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(54) Title: LOW GELLING DETERGENT COMPOSITIONS AND A PROCESS FOR MAKING SUCH COMPOSITIONS

(57) Abstract

A granular laundry detergent composition is disclosed having a bulk density of at least 650 g/l which comprises (a) discrete particles comprising from 25 % by weight to 60 % by weight of anionic surfactant; (b) inorganic perhydrate bleach; (c) peroxyacid bleach precursor, wherein the peroxyacid bleach precursor is coated, the coating material being selected from water-soluble acidic polymers. The composition has a low tendency to form a gel upon contact with water, and minimises damage to delicate, coloured fabrics. A process for making a granular laundry detergent composition which has a low tendency to form a gel upon contact with water is also disclosed.

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LOW GELLING DETERGENT COMPOSITIONS AND
A PROCESS FOR MAKING SUCH COMPOSITIONS

Technical Field

The present invention relates to a low gelling laundry detergent compositions having a high bulk density, and comprising a bleach and bleach activator. The composition is particularly well suited to minimise or eliminate fabric damage, especially to delicate coloured fabrics.

Background of the Invention

It has long been recognised that granular powders can form undesirable gels upon contact with water (ie at the start of the wash cycle). These gels are caused, at least in part, by the presence of highly viscous surfactant phases that may arise when the detergent comes into contact with water, either in the dispensing drawer of the washing machine, or in a dispensing device which is placed into the drum of the machine. It has also been recognised that the formation of gels has undesirable properties including poor dispensing, lower performance because of slower solubility of active agents into the wash water, and deposition of residues (ie the gel) on to fabrics.

It has more recently been recognised that gels deposited on to fabrics early in the wash cycle can cause high local concentrations of active bleaching agents (eg. peroxide) which can cause local damage to fabrics, such as discoloration.

EP510746, published on 28th October, 1992 discloses high active, low gelling surfactant particles which may be admixed with other ingredients including bleach and bleach activator in order to make a finished composition. Acid coated bleach activator particles are not disclosed.

It is the aim of the invention to provide a compact, granular detergent composition comprising high active surfactant particles as well as inorganic perhydrate bleach and peroxyacid bleach precursor (or "bleach activator"), which has a very low tendency to gel thereby minimising or eliminating fabric damage. A further aim of the invention is to provide a process route for making low gelling compositions of this type.

Detailed Description of the Invention

Compositions of the present invention reduce or eliminate the fabric damage caused by gel sticking to fabrics and causing very high local concentration of bleaching agent. The essential components of the present invention are:

- a) particles comprising a high level (from 25% to 60%) of anionic surfactant;
- b) inorganic perhydrate bleach;
- c) acid coated peroxyacid bleach precursor

High Active Surfactant Containing Particles

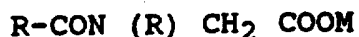
A wide range of surfactants can be used in the detergent compositions. A typical listing of anionic, nonionic, ampholytic and zwitterionic classes, and species of these

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 particles of the present invention will contain from 25% by weight to 60% by weight, preferably 35% by weight to 45% by weight of anionic surfactant. The finished compositions of the present invention will contain from 2% by weight to 25% by weight of anionic surfactant.

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, especially 11 to 13 carbon atoms in the alkyl radical, and alpha-sulphonated methyl fatty acid esters in which the fatty acid is derived from a C₁₂-C₁₈ fatty source, preferably from a C₁₆-C₁₈ 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 16 to 18 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 such system comprises a mixture of C₁₄-C₁₅ alkyl sulphate and C₁₆-C₁₈ alkyl sulphate in a weight ratio of C₁₄-C₁₅: C₁₆-C₁₈ of from 3:1 to 1:1. The alkyl sulphates may also be combined with alkyl ethoxy sulphates having from 10 to 20, preferably 10 to 16 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

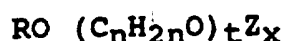


wherein R is a C₉-C₁₇ linear or branched alkyl or alkenyl group, R' is a C₁-C₄ alkyl group and M is an alkali metal ion. Preferred examples are the lauroyl, Cocoyl (C₁₂-C₁₄), myristyl and oleyl methyl sarcosinates in the form of their sodium salts.

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 C₉-C₁₅ primary alcohol ethoxylates containing 3-8 moles of ethylene oxide per mole of alcohol, particularly the C₁₄-C₁₅ primary alcohols containing 6-8 moles of ethylene oxide per mole of alcohol and the C₁₂-C₁₄ 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



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.

A further class of surfactants are the semi-polar surfactants such as amine oxides. Suitable amine oxides are selected from mono C₈-C₂₀, preferably C₁₀-C₁₄ N-alkyl or alkenyl amine oxides and propylene-1,3-diamine dioxides wherein the remaining N positions are substituted by methyl, hydroxyethyl or hydroxypropyl groups.

Cationic surfactants can also be used in the detergent compositions herein and suitable quaternary ammonium surfactants are selected from mono C₈-C₁₆, preferably C₁₀-C₁₄ N-alkyl or alkenyl ammonium surfactants wherein remaining N positions are substituted by methyl, hydroxyethyl or hydroxypropyl groups.

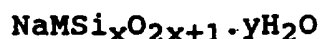
The surfactant containing particles will further comprise components selected from a wide range of possible ingredients which are commonly used in laundry detergents. Preferably the particles will contain some detergent builder:

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.

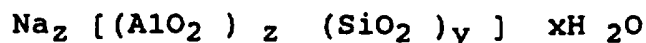
Suitable silicates are those having an $\text{SiO}_2:\text{Na}_2\text{O}$ ratio in the range from 1.6 to 3.4, the so-called amorphous silicates of $\text{SiO}_2 : \text{Na}_2\text{O}$ ratios from 2.0 to 2.8 being preferred. These materials can be added at various points of the manufacturing process, 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



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 $\text{Na}_2\text{Si}_2\text{O}_5$. These materials are available from Hoechst AG FRG as respectively NaSKS-11 and NaSKS-6. The most preferred material is δ - $\text{Na}_2\text{Si}_2\text{O}_5$, (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



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 and mixtures thereof. In an especially preferred embodiment, the crystalline aluminosilicate ion exchange material is Zeolite A and has the formula



wherein x is from 20 to 30, especially 27. Zeolite X of formula $\text{Na}_{86} [(\text{AlO}_2)_{86} (\text{SiO}_2)_{106}] \cdot 276 \text{H}_2\text{O}$ is also suitable, as well as Zeolite HS of formula $\text{Na}_6 [(\text{AlO}_2)_6 (\text{SiO}_2)_6] \cdot 7.5 \text{H}_2\text{O}$.

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. 1,379,241, lactoxysuccinates described in British Patent No.

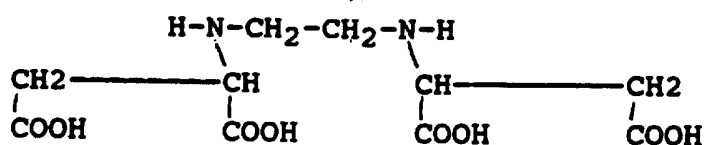
1,389,732, and aminosuccinates described in Netherlands Application 7205873, and the oxypolycarboxylate materials such as 2-oxa-1,1,3-propane tricarboxylates described in British Patent No. 1,387,447.

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.

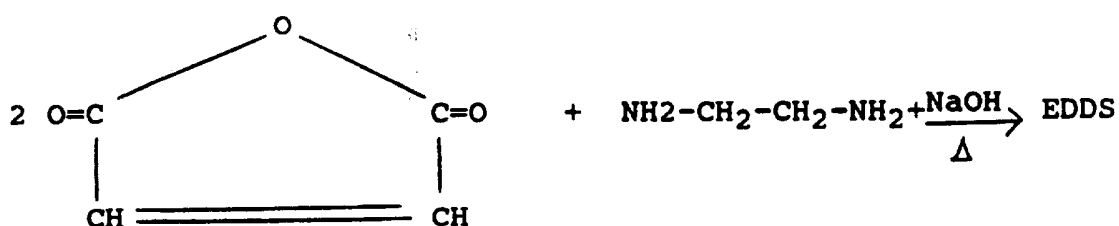
Another preferred polycarboxylate builder is ethylenediamine-N,N'-disuccinic acid (EDDS) or the alkali metal, alkaline earth metal, ammonium, or substituted ammonium salts thereof, or mixtures thereof. Preferred EDDS compounds are the free acid form and the sodium or magnesium salt thereof. Examples of such preferred sodium salts of EDDS include NaEDDS, Na₂EDDS and Na₄EDDS.

Examples of such preferred magnesium salts of EDDS include Mg EDDS and Mg₂EDDS. The magnesium salts are the most preferred for inclusion in compositions in accordance with the invention.

The structure of the acid form of EDDS is as follows :



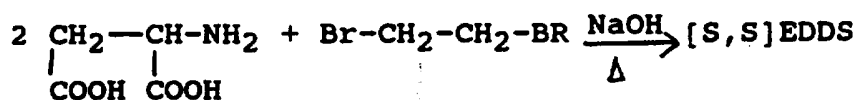
EDDS can be synthesised, for example, from readily available, inexpensive starting material such as maleic anhydride and ethylene diamine as follows :



A more complete disclosure of methods for synthesising EDDS from commercially available starting materials can be found in US Patent 3,158,635, Kezerian and Ramsay, issued November 24, 1964.

The synthesis of EDDS from maleic anhydride and ethylene diamine yields a mixture of three optical isomers, [R,R], [S,S], and [S,R], due to the two asymmetric carbon atoms. The biodegradation of EDDS is optical isomerspecific, with the [S,S] isomer degrading most rapidly and extensively, and for this reason the [S,S] isomer is most preferred for inclusion in the compositions of the invention.

The [S,S] isomer of EDDS can be synthesised from L-aspartic acid and 1,2-dibromoethane, as follows :



A more complete disclosure of the reaction of L-aspartic acid with 1,2-dibromoethane to form the [S,S] isomer of EDDS can be found in Neal and Rose, Stereospecific Ligands and Their Complexes of Ehtylenediaminediscuccinic Acid, Inorganic Chemistry, Vol 7 (1968), pp. 2405-2412.

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"

Inorganic perhydrate bleach

The compositions of the present invention will include an inorganic perhydrate bleach, normally in the form of the sodium salt, as the source of alkaline hydrogen peroxide in the wash liquor. This perhydrate is normally incorporated at a level of from 3% to 35% by weight, more preferably from 5% to 30% by weight and most preferably from 8% to 25% by weight of the total composition.

The perhydrate may be any of the inorganic salts such as perborate, percarbonate, perphosphate and persilicate salts but is conventionally an alkali metal perborate or percarbonate. Whilst fabric colour damage arising from compositions in accordance with the invention is low, irrespective of whether a perborate or percarbonate salt is employed, the improvement in comparison with uncoated precursor particulates is more noticeable with percarbonate bleach as this causes greater fabric colour damage in the absence of any coating on the bleach precursor.

Sodium percarbonate, which is the preferred perhydrate, is an addition compound having a formula corresponding to $2\text{Na}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}_2$, 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. A suitable coating is sodium silicate of $\text{SiO}_2:\text{Na}_2\text{O}$ 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. Another 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 Interlox 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 $\text{Na}_2\text{SO}_4.n.\text{Na}_2\text{CO}_3$ 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. Magnesium silicate can also be included in the coating.

The particle size range of the crystalline percarbonate is from 350 micrometers to 450 micrometers with a mean of approximately 400 micrometers. When coated, about 60% to 80% by weight of the crystals have a size greater than 425 micrometers with a mean of approximately 650 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. Accordingly, in detergent compositions utilising percarbonate as the perhydrate salt, the total level of

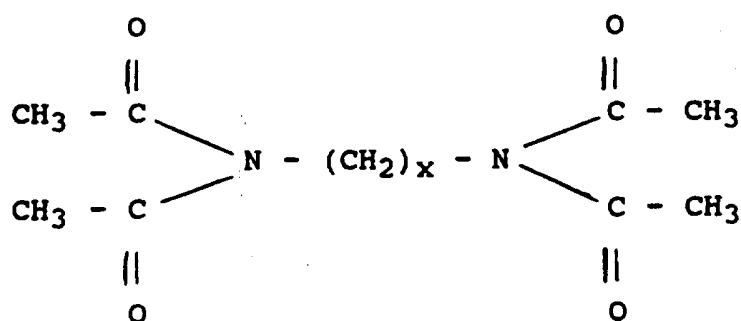
Iron, Copper and Manganese ions in the product should not exceed 25 ppm and preferably should be less than 20 ppm in order to avoid an unacceptably adverse effect on percarbonate stability. Detergent compositions in which alkali metal percarbonate bleach has enhanced stability are disclosed in the Applicants copending British Patent Application No. 9021761.3 (Attorney's Docket No. CM343).

Acid Coated 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,N¹N¹ 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.

Solid peroxyacid bleach precursors useful in the present invention have a $M_{pt} > 30^{\circ}\text{C}$ and preferably $> 40^{\circ}\text{C}$. Such precursors will normally be in fine powder or crystalline form in which at least 90% by weight of the powder has a particle size < 150 micrometers.

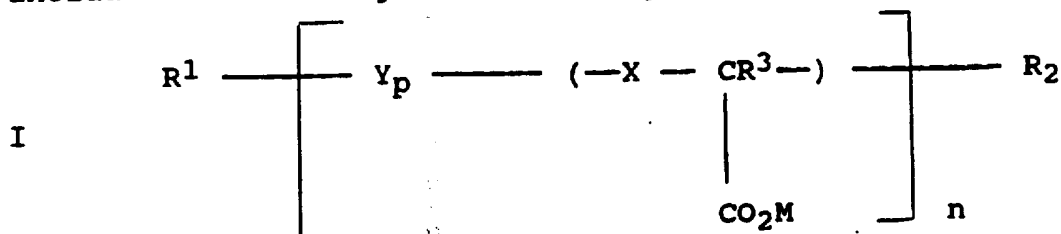
Another essential ingredient of the compositions according to the present invention is a water-soluble acidic polymer. Said polymer is used in the compositions according to the present invention as the coating material to coat said peroxyacid bleach precursor. In a preferred embodiment of the present invention, said peroxyacid bleach precursor is co-agglomerated, preferably with a water-soluble acidic polymer. In one embodiment of the invention the binder material and the coating material are different water-soluble acidic polymers, but in another, preferred embodiment of the present invention, the binder material and the coating material are the same water-soluble acidic polymer.

Suitable polymers for use herein are water-soluble. By water-soluble, it is meant herein that the polymers have a solubility greater than 5 g/l at 20°C .

Suitable polymers for use herein are acidic. By acidic, it is meant herein that a 1% solution of said polymers has a pH of less than 7, preferably less than 5.5.

Suitable polymers for use herein have a molecular weight in the range of from 1000 to 280,000, preferably from 1500 to 150,000, preferably, suitable polymers for use herein have a melting point superior to 30°C .

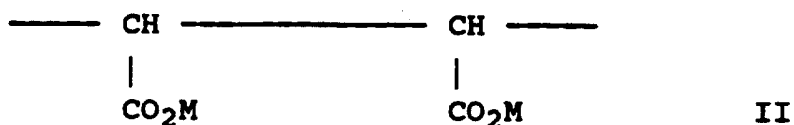
Suitable polymers which meet the above criteria and are therefore particularly useful in the present invention, include those having the following empirical formula I :



wherein X is O or CH₂; Y is a comonomer or comonomer mixture; R¹ and R² are bleach-stable polymer-end groups; R³ is H, OH or C₁₋₄ alkyl; M is H, and mixtures thereof with alkali metal, alkaline earth metal, ammonium or substituted ammonium; p is from 0 to 2; and n is at least 10, and mixtures thereof. the proportion of M being H in such polymers must be such as to ensure that the polymer is sufficiently acidic to meet the acidity criteria as hereinbefore defined.

Polymers according to formula I are known in the field of laundry detergents, and are typically used as chelating agents, as for instance in GB-A-1,597,756. Preferred polycarboxylate polymers fall into several categories. A first category belongs to the class of copolymeric polycarboxylate polymers which, formally at least, are formed from an unsaturated polycarboxylic acid such as maleic acid, citraconic acid, itaconic acid and mesaconic acid as first monomer, and an unsaturated monocarboxylic acid such as acrylic acid or an alpha -C₁₋₄ alkyl acrylic acid as second monomer. Referring to formula I, therefore, preferred polycarboxylate polymers of this type are those in which X is CH₂, R³ is H or C₁₋₄ alkyl, especially methyl, p is from about 0.1 to about 1.9, preferably from about 0.2 to about 1.5, n averages from about 10 to about 1500, preferably from about 50 to about

1000, more preferably from 100 to 800, especially from 120 to 400 and Y comprises monomer units of formula II



Such polymers are available from BASF under the trade name Sokalan(R) CP5 (neutralised form) and Sokalan(R) CP45 (acidic form).

A second category belongs to the class of polycarboxylate polymers in which referring to formula I, X is CH₂, R³ is OH, p is from 0 to 0.1, preferably 0 and n averages from about 50 to about 1500, preferably from about 100 to 1000. Y, if present, can be a polycarboxylic acid such as II above, or an ethylene oxide moiety.

A third category belongs to the class of acetal polycarboxylate polymers in which, referring to formula I, X is (OR⁴)₂, where R⁴ is C1-C4 alkyl, R³ is H, p is from 0 to 0.1, preferably 0 and n averages from 10 to 500. If present, Y again can be a polycarboxylic acid such as II above or an ethyleneoxide moiety.

A fourth category belongs to the class of polycarboxylate polymers in which referring to formula I, X is CH₂, R³ is H or C₁₋₄ alkyl, p is 0 and n averages from about 10 to 1500, preferably from about 500 to 1000.

A fifth category of polycarboxylate polymers has the formula I in which X is CH₂, R³ is H or C1-4 alkyl, especially methyl, p is from 0.01 to 0.09, preferably from 0.02 to 0.06, n averages from about 10 to about 1500, preferably from about 15 to about 300 and Y is a polycarboxylic acid formed from maleic acid, citraconic acid, itaconic acid or mesaconic acid, highly preferred being maleic acid-derived comonomers of formula II above.

The bleach-stable polymer end groups in formula I suitably include alkyl groups, oxyalkyl groups and alkyl carboxylic acid groups and salts and esters thereof.

In formula I above, M is H or mixtures thereof with alkali metal, alkaline earth metal, ammonium or substituted ammonium. The proportion of M which is H is such as to ensure that the polymer meets the pH criteria described herein above.

In the above, n, the degree of polymerization of the polymer can be determined from the weight average polymer molecular weight by dividing the latter by the average monomer molecular weight. Thus, for a maleic-acrylic copolymer having a weight average molecular weight of 15,500 and comprising 30 mole % of maleic acid derived units, n is 182 (i.e. $15,500 / (116 \times 0.3 + 72 \times 0.7)$).

In case of doubt, weight-average polymer molecular weights can be determined herein by gel permeation chromatography using Water [mu] Porasil (RTM) GPC 60 A2 and [mu] Bondagel (RTM) E-125, E-500 and E-1000 in series, temperature-controlled columns at 40°C against sodium polystyrene sulphonate polymer standards, available from Polymer Laboratories Ltd., Shropshire, UK, the polymer standards being 0.15M sodium dihydrogen phosphate and 0.02M tetramethyl ammonium hydroxide at pH 7.0 in 80/20 water/acetonitrile.

Mixtures of polycarboxylate polymers are also suitable herein, especially mixtures comprising a high molecular weight component having an n value of at least 100, preferably at least 120, and a low molecular weight component having an n value of less than 100, preferably from 10 to 90, more preferably from 20 to 80. Such mixtures are optimum from the viewpoint of providing

excellent bleach stability and anti-incrustation performance in the context of a zero-phosphate detergent formula.

In mixtures of this type, the weight ratio of high molecular weight component to low molecular weight component is generally at least 1:1, preferably from about 1:1 to about 20:1, more preferably from about 1.5:1 to about 10:1, especially from about 2:1 to about 8:1. Preferred polycarboxylate polymers of the low molecular weight type are polycarboxylate polymers of the fourth category (homopolyacrylate polymers) listed above.

Of all the above, highly preferred polycarboxylate polymers herein are those of the first category in which n averages from 100 to 800, preferably from 120 to 400 and mixtures thereof with polycarboxylate polymers of the fourth category in which n averages from 10 to 90, preferably from 20 to 80.

Other suitable polymers for use herein include polymers derived from amino acids such as polyglutamine acid, as disclosed in co-pending application GB 91-20653.2, and polyaspartic acid, as disclosed in EP 305 282, and EP 351 629.

A process for manufacturing a solid peroxyacid bleach precursor according to the present invention includes the steps of :

- co-agglomerating a peroxyacid bleach precursor with a binder material as hereinbefore defined;
- optionally drying said co-agglomerate;
- coating said dried co-agglomerate with a coating material as hereinbefore defined;
- drying said coated co-agglomerate.

According to the present invention the peroxyacid bleach precursor powder must be co-agglomerated into a water-soluble acidic polymer binder material as hereinabove defined. Any agglomerating technique known to the man skilled in the art is suitable for use herein. As a preferred embodiment, a co-agglomerate is formed which is a particulate material, at least 85% of which has a particle size between 400 and 1700 micrometers.

The co-agglomerated particulate material does not itself provide the benefits of the invention, and said co-agglomerated material needs to be coated with a water-soluble acidic polymer as hereinabove defined.

The coating of the co-agglomerated material with the coating material can be carried out in several ways and the process itself is not critical to the present invention.

The coating material may be sprayed on as a molten material or as a solution or dispersion in a solvent/carrier liquid which is subsequently removed by evaporation. The coating material can also be applied as a powder coating e.g. by electrostatic techniques although this is less preferred as the adherence of powdered coating material is more difficult to achieve and can be more expensive.

Molten coating is a preferred technique for coating materials of $M_{pt} < 80^{\circ}\text{C}$ but is less convenient for higher Melting Point acids (i.e. $> 100^{\circ}\text{C}$). For coating materials of $M_{pt} > 80^{\circ}\text{C}$, spray on as a solution or dispersion is preferred. Organic solvents such as ethyl and isopropyl alcohol can be used to form the solutions or dispersions, although this will necessitate a solvent recovery stage in order to make their use economic. However, the use of organic solvents also gives rise to safety problems such

as flammability and operator safety and thus aqueous solutions or dispersions are preferred.

Aqueous solutions are particularly advantageous as the coating materials herein have a high aqueous solubility, provided the solution has a sufficiently low viscosity to enable it to be handled. Preferably a concentration of at least 25% by weight of the coating material in the solvent is used in order to reduce the drying/evaporation load after surface treatment has taken place. The treatment apparatus can be any of those normally used for this purpose, such as inclined rotary pans, rotary drums and fluidised beds.

The solid peroxyacid bleach precursor compositions according to the present invention from 30% to 93%, preferably 70% to 88%, by weight of the total composition of said peroxyacid bleach precursor, and from 7% to 70% of said polymer, preferably 12% to 30%.

Solid peroxyacid bleach precursor compositions in accordance with the invention can be used in a variety of applications. Thus the peroxyacid bleach compositions may themselves be incorporated into other solid compositions such as tablets, extrudates and agglomerates. The compositions can also be suspended in nonaqueous liquid compositions in which the organic acid surface treating material is insoluble and inert. However, the preferred application for the solid peroxybleach precursor compositions of the invention is as particulate components of granular detergent compositions, particularly the so-called concentrated detergent compositions that are added to a washing machine by means of a dosing device placed in the machine drum with the soiled fabric load. Concentrated granular detergent compositions dispensed into the wash liquor via a dosing device are more subject to dissolution problems than compositions added via the

dispensing compartment of a washing machine because, in the initial stages of a wash cycle, the agitation in the immediate environment of the product is inhibited by the presence of the fabric load. Whilst this can constitute a benefit in permitting the development of high transient concentrations of builder and surfactant, the development of high transient peroxyacid concentrations can, as noted previously, lead to fabric and colour damage. The compositions of the present invention, when incorporated into concentrated detergent products delivered to the wash liquor via a dispensing device, mitigate if not eliminate this problem.

Detergent compositions incorporating the coated peroxy acid bleach precursor particulates will normally contain from 0.5% to 20% of the precursor, more frequently from 1% to 9% and most preferably from 3% to 8%, on a composition weight basis.

Optional Ingredients

Detergent Compositions of the present invention may, optionally, include anti-redeposition and soil suspension agents, 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 hydroxyethylcellulose, 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

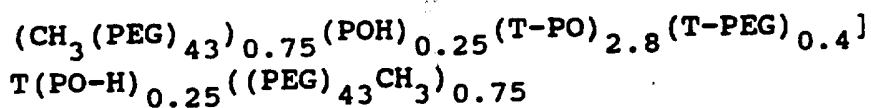
copolymer. These materials are normally used at levels of from 0.5% to 10% by weight, more preferably from 0.75% to 8%, most preferably from 1% to 6% by weight of the composition.

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 copolymeric 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.

Preferred optical brighteners are anionic in character, examples of which are disodium 4,4¹-bis-(2-diethanolamino-4-anilino -s- triazin-6- ylamino)stilbene-2:2¹ disulphonate, disodium 4,4¹-bis-(2-morpholino -4-anilino-2-triazin-6-ylaminostilbene-2:2¹-disulphonate, disodium 4,4¹-bis-(2,4-dianilino-s-triazin-6-ylamino)stilbene-2:2¹ - disulphonate, monosodium 4¹,4¹¹-bis-(2,4-dianilino-s-triazin-6 ylamino)stilbene-2- sulphonate, disodium 4,4¹-bis-(2-anilino-4-(N-methyl-N-2-hydroxyethylamino)-2-triazin-6-ylamino)stilbene-2,2¹ - disulphonate, disodium 4,4¹-bis-(4-phenyl-2,1,3-triazol-2-yl)stilbene-2,2¹ disulphonate, disodium 4,4¹bis(2-anilino-4-(1-methyl-2-hydroxyethylamino)-s-triazin-6-ylamino)stilbene-2,2¹disulphonate and sodium 2(stilbyl-4¹¹-(naphtho-1¹,2¹:4,5)-1,2,3 - triazole-2¹¹- 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



where PEG is $-(\text{OC}_2\text{H}_4)\text{O}-$, PO is $(\text{OC}_3\text{H}_6\text{O})$ and T is $(\text{pCOC}_6\text{H}_4\text{CO})$.

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 silica-silicone 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 m²/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 C₂₀-C₂₄ 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 exemplified 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 C₁₂-C₁₄ 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. 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 anionic surfactant is used, which 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.

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 inorganic perhydrate bleach, and with the particles containing the acid coated bleach precursor (made according to the process described hereinabove).

In a particularly preferred embodiment granular silicate is added in the form of crystalline layered sodium silicate which may be prepared according to the disclosures of DE-A-3417649 and DE-A-3742043. Compositions containing these granules have been found to have a particularly low tendency to gel.

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 particles.

Appropriate choice of constituent 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.

Tendency to Gel

It is an aim of the present invention to provide a finished laundry detergent composition which has a low tendency to form a gel. The following test procedure has been

established to measure the tendency of a composition to gel, and to provide a method of fixing a criterion

TEST PROCEDURE

1. Sample down to a 100g quantity of composition using a Pascal Sampler.
2. Place sampled product in a heated cabinet at about 40°C for minimum of 4 hours. Remove the sample and allow to stabilise at 30°C+/-2°C.
3. In a beaker, weigh out 40g of water at 25°C.
4. Record the temperature of the product and add the preweighed 100g sample to the water. To aid mixing, the powder should always be added to the water in this way.
5. HAND MIX vigorously using a spatula for 25+/-2 seconds to form paste. Ensure no dry powder pockets are visible either round the side of the beaker or in the paste. When mixing is complete, start a stopwatch.
6. On each of three flat plastic surfaces (e.g. beaker lids) weigh 10g +/-0.2g of the paste. At exactly 2 minutes after paste mixing was completed, add one quantity of paste to each of three tergotometer beakers, already containing 1000ml of water at 25°C. Addition of paste is crucial : it MUST be introduced into the beaker in one single lump. Any error in the 10g addition should be measured via tare of residual paste and used to adjust the final grade to correspond with 10.0g exact addition.

7. Switch on stirrer for 3 MINUTES, ensuring pastes have first sunk to the base of each beaker.
8. Filter solutions separately using a Buchner Funnel.
Minimise free water on paper by filtering for one minute after water is no longer visible.
9. Weigh filter paper Circles plus residues.
10. Calculate weight of Residue on each filter paper.
Express result in terms of the mean and standard deviation of 3 replicates.

Testing in the laboratory and with consumers has shown that a gel residue of 2g or less indicates that the composition will have a suitably low tendency to gel under real-life washing conditions resulting in very little, or no fabric damage.

Example 1

High Active Paste agglomerates were made making a surfactant paste comprising:

- 60% linear alkyl benzene sulphonate, sodium salt
- 18.5% tallow alkyl sulphate, sodium salt
- 1.5% alkyl ether sulphate, average of 3 ether groups per molecule, sodium salt
- 20% water

The paste was then pumped into a Lodige CB (Trade name) high shear mixer at a rate of 4000 kg/hr, at the same time as 3000 kg/hr zeolite (powder, 80% active) and 2400 kg/hr sodium carbonate and 150 kg/hr sodium carboxymethyl cellulose (powder, 70% active) were added. Agglomeration of the resulting mixture was completed in a Lodige KM (Trade name). The resulting agglomerates were then dried in a fluid bed, water being removed at a rate of 680 kg/hr.

Tetra Acetyl Ethylene Diamine (TAED) in fine powder form (purity ca 99.0%, particle size 90% by weight less than 150 micrometers) was agglomerated with a 40% aqueous solution of Sokalan(R) CP45 at a binder level of 24% (by weight). The agglomeration was carried out in a plough-share mixer and the resultant, wet, agglomerate was then dried in a fluid-bed dryer.

After drying, the agglomerate was then spray-coated with a further quantity (12.5% by weight) of the said polymer solution. The coated agglomerate was then dried again using a fluid-bed and screened to provide a finished material with particle size where more than 90% lay between 425 micrometers and 1700 micrometers.

The composition of the final agglomerate was as follows :

| | |
|---------------------|-----------|
| TAED | 82.0% |
| Sokalan(R) CP45 | 15.0% |
| Water/miscellaneous | up to 100 |

A reference TAED agglomerate was prepared by agglomerating the same TAED powder with molten TAE25 as binder in the same mixing device as above. Particles were then cooled and sized to the same standards as above. Agglomerate composition was :

| | |
|-------|-------|
| TAED | 87.0% |
| TAE25 | 13% |

The surfactant and TAED agglomerates were tested for colour damage potential when incorporated into the following detergent matrix (composition in parts by weight) :

| | |
|--|-----|
| C12 Lin. Alkyl Benzene Sulfonate | 9.0 |
| Tallow Alkyl Sulphate | 2.7 |
| Dobanol 45E7 | 3.8 |
| Zeolite A (6.7% from agglom., 13.3% dry added) | 20 |

| | |
|---|------|
| Citrate | 6.5 |
| Carbonate (6.7% from agglom., 8.3% dry added) | 15.0 |
| Silicate ($\text{SiO}_2:\text{Na}_2\text{O}=2:1$) | 3.5 |
| Perborate monohydrate | 16.0 |
| Sokalan(R) CP45* | 4.0 |
| CMC (from agglomerates) | 0.4 |
| TAED | 5.0 |

Miscellaneous (including water, perfume, enzymes, suds suppressor etc.) up to 100

- * The detergent matrix already contains Sokalan(R) CP45 as a co-builder, independently from the Sokalan(R) CP45 present in the agglomerates.

The formulations containing the TAED agglomerates were subjected to a full scale washing machine test using Miele automatic washing machines (Model W754) set to the Short Wash cycle at 40°C.

Bleach-sensitive coloured fabric swatches were used, 43 cm² swatches being wrapped around the dispensing device in which 100g of the formulation was added. In each machine, 3.3 kg of white cotton bedsheets were used as ballast. 12 litres of water of 150 ppm hardness (expressed as CaCO_3) with a Ca:Mg ratio of 3:1 was fed to each machine. The swatches were made of 100% lambswool woven fabric with purple 48 dye (Design No. W3970) supplied by Borval Fabrics, Albert Street, Huddersfield, West Yorkshire, England. 24 replicates of each treatment were performed and the swatches were then graded visually for fabric colour damage by an expert panel using the following grading system.

Three coloured swatches demonstrating differing degrees of colour damage are used as standards to establish a 4 point scale in which 1 represents 'virtually no damage' and 4 represents 'very damaged'. The three standards are used to

define the mid points between the various descriptions of colour damage viz

| | |
|---|---------------------|
| 1 | virtually no damage |
| 2 | slight damage |
| 3 | damage |
| 4 | very damaged |

Two expert panellists are used and their results are averaged.

Using this technique to compare colour damage resulting from use of the formulations above the following results were obtained

| <u>Formulations</u> | <u>% of swatches having grade</u> | | | | <u>Overall Grade</u> |
|-------------------------------------|-----------------------------------|------|------|------|----------------------|
| | 1 | 2 | 3 | 4 | |
| (Reference) TAE25/TAED | 4.2 | 4.2 | 20.8 | 70.8 | 3.58 |
| (Invention) Sokalan(R) CP45/TAED | 4.2 | 33.3 | 20.8 | 41.7 | 3.0 |

It can be seen that the formulation incorporating the agglomerate in accordance with the invention produces appreciably less fabric colour damage than the reference agglomerate.

The formulation of this example made according to the invention was further tested according to the test procedure in the section "Tendency to Gel" above. The weight of gel recovered after following this test procedure was less than 1g. In contrast the reference product (using TAED/TAE25 agglomerates) resulted in a gel of more than 2g when subjected to the same test.

Example 2

A detergent composition was made according to the same process as that described in example 1. However in this example, the silicate ($\text{SiO}_2\text{:Na}_2\text{O}=2\text{:}1$) was replaced by a crystalline, layered silicate (SKS-6 [TM]) which was prepared by forming an agglomerate with citric acid, and the perborate was replaced by percarbonate.

The agglomerates were tested in the following detergent matrix (composition in parts by weight):

| | |
|---|-----------|
| C12 Lin. Alkyl Benzene Sulfonate | 9.0 |
| Tallow Alkyl Sulphate | 2.7 |
| Dobanol 45E7 | 3.8 |
| Zeolite A (6.7% from agglom., 13.3% dry added) | 20 |
| Citrate | 0.5 |
| Carbonate (6.7% from agglom., 8.3% dry added) | 15.0 |
| Silicate (SKS-6 [TM])/citric | 9.0 |
| Percarbonate | 16.0 |
| Sokalan(R) CP45* | 4.0 |
| CMC (from agglomerates) | 0.4 |
| TAED | 5.0 |
| Miscellaneous (including water, perfume, enzymes, suds suppressor etc.) | up to 100 |

Using the same technique as in example 1 to compare colour damage resulting from use of the formulations above the following results were obtained:

| <u>Formulations</u> | <u>% of swatches having grade</u> | | | | <u>Overall Grade</u> |
|-------------------------------|-----------------------------------|------|------|------|----------------------|
| | 1 | 2 | 3 | 4 | |
| (Invention) with SKS-6/citric | 16.6 | 41.7 | 33.3 | 4.17 | 2.33 |

The composition of example 2 was further tested according to the test procedure in the section "Tendency to Gel" above. The weight of gel recovered after following this test procedure was less than 1g.

WHAT IS CLAIMED IS:

1. A granular laundry detergent composition having a bulk density of at least 650 g/l which comprises;
 - discrete particles comprising from 25% by weight to 60% by weight of anionic surfactant;
 - inorganic perhydrate bleach;
 - peroxyacid bleach precursor;characterised in that the peroxyacid bleach precursor is coated, the coating material being selected from water-soluble acidic polymers.
2. A granular laundry detergent composition according to claim 1, wherein the coating material is a water soluble acidic polymer, said polymer having a water solubility greater than 5g/l at 20°C, a molecular weight of from 1000 to 250000, and wherein a 1% solution of said polymer has a pH of less than 7.
3. A granular laundry detergent composition according to either of claims 1 or 2 in which the peroxyacid bleach precursor is tetraacetyl ethylene diamine.
4. A granular laundry detergent composition according to any of the previous claims in which the inorganic perhydrate bleach is a salt of percarbonate, preferably sodium percarbonate.
5. A granular laundry detergent composition according to any of the previous claims in which the composition further comprises a salt of a crystalline, layered silicate
6. A granular laundry detergent composition according to any of the previous claims in which the finished composition comprises from 2% to 25% by weight of

anionic surfactant, from 3% to 35% by weight of perborate, percarbonate or a mixture of these, and from 0.5% to 20% by weight of peroxyacid bleach precursor.

7. A low gelling granular laundry detergent composition according to any of the previous claims wherein a 100g sample of the composition can be mixed with 25g of water at 25°C for 25 seconds to form a paste, and wherein 10g of said paste placed in 1000ml of water at 25°C and stirred with a stirrer which rotates at 250rpm for 3 minutes, leaves a gel residue of less than 2g.
8. A process for making a granular laundry detergent which comprises the steps of:
 - agglomerating a powder, or a mixture of powders in a high shear mixer with a surfactant paste, said surfactant paste comprising from 50% by weight to 95% by weight, preferably 70% by weight to 85% by weight of anionic surfactant, to form a free flowing powder, said free flowing powder comprising from 25% by weight to 60% by weight of anionic surfactant;
 - admixing with said free flowing powder a second free flowing powder which comprises an inorganic perhydrate bleach;
 - admixing with said free flowing powders a third free flowing powder which comprises a peroxyacid bleach precursor and which is substantially coated with water-soluble acidic polymers;
 - combining said free flowing powders with additional detergent ingredients which may be incorporated by any suitable means, such as drymixing, spraying on.
9. A process according to the previous claim in which a free flowing powder comprising crystalline layered silicate is additionally admixed to the composition.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US93/06819

A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) : C11D 1/02, 3/39, 3/395, 11/00, 17/06; D06L 3/02

US CL : Please See Extra Sheet.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 252/99, 102, 174, 174.13, 174.24, 186.27, 186.31, 186.38, 186.39, 186.40, 534, 539

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


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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|-----------|--|-----------------------|
| Y | USA, 3,933,673 (Davies) 20 January 1976 see Col. 7, lines 11-17. | 1-3, 8 & 9 |
| Y | US,A, 4,444,674 (Gray) 24 April 1984 see examples VII-XVI. | 1-3, 8 & 9 |
| Y | US,A, 4,522,739 (Gray) 11 June 1985 see Example 1 and Col. 12, lines 6-17. | 1-3, 8 & 9 |
| Y | US,A, 5,002,691 (Bolkan et al) 03 March 1991 see Col. 14, line 30- Col. 15, line 42 and Col. 21, lines 15-61. | 1-3, 8 & 9 |
| Y | US,A, 5009,804 (Clayton et al) 23 April 1991 see Col. 2, lines 31-46; Col. 13, lines 24-59 and Examples 1 & 2. | 1-3, 8 & 9 |

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

| | | |
|--|----|--|
| * Special categories of cited documents: | *T | later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention |
| *A document defining the general state of the art which is not considered to be part of particular relevance | *X | document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone |
| *E earlier document published on or after the international filing date | *Y | document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art |
| *L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) | *Z | document member of the same patent family |
| *O document referring to an oral disclosure, use, exhibition or other means | | |
| *P document published prior to the international filing date but later than the priority date claimed | | |

| | |
|---|---|
| Date of the actual completion of the international search 11 SEPTEMBER 1993 | Date of mailing of the international search report 26 OCT 1993 |
| Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. NOT APPLICABLE | Authorized officer:  DENNIS L. ALBRECHT Telephone No. (703) 308-2525 |

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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|-----------|--|-----------------------|
| Y | US,A, 5,078,895 (Dany et al) 07 January 1992 see the entire document. | 9 |
| Y | US,A, 5,100,576 (Cramer et al) 31 March 1992 see the entire document. | 1-3, 8 & 9 |
| Y,P | US,A, 5,167,852 (Emery et al) 01 December 1992 see Col. 12, lines 64-68 | 1-3, 8 & 9 |

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Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☒ Claims Nos.: 4-7
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
☐ No protest accompanied the payment of additional search fees.

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