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(54) Detergent compositions comprising percarbonate bleaching agents.

(57) A granular detergent composition having a bulk density of at least 650 g/l, comprising:
i) granular surfactant agglomerates which comprise from 25% to 60% by weight of anionic surfactant and which have a average particle size of less than 480 micrometers; and
ii) from 2% to 50% by weight of granular alkalimetal percarbonate.

EP 0 639 637 A1

The present invention relates to detergent compositions comprising percarbonate bleach particles. In particular it relates to compositions which have a high bulk density, improved characteristics of dispensing from either the drawer of a washing machine, or other dispensing device, thereby giving improved cleaning performance of bleaching compositions.

Perborate bleach has been commonly used in detergent compositions. However it has a tendency to promote gelling in the presence of surfactants and water which may prevent the detergent composition from being rapidly and effectively dispersed in the wash solution.

Percarbonate bleach is currently being proposed as an alternative to perborate bleach which has commonly been used in detergent compositions in the past. Sodium percarbonate is an attractive perhydrate for use in detergent compositions because it dissolves readily in water, is weight efficient and, after giving up its available oxygen, provides a useful source of carbonate ions for detergency purposes.

Particulate detergent components comprising surfactants and percarbonate have been proposed in the prior art.

WO92/6163, published on 16th April, 1992, discloses granular compositions which comprise percarbonate and surfactant particles. It states that a substantial amount of the surfactant particles should have a particle size lying between 250 micrometers and 700 micrometers.

The application, which is mainly concerned with percarbonate stability, also mentions the possibility of coating percarbonate with protective layer comprising carbonate and sulphate.

EP510746, published on 28th October, 1992 describes surfactant agglomerates having an average particle size of from 200 to 1000 micrometers. "Bleaching agents" and "perborate" are specifically disclosed as optional components, but percarbonate is not mentioned.

A disadvantage which may be associated with high density surfactant agglomerates is that they have slower rates of surfactant dissolution when compared to low density products. This can reduce the overall cleaning performance because a slow rate of surfactant dissolution causes a slow rate of fabric/soil wetting and a slow rate of control of fabric softener cationic active residues on fabrics.

A proposed solution is to use more rapidly water soluble surfactants having a low Krafft point, and fine surfactant agglomerate particle size in order to give more rapid rates of surfactant dissolution.
However the combination of perborate monohydrate and fine particles of water soluble anionic surfactant cause unacceptable level of drawer dispenser or granulette dosing device residues. Any reduction of perborate monohydrate level reduces the performance at low temperature.

It has now been found that the use of certain alkalimetal percarbonate materials with fine particles of water soluble surfactant particles with high density show a good dispensing profile and fast rates of surfactant and bleach dissolution.

Summary of the Invention

A granular detergent composition having a bulk density of at least 650 g/l, comprising:

i) granular surfactant agglomerates which comprise from 25% to 60% by weight of anionic surfactant and which have a average particle size of less than 480 micrometers; and
ii) from 2% to 50% by weight of granular alkalimetal percarbonate.

Detailed Description of the Invention

A granular detergent composition having a bulk density of at least 650 g/l, comprising a granular surfactant agglomerates which comprise from 25% to 60% by weight of anionic surfactant, and from 2% to 50% by weight of granular alkalimetal percarbonate.

The average agglomerate particle size is less than 480 micrometers, preferably less than 400 micrometers, and more preferably less than 350 micrometers.

At least 50% by weight of the anionic surfactant which is present in the agglomerates is chosen from those anionic surfactants having a Krafft point of less than 38°C.

Preferred anionic surfactants are chosen from the group consisting of linear alkyl benzene sulphonate with average chain length below $C_{12.2}$, alkyl sulphate having an alkyl chain which is predominantly C_{11-15}, preferably C_{12-15} (branched), more preferably C_{12-14} (linear), alkyl ether sulphate or mixtures of these. Most preferably alkyl sulphate and/or alkyl ether sulphate are used and linear alkyl benzene sulphonate is excluded.

Preferred nonionic surfactants for use in the surfactant agglomerates include polyhydroxy fatty acid amides, alkyl poly glucosides, alkyl polyglycerol ether, ethoxylated nonionic surfactant, hydrophobic diols such as dodecane diols, and mixtures thereof.

The granular percarbonate of the present invention may be advantageously coated with a soluble salt. Preferably a coating which comprises sodium carbonate, sodium sulphate, citrate or mixtures of these is used.

Preferred levels of percarbonate are from 8% to 30% by weight, whereas perborate should be present at a level of less than 3% by weight, and preferably perborate should be excluded from the compositions of the present invention.

High Active Surfactant Containing Particles

A wide range of surfactants can be used in the detergent compositions. A typical listing of anionic, nonionic, ampholytic and zwitterionic classes, and species of these surfactants, is given in U.S.P. 3,929,678 issued to Laughlin and Heuring on December, 30, 1975. A list of suitable cationic surfactants is given in U.S.P. 4,259,217 issued to Murphy on March 31, 1981.

The most suitable anionic surfactants for use in the present invention are those having a Krafft point of less than 38°C. This can be measured by mixing 1g of an anionic surfactant into 100 mls of distilled water and cooling the mixture in an ice bath, allowing it to become cloudy. The solution is then slowly heated and the temperature at which it becomes transparent is recorded. This temperature is the Krafft point.

Mixtures of low Krafft point (i.e. less than 38°C) anionic surfactant and high Krafft point (i.e. more than 38°C) may be used in the present invention, although it is preferred that the low Krafft point anionics represent at least 50% by weight of the total anionic surfactant present in the surfactant particle.

Mixtures of anionic surfactants are suitable herein, particularly blends of sulphate, sulphonate and/or carboxylate surfactants. Mixtures of sulphonate and sulphate surfactants are normally employed in a sulphonate to sulphate weight ratio of from 5:1 to 1:2, preferably from 3:1 to 2:3, more preferably from 3:1 to 1:1. Preferred sulphonates include alkyl benzene sulphonates having from 9 to 15, most preferably less than 12 carbon atoms in the alkyl radical, and alpha-sulphonated methyl fatty acid esters in which the fatty acid is derived from a C_{10}-C_{18} fatty source, preferably from a C_{10}-C_{14} fatty source. In each instance the cation is an alkali metal, preferably sodium. Preferred sulphate surfactants in such sulphonate sulphate mixtures are alkyl sulphates having from 12 to 22, preferably 10 to 14 carbon atoms in the alkyl radical. Another useful surfactant system comprises a mixture of two alkyl sulphate materials whose respective mean chain lengths differ from each other. One examples of typical anionic surfactant systems includes a mixture of C_{12}-C_{14} alkyl sulphate and C_{16}-C_{18} alkyl sulphate in a weight ratio of C_{12}-C_{14}: C_{16}-C_{18} of from 2:1. Another example is a mixture of C_{12}-C_{15} alkyl sulphate and C_{14}-C_{15} alkyl sulphate in a weight ratio of C_{12}-C_{15}: C_{14}-C_{15} of from 1.5:1. The alkyl sulphates may also be combined with alkyl ethoxy sulphates having from 10 to 20, preferably 10 to 14 carbon atoms in the alkyl radical and an average degree of ethoxylation of 1 to 6. The cation in each instance is again an alkali metal, preferably sodium.

Other anionic surfactants suitable for the purposes of the invention are the alkali metal sarcosinates of formula

$R\text{-}CON\ (R)\ CH_2\ COOM$

wherein R is a C_9-C_{17} linear or branched alkyl or alkenyl group, R' is a C_1-C_4 alkyl group and M is an alkali metal ion. Preferred examples are the lauroyl, Cocoyl (C_{12}-C_{14}),myristyl and oleyl methyl sarcosinates in the form of their sodium salts.

Also useful are the sulphonation products of fatty acid methyl esters containing a alkyl group with from 10 to 20 carbon atoms. Preferred are the C10-14 methyl ester sulphonates (MES).

Whilst not being the main component of the anionic surfactant of the present invention water-soluble salts of the higher fatty acids, i.e., "soaps", can be used in the compositions herein. This includes alkali metal soaps such as the sodium, potassium, ammonium, and alkylammonium salts of higher fatty acids containing from about 8 to about 24 carbon atoms, and preferably from about 12 to about 18 carbon atoms. Soaps can be made by direct saponification of fats and oils or by the neutralization of free fatty acids. Particularly useful are the sodium and potassium salts of the mixtures of fatty acids derived from coconut oil and tallow, i.e., sodium or potassium tallow and coconut soap.

The particles of the present invention will contain from 25% by weight to 60% by weight, preferably 35% by weight to 55% by weight of anionic surfactant. The finished compositions of the present invention will contain from 2% to 30% by weight, preferably 5% to 25% by weight of anionic surfactant.

One class of nonionic surfactants useful in the present invention comprises condensates of ethylene oxide with a hydrophobic moiety, providing surfactants having an average hydrophilic-lipophilic balance (HLB) in the range from 8 to 17, preferably from 9.5 to 13.5, more preferably from 10 to 12.5. The hydrophobic (lipophilic) moiety may be aliphatic or aromatic in nature and the length of the polyoxyethylene group which is condensed with any particular hydrophobic group can be readily adjusted to yield a water-soluble compound having the desired degree of balance between hydrophilic and hydrophobic elements.

Especially preferred nonionic surfactants of this type are the C_9-C_{15} primary alcohol ethoxylates containing 3-9 moles of ethylene oxide per mole of alcohol, particularly the C_{13}-C_{15} primary alcohols containing 6-9 moles of ethylene oxide per mole of alcohol and the C_{11}-C_{15} primary alcohols containing 3-5 moles of ethylene oxide per mole of alcohol.

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

$RO\ (C_nH_{2n}O)_tZ_x$

wherein Z is a moiety 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 0070074, 0070077, 0075996 and 0094118.

Still another class of nonionic surfactants comprises alkyl poly glycerol ethers which may be represented by the formula R - (O - CH2 - CHOH - CH2)n - OH, where R is a C8-18 alkyl group and n is from 0 to 6.

Still another class of nonionic surfactants comprises polyhydroxy fatty acid amides which 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. In a highly preferred embodiment of the invention N-methyl glucamine is reacted with a C12-C20 methyl ester. It also says that the formulator of granular detergent compositions may find it convenient to run the amidation reaction in the presence of solvents which comprise alkoxylated, especially ethoxylated (EO 3-8) C12-C15 alcohols.

A further class of surfactants are the semi-polar surfactants such as amine oxides. Suitable amine oxides are selected from mono C_8-C_{20}, preferably C_{10}-C_{14} N-alkyl or alkenyl amine oxides and propylene-1,3-diamine dioxides wherein the remaining N positions are substituted by methyl, hydroxyethyl or hydroxpropyl groups.

Cationic surfactants can also be used in the detergent compositions herein and suitable quaternary ammonium surfactants are selected from mono C_8-C_{16}, preferably C_{10}-C_{14} N-alkyl or alkenyl ammonium surfactants wherein remaining N positions are substituted by methyl, hydroxyethyl or hydroxypropyl groups.

The surfactant containing particles will further comprise components selected from a wide range of possible ingredients which are commonly used in laundry detergents. Preferably the particles will contain some detergent builder:

These can include, but are not restricted to alkali metal carbonates, bicarbonates, silicates, aluminosilicates, monomeric polycarboxylates, homo or copolymeric polycarboxylic acids or their salts in which the polycarboxylic acid comprises at least two carboxylic radicals separated from each other by not more than two carbon atoms, organic phosphonates and aminoalkylene poly (alkylene phosphonates) and mixtures of any of the foregoing. The builder system is present in an amount of from 25% to 60% by weight of the composition, more preferably from 30% to 60% by weight.

Preferred builder systems are free of boron compounds and any polymeric organic materials are preferably biodegradable.

Suitable silicates are those having an SiO_2:Na_2O ratio in the range from 1.6 to 3.4, the so-called amorphous silicates of SiO_2 : Na_2O ratios from 2.0 to 2.8 being preferred. These materials can be added at various points of the manufacturing process, such as in the form of an aqueous solution serving as an agglomerating agent for other solid components, or, where the silicates are themselves in particulate form, as solids to the other particulate components of the composition.

Within the silicate class, highly preferred materials are crystalline layered sodium silicates of general formula

$NaMSi_xO_{2x+1}.yH_2O$

wherein M is sodium or hydrogen, x is a number from 1.9 to 4 and y is a number from 0 to 20. Crystalline layered sodium silicates of this type are disclosed in EP-A-0164514 and methods for their preparation are disclosed in DE-A-3417649 and DE-A-3742043. For the purposes of the present invention, x in the general formula above has a value of 2, 3 or 4 and is preferably 2. More preferably M is sodium and y is 0 and preferred examples of this formula comprise the α,β,γ and δ forms of $Na_2Si_2O_5$. These materials are available from Hoechst AG FRG as respectively NaSKS-11 and NaSKS-6. The most preferred material is δ - $Na_2Si_2O_5$, (NaSKS-6). Crystalline layered silicates are incorporated either as dry mixed solids, or as solid components of agglomerates with other components.

Whilst a range of aluminosilicate ion exchange materials can be used, preferred sodium aluminosilicate zeolites have the unit cell formula

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

wherein z and y are at least 6; the molar ratio of z to y is from 1.0 to 0.5 and x is at least 5, preferably from 7.5 to 276, more preferably from 10 to 264. The aluminosilicate materials are in hydrated form and are preferably crystalline, containing from 10% to 28%, more preferably from 18% to 22% water in bound form.

The above aluminosilicate ion exchange materials are further characterised by a particle size diameter of from 0.1 to 10 micrometers, preferably from 0.2 to 4 micrometers. The term "particle size diameter" herein represents the average particle size diameter of a given ion exchange material as determined by conventional analytical techniques such as, for example, microscopic determination utilizing a scanning electron microscope or by means of a laser granulometer. The aluminosilicate ion exchange materials are further characterised by their calcium ion exchange capacity, which is at least 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 300 mg eq./g to 352 mg eq./g. The aluminosilicate ion exchange materials herein are still further characterised by their calcium ion exchange rate which is at least 130 mg equivalent of $CaCO_3$/litre/minute/-(g/litre) [2 grains Ca^{++}/gallon/minute/gram/gallon)] of aluminosilicate (anhydrous basis), and which generally lies within the range of from 130 mg equivalent of $CaCo_3$/litre/minute/(gram/litre) [2 grains/gallon/minute/(gram/gallon)] to 390 mg equivalent of $CaCO_3$/litre/minute/ (gram/litre) [6 grains/gallon/minute/(gram/gallon)], based on calcium ion hardness.

Optimum aluminosilicates for builder purposes exhibit a calcium ion exchange rate of at least 260 mg equivalent of $CaCO_3$/litre/ minute/ (gram/litre) [4 grains/gallon/minute/ (gram/gallon)].

Aluminosilicate ion exchange materials useful in the practice of this invention are commercially available and can be naturally occurring materials, but are preferably synthetically derived. A method for producing aluminosilicate ion exchange materials is discussed in US Patent No. 3,985,669. Preferred synthetic crystalline aluminosilicate ion exchange materials useful herein are available under the designations Zeolite A, Zeolite B, Zeolite X, Zeolite HS, Zeolite MAP and mixtures thereof. In an especially preferred embodiment, the crystalline aluminosilicate ion exchange material is Zeolite A and has the formula

$Na_{12} [(AlO_2)_{12} (SiO_2)_{12}]. xH_2O$

wherein x is from 20 to 30, especially 27. Zeolite X of formula $Na_{86} [(A1O_2)_{86}(SiO_2)_{106})$. 276 H_2O is also suitable, as well as Zeolite HS of formula $Na_6 [(A1O_2)_6(SiO_2)_6]$ 7.5 H_2O).

Suitable water-soluble monomeric or oligomeric carboxylate builders include lactic acid, glycolic acid and ether derivatives thereof as disclosed in Belgian Patent Nos. 831,368, 821,369 and 821,370. Polycarboxylates containing two carboxy groups include the water-soluble salts of succinic acid, malonic acid, (ethylenedioxy) diacetic acid, maleic acid, diglycolic acid, tartaric acid, tartronic acid and fumaric acid, as well as the ether carboxylates described in German Offenlegenschrift 2,446,686, and 2,446,687 and U.S. Patent No. 3,935,257 and the sulfinyl carboxylates described in Belgian Patent No. 840,623. Polycarboxylates containing three carboxy groups include, in particular, water-soluble citrates, aconitrates and citraconates as well as succinate derivatives such as the carboxymethyloxysuccinates described in British Patent No. 1,379,24l, lactoxysuccinates described in British Patent No. 1,389,732, and aminosuccinates described in Netherlands Application 7205873, and the oxypolycarboxylate materials such as 2-oxa-1,1,3-propane tricarboxylates described in British Patent No. 1,387,447.

Polycarboxylates containing four carboxy groups include oxydisuccinates disclosed in British Patent No. 1,261,829, 1,1,2,2-ethane tetracarboxylates, 1,1,3,3-propane tetracarboxylates and 1,1,2,3-propane tetracarboxylates. Polycarboxylates containing sulfo substituents include the sulfosuccinate derivatives disclosed in British Patent Nos. 1,398,421 and 1,398,422 and in U.S. Patent No. 3,936,448, and the sulfonated pyrolysed citrates described in British Patent No. 1,439,000.

Another preferred polycarboxylate builder is ethylenediamine-N,N'-disuccinic acid (EDDS) or the alkali metal, alkaline earth metal, ammonium, or substituted ammonium salts thereof, or mixtures thereof.

Alicyclic and heterocyclic polycarboxylates include cyclopentane-cis,cis,cis-tetracarboxylates, cyclopentadienide pentacarboxylates, 2,3,4,5-tetrahydrofuran - cis, cis, cis-tetracarboxylates, 2,5-tetrahydrofuran - cis - dicarboxylates, 2,2,5,5-tetrahydrofuran - tetracarboxylates, 1,2,3,4,5,6-hexane - hexacarboxylates and carboxymethyl derivatives of polyhydric alcohols such as sorbitol, mannitol and xylitol. Aromatic polycarboxylates include mellitic acid, pyromellitic acid and the phthalic acid derivatives disclosed in British Patent No. 1,425,343.

Of the above, the preferred polycarboxylates are hydroxycarboxylates containing up to three carboxy groups per molecule, more particularly citrates.

The parent acids of the monomeric or oligomeric polycarboxylate chelating agents or mixtures thereof with their salts, e.g. citric acid or citrate/citric acid mixtures are also contemplated as components of builder systems of detergent compositions in accordance with the present invention.

Other suitable water soluble organic salts are the homo- or co-polymeric polycarboxylic acids or their salts in which the polycarboxylic acid comprises at least two carboxyl radicals separated from each other by not more than two carbon atoms. Polymers of the latter type are disclosed in GB-A-1,596,756. Examples of such salts are polyacrylates of MWt 2000-5000 and their copolymers with maleic anhydride, such copolymers having a molecular weight of from 20,000 to 70,000, especially about 40,000. Such builder polymeric materials may be identical to the polymeric materials as binder materials and coating materials, as described hereinabove. These materials are normally used at levels of from 0.5% to 10% by weight more preferably from 0.75% to 8%, most preferably from 1% to 6% by weight of the composition.

Organic phosphonates and amino alkylene poly (alkylene phosphonates) include alkali metal ethane 1-hydroxy diphosphonates, nitrilo trimethylene phosphonates, ethylene diamine tetra methylene phosphonates and diethylene triamine penta methylene phosphonates, although these materials are less preferred where the minimisation of phosphorus compounds in the compositions is desired.

Examples of other components which may be used in laundry detergents, and which may be incorporated into the surfactant particles are described below under "Optional Ingredients"

Percarbonate bleach

The compositions of the present invention will include a percarbonate bleach, normally in the form of the sodium salt, as the source of alkaline hydrogen peroxide in the wash liquor. This percarbonate is normally incorporated at a level of from 2% to 50% by weight, more preferably from 5% to 30% by weight and most preferably from 8% to 25% by weight of the total composition.

Sodium percarbonate is an addition compound having a formula corresponding to $2Na_2CO_3.3H_2O_2$, and is available commercially as a crystalline solid. Most commercially available material includes a low level of a heavy metal sequestrant such as EDTA, 1-hydroxyethylidene 1, 1-diphosphonic acid (HEDP) or an amino-phosphonate, that is incorporated during the manufacturing process. For the purposes of the detergent composition aspect of the present invention, the percarbonate can be incorporated into detergent compositions without additional protection, but preferred executions of such compositions utilise a coated form of the material. The preferred coating is a mixed salt of an alkali metal sulphate and carbonate. Such coatings together with coating processes have previously been described in GB-1,466,799, granted to Interox on 9th March 1977. The weight ratio of the mixed salt coating material to percarbonate lies in the range from 1:200 to 1:4, more preferably from 1:99 to 1:9, and most preferably from 1:49 to 1:19. Preferably, the mixed salt is of sodium sulphate and sodium carbonate which has the general formula $Na_2SO_4.n.Na_2CO_3$ wherein n is from 0.1 to 3, preferably n is from 0.3 to 1.0 and most preferably n is from 0.2 to 0.5. Another preferred coating material is citrate, or mixtures of citrate with sulphate or carbonate. Water soluble surfactants may also be used as coating materials.

An alternative, although less preferred coating material is sodium silicate of $SiO_2:Na_2O$ ratio from 1.6:1 to 3.4:1, preferably 2.8:1, applied as an aqueous solution to give a level of from 2% to 10%, (normally from 3% to 5%) of silicate solids by weight of the percarbonate. Magnesium silicate can also be included in the coating. However silicate should not be the major coating agent in order to maintain good dispensing properties. If present, the silicate level in the coating should be less than 3% by weight of the percarbonate.

The particle size range of the crystalline percarbonate is from 150 micrometers to 1500 micrometers, preferably from 250 micrometers to 1000 micrometers with a mean particle size of from 500 micrometers to 700 micrometers.

Whilst heavy metals present in the sodium carbonate used to manufacture the percarbonate can be controlled by the inclusion of sequestrants in the reaction mixture, the percarbonate still requires protection from heavy metals present as impurities in other ingredients of the product.

In order for the benefits of the present invention to be fully realised, it is highly desirable that the percarbonate material chosen can be rapidly disolved in the wash and the active bleaching species are readily formed. In order to choose suitable percarbonate materials the available oxygen (AvO2) level can be measured using thiosulphate/ potassium iodide/ ammonium molybdate titration on aliquots taken from a stirred aqueous solution of the 1% wt./wt. concentration of the detergent composition which contains the percarbonate after 2, 4 and 5 minutes. A sample of the composition is dissolved in a Sotax apparatus in deionised water which has been adjusted to 25°dH water hardness by the addition of calcium chloride and magnesium chloride (with Ca:Mg = 3:1), at 10°C. The solution is stirred at 150 rpm. A given percarbonate is considered to be suitable for use in the present invention if it releases at least 40% of the total AvO2 after 2 minutes, at least 80% of the total AvO2 after 4 minutes, and at least 90% of the total AvO2 after 5 minutes.

Compositions of the present invention, which contain percarbonate, have a greatly reduced tendency to form undesirable gels in the presence of surfactants and water than similar compositions which contain perborate. Without wishing to be bound by theory, it is believed that this is because the type of percarbonate which is selected here has a lower surface area and lower porosity than perborate monohydrate.This low surface area and low porosity prevents the co-gelling with fine particles of surfactant agglomerates and is therefore not detrimental to dispensing.

Optional Ingredients

Detergent compositions of the present invention may, optionally, include anti-redeposition and soil suspension agents, bleach activators, optical brighteners, soil release agents, suds suppressors, enzymes, fabric softening agents, perfumes and colours, as well as other ingredients known to be useful in laundry detergents.

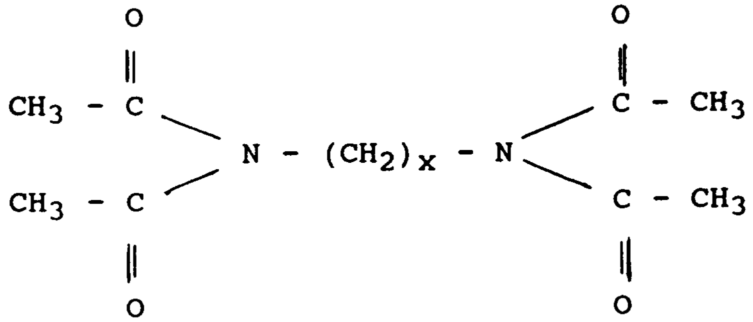
Anti-redeposition and soil-suspension agents suitable herein include cellulose derivatives such as methylcellulose, carboxymethylcellulose and hydroxyethycellulose, and homo-or co-polymeric polycarboxylic acids or their salts. Polymers of this type include copolymers of maleic anhydride with ethylene, methylvinyl ether or methacrylic acid, the maleic anhydride constituting at least 20 mole percent of the copolymer. These materials are normally used at levels of from 0.5% to 10% by weight, more preferably from 0.75% to 8%, most preferably from 1% to 6% by weight of the composition.

Other useful polymeric materials are the polyethylene glycols, particularly those of molecular weight 1000-10000, more particularly 2000 to 8000 and most preferably about 4000. These are used at levels of from 0.20% to 5% more preferably from 0.25% to 2.5% by weight. These polymers and the previously mentioned homo- or co-polymeric polycarboxylate salts are valuable for improving whiteness maintenance, fabric ash deposition, and cleaning performance on clay, proteinaceous and oxidizable soils in the presence of transition metal impurities.

In a preferred embodiment of the present invention, the composition comprises peroxyacid bleach precursor. The solid peroxyacid bleach precursors of the present invention comprise precursors containing one or more N- or O- acyl groups, which precursors can be selected from a wide range of classes.

Suitable classes include anhydrides, esters, imides and acylated derivatives of imidazoles and oximes, and examples of useful materials within these classes are disclosed in GB-A-1586789. The most preferred classes are esters such as are disclosed in GB-A-836988, 864,798, 1147871 and 2143231 and imides such as are disclosed in GB-A-855735 & 1246338.

Particularly preferred precursor compounds are the N-,N,N^{1}N^1 tetra acetylated compounds of formula



wherein x can be 0 or an integer between 1 & 6.

Examples include tetra acetyl methylene diamine (TAMD) in which $x=1$, tetra acetyl ethylene diamine (TAED) in which $x=2$ and tetraacetyl hexylene diamine (TAHD) in which $x=6$. These and analogous compounds are described in GB-A-907356. The most preferred peroxyacid bleach precursor is TAED.

Other activators are perbenzoic acid precursors such as benzoyloxybenzene sulphonate (BOBS) and benzoyl caprolactam.

Is is most preferred that a peroxyacid bleach precursor is present at a level of at least 0.5% by weight of the composition. The particles of peroxyacid bleach precursor preferably have a particle size of from 100 micrometers to 1500 micrometers.

These peroxyacid bleach precursors can be partially replaced by preformed peracids such as N,N phthaloylaminoperoxy acid (PAP), nonyl amide of peroxyadipic acid (NAPAA), 1,2 diperoxydodecanedioic acid (DPDA) and trimethyl ammonium propenyl imidoperoxy mellitic acid (TAPIMA). Other bleach precursors include glycolate esters (described in EP 507475); 4h-3,1 - benzoxazin - 4 ones; cationic precursors (described in EP 458396 and EP 464880); ester carbonate activators (described in EP 475511), NOBS, iso-NOBS.

Preferred optical brighteners are anionic in character, examples of which are disodium $4,4^1$-bis-(2-diethanolamino-4-anilino -s- triazin-6- ylamino)stilbene-$2:2^1$ disulphonate, disodium $4,4^1$-bis-(2-morpholino -4-anilino-2-triazin-6-ylaminostilbene-$2:2^1$-disulphonate,disodium 4, 4^1-bis-(2,4-dianilino-s-triazin-6-ylamino)-stilbene-$2:2^1$ - disulphonate, monosodium $4^1{,}4^{11}$-bis-(2,4-dianilino-s-triazin-6 ylamino)stilbene-2- sulphonate, disodium $4,4^1$-bis-(2-anilino-4-(N-methyl-N-2-hydroxyethylamino)-2-triazin-6-ylamino)stilbene-$2,2^1$ - disulphonate, disodium $4,4^1$-bis-(4-phenyl-2,1,3-triazol-2-yl)stilbene-$2,2^1$ disulphonate, disodium $4,4^1$bis(2-anilino-4-(1-methyl-2-hydroxyethylamino)-s-triazin-6-ylamino)stilbene-$2,2^1$disulphonate and sodium 2(stilbyl-4^{11}-(naphtho-$1^1,2^1$:4,5)-1,2,3 - triazole-2^{11}- sulphonate.

Soil-release agents useful in compositions of the present invention are conventionally copolymers or terpolymers of terephthalic acid with ethylene glycol and/or propylene glycol units in various arrangements. Examples of such polymers are disclosed in the commonly assigned US Patent Nos. 4116885 and 4711730 and European Published Patent Application No. 0272033. A particular preferred polymer in accordance with EP-A-0272033 has the formula

$$(CH_3(PEG)_{43})_{0.75}(POH)_{0.25}(T\text{-}PO)_{2.8}(T\text{-}PEG)_{0.4}]T(PO\text{-}H)_{0.25}((PEG)_{43}CH_3)_{0.75}$$

where PEG is $-(OC_2H_4)O-$, PO is (OC_3H_6O) and T is $(pCOC_6H_4CO)$.

Certain polymeric materials such as polyvinyl pyrrolidones typically of MWt 5000-20000, preferably 10000-15000, also form useful agents in preventing the transfer of labile dyestuffs between fabrics during the washing process.

Another optional detergent composition ingredient is a suds suppressor, exemplified by silicones, and silicasilicone mixtures. Silicones can be generally represented by alkylated polysiloxane materials while silica is normally used in finely divided forms, exemplified by silica aerogels and xerogels and hydrophobic silicas of various types. These materials can be incorporated as particulates in which the suds suppressor is advantageously releasably incorporated in a water-soluble or water-dispersible, substantially non-surface-active detergent-impermeable carrier. Alternatively the suds suppressor can be dissolved or dispersed in a liquid carrier and applied by spraying on to one or more of the other components.

As mentioned above, useful silicone suds controlling agents can comprise a mixture of an alkylated siloxane, of the type referred to hereinbefore, and solid silica. Such mixtures are prepared by affixing the silicone to the surface of the solid silica. A preferred silicone suds controlling agent is represented by a hydrophobic silanated (most preferably trimethyl-silanated) silica having a particle size in the range from 10 nanometers to 20 nanometers and a specific surface area above 50 m^2/g, intimately admixed with dimethyl silicone fluid having a molecular weight in the range from about 500 to about 200,000 at a weight ratio of silicone to silanated silica of from about 1:1 to about 1:2.

A preferred silicone suds controlling agent is disclosed in Bartollota et al. US Patent 3,933,672. Other particularly useful suds suppressors are the self-emulsifying silicone suds suppressors, described in German Patent Application DTOS 2,646,126 published April 28, 1977. An example of such a compound is DC0544, commercially available from Dow Corning, which is a siloxane/glycol copolymer.

The suds suppressors described above are normally employed at levels of from 0.001% to 0.5% by weight of the composition, preferably from 0.01% to 0.1% by weight.

The preferred methods of incorporation comprise either application of the suds suppressors in liquid form by spray-on to one or more of the major components of the composition or alternatively the formation of the suds suppressors into separate particulates that can then be mixed with the other solid components of the composition. The incorporation of the suds modifiers as separate particulates also permits the inclusion therein of other suds controlling materials such as C_{20}-C_{24} fatty acids, microcrystalline waxes and high MWt copolymers of ethylene oxide and propylene oxide which would otherwise adversely affect the dispersibility of the matrix. Techniques for forming such suds modifying particulates are disclosed in the previously mentioned Bartolotta et al US Patent No. 3,933,672.

Another optional ingredient useful in the present invention is one or more enzymes.

Preferred enzymatic materials include the commercially available amylases, neutral and alkaline proteases, lipases, esterases and cellulases conventionally incorporated into detergent compositions. Suitable enzymes are discussed in US Patents 3,519,570 and 3,533,139.

Fabric softening agents can also be incorporated into detergent compositions in accordance with the present invention. These agents may be inorganic or organic in type. Inorganic softening agents are examplified by the smectite clays disclosed in GB-A-1,400,898. Organic fabric softening agents include the water insoluble tertiary amines as disclosed in GB-A-1514276 and EP-B-0011340.

Their combination with mono C_{12}-C_{14} quaternary ammonium salts is disclosed in EP-B-0026527 & 528. Other useful organic fabric softening agents are the dilong chain amides as disclosed in EP-B-0242919. Additional organic ingredients of fabric softening systems include high molecular weight polyethylene oxide materials as disclosed in EP-A-0299575 and 0313146.

Levels of smectite clay are normally in the range from 5% to 15%, more preferably from 8% to 12% by weight, with the material being added as a dry mixed component to the remainder of the formulation. Organic fabric softening agents such as the water-insoluble tertiary amines or dilong chain amide materials are incorporated at levels of from 0.5% to 5% by weight, normally from 1% to 3% by weight, whilst the high molecular weight polyethylene oxide materials and the water soluble cationic materials are added at levels of from 0.1% to 2%, normally from 0.15% to 1.5% by weight. Where a portion of the composition is spray dried, these materials can be added to the aqueous slurry fed to the spray drying tower, although in some instances it may be more convenient to add them as a dry mixed particulate, or spray them as a molten liquid on to other solid components of the composition.

Processing

The high active surfactant particles of the present invention may take the form of flakes, prills, marumes, noodles, ribbons, but preferably take the form of granules. In order to achieve the low gelling properties which are an essential feature of the present invention, it has now been found that the most preferred way to process the particles is by agglomerating powders (such as those described hereinabove e.g. aluminosilicate, carbonate) with high active surfactant pastes and to control the particle size of the resultant agglomerates within specified limits. Such a process involves mixing an effective amount of powder with a high active surfactant paste in one or more agglomerators such as a pan agglomerator, a Z-blade mixer or more preferably an in-line mixer such as those manufactured by Schugi (Holland) BV, 29 Chroomstraat 8211 AS, Lelystad, Netherlands, and Gebruder Lodige Maschinenbau GmbH, D-4790 Paderborn 1, Elsenerstrasse 7-9, Postfach 2050, Germany. Most preferably a high shear mixer is used such as a Lodige CB (Trade Name).

A high active surfactant paste comprising from 50% by weight to 95% by weight, preferably 70% by weight to 85% by weight of surfactant is used. The surfactant sustem may comprise any of the groups of anionic, nonionic, cationic, amphoteric, and zwitterionic surfactants, or mixtures of these. The paste may be pumped into the agglomerator at a temperature high enough to maintain a pumpable viscosity, but low enough to avoid degradation of the anionic surfactants used. An operating temperature of the paste of 50 ° C to 80 ° C is typical.

A particularly suitable process of making surfactant particles from high active surfactant pastes is more fully described in EP 510 746, published on 28th October, 1992.

The term mean particle size as defined herein is calculated by sieving a sample of the composition into a number of fractions (typically 5 fractions) on a series of Tyler sieves. The weight fractions thereby obtained are plotted against the aperture size of the sieves. The mean particle size is taken to be the aperture size through which 50% by weight of the sample would pass. For the purposes of the present invention the surfactant containing granules should have a mean partle size of less than 480 micrometers, preferably less than 400 micrometers, and most preferably less than 350 micrometers.

According to the present invention, the free-flowing surfactant particles made by the process described above are then mixed with other detergent components in order to produce a finished detergent composition.

The surfactant particles are mixed with the particles containing the alkalimetal percarbonate.

All of the ingredients of the final composition may be mixed or blended in any suitable piece of equipment, such as a rotating drum. Liquid ingredients such as nonionic surfactant and perfume may be sprayed on to the surface of one or more of the constituent granules, or onto the finished composition.

Appropriate choice of consitituent particles is required in order to ensure that the finished composition has a bulk density of at least 650 g/l, preferably 750-1100 g/l.

EXAMPLES

In these examples the following abbreviations have been used:

DTPMP:	Diethylene triamine penta (methylene phosphonic acid), supplied by Monsanto as Dequest 2060 (trade name).
Sokolan CP5:	Co-polymer of acrylic and maleic acid, supplied by BASF.
C14/15AE7:	Ethoxylated alcohol having C14 to C15 chain length and an average of 7 ethoxy groups per molecule
C16/18AE11:	Ethoxylated alcohol having C16 to C18 chain length and an average of 11 ethoxy groups per molecule
LAS:	linear alkyl benzene sulphonate
C16/18AS:	Alkyl sulphate having alkyl chain length of predominantly C16 to C18
C12/15AS:	Alkyl sulphate having alkyl chain length of predominantly C12 to C15
C12/15AE3:	Ethoxylated alcohol having C12 to C15 chain length and an average of 3 ethoxy groups per molecule
CMC:	Carboxy methyl cellulose
PB1:	Sodium perborate, monohydrate
PB4:	Sodium perborate, tetrahydrate
TAED:	N,N,N,N-tetraacetylethylene diamine
Percarbonate:	Sodium percarbonate coated with 2.5% carbonate/sulphate.
Silicate:	Granular silicate with a mean particle size of 600 micrometers, supplied by Akzo.

▓	A Invention	B Invention	C Invention	D Comparative	E Comparative
Non agglomerated spray dried components					
a) Zeolite A	13%	-	-	13%	13%
b) DTPMP	0.4%	-	-	0.4%	0.4%
c) Sokalan CP5	4%	-	-	4%	4%
d) C14/15AE7	4%	-	-	4%	4%
e) C16/18AE11	1%	-	-	1%	1%
Agglomerates					
f) LAS	7%	-	7%	7%	7%
g) C16/18 AS	2%	-	-	2%	2%
h) C12/15 AE3S	0.2%	-	-	0.2%	0.2%
i) Zeolite A	7%	-	20%	7%	7%
j) C12/15 AS	-	9%	-	-	-
k) C12/15 AE3	-	5%	3%	-	-
l) C14/15 AE7	-	4%	3%	-	-
m) CMC	0.3%	-	-	0.3%	0.3%
n) Carbonate Na	8%	-	-	8%	8%
o) Zeolite MAP	-	25%	-	-	-
Agglomerate Particle Size (micrometers)	Mean : 340	Mean : 340	Mean : 340	Mean: 340	Mean: 600
Density of the agglomerate	700g/l	750g/l	750g/l	700g/l	700g/l
p) Percarbonate	18%	18%	18%	-	-
q) PB1	-	-	-	8%	8%
r) PB4	-	-	-	12%	12%
s) TAED	5%	5%	5%	5%	5%
t) Na Carbonate	8%	8%	8%	8%	8%
u) Na Silicate 2.0R	3%	3%	3%	3%	3%

v) Citrate	5%	5%	5%	5%	5%
w) Savinase 4.0 KNPU/g	1.4%	-	-	1.4%	1.4%
x) Lipolase 100,000LU/g	0.4%	-	-	0.4%	0.4%
Total Balance (Misc./Water)	100%	100%	100%	100%	100%

The compositions of examples A to E were prepared by:

1) spray drying a slurry comprising components a) to c);
2) spraying components d) and e) on to the spray dried powder.
3) forming agglomerates in a Loedige (Trade Name) high speed mixer from components f) to o); and
4) dry mixing the spray dried powder and the agglomerates together with components p) to x)

Comparative example D was found to give poor dispensing, but a good rate of dissolution due to the small particle size (mean = 340 micrometers) of the surfactant containing agglomerates.

Comparative example E shows good dispensing but a poor rate of dissolution due to the larger particle size (mean = 600 micrometers).

Example A shows both good dispensing and a good rate of dissolution due to the small agglomerate size (mean = 340 micrometers) and the presence of percarbonate as the bleaching agent in the composition.

Compositions of examples A, D, and E were tested in realistic washing conditions in a washing machine. A was found to outperform both D and E over a wide range of stains, especially at low washing temperatures.

Claims

1. A granular detergent composition having a bulk density of at least 650 g/l, comprising:
   i) granular surfactant agglomerates which comprise from 25% to 60% by weight of anionic surfactant; and
   ii) from 2% to 50% by weight of granular alkalimetal percarbonate, characterised in that said granular surfactant agglomerates have an average particle size of less than 480 micrometers

2. A granular detergent composition according to claim 1 wherein the agglomerate particle size is less than 400 micrometers, preferably less than 350 micrometers.

3. A granular detergent composition according to either of claims 1 or 2 wherein at least 50% by weight of the anionic surfactant which is present in component i) is chosen from those anionic surfactants having a Krafft point of less than 38°C.

4. A granular detergent composition according to claim 3 wherein the anionic surfactant is chosen from the group consisting of alkyl sulphate having alkyl chain length of predominantly C11 to C15, alkyl ether sulphate, linear alkyl benzene sulphonate, or mixtures of these.

5. A granular detergent composition according to claim 4 wherein the anionic surfactant is chosen from alkyl sulphate having alkyl chain length of predominantly C12 to C15, preferably C12 to C14, alkyl ether sulphate, or mixtures of these.

6. A granular detergent composition according to claim 1 wherein the percarbonate granules are coated with a coating material which comprises a soluble salt.

7. A granular detergent composition according to claim 6 wherein said coating material comprises sodium carbonate, sodium sulphate, citrate, or mixtures of these.

8. A granular detergent composition according to claim 1 wherein the levels of percarbonate is from 8% to 30% by weight, and the level of perborate is less than 3% by weight.

9. A granular detergent composition according to claim 1 wherein said granular surfactant agglomerates further comprise nonionic surfactants chosen from the group consisting of polyhydroxy fatty acid amides, alkyl polyglucosides, alkyl polyglycerol ether, ethoxylated nonionic surfactant, hydrophobic diols such as dodecane diols, and mixtures thereof.

European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 93 20 2405

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.6)
X	WO-A-92 18594 (PROCTER & GAMBLE CO.) * page 21, paragraph 2 -paragraph 3 * * page 29, paragraph 4 * ---	1-9	C11D17/06 C11D3/39
D,X	WO-A-92 06163 (PROCTER & GAMBLE CO.) * page 17, paragraph 3 * * page 18, paragraph 1 * * page 29, paragraph 2 * * page 29, last paragraph * -----	1-9	

TECHNICAL FIELDS SEARCHED (Int.Cl.6)

C11D

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
BERLIN	3 February 1994	Pelli Wablat, B

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

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