meq/100 g. of clay. The starting clays for the organically modified clays can be similarly described. The term "expandable" as used to describe clays relates to the ability of the layered clay structure to be swollen, or expanded, on contact with water. The three-layer expandable clays used herein are those materials classified geologically as smectites.

There are two distinct classes of smectite-type clays that can be broadly differentiated on the basis of the numbers of octahedral metal-oxygen arrangements in the central layer for a given number of silicon-oxygen atoms in outer layers.

The clays employed in these compositions contain cationic counterions such as protons, sodium ions, potassium ions, calcium ions, and lithium ions. It is customary to distinguish between clays on the basis of one cation predominantly or exclusively absorbed. For example, a sodium clay is one in which the absorbed cation is predominantly sodium. Such absorbed cations can become involved in exchange reactions with cations present in aqueous solutions. A typical exchange reaction involving a smectite-type clay is expressed by the following equation :

$$\text{smectite clay (Na)}^+ + NH_4OH \Rightarrow \text{smectite clay } (NH_4)^+ + NaOH.$$

Since in the foregoing equilibrium reaction, an equivalent weight of ammonium ion replaces an equivalent weight of sodium, it is customary to measure cation exchange capacity (sometimes termed "base exchange capacity") in terms of milliequivalents per 100 g. of clay (meq/100g). The cation exchange capacity of clays can be measured in several ways, including by electrodialysis, by exchange with ammonium ion followed by titration, or by a methylene blue procedure, all as fully set forth in Grimshaw, "The Chemistry and Physics of Clays", pp. 264-265, Interscience (1971).

The cation exchange capacity of a clay material relates to such factors as the expandable properties of the clay, the charge of the clay (which in turn is determined at least in part by the lattice structure), and the like. The ion exchange capacity of clays varies widely in the range from about 2 meq/100 g. of kaolinites to about 150 meq/100 g., and greater, for certain smectite clays.

The amount of smectite clay present in the clay particles of the present invention is not limited. However, it is at higher levels (for example, at least 50% by weight) of clay in the particle that the problem of poor whiteness is most evident, and consequently that the present invention is most useful. Preferably the agglomerates used will comprise from 50% to 85% by weight of the agglomerate, and even more preferably from 55% to 70% by weight.

The component may also comprise one or more surfactants chosen from anionic, cationic, nonionic, zwitterionic and amphoteric surfactants, in addition to the clay particles. Indeed the inclusion of such surfactants may be of considerable advantage in order to improve the rate of disintegration of the clay containing component in the wash water.

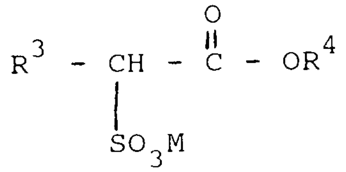
Anionic Surfactants

The components and compositions of the present invention may comprise one or more anionic surfactants chosen from those described below.

Alkyl Ester Sulfonate Surfactant

Alkyl Ester sulfonate surfactants hereof include linear esters of C_8-C_{20} carboxylic acids (i.e. fatty acids) which are sulfonated with gaseous SO_3 according to "The Journal of the American Oil Chemists Society'" 52 (1975), pp. 323-329. Suitable starting materials would include natural fatty substances as derived from tallow, palm oil, etc.

The preferred alkyl ester sulfonate surfactant, especially for laundry applications, comprises alkyl ester sulfonate surfactants of the structural formula:



$$R^3 - \underset{SO_3M}{\underset{|}{CH}} - \overset{O}{\overset{\|}{C}} - OR^4$$

wherein R^3 is a C_8-C_{20} hydrocarbyl, preferably an alkyl, or combination thereof, R^4 is a C_1-C_6 hydrocarbyl, preferably an alkyl, or combination thereof, and M is a cation which forms a water soluble salt with the alkyl ester sulfonate. Suitable salt-forming cations include metals such as sodium, potassium, and lithium, and substituted or unsubstituted ammonium cations, such as monoethanolamine, diethanolamine, and triethanolamine. Preferably, R^3 is C_{10}-C_{16} alkyl, and R^4 is methyl, ethyl or isopropyl.

Especially preferred are the methyl ester sulfonates wherein R^3 is C_{14}-C_{16} alkyl.

Alkyl Sulfate Surfactant

Alkyl sulfate surfactants hereof are water soluble salts or acids or the formula $ROSO_3M$ wherein R preferably is a C_{10}-C_{24} hydrocarbyl, preferably an alkyl or hydroxyalkyl having a C_{10}-C_{20} alkyl component, more preferably a C_{12}-C_{18} alkyl or hydroxyalkyl, and M is H or a cation, e.g., an alkali metal cation (e.g., sodium, potassium, lithium), or ammonium or substituted ammonium (e.g., methyl-, dimethyl-, and trimethyl ammonium cations and quaternary ammonium cations, such as tetramethyl-ammonium and dimethyl piperdinium cations and quarternary ammonium cations derived from alkylamines such as ethylamine, diethylamine, triethylamine, and mixtures thereof, and the like). Typically, alkyl chains of C_{12-16} are preferred for lower wash temperatures (e.g., below about 50 ° C) and C_{16-18} alkyl chains are preferred for higher wash temperatures (e.g., above about 50 ° C).

Alkyl Alkoxylated Sulfate Surfactant

Alkyl alkoxylated sulfate surfactants hereof are water soluble salts or acids of the formula $RO(A)_mSO_3M$ wherein R is an unsubstituted C_{10}-C_{24} alkyl or hydroxyalkyl group having a C_{10}-C_{24} alkyl component, preferably a C_{12}-C_{20} alkyl or hydroxyalkyl, more preferably C_{12}-C_{18} alkyl or hydroxyalkyl, A is an ethoxy or propoxy unit, m is greater than zero, typically between about 0.5 and about 6, more preferably between about 0.5 and about 3, and M is H or a cation which can be, for example, a metal cation (e.g., sodium, potassium, lithium, calcium, magnesium, etc.), ammonium or substituted-ammonium cation. Alkyl ethoxylated sulfates as well as alkyl propoxylated sulfates are contemplated herein. Specific examples of substituted ammonium cations include methyl-, dimethyl-, trimethyl-ammonium and quaternary ammonium cations, such as tetramethyl-ammonium, dimethyl piperdinium and cations derived from alkanolamines such as ethylamine, diethylamine, triethylamine, mixtures thereof, and the like. Exemplary surfactants are C_{12}-C_{18} alkyl polyethoxylate (1.0) sulfate, C_{12}-$C_{18}E(1.0)M$), C_{12}-C_{18} alkyl polyethoxylate (2.25) sulfate, C_{12}-$C_{18}E(2.25)M$), C_{12}-C_{18} alkyl polyethoxylate (3.0) sulfate C_{12}-$C_{18}E(3.0)$, and C_{12}-C_{18} alkyl polyethoxylate (4.0) sulfate C_{12}-$C_{18}E(4.0)M$), wherein M is conveniently selected from sodium and potassium.

Other Anionic Surfactants

Other anionic surfactants useful for detersive purposes can also be included in the laundry detergent compositions of the present invention. These can include salts (including, for example, sodium, potassium, ammonium, and substituted ammonium salts such as mono-, di- and triethanolamine salts) of soap, C_9-C_{20} linear alkylbenzenesulphonates, C_8-C_{22} primary or secondary alkanesulphonates, C_8-C_{24} olefinsulphonates, sulphonated polycarboxylic acids prepared by sulphonation of the pyrolyzed product of alkaline earth metal citrates, e.g., as described in British patent specification No. 1,082,179, C_8-C_{24} alkylpolyglycolethersulfates (containing up to 10 moles of ethylene oxide); acyl glycerol sulfonates, fatty oleyl glycerol sulfates, alkyl phenol ethylene oxide ether sulfates, paraffin sulfonates, alkyl phosphates, isethionates such as the acyl isethionates, N-acyl taurates, alkyl succinamates and sulfosuccinates, monoesters of sulfosuccinate (especially saturated and unsaturated C_{12}-C_{18} monoesters) diesters of sulfosuccinate (especially saturated and unsaturated C_6-C_{14} diesters),acyl sarcosinates, sulfates of alkylpolysaccharides such as the sulfates of alkylpolyglucoside (the nonionic nonsulfated compounds being described below), branched primary alkyl sulfates, alkyl polyethoxy carboxylates such as those of the formula $RO(CH_2CH_2O)_kCH_2COO\text{-}M^+$ wherein R is a C_8-C_{22} alkyl, k is an integer from 0 to 10, and M is a soluble salt-forming cation. Resin acids and hydrogenated resin acids are also suitable, such as rosin, hydrogenated rosin, and resin acids and hydrogenated resin acids present in or derived from tall oil. Further examples are given in "Surface Active Agents and Detergents" (Vol. I and II by Schwartz, Perry and Berch). A variety of such surfactants are also generally disclosed in U.S. Patent 3,929,678, issued December 30, 1975 to Laughlin, et al. at Column 23, line 58 through Column 29, line 23 (herein incorporated by reference).

When included therein, the laundry detergent compositions of the present invention typically comprise from about 1 % to about 40 %, preferably from about 3 % to about 20 % by weight of such anionic surfactants.

Nonionic Surfactants

Particularly preferred for use in the present invention are nonionic surfactants such as the polyethylene oxide condensates of alkyl phenols, e.g., the condensation products of alkyl phenols having an alkyl group containing from about 6 to 16 carbon atoms, in either a straight chain or branched chain configuration, with from about 4 to 25 moles of ethylene oxide per mole of alkyl phenol.

Preferred nonionics are the water-soluble condensation products of aliphatic alcohols containing from 8 to 22 carbon atoms, in either straight chain or branched configuration, with an average of up to 25 moles of ethylene oxide per mole of alcohol. Particularly preferred are the condensation products of alcohols having an alkyl group containing from about 9 to 15 carbon atoms with from about 2 to 10 moles of ethylene oxide per mole of alcohol; and condensation products of propylene glycol with ethylene oxide. Most preferred are condensation products of alcohols having an alkyl group containing from about 12 to 15 carbon atoms with an average of about 3 moles of ethylene oxide per mole of alcohol.

A second class of nonionic surfactants is the polyhydroxy fatty acid amides. Polyhydroxy fatty acid amides may be produced by reacting a fatty acid ester and an N-alkyl polyhydroxy amine. The preferred amine for use in the present invention is N-(R1)-CH2(CH2OH)4-CH2-OH and the preferred ester is a C12-C20 fatty acid methyl ester. Most preferred is the reaction product of N-methyl glucamine with C12-C20 fatty acid methyl ester.

Methods of manufacturing polyhydroxy fatty acid amides have been described in WO 92 6073, published on 16th April, 1992. This application describes the preparation of polyhydroxy fatty acid amides in the presence of solvents.

Another class of nonionic surfactants comprises alkyl polyglucoside compounds of the general formula:

$$RO\,(C_nH_{2n}O)_t\,Z_x$$

wherein Z is a moity derived from glucose; R is a saturated hydrophobic alkyl group that contains from 12 to 18 carbon atoms; t is from 0 to 10 and n is 2 or 3; x is from 1.3 to 4, the compounds including less than 10% unreacted fatty alcohol and less than 50% short chain alkyl polyglucosides. Compounds of this type and their use in detergent compositions are disclosed in EP-B 070 074, 070 077, 075 996 and 094 118.

Other Surfactants

The laundry detergent compositions of the present invention may also contain cationic, ampholytic, zwitterionic, and semi-polar surfactants, as well as nonionic surfactants other than those already described herein, including the semi-polar nonionic amine oxides described below.

Cationic detersive surfactants suitable for use in the laundry detergent compositions of the present invention are those having one long-chain hydrocarbyl group. Examples of such cationic surfactants include the ammonium surfactants such as alkyldimethylammonium halogenides, and those surfactants having the formula :

$R^1R^2R^3R^4N^+X^-$

wherein R^1 is an alkyl or alkyl benzyl group having from about 8 to about 18 carbon atoms in the alkyl chain, each of R^2, R^3, R^4 is independently C_1-C_4 alkyl, C_1-C_4 hydroxy alkyl, benzyl, and -$(C_2H_4)x$H where x has a value from 2 to 5, and X^- is an anion. Not more than one of R_2, R_3, R_4 should be benzyl.
The preferred alkyl chain length for R^1 is C_{12}-C_{15}, particularly where the alkyl group is a mixture of chain lengths derived from coconut or palm kernel fat, or is derived synthetically by olefin build up or OXO alcohols synthesis. Preferred groups for R_2, R_3, R_4 are methyl and hydroxyethyl groups, and the anion X may be selected from halide, methosulphate, acetate and phosphate ions. Examples of suitable quaternary ammonium compounds for use herein are:

coconut trimethyl ammonium chloride or bromide
coconut methyl dihydroxyethyl ammonium chloride or bromide
decyl triethyl ammonium chloride or bromide
decyl dimethyl hydroxyethyl ammonium chloride or bromide
C12-14 dimethyl hydroxyethyl ammonium chloride or bromide
myristyl trimethyl ammonium methyl sulphate
lauryl dimethyl benzyl ammonium chloride or bromide
lauryl methyl (ethenoxy)$_4$ ammonium chloride or bromide

The above water-soluble cationic components of the compositions of the present invention, are capable of existing in cationic form in a 0.1% aqueous solution at pH10.

Other cationic surfactants useful herein are also described in US Patent 4,228,044, Cambre, issued October 14, 1980, incorporated herein by reference.

When included therein, the laundry detergent compositions of the present invention typically comprise from 0 % to about 25 %, preferably from about 3 % to about 15 % by weight of such cationic surfactants.

Ampholytic surfactants are also suitable for use in the laundry detergent compositions of the present invention. These surfactants can be broadly described as aliphatic derivatives of secondary or tertiary amines, or aliphatic derivatives of heterocyclic secondary and tertiary amines in which the aliphatic radical can be straight- or branched chain. One of the aliphatic substituents contains at least 8 carbon atoms, typically from about 8 to about 18 carbon atoms, and at least one contains an anionic water-solubilizing group e.g. carboxy, sulfonate, sulfate. See U.S. Patent No. 3,929,678 to Laughlin et al., issued December 30, 1975 at column 19, lines 18-35 (herein incorporated by reference) for examples of ampholytic surfactants.

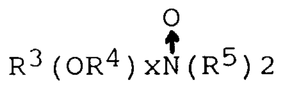
When included therein, the laundry detergent compositions of the present invention typically comprise from 0 % to about 15 %, preferably from about 1 % to about 10 % by weight of such ampholytic surfactants.

Zwitterionic surfactants are also suitable for use in laundry detergent compositions. These surfactants can be broadly described as derivatives of secondary and tertiary amines, derivates of heterocyclic secondary and tertiary amines, or derivatives of quaternary ammonium, quarternary phosphonium or tertiary sulfonium compounds. See U.S. Patent No. 3,929,678 to Laughlin et al., issued December 30, 1975 at columns 19, line 38 through column 22, line 48 (herein incorporated by reference) for examples of zwitterionic surfactants.

When included therein, the laundry detergent compositions of the present invention typically comprise from 0 % to about 15 %, preferably from about 1 % to about 10 % by weight of such zwitterionic surfactants.

Semi-polar nonionic surfactants are a special category of nonionic surfactants which include water-soluble amine oxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and 2 moieties selected from the group consisting af alkyl groups and hydrocyalkyl groups containing from about 1 to about 3 carbon atoms; water-soluble phosphine oxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and 2 moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from about 1 to about 3 carbon atoms.

Semi-polar nonionic detergent surfactants include the amine oxide surfactants having the formula :



$$R^3(OR^4)x\overset{\overset{O}{\uparrow}}{N}(R^5)2$$

wherein R^3 is an alkyl, hydroxyalkyl, or alkyl phenyl group or mixtures thereof containing from about 8 to about 22 carbon atoms; R^4 is an alkylene or hydroxyalkylene group containing from about 2 to about 3 carbon atoms or mixtures thereof; x is from 0 to about 3; and each R^5 is an alkyl or hydroxyalkyl group containing from about 1 to about 3 carbon atoms or a polyethylene oxide group containing from about 1 to about 3 ethylene oxide groups. The R^5 groups can be attached to each other, e.g., through an oxygen or nitrogen atom, to form a ring structure.

The amine oxide surfactants in particular include C_{10}-C_{18} alkyl dimenthyl amine oxides and C_8-C_{12} alkoxy ethyl dihydroxy ethyl amine oxides.

When included therein, the laundry detergent compositions of the present invention typically comprise from 0 % to about 15 %, preferably from about 1 % to about 10 % by weight of such semi-polar nonionic surfactants.

Finely Divided particulate Material

The other essential feature of the present invention is the finely divided particulate material which comprises sodium aluminosilicate and silica.

Sodium aluminosilicate may take many forms. One example is crystalline aluminosilicate ion exchange material of the formula

$$Na_z[(AlO_2)_z \cdot (SiO_2)_y] \cdot xH_2O$$

wherein z and y are at least about 6, the molar ratio of z to y is from about 1.0 to about 0.4 and z is from about 10 to about 264. Amorphous hydrated aluminosilicate materials useful herein have the empirical formula

$$M_z(zAlO_2 \cdot ySiO_2)$$

wherein M is sodium, potassium, ammonium or substituted ammonium, z is from about 0.5 to about 2 and y is 1, said material having a magnesium ion exchange capacity of at least about 50 milligram equivalents of $CaCO_3$ hardness per gram of anhydrous aluminosilicate. Hydrated sodium Zeolite A with a particle size of from about 1 to 10 microns is preferred.

The aluminosilicate ion exchange builder materials herein are in hydrated form and contain from about 10% to about 28% of water by weight if crystalline, and potentially even higher amounts of water if amorphous. Highly preferred crystalline aluminosilicate ion exchange materials contain from about 18% to about 22% water in their crystal matrix. The crystalline aluminosilicate ion exchange materials are further characterized by a particle size diameter of from about 0.1 micron to about 10 microns. Amorphous materials are often smaller, e.g., down to less than about 0.01 micron. Preferred ion exchange materials have a particle size diameter of from about 0.2 micron to about 4 microns. The term "particle size diameter" herein represents the average particle size diameter by weight of a given ion exchange material as determined by conventional analytical techniques such as, for example, microscopic determination utilizing a scanning electron microscope. The crystalline aluminosilicate ion exchange materials herein are usually further characterized by their calcium ion exchange capacity, which is at least about 200 mg equivalent of $CaCO_3$ water hardness/g of aluminosilicate, calculated on an anhydrous basis, and which generally is in the range of from about 300 mg eq./g to about 352 mg eq./g. The aluminosilicate ion exchange materials herein are still further characterized by their calcium ion exchange rate which is at least about 2 grains Ca^{++}/gallon/minute/gram/gallon of aluminosilicate (anhydrous basis), and generally lies within the range of from about 2 grains/gallon/minute/gram/gallon to about 6 grains/gallon/minute/gram/gallon, based on calcium ion hardness. Optimum aluminosilicate for builder purposes exhibit a calcium ion exchange rate of at least about 4 grains/gallon/minute/gram/gallon.

The amorphous aluminosilicate ion exchange materials usually have a Mg^{++} exchange of at least about 50 mg eq. $CaCO_3$/g (12 mg Mg^{++}/g) and a Mg^{++} exchange rate of at least about 1 grain/gallon/minute/gram/gallon. Amorphous materials do not exhibit an observable diffraction pattern when examined by Cu radiation (1.54 Angstrom Units).

Aluminosilicate ion exchange materials useful in the practice of this invention are commercially available. The aluminosilicates useful in this invention can be crystalline or amorphous in structure and can be naturally occurring aluminosilicates or synthetically derived. A method for producing aluminosilicate ion exchange materials is discussed in U.S. Pat. No. 3,985,669, Krummel et al., issued Oct. 12, 1976, incorporated herein by reference. Preferred synthetic crystalline aluminosilicate ion exchange materials useful herein are available under the designations Zeolite A, Zeolite B, Zeolite M, Zeolite P and Zeolite X. In an especially preferred embodiment, the crystalline aluminosilicate ion exchange material has the formula

$Na_{12}[(AlO_2)_{12}(SiO2)_{12}]\bullet xH_2O$

wherein x is from about 20 to about 30, especially about 27 and has a particle size generally less than about 5 microns.

Silica

Silica is a highly dispersed amorphous silicon dioxide. It is commercially available in many forms. Most commonly silica has a tapped density of from 50 g/l to 120 g/l. The specific surface area of the particles ranges from 25 square metres per gram to 800 square metres per gram. The surface of silica particles can be chemically modified to change their behaviour with respect to water. For example,silica particles may be treated with organosilanes to make the particles predominantly hydrophobic. It has been found that silicas must be fully or partly hydrophobised to be useful in the present invention.

In commercial practice, silica is usually prepared by one of two techniques; either by precipitation or by high temperature flame hydrolysis. Precipitated silicas generally have an agglomerate size of from 3 micrometers to 100 micrometers, whereas fumed silicas (made by flame hydrolysis) usually have primary particles which are generally spherical and have an average diameter of from 7nm to 40nm. Fumed silicas having an average primary particle size of from 7 to 25 nanometers are preferred in the present invention.

Examples of silicas which are particularly useful in the present invention include those supplied by Degussa AG, Frankfurt, Germany under the Trade Name "Aerosil". Aerosil R972 has been found to be particularly useful. This silica is a hydrophobic, fumed silica which has a specific surface area of about 110 square metres per gram and an average primary particle size of 16 nanometers.

Mixing the Finely Divided Particulate Material

For use in the present invention, the sodium aluminosilicate and the silica should be premixed in a ratio of from 100:1 to 5:1. Preferably the ratio will be from 20:1 to 4:1, and most preferably around 10:1. The resulting premix is a free-flowing powder which is much easier to handle than either the zeolite power on its own, or the silica powder on its own. Sodium aluminosilicate powder alone is usually cohesive and does not flow well. Silica powder on its own is very dusty, due to the very small particle size and low bulk density. However the finely divided particulate materials of the present invention are a free-flowing, non-dusty powder.

It is necessary to mix the finely divided particulate material with the rest of the detergent composition. In order to achieve the benefits of the present invention, a level of the finely divided particulate material of from 3% to 15% by weight of the detergent composition is then mixed to coat the surfaces of the clay agglomerates. Preferably the finely divided particulate material should substantially coat the surface of the granular component. Preferably the level of the finely divided particulate material is from 5% to 12% by weight, and most preferably about 10% by weight of the granular component.

Optional Ingredients

Other ingredients which are known for use in the components and compositions may also be used as optional ingredients in the present invention. Examples of builders (other than aluminosilicates and silicas which have been described hereinabove), chelants, and polymers are included here in more detail.

The granular detergents of the present invention can contain neutral or alkaline salts which have a pH in solution of seven or greater, and can be either organic or inorganic in nature. The builder salt assists in providing the desired density and bulk to the detergent granules herein. While some of the salts are inert, many of them also function as detergency builder materials in the laundering solution.

Examples of neutral water-soluble salts include the alkali metal, ammonium or substituted ammonium chlorides, fluorides and sulfates. The alkali metal, and especially sodium, salts of the above are preferred. Sodium sulfate is typically used in detergent granules and is a particularly preferred salt. Citric acid and, in general, any other organic or inorganic acid may be incorporated into the granular detergents of the present invention as long as it is chemically compatible with the rest of the agglomerate composition.

Other useful water-soluble salts include the compounds commonly known as detergent builder materials. Builders are generally selected from the various water-soluble, alkali metal, ammonium or substituted ammonium phosphates, polyphosphates, phosphonates, polyphosphonates, carbonates, silicates, borates, and polyhydroxysulfonates. Preferred are the alkali metal, especially sodium, salts of the above.

Specific examples of inorganic phosphate builders are sodium and potassium tripolyphosphate, pyrophosphate, polymeric metaphosphate having a degree of polymerization of from about 6 to 21, and orthophosphate. Examples of polyphosphonate builders are the sodium and potassium salts of ethylene diphosphonic acid, the sodium and potassium salts of ethane 1-hydroxy-1,1-diphosphonic acid and the sodium and potassium salts of ethane, 1,1,2-triphosphonic acid. Other phosphorus builder compounds are disclosed in U.S. Pat. Nos. 3,159,581; 3,213,030; 3,422,021; 3,422,137; 3,400,176 and 3,400,148, incorporated herein by reference.

Examples of nonphosphorus, inorganic builders are sodium and potassium carbonate, bicarbonate, sesquicarbonate, tetraborate decahydrate, and silicate having a molar ratio of SiO_2 to alkali metal oxide of from about 0.5 to about 4.0, preferably from about 1.0 to about 2.4.

As mentioned above powders normally used in detergents such as zeolite, carbonate, silica, silicate, citrate, phosphate, perborate, percarbonate etc. and process aids such as starch, can be used in preferred embodiments of the present invention.

Polymers

Also useful are various organic polymers, some of which also may function as builders to improve detergency. Included among such polymers may be mentioned sodium carboxy-lower alkyl celluloses, sodium lower alkyl celluloses and sodium hydroxy-lower alkyl celluloses, such as sodium carboxymethyl cellulose, sodium methyl cellulose and sodium hydroxypropyl cellulose, polyvinyl alcohols (which often also include some polyvinyl acetate), polyacrylamides, polyacrylates and various copolymers, such as those of maleic and acrylic acids. Molecular weights for such polymers vary widely but most are within the range of 2,000 to 100,000.

Polymeric polycarboxylate builders are set forth in U.S. Patent 3,308,067, Diehl, issued March 7, 1967. Such materials include the water-soluble salts of homo-and copolymers of aliphatic carboxylic acids such as maleic acid, itaconic acid, mesaconic acid, fumaric acid, aconitic acid, citraconic acid and methylenemalonic acid.

Other Optionals Ingredients

Other ingredients commonly used in detergent compositions can be included in the components and compositions of the present invention. These include color speckles, bleaching agents and bleach activators, suds boosters or suds suppressors, antitarnish and anticorrosion agents, soil suspending agents, soil release agents, dyes, fillers, optical brighteners, germicides, pH adjusting agents, nonbuilder alkalinity sources, hydrotropes, enzymes, and enzyme-stabilizing agents.

Other ingredients that may be included in the compositions of the present invention are perfumes. The perfumes may be non-encapsulated and/or encapsulated perfumes. Examples of suitable encapsulated perfumes are described in co-pending European Patent Application number 93870036.6, filed on February 26th, 1993.

Process Details

Another aspect of the present invention is the process of making granular components which comprise smectite clay and which have good colour properties (i.e. whiteness)

Granular detergent components which comprise smectite clays may be made by many methods which are known to the man skilled in the art including spray drying, and various types of granulation, or combinations of these techniques. One particularly useful method of granulation is known as agglomeration. The term agglomeration is taken herein to mean the build-up of small particles (such as the clay particles) to form the granular detergent component (the agglomerate) having the required particle size.

Particles suitable for use in an agglomeration process, in addition to the clay, may be in the form of powders of sodium aluminosilicate, carbonate, sulphate, citrate, silica, or mixtures of these, and the agglomeration may be effected in the presence of a binder. One method of doing this is by combining the powders with a liquid or pasty component which may comprise surfactant in a fine dispersion mixer or granulator. One particularly preferred binder is the solution of a complex of anionic and cationic surfactants. For example a solution comprising linear alkyl benzene sulphonate and a quaternary ammonium compound in a molar ratio of from 0.1:1 to 3.0:1, preferably from 1.3:1 to 2.5:1, and more preferably from 1.5:1 to 2.0:1.

Suitable pieces of equipment in which to carry out the fine dispersion mixing or granulation of the present invention are mixers of the Fukae^R FS-G series manufactured by Fukae Powtech Kogyo Co., Japan;

this apparatus is essentially in the form of a bowl-shaped vessel accessible via a top port, provided near its base with a stirrer having a substantially vertical axis, and a cutter positioned on a side wall. The stirrer and cutter may be operated independently of one another and at separately variable speeds. The vessel can be fitted with a cooling jacket or, if necessary, a cryogenic unit.

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

Other preferred suitable equipment can include Eirich^R, series RV, manufactured by Gustau Eirich Hardheim, Germany; Lödige^R, series FM for batch mixing, series Baud CB and KM for continuous mixing/agglomeration, manufactured by Lödige Machinenbau GmbH, Paderborn, Germany; Drais^R T160 series, manufactured by Drais Werke GmbH, Mannheim Germany; and Winkworth^R RT 25 series, manufactured by Winkworth Machinery Ltd., Berkshire, England.

The Littleford Mixer, Model #FM-130-D-12, with internal chopping blades and the Cuisinart Food Processor, Model #DCX-Plus, with 7.75 inch (19.7 cm) blades are two examples of suitable mixers. Any other mixer with fine dispersion mixing and granulation capability and having a residence time in the order of 0.1 to 10 minutes can be used. The "turbine-type" impeller mixer, having several blades on an axis of rotation, is preferred. The invention can be practised as a batch or a continuous process.

The following steps may be used in this aspect of the invention:

i) fine dispersion mixing or granulation of smectite clay in the presence of a binder to form agglomerates having a bulk density of at least 600 g/l ;

ii) mixing said agglomerates with an effective amount of a finely divided particulate material, said finely divided particulate material comprising sodium aluminosilicate and hydrophobic silica, wherein the ratio of the sodium aluminosilicate to silica in component ii) is from 100:1 to 5:1.

It is expected that the finely divided particulate materials of the present invention will be added towards the end of the process and will help to prevent further agglomeration of the components which could lead to oversized particle distribution. The finely divided particulate material may be incorporated by any suitable means, a rotating drum or mixer of the ploughshare type are most preferred.

One particularly preferred process method is to prepare the agglomerates of clay particles by an agglomeration technique such as the fine dispersion mixing and granulation process described above, and to spray some or all of the surfactant, preferably nonionic surfactant, on to clay particles in a suitable mixer or rotating drum. Excess water may then be removed if necessary, for example using a fluidised bed dryer. The dry agglomerates are then mixed with the finely divided particulate material in order to ensure a good coating of the finely divided particles over the surface of the clay agglomerates. A mixer such as a rotating drum or any of the mixers described above may be found to be suitable for this.

The most preferred embodiment of this aspect of the invention is described below.

Agglomerates of clay particles are made by spraying a solution comprising a complex of anionic and cationic surfactant on to clay particles in a high shear mixer such as a Loedige CB [Trade Name], forming wet agglomerates of the clay particles in a low shear mixer such as a Loedige KM [Trade Name], and subsequently drying the wet clay agglomerates in a dryer, such as a fluid bed dryer and spraying nonionic surfactant on to the dry agglomerates in a rotating drum mixer. It has been found that it is possible to control key physical characteristics of the agglomerates such as porosity, moisture and particle size in order to optimise the characteristics and performance of the finished composition. For example, the process parameters such as the residence time through the low shear mixer may be adjusted in order to control the porosity. Preferably the porosity of the finished component will be from 5% to 24%, more preferably from 10% to 15%, as measured by mercury porosimetry. The moisture level of the component can be controlled by the amount of drying. Preferably the moisture content of the component is from 2% to 18% by weight, and more preferably from 4% to 14% by weight. Undersize and oversize particles may then be removed by any suitable means, including sieving, classification by cyclone etc. Preferably the weight fraction of the component having a mean particle size of less than 250 micrometers is less than 10%, preferably less than 5%, and more preferably less than 1%. Preferably the weight fraction of the component having a mean particle size of greater than 1200 micrometers is less than 10%, and preferably less than 5%.

Finally the resulting agglomerates are mixed with from 3% to 15% by weight of the finely divided particulate material.

Controlling the parameters as defined above results in a product having excellent dispensing and rate of dissolution properties.

Examples

A clay agglomerate (component (i)) was prepared having the following composition (all percentages are by weight):

Linear Alkyl Benzene Sulphonate (LAS)	13%
C12-14 Dimethyl Hydroxyethyl Ammonium Chloride	8%
Montmorillonite Clay	70%
Zeolite A	4%
Water	5%

A mixture of finely divided particulate material (component (ii))was prepared containing:
Sodium Aluminosilicate (zeolite A) and hydrophobic silica (Aerosil R972 [Trade Name], supplied by Degussa), in the ratio of 20:1
The clay agglomerates of component (i) were prepared by pre-complexing the anionic and cationic surfactants. This was done by mixing solutions of LAS (78% active) and the dimethyl hydroxyethyl ammonium chloride (40% active) together in the appropriate proportions.

The resulting solution was sprayed on to the clay and finely dispersed around the clay particles in order to start granulation (i.e. agglomeration of the clay particles). This was done continuously using a Loedige CB [Trade Name] with a residence time of about 5 seconds.

The wet agglomerates were dusted with Zeolite A while passing through a Loedige KM [Trade Name] with a residence time of about 30 seconds, and subsequently dried in a fluidised bed to reduce the water content to 5%.

Example 1

The clay agglomerates described above were further processed by spraying on 5% by weight of the finished component of nonionic surfactant (C12-15 alkyl ethoxy sulphate, with an average of 3 ethoxy groups per molecule; Dobanol [Trade Name] supplied by Shell) in a rotating drum mixer.

The clay agglomerates were then dusted with 5% by weight of the finished component of the finely divided particulate material (component (ii)) described above. This was done by thoroughly mixing components (i) and (ii) using a rotating drum mixer.

Example 2

The product described in example 1 was repeated replacing the nonionic surfactant by C14-15 alkyl ethoxy sulphate, with an average of 7 ethoxy groups per molecule; Dobanol [Trade Name] supplied by Shell.

Example 3

The product described in example 1 was repeated replacing the nonionic surfactant by C16-18 (tallow) alkyl ethoxy sulphate, with an average of 11 ethoxy groups per molecule.

Example 4

The product described in example 1 was repeated and the clay agglomerates were dusted using different levels of the finely divided particulate material (component ii). The levels used were 2.5% by weight of the finished component, and 7.5% by weight of the finished component .

Comparative Example 5

All the steps of example 1 were repeated apart from the final step of dusting the clay agglomerates with the finely divided particulate material. In this comparative example the finely divided particulate material was omitted.

The components made by examples 1 to 5 were evaluated in two ways: firstly, by measuring the whiteness of the clay agglomerates using the Hunter Scale (L,a,b values); and secondly by blending them into a white granular laundry detergent (Ariel Ultra [Trade Name] supplied by Procter & Gamble) at a level of 20% by weight, and visually grading the product.

The component of examples 1 to 4 was found to have a very good aesthetic appearance in which it was very difficult to identify the clay agglomerates from the rest of the white powder even under close examination. Furthermore, in examples 1 and 4 it was found that the L value of the Hunter colour scale was increased at higher levels of finely divided particulate material used. (Higher L value indicates better whiteness).

The component of comparative example 5, however, was found to have a poorer aesthetic appearance in which the clay agglomerates were easily identifiable from the rest of the powder. Furthermore the clay agglomerates used in example 5 had a lower L value on the Hunter colour scale that any of the examples 1 to 4.

Claims

1. A granular detergent component or composition having a bulk density of at least 600 g/l which comprises:
   (i) a granular component which comprises smectite clay ; and
   (ii) a finely divided particulate material characterised in that the finely divided particulate material is present at a level of from 0.5% to 15% by weight of the detergent component or composition and that the finely divided particulate material comprises sodium aluminosilicate and hydrophobic silica wherein the ratio of the sodium aluminosilicate to hydrophobic silica in component (ii) is from 100:1 to 5:1.

2. A detergent component or composition according to claim 1 wherein the ratio of the sodium aluminosilicate to silica in component (ii) is from 20:1 to 4:1, and preferably around 10:1.

3. A detergent component or composition according to either of the previous claims wherein the silica is a hydrophobic fumed silica having a average primary particle size of from 7 to 25 nanometers.

4. A detergent component or composition according to any of the previous claims wherein the sodium aluminosilicate is a hydrated, crystalline aluminosilicate.

5. A detergent component or composition according to any of the previous claims wherein the granular component (i) comprises from 50% to 85% by weight of smectite clay.

6. A detergent component or composition according to any of the previous claims wherein the finely divided particulate material (ii) substantially coats the surface of the granular component i)

7. A process for making a free-flowing detergent powder having a bulk density of at least 600 g/l which comprises the steps of:
   (i) fine dispersion mixing or granulation of clay in the presence of a binder to form agglomerates; and
   (ii) mixing said agglomerates with an effective amount of a finely divided particulate material, said finely divided particulate material comprising sodium aluminosilicate and hydrophobic silica, wherein the ratio of the sodium aluminosilicate to silica in component (ii) is from 100:1 to 5:1.

8. A process according to claim 7 wherein the finely divided particulate material is added at a level of from 0.5% to 15% by weight of the finished detergent component or composition.

9. A process according to either of claims 7 or 8 wherein the ratio of the sodium aluminosilicate to hydrophobic silica in the premixed powder of step (ii) is from 20:1 to 4:1, and preferably around 10:1.

10. A process according to any of claims 7 to 9 wherein the agglomerates formed in step (i) are treated in a drying step to reduce the moisture level.

11. A process according to any of claims 7 to 10 wherein the agglomerates formed in step (i) are treated by spraying a nonionic surfactant on to said agglomerates.

European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 93 20 1563

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.5)
A	EP-A-0 452 016 (ECC INTERNATIONAL) * page 2, line 25 - line 41; example 1 *	1,7	C11D3/12 C11D17/06 C11D17/00
A	DE-A-39 42 066 (HENKEL) * examples *	1,7	
D,A	EP-A-0 385 748 (UNILEVER) * page 4, line 32 - line 35; example 1b *	1,7	
D,A	FR-A-2 524 903 (COLGATE-PALMOLIVE) * example 4 *	1	

TECHNICAL FIELDS SEARCHED (Int.Cl.5)

C11D

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	8 November 1993	PFANNENSTEIN, H

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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