(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 0 816 483 A1

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
07.01.1998 Bulletin 1998/02

(51) Int. Cl.^{6}: **C11D 3/39**, C11D 1/72

(21) Application number: **96870084.9**

(22) Date of filing: **27.06.1996**

(84) Designated Contracting States:
AT BE CH DE DK ES FR GB GR IE IT LI LU NL PT SE

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(54) Granular bleaching compositions

(57) The present invention relates to granular bleaching compositions comprising an alcohol alkoxylate nonionic surfactant, a hydrogen peroxide source and a bleach precursor having a Krafft point of at least 10°C, whereby the bleach precursor exhibits an effective perhydrolysis rate.

Printed by Xerox (UK) Business Services
2.15.7/3.4

Description

Technical field of the Invention

The present invention relates to a granular bleaching composition containing a hydrogen peroxide source and a peroxyacid bleach precursor, wherein the bleach precursor exhibits an effective perhydrolysis rate.

Background of the invention

The satisfactory removal of coloured naturally derived soils/stains such as blood, egg, chocolate, gravy from soiled/stained substrates is a particular challenge to the formulator of a bleaching composition for use in a washing method such as a laundry or machine dishwashing method.

Traditionally, the removal of such coloured soils/stains has been enabled by the use of bleach components such as oxygen bleaches, including hydrogen peroxide and organic peroxyacids. The organic peroxyacids are often obtained by the in situ perhydrolysis reaction between hydrogen peroxide and an organic peroxyacid bleach precursor. Of these bleach precursors, those having a Krafft point of at least 10°C have been seen most useful in the removal of such coloured soils/stains. Suitable examples of bleach precursors having a Krafft point of at least 10°C are the amide substituted peroxyacid precursor compounds such as (6-octanamido-caproyl) oxy benzene sulfonate, (6-nonanamidocaproyl) oxy benzene sulfonate and (6-decanamido-caproyl) oxy benzene sulfonate as described in EP-A-0170386.

However, a problem encountered with the use of bleach precursors having a Krafft point of at least 10°C is their low perhydrolysis rate. Not to be bound by theory, it is believed that the low perhydrolysis rate is associated to the low dissolution rate of the precursor. As a result, the cleaning performance is reduced. The potential for such a problem is now even more acute with the move in consumer washing habits towards lower washing temperature. Problems can also, in particular, be encountered when said bleach precursors are used under high water hardness conditions, resulting upon dissolution in the formation of calcium salts of bleach precursor with low solubility. Such a problem of reduced perhydrolysis is further increased where the bleach precursor is present in a form that exhibits a low rate of dissolution, e.g as divalent and/or trivalent metal salt, thus affecting the perhydrolysis rate.

A further problem, associated with the bleach precursors having slow perhydrolysis rate, appears when the soiled fabrics also comprise a catalase enzyme. Hence, due to the slow perhydrolysis of the precursor, the catalase will destroy the hydrogen peroxide component before the bleach activator is properly perhydrolysed. As a result, the concentration of peracid present in the wash is reduced and so is the bleaching performance.

Accordingly, the formulator of a granular bleaching composition is faced with the challenge of formulating a granular bleaching composition which provides effective perhydrolysis of the precursor.

To solve this problem of low perhydrolysis rate, the use of a dispensing means to deliver the detergent product directly to the wash solution has been proposed as described in co-pending application PCT/US95/14077.

Notwithstanding the advances in the art, there is still a need for alternative compositions which provide effective dissolution of the bleach precursors having a Krafft point of at least 10°C.

The Applicant has now found that the use of high levels of alcohol alkoxylate nonionic surfactants relative to the levels of bleach precursors having a Krafft point of at least 10°C, within a granular bleaching composition or within the aqueous wash liquor, also fulfills such a need.

An advantage of the invention is that it provides bleach precursors containing bleaching compositions with an effective rate of perhydrolysis.

Another advantage of the invention is that it provides compositions which enable the use of divalent and/or trivalent metal salts.

A further advantage of the invention is that it provides compositions with improved resistance to the catalase.

Summary of the Invention

The present invention is a granular bleaching composition comprising an alcohol alkoxylate nonionic surfactant, a hydrogen peroxide source and a bleach precursor having a Krafft point of at least 10°C, said alcohol alkoxylate nonionic surfactant and said precursor being present in a molar ratio of nonionic surfactant to bleach precursor of at least 3:1.

In another aspect of the invention a method of washing laundry is provided which comprises the step of contacting the fabrics with an aqueous liquor of a granular bleaching composition comprising an alcohol alkoxylate nonionic surfactant, a hydrogen peroxide source and a bleach precursor having a Krafft point of at least 10°C, said surfactant and said precursor being present in a molar ratio of nonionic surfactant to bleach precursor of at least 3:1. By the present method, effective perhydrolysis of the bleach precursor is obtained.

Detailed description of the invention

Alcohol alkoxylate nonionic surfactant

An essential component of the invention is an alcohol alkoxylate nonionic surfactant. Not to be bound by theory, it is believed that such type of surfactant helps to dissolve the bleach precursors having a Krafft point of at least 10°C by forming mixed micelles, thereby preventing to some extent the precipitation of said bleach precursor in presence of hardness. The comicellisation is also believed to speed up the perhydrolysis by making the precursor molecule more accessible to the hydrogen peroxide.

Typical levels of such nonionic surfactant are from 0.1% to 20% by weight, preferably 3% to 10% by weight and more preferably from 4% to 8% by weight of the composition.

Suitable alcohol alkoxylate nonionic surfactants are the class of compounds which may be broadly defined as compounds produced by the condensation of alkylene oxide groups (hydrophilic in nature) with an organic hydrophobic compound, which may be branched or linear aliphatic (e.g. Guerbet or secondary alcohols) or alkyl aromatic in nature. The length of the hydrophilic or polyoxyalkylene radical 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.

Suitable exemplary classes of such alcohol alkoxylate nonionic surfactant are listed below:

1. The polyethylene, polypropylene, and polybutylene oxide condensates of alkyl phenols. In general, the polyethylene oxide condensates are preferred. These compounds include the condensation products of alkyl phenols having an alkyl group containing from 6 to 12 carbon atoms in either a straight- or branched-chain configuration with the alkylene oxide. In a preferred embodiment, the ethylene oxide is present in an amount equal to from 5 to 25 moles of ethylene oxide per mole of alkyl phenol. Commercially available nonionic surfactants of this type include Igepal™ CO-630, marketed by the GAF Corporation; and Triton™ X-45, X-114, X-100, and X-102, all marketed by the Rohm & Haas Company.

2. The condensation products of aliphatic alcohols with from 1 to 25 moles of ethylene oxide. The alkyl chain of the aliphatic alcohol can either be straight or branched, primary or secondary, and generally contains from 8 to 22 carbon atoms. Particularly preferred are the condensation products of alcohols having an alkyl group containing from 10 to 20 carbon atoms with from 2 to 10 moles of ethylene oxide per mole of alcohol. Examples of commercially available nonionic surfactants of this type include Tergitol™ 15-S-9 (the condensation product of C_{11}-C_{15} linear alcohol with 9 moles ethylene oxide), Tergitol™ 24-L-6 NMW (the condensation product of C_{12}-C_{14} primary alcohol with 6 moles ethylene oxide with a narrow molecular weight distribution), both marketed by Union Carbide Corporation; Neodol™ 45-9 (the condensation product of C_{14}-C_{15} linear alcohol with 9 moles of ethylene oxide), Neodol™ 23-6.5 (the condensation product of C_{12}-C_{13} linear alcohol with 6.5 moles of ethylene oxide), Neodol™ 45-7 (the condensation product of C_{14}-C_{15} linear alcohol with 7 moles of ethylene oxide), Neodol™ 45-4 (the condensation product of C_{14}-C_{15} linear alcohol with 4 moles of ethylene oxide), marketed by Shell Chemical Company, and Kyro™ EOB (the condensation product of C_{13}-C_{15} alcohol with 9 moles ethylene oxide), marketed by The Procter & Gamble Company.

3.The condensation products of ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol. The hydrophobic portion of these compounds preferably has a molecular weight of from 1500 to 1800 and exhibits water insolubility. The addition of polyoxyethylene moieties to this hydrophobic portion tends to increase the water solubility of the molecule as a whole, and the liquid character of the product is retained up to the point where the polyoxyethylene content is 50% of the total weight of the condensation product, which corresponds to condensation with up to 40 moles of ethylene oxide. Examples of compounds of this type include certain of the commercially available Pluronic™ surfactants, marketed by BASF.

4.The condensation products of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylenediamine. The hydrophobic moiety of these products consists of the reaction product of ethylenediamine and excess propylene oxide, and generally has a molecular weight of from 2500 to 3000. This hydrophobic moiety is condensed with ethylene oxide to the extent that the condensation product contains from 40% to 80% by weight of polyoxyethylene and has a molecular weight of from 5,000 to 11,000. Examples of this type of nonionic surfactant include certain of the commercially available Tetronic™ compounds, marketed by BASF.

Mixtures of any of the above mentioned nonionic alkoxylated surfactants may be used.

The nonionic surfactant may be included within the bleaching composition of the invention by any means as long as the molar ratio requirement within the composition, as defined herein after, is fulfilled. It may be processed together with the bleach precursor having a Krafft point of at least 10°C so as to form an agglomerate, or provide a coating. It may also be included as a separate component from the bleach into the detergent composition. Mixtures of any of these processes can be used.

Hydrogen peroxide source

An essential component of the invention is a hydrogen peroxide source. Preferred sources of hydrogen peroxide include perhydrate bleaches. The perhydrate is typically 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 0.1% to 60%, preferably from 3% to 40% by weight, more preferably from 5% to 35% by weight and most preferably from 8% to 30% by weight of the composition.

The perhydrate may be any of the alkalimetal inorganic salts such as perborate monohydrate or tetrahydrate, percarbonate, perphosphate and persilicate salts but is conventionally an alkali metal perborate or percarbonate.

Sodium percarbonate, which is the preferred perhydrate, is an addition compound having a formula corresponding to 2Na2CO3.3H2O2, 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 bleaching composition aspect of the present invention, the percarbonate can be incorporated into bleaching compositions without additional protection, but preferred executions of such compositions utilise a coated form of the material. A variety of coatings can be used including borate, boric acid and citrate or sodium silicate of SiO2:Na2O 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. However, the most preferred coating is a mixture of sodium carbonate and sulphate or sodium chloride.

The particle size range of the crystalline percarbonate is from 350 micrometers to 1500 micrometers with a mean of approximately 500-1000 micrometers.

Bleach precursor having a Krafft point of at least 10°C

The other essential component of the invention is a bleach precursor having a Krafft point of at least 10°C, preferably at least 50°C, more preferably of at least 60°C. By Krafft point is meant the temperature above which a solution of 10% by weight of said bleach precursor in deionised water becomes perfectly clear transparent. By " clear transparent" is meant a substance which permits the passage of rays of the visible spectrum. The bleach precursors suitable for use herein are preferably of the anionic type.

Suitable anionic bleach precursors for the purpose of the invention comprise at least one acyl group forming the peroxyacid moiety bonded to a leaving group through an -O- or-N- linkage.

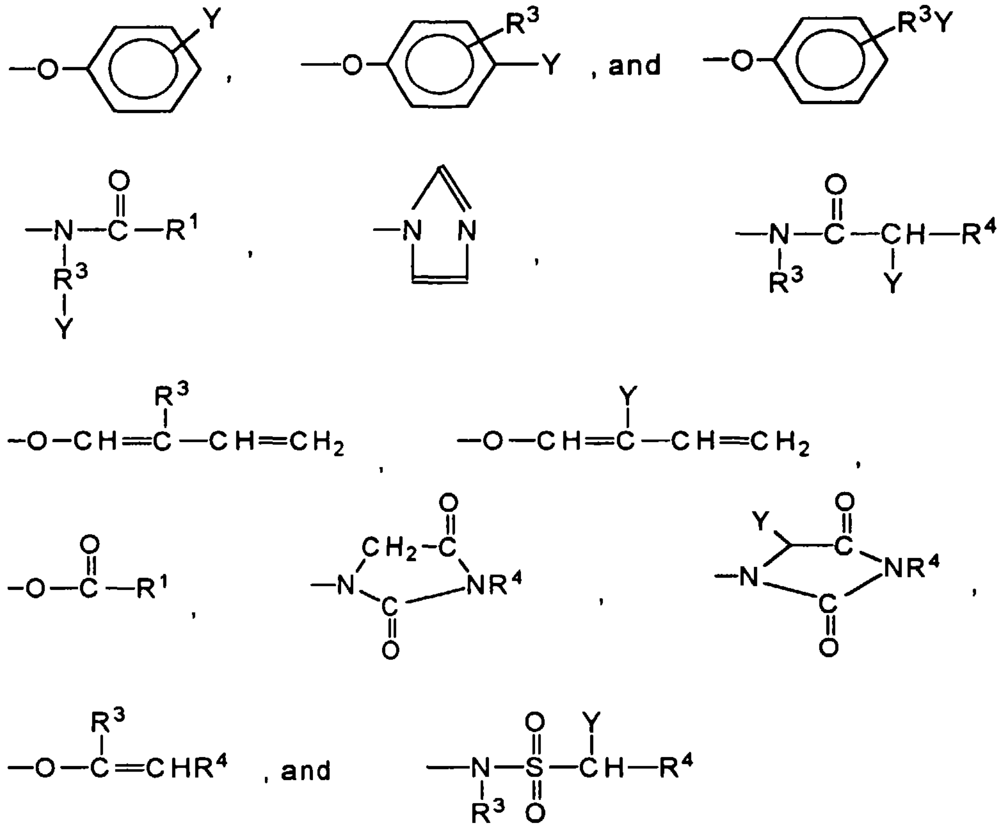
Suitable anionic peroxyacid bleach precursors for the purpose of the invention are the amide substituted compounds of the following general formulae:

$$R1N(R5)C(O)R2C(O)L \text{ or } R1C(O)N(R5)R2C(O)L$$

wherein R1 is an alkyl, alkylene, aryl or alkaryl group with from 1 to 14 carbon atoms, R2 is an alkylene, arylene, and alkarylene group containing from 1 to 14 carbon atoms, and R5 is H or an alkyl, aryl, or alkaryl group containing 1 to 10 carbon atoms and L can be essentially any leaving group. R1 preferably contains from 6 to 12 carbon atoms. R2 preferably contains from 4 to 8 carbon atoms. R1 may be straight chain or branched alkyl, substituted aryl or alkylaryl containing branching, substitution, or both and may be sourced from either synthetic sources or natural sources including for example, tallow fat. Analogous structural variations are permissible for R2. R2 can include alkyl, aryl, wherein said R2 may also contain halogen, nitrogen, sulphur and other typical substituent groups or organic compounds. R5 is preferably H or methyl. R1 and R5 should not contain more than 18 carbon atoms total. Amide substituted bleach activator compounds of this type are described in EP-A-0170386.

The leaving group, hereinafter L group, must be sufficiently reactive for the perhydrolysis reaction to occur within the optimum time frame (e.g., a wash cycle). However, if L is too reactive, this activator will be difficult to stabilize for use in a bleaching composition.

Preferred L groups are selected from:



and mixtures thereof, wherein R1 is an alkyl, aryl, or alkaryl group containing from 1 to 14 carbon atoms, R3 is an alkyl chain containing from 1 to 8 carbon atoms, R4 is H or R3, and Y is H or a solubilizing group. Any of R1, R3 and R4 may be substituted by essentially any functional group including, for example alkyl, hydroxy, alkoxy, halogen, amine, nitrosyl, amide and ammonium or alkyl ammonium groups

The preferred solubilizing groups are -SO3-M+, -CO2-M+, -SO4-M+, -N+(R3)4X- and O<--N(R3)3 and most preferably -SO3-M+ and -CO2-M+ wherein R3 is an alkyl chain containing from 1 to 4 carbon atoms, M is a cation which provides solubility to the bleach activator and X is an anion which provides solubility to the bleach activator. Preferably, M is an alkali metal, ammonium or substituted ammonium cation, with sodium and potassium being most preferred, and X is a halide, hydroxide, methylsulfate or acetate anion.

Preferred examples of bleach precursors of the above formulae include amide substituted peroxyacid precursor compounds selected from (6-octanamido-caproyl)oxybenzenesulfonate, (6-nonanamidocaproyl)oxy benzene sulfonate, (6-decanamido-caproyl)oxybenzenesulfonate, and mixtures thereof as described in EP-A-0170386.

The Applicant also found that further anionic bleach precursors having a Krafft point of at least 10°C could be used instead of or in combination of the above mentioned anionic bleach precursors. Such precursors are the above mentioned anionic bleach precursor present as a divalent and/or trivalent metal salt. This finding is especially surprising as such bleach precursor salts have a low solubility. Typical examples of such low solubility bleach precursors include Mg [(6-octanamido-caproyl)oxybenzenesulfonate]$_2$, Mg [(6-nonanamido caproyl) oxy benzenesulfonate]$_2$, Mg [(6-decanamido-caproyl)oxybenzene sulfonate]$_2$, Ca [(6-octanamido-caproyl)oxybenzenesulfonate]$_2$, Ca [(6-nonanamido-caproyl) oxy benzenesulfonate]$_2$, Ca [(6-decanamido-caproyl)oxy benzenesulfonate]$_2$, and mixtures thereof. It is therefore an advantage of the invention that it allows the use of anionic bleach precursors present as divalent and/or trivalent metal salts.

Mixtures of any of the peroxyacid bleach precursor, hereinbefore described, may also be used.

Preferred among the above-mentioned peroxyacid bleach precursors are the amide-substituted peroxyacid precursor compounds selected from (6-octanamido-caproyl)oxybenzenesulfonate, (6-nonanamidocaproyl)oxy benzene sulfonate, (6-decanamido-caproyl)oxybenzenesulfonate, and mixtures thereof.

Typical levels of the peroxyacid bleach precursors having a Krafft point of at least 10°C within the bleaching compositions are from 0.1% to 25%, preferably from 1% to 20% and most preferably 3 to 15% by weight of the composition.

It is also an essential requirement of the bleaching composition of the invention that the nonionic surfactant and the precursor be present in a molar ratio of at least 3:1, preferably above 4:1.

Optional co-precursors

Optional bleach co-precursors may be used in addition to the bleach precursor having a Krafft point of at least 10°C so as to provide a bleaching composition with a broader spectrum of soil removal.

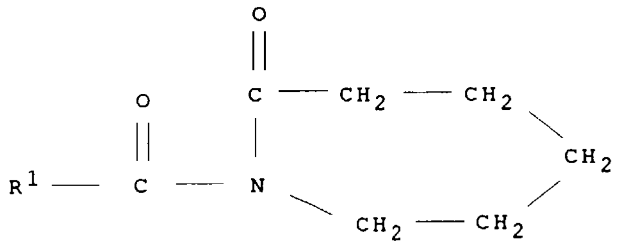
Suitable bleach co-precursors include the tetraacetyl ethylene diamine (TAED) bleach precursor.

Still another class of bleach co-precursor is the class of precursors exhibiting surfactancy properties and having a Krafft point of less than 10°C.

Suitable bleach co-precursors having a Krafft point of less than 10°C is the class of alkyl percarboxylic acid bleach precursors. Preferred alkyl percarboxylic acid precursors include the monovalent salts of nonanoyl oxy benzene sulphonate (NOBS described in US 4,412,934) and 3,5,5-tri-methyl hexanoyl oxybenzene sulfonate (ISONOBS described in EP120,591).

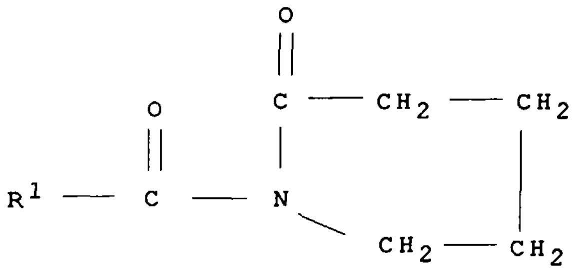
Still another class of bleach precursors suitable as a co-precursor having a Krafft point of less than 10°C are the N-acylated precursor compounds of the lactam class disclosed generally in GB-A-955735. Preferred materials of this class comprise the caprolactams.

Suitable caprolactam bleach precursors are of the formula:



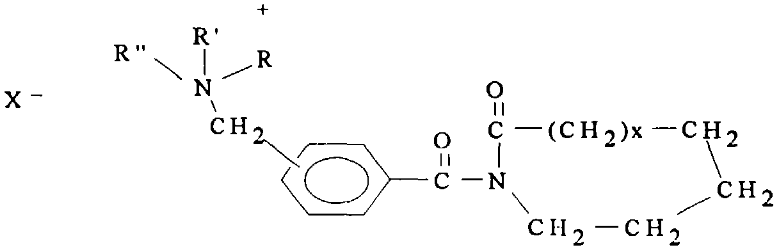
wherein R^1 is an alkyl, aryl, alkoxyaryl or alkaryl group containing from 6 to 12 carbon atoms. Preferred hydrophobic N-acyl caprolactam bleach precursor materials are selected from benzoyl caprolactam, octanoyl caprolactam, nonanoyl caprolactam, decanoyl caprolactam, undecenoyl caprolactam, 3,5,5-trimethylhexanoyl caprolactam and mixtures thereof. A most preferred is nonanoyl caprolactam.

Suitable valero lactams have the formula:



wherein R^1 is an alkyl, aryl, alkoxyaryl or alkaryl group containing from 6 to 12 carbon atoms. More preferably, R^1 is selected from phenyl, heptyl, octyl, nonyl, 2,4,4-trimethylpentyl, decenyl and mixtures thereof.

Other suitable bleach co-precursors having a Krafft point of less than 10°C are the cationic bleach precursors. Suitable cationic peroxyacid co-precursors include any of the ammonium or alkyl ammonium substituted alkyl or benzoyl oxybenzene sulfonates, N-acylated caprolactams, N-acylated valerolactams and monobenzoyltetraacetyl glucose benzoyl peroxides. Preferred cationic bleach precursors are derived from the valerolactam and acyl caprolactam compounds, of formula:



wherein x is 0 or 1, substituents R, R' and R" are each C1-C10 alkyl or C2-C4 hydroxy alkyl groups, or $[(C_yH_{2y})O]_n$-R"' wherein y=2-4, n=1-20 and R"' is a C1-C4 alkyl group or hydrogen and X is an anion.

Highly preferred among these additional bleach co-precursors is the tetraacetyl ethylene diamine (TAED) bleach precursor.

When present, said co-precursors will normally be incorporated at a level of from 0.1% to 60%, preferably from 1% to 40% and most preferably 3 to 25% by weight of the bleaching composition.

The bleaching composition of the invention, may also comprise optional ingredients conventional to detergent compositions. Accordingly, the term bleaching composition and detergent composition will be used hereinafter synonymously. Typically, such optional ingredients include additional surfactants, builders, detergent adjunct materials and mixtures thereof.

Additional surfactants

Optional surfactants may be used in addition to the alcohol alkoxylate nonionic surfactant. Typically, such optional surfactants include one or more surfactants selected from anionic, cationic, nonionic, ampholytic, amphoteric and zwitterionic surfactants and mixtures thereof. 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. Further examples are given in "Surface Active Agents and Detergents" (Vol. I and II by Schwartz, Perry and Berch). A list of suitable cationic surfactants is given in U.S.P. 4,259,217 issued to Murphy on March 31, 1981.

Non-limiting examples of surfactants useful herein include the conventional C_{11}-C_{18} alkyl benzene sulfonates ("LAS") and primary, branched-chain and random C_{10}-C_{20} alkyl sulfates ("AS"), the C_{10}-C_{18} secondary (2,3) alkyl sulfates of the formula $CH_3(CH_2)_x(CHOSO_3^-M^+)CH_3$ and $CH_3\,(CH_2)_y(CHOSO_3^-M^+)\,CH_2CH_3$ where x and (y + 1) are integers of at least 7, preferably at least 9, and M is a water-solubilizing cation, especially sodium, unsaturated sulfates such as oleyl sulfate, the C_{10}-C_{18} alkyl alkoxy sulfates ("AE_xS"; especially EO 1-7 ethoxy sulfates), C_{10}-C_{18} alkyl alkoxy carboxylates (especially the EO 1-5 ethoxycarboxylates), the C_{10-18} glycerol ethers, the C_{10}-C_{18} alkyl polyglycosides and their corresponding sulfated polyglycosides, and C_{12}-C_{18} alpha-sulfonated fatty acid esters. If desired, the conventional amphoteric surfactants such as the C_{12}-C_{18} betaines and sulfobetaines ("sultaines"), C_{10}-C_{18} amine oxides, and the like, can also be included in the overall compositions. The C_{10}-C_{18} N-alkyl polyhydroxy fatty acid amides can also be used. Typical examples include the C_{12}-C_{18} N-methylglucamides. See WO 9,206,154. Other sugar-derived surfactants include the N-alkoxy polyhydroxy fatty acid amides, such as C_{10}-C_{18} N (3-methoxypropyl) glucamide. The N-propyl through N-hexyl C_{12}-C_{18} glucamides can be used for low sudsing. C_{10}-C_{20} conventional soaps may also be used. If high sudsing is desired, the branched-chain C_{10}-C_{16} soaps may be used. Other suitable surfactants suitable for the purpose of the invention are the anionic alkali metal sarcosinates of formula:

$$R\text{-}CON(R^1)CH_2COOM$$

wherein R is a C_9-C_{17} linear or branched alkyl or alkenyl group, R^1 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.

Mixtures of anionic and nonionic surfactants are especially useful. Other conventional useful surfactants are listed in standard texts.

The total amount of optional surfactants will generally be up to 70%, typically 1 to 55% by weight of the bleaching composition. Preferably, high levels of surfactants present in a total amount of at least 11% by weight, more preferably 20% by weight of the composition have been found to be beneficial to the cleaning performance of the composition. Most preferably, a better cleaning performance is observed where at least one of the surfactant components is an anionic surfactant.

Builders

Detergent builders can also optionally be included in the compositions herein to assist in controlling mineral hardness. Inorganic as well as organic builders can be used. Builders are typically used in fabric laundering compositions to assist in the removal of particulate soils.

The level of builder can vary widely depending upon the end use of the composition and its desired physical form. When present, the compositions will typically comprise at least 1% builder. Granular formulations typically comprise from 5% to 80%, more preferably less than 25% by weight, of the detergent builder. Lower or higher levels of builder, however, are not meant to be excluded.

Inorganic or phosphate-containing detergent builders include, but are not limited to, the alkali metal, ammonium and alkanolammonium salts of polyphosphates (exemplified by the tripolyphosphates, pyrophosphates, and glassy polymeric meta-phosphates).

Non-phosphate builders may also be used. These can include, but are not restricted to phytic acid, silicates, alkali metal carbonates (including bicarbonates and sesquicarbonates), sulphates, aluminosilicates, monomeric polycarboxylates. Examples of silicate builders are the crystalline layered silicates, such as the layered sodium silicates described in U.S. 4,664,839. NaSKS-6 is the trademark for a crystalline layered silicate marketed by Hoechst (commonly abbreviated herein as "SKS-6"). Unlike zeolite builders, the Na SKS-6 silicate builder does not contain aluminium. NaSKS-6 has the delta-$Na_2Si_2O_5$ morphology form of layered silicate. It can be prepared by methods such as those described in DE-A-3,417,649 and DE-A-3,742,043. SKS-6 is a highly preferred layered silicate for use herein, but other such layered silicates, such as those having the general formula $NaMSi_xO_{2x+1}.yH_2O$ wherein M is sodium or hydrogen, x is a number from 1.9 to 4, preferably 2, and y is a number from 0 to 20, preferably 0 can be used herein. Various other layered silicates from Hoechst include NaSKS-5, NaSKS-7 and NaSKS-11, as the alpha, beta and gamma forms. As noted above, the delta-$Na_2Si_2O_5$ (NaSKS-6 form) is most preferred for use herein. Other silicates may also be useful such as for example magnesium silicate, which can serve as a crispening agent in granular formulations, as a stabilising agent for oxygen beaches, and as a component of suds control systems.

Aluminosilicate builders are of great importance in most currently marketed heavy duty granular detergent compositions. Aluminosilicate builders include those having the empirical formula:

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

wherein z and y are integers of at least 6, the molar ratio of z to y is in the range from 1.0 to 0.5, and x is an integer from 15 to 264.

Useful aluminosilicate ion exchange materials are commercially available. These aluminosilicates can be crystalline or amorphous in structure and can be naturally-occurring aluminosilicates or synthetically derived. A method for producing aluminosilicate ion exchange materials is disclosed in U.S. 3,985,669. Preferred synthetic crystalline aluminosilicate ion exchange materials useful herein are available under the designations Zeolite A, Zeolite P (B), Zeolite MAP and Zeolite X. In an especially preferred embodiment, the crystalline aluminosilicate ion exchange material has the formula:

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

wherein x is from 20 to 30, especially 27. This material is known as Zeolite A. Dehydrated zeolites (x = 0 - 10) may also be used herein. Preferably, the aluminosilicate has a particle size of 0.1-10 microns in diameter.

Suitable organic detergent builders include, but are not restricted to, a wide variety of polycarboxylate compounds. As used herein, "polycarboxylate" refers to compounds having a plurality of carboxylate groups, preferably at least 3 carboxylates. Polycarboxylate builder can generally be added to the composition in acid form, but can also be added in the form of a neutralised salt. When utilized in salt form, alkali metals, such as sodium, potassium, and lithium, or alkanolammonium salts are preferred.

Included among the polycarboxylate builders are a variety of categories of useful materials. One important category of polycarboxylate builders encompasses the ether polycarboxylates, including oxydisuccinate, as disclosed in U.S. 3,128,287 and U.S. 3,635,830. See also "TMS/TDS" builders of U.S. 4,663,071. Suitable ether polycarboxylates also include cyclic compounds, particularly alicyclic compounds, such as those described in U.S. 3,923,679; 3,835,163; 4,158,635; 4,120,874 and 4,102,903.

Other useful detergency builders include the ether hydroxypolycarboxylates, copolymers of maleic anhydride with ethylene or vinyl methyl ether, or acrylic acid, 1, 3, 5-trihydroxy benzene-2, 4, 6-trisulphonic acid, and carboxymethyloxysuccinic acid, the various alkali metal, ammonium and substituted ammonium salts of polyacetic acids such as ethylenediamine tetraacetic acid and nitrilotriacetic acid, as well as polycarboxylates such as mellitic acid, succinic acid, oxydisuccinic acid, polymaleic acid, benzene 1,3,5-tricarboxylic acid, carboxymethyloxysuccinic acid, and soluble salts thereof.

Citrate builders, e.g., citric acid and soluble salts thereof (particularly sodium salt), are polycarboxylate builders which can be used in granular compositions, especially in combination with zeolite and/or layered silicate builders. Oxydisuccinates are also especially useful in such compositions and combinations.

Also suitable in the compositions of the invention are the 3,3-dicarboxy-4-oxa-1,6-hexanedioates and the related compounds disclosed in U.S. 4,566,984. Useful succinic acid builders include the C_5-C_{20} alkyl and alkenyl succinic acids and salts thereof. A particularly preferred compound of this type is dodecenylsuccinic acid. Specific examples of succinate builders include: laurylsuccinate, myristylsuccinate, palmitylsuccinate, 2-dodecenylsuccinate (preferred), 2-pentadecenylsuccinate, and the like. Laurylsuccinates are the preferred builders of this group, and are described in EP 0,200,263. Other suitable polycarboxylates are disclosed in U.S. 4,144,226 and in U.S. 3,308,067. See also U.S. 3,723,322.

Fatty acids, e.g., C_{12}-C_{18} monocarboxylic acids, can also be incorporated into the compositions alone, or in combination with the aforesaid builders, especially citrate and/or the succinate builders, to provide additional builder activity. Such use of fatty acids will generally result in a diminution of sudsing, which should be taken into account by the formulator.

Detergent adjunct materials

The compositions herein can optionally include one or more other detergent adjunct materials or other materials for assisting or enhancing cleaning performance, treatment of the substrate to be cleaned, or to modify the aesthetics of the composition (e.g. colorants, dyes, etc.). The following are illustrative examples of such adjunct materials.

Enzymes

The enzymes to be incorporated include proteases, amylases, lipases, cellulases, and peroxidases, as well as mixtures thereof. Other types of enzymes may also be included. They may be of any suitable origin, such as vegetable, animal, bacterial, fungal and yeast origin. However, their choice is governed by several factors such as pH-activity and/or stability optima, thermostability and stability versus active detergents and builders. In this respect bacterial or fungal enzymes are preferred, such as bacterial amylases and proteases, and fungal cellulases.

Enzymes are normally incorporated at levels sufficient to provide up to 5 mg by weight, more typically 0.01 mg to 3 mg, of active enzyme per gram of the composition. Stated otherwise, the compositions herein will typically comprise from 0.001% to 5%, preferably 0.01%-1% by weight of a commercial enzyme preparation.

Suitable examples of proteases are the subtilisins which are obtained from particular strains of B. subtilis and B. licheniforms. Another suitable protease is obtained from a strain of Bacillus, having maximum activity throughout the pH range of 8-12, developed and sold by Novo Industries A/S under the registered trade name ESPERASE. The preparation of this enzyme and analogous enzymes is described in GB 1,243,784 of Novo. Proteolytic enzymes suitable for removing protein-based stains that are commercially available include those sold under the tradenames ALCALASE and SAVINASE by Novo Industries A/S (Denmark) and MAXATASE by International Bio-Synthetics, Inc. (The Netherlands). Other proteases include Protease A (see EP 130,756) and Protease B (see EP257189).

Amylases include, for example, α-amylases described in GB 1,296,839 (Novo), RAPIDASE, International Bio-Synthetics, Inc. and TERMAMYL, Novo Industries. Fungamyl (Novo) is especially useful.

The cellulases usable in the present invention include both bacterial or fungal cellulase. Preferably, they will have a pH optimum of between 5 and 9.5. Suitable cellulases are disclosed in U.S. 4,435,307, which discloses fungal cellulase produced from Humicola insolens and Humicola strain DSM1800 or a cellulase 212-producing fungus belonging to the genus Aeromonas, and cellulase extracted from the hepatopancreas of a marine mollusk (Dolabella Auricula Solander). Suitable cellulases are also disclosed in GB-A-2.075.028; GB-A-2.095.275 and DE-OS-2.247.832. ENDO A, CAREZYME both from Novo Industries A/S are especially useful.

Suitable lipase enzymes for detergent usage include those produced by microorganisms of the Pseudomonas group, such as Pseudomonas stutzeri ATCC 19.154, as disclosed in GB 1,372,034. See also lipases in Japanese Patent Application 53,20487, laid open to public inspection on February 24, 1978. This lipase is available from Amano Pharmaceutical Co. Ltd., Nagoya, Japan, under the trade name Lipase P "Amano," hereinafter referred to as "Amano-P." Other commercial lipases include Amano-CES, lipases ex Chromobacter viscosum, e.g. Chromobacter viscosum var. lipolyticum NRRLB 3673, commercially available from Toyo Jozo Co., Tagata, Japan; and further Chromobacter viscosum lipases from U.S. Biochemical Corp., U.S.A. and Disoynth Co., The Netherlands, and lipases ex Pseudomonas gladioli. The LIPOLASE enzyme derived from Humicola lanuginosa and commercially available from Novo (see also EP 341,947) is a preferred lipase for use herein. Peroxidase enzymes are used in combination with oxygen sources, e.g., percarbonate, perborate, persulfate, hydrogen peroxide, etc. They are used for "solution bleaching," i.e. to prevent transfer of dyes or pigments removed from substrates during wash operations to other substrates in the wash solution.

Peroxidase enzymes are known in the art, and include, for example, horseradish peroxidase, ligninase, and haloperoxidase such as chloro- and bromo-peroxidase. Peroxidase-containing detergent compositions are disclosed, for example, in WO 89/099813.

A wide range of enzyme materials and means for their incorporation into synthetic detergent compositions are also disclosed in U.S. 3,553,139. Enzymes are further disclosed in U.S. 4,101,457 and in U.S. 4,507,219. Enzymes for use in detergents can be stabilized by various techniques. Enzyme stabilisation techniques are disclosed and exemplified in U.S. 3,600,319 and EP 0,199,405. Enzyme stabilisation systems are also described, for example, in U.S. 3,519,570.

Polymeric Dispersing Agents

Polymeric dispersing agents can be utilized at levels from 0.5% to 8%, by weight, in the compositions herein, especially in the presence of zeolite and/or layered silicate builders. Suitable polymeric dispersing agents include polymeric polycarboxylates and polyethylene glycols, although others known in the art can also be used.

Polymeric polycarboxylate materials can be prepared by polymerizing or copolymerizing suitable unsaturated monomers, preferably in their acid form. Unsaturated monomeric acids that can be polymerized to form suitable polymeric polycarboxylates are selected from acrylic acid, maleic acid (or maleic anhydride), fumaric acid, itaconic acid, aconitic acid, mesaconic acid, citraconic acid and methylenemalonic acid. The presence in the polymeric polycarboxylates herein of monomeric segments, containing no carboxylate radicals such as vinylmethyl ether, styrene, ethylene, etc. is suitable provided that such segments do not constitute more than 40% by weight.

Polymeric polycarboxylate materials can also optionally include further monomeric units such as nonionic spacing units. For example, suitable nonionic spacing units may include vinyl alcohol or vinyl acetate.

Particularly preferred polymeric polycarboxylates are co-polymers derived from monomers of acrylic acid and maleic acid. The average molecular weight of such polymers in the acid form preferably ranges from 2,000 to 10,000, more preferably from 4,000 to 7,000 and most preferably from 4,000 to 5,000. Water-soluble salts of such acrylic/maleic acid polymers can include, for example, the alkali metal, ammonium and substituted ammonium salts. Soluble polymers of this type are known materials. Use of polyacrylates of this type in detergent compositions has been disclosed, for example, in Diehl, U.S. Patent 3,308,067, issued march 7, 1967. The ratio of acrylate to maleate segments in such copolymers will generally range from 30:1 to 1:1, more preferably from 10:1 to 2:1. Soluble acrylate/maleate copolymers of this type are known materials which are described in EP 66915 as well as in EP 193,360, which also describes such polymers comprising hydroxypropylacrylate. Of these acrylic/maleic-based copolymers, the water-soluble salts of copolymers of acrylic acid and maleic acid are preferred.

Another class of polymeric polycarboxylic acid compounds suitable for use herein are the homo-polymeric polycarboxylic acid compounds derived from acrylic acid. The average molecular weight of such homo-polymers in the acid form preferably ranges from 2,000 to 100,000, more preferably from 3,000 to 75,000, most preferably from 4,000 to 65,000.

A further example of polymeric polycarboxylic compounds which may be used herein include the maleic/acrylic/vinyl alcohol terpolymers. Such materials are also disclosed in EP 193,360, including, for example, the 45/45/10 terpolymer of acrylic/maleic/vinyl alcohol.

Another example of polymeric polycarboxylic compounds which may be used herein include the biodegradable polyaspartic acid and polyglutamic acid compounds.

Clay Soil Removal/Anti-redeposition Agents

Granular bleaching compositions which contain these compounds typically contain from 0.01% to 10.0% by weight of the water-soluble ethoxylates amines.

The most preferred soil release and anti-redeposition agent is ethoxylated tetraethylenepentamine. Exemplary ethoxylated amines are further described in U.S. 4,597,898. Another group of preferred clay soil removal-antiredeposition agents are the cationic compounds disclosed in EP 111,965. Other clay soil removal/antiredeposition agents which can be used include the ethoxylated amine polymers disclosed in EP 111,984; the zwitterionic polymers disclosed in EP 112,592; and the amine oxides disclosed in U.S. 4,548,744 and the carboxy methyl cellulose (CMC) materials. These materials are well known in the art.

Polymeric Soil Release Agent

Polymeric soil release agents are characterised by having both hydrophilic segments, to hydrophilize the surface of hydrophobic fibers, such as polyester and nylon, and hydrophobic segments, to deposit upon hydrophobic fibers and remain adhered thereto through completion of washing and rinsing cycles and, thus, serve as an anchor for the hydrophilic segments. This can enable stains occurring subsequent to treatment with the soil release agent to be more easily cleaned in later washing procedures.

The polymeric soil release agents useful herein especially include those soil release agents having: (a) one or more nonionic hydrophile components consisting essentially of (i) polyoxyethylene segments with a degree of polymerization of at least 2, or (ii) oxypropylene or polyoxypropylene segments with a degree of polymerization of from 2 to 10, wherein said hydrophile segment does not encompass any oxypropylene unit unless it is bonded to adjacent moieties at each end by ether linkages, or (iii) a mixture of oxyalkylene units comprising oxyethylene and from 1 to 30 oxypropylene units wherein said mixture contains a sufficient amount of oxyethylene units such that the hydrophile component has hydrophilicity great enough to increase the hydrophilicity of conventional polyester synthetic fiber surfaces upon deposit of the soil release agent on such surface, said hydrophile segments preferably comprising at least 25% oxyethylene units and more preferably, especially for such components having 20 to 30 oxypropylene units, at least 50% oxyethylene units; or (b) one or more hydrophobe components comprising (i) C_3 oxyalkylene terephthalate segments, wherein, if said hydrophobe components also comprise oxyethylene terephthalate, the ratio of oxyethylene terephthalate:C_3 oxyalkylene terephthalate units is 2:1 or lower, (ii) C_4-C_6 alkylene or oxy C_4-C_6 alkylene segments, or mixtures therein, (iii) poly (vinyl ester) segments, preferably polyvinyl acetate), having a degree of polymerization of at least 2, or (iv) C_1-C_4 alkyl ether or C_4 hydroxyalkyl ether substituents, or mixtures therein, wherein said substituents are present in the form of C_1-C_4 alkyl ether or C_4 hydroxyalkyl ether cellulose derivatives, or mixtures therein, and such cellulose derivatives are amphiphilic, whereby they have a sufficient level of C_1-C_4 alkyl ether and/or C_4 hydroxyalkyl ether units to deposit upon conventional polyester synthetic fiber surfaces and retain a sufficient level of hydroxyls, once adhered to such conventional synthetic fiber surface, to increase fiber surface hydrophilicity, or a combination of (a) and (b).

Typically, the polyoxyethylene segments of (a)(i) will have a degree of polymerization of from 200, although higher levels can be used, preferably from 3 to 150, more preferably from 6 to 100. Suitable oxy C_4-C_6 alkylene hydrophobe segments include, but are not limited to, end-caps of polymeric soil release agents such as $MO_3S(CH_2)_nOCH_2CH_2O$-, where M is sodium and n is an integer from 4-6, as disclosed in U.S. 4,721,580.

Polymeric soil release agents useful in the present invention also include cellulosic derivatives such as hydroxyether cellulosic polymers, copolymeric blocks of ethylene terephthalate or propylene terephthalate with polyethylene oxide or polypropylene oxide terephthalate, and the like. Such agents are commercially available and include hydroxyethers of cellulose such as METHOCEL (Dow) and carboxy alkyl of cellulose such as Metolose (Shin Etsu). Cellulosic soil release agents for use herein also include those selected from C_1-C_4 alkyl and C_4 hydroxyalkyl cellulose; see U.S. 4,000,093.

Soil release agents characterised by poly(vinyl ester) hydrophobe segments include graft copolymers of poly(vinyl ester), e.g., C_1-C_6 vinyl esters, preferably poly(vinyl acetate) grafted onto polyalkylene oxide backbones, such as polyethylene oxide backbones (see EP 0 219 048). Commercially available soil release agents of this kind include the SOKALAN type of material, e.g., SOKALAN HP-22, available from BASF (West Germany).

One type of preferred soil release agent is a copolymer having random blocks of ethylene terephthalate and polyethylene oxide (PEO) terephthalate. The molecular weight of this polymeric soil release agent is in the range of from 25,000 to 55,000. See U.S. 3,959,230 and U.S. 3,893,929.

Another preferred polymeric soil release agent is a polyester with repeat units of ethylene terephthalate units which contains 10-15% by weight of ethylene terephthalate units together with 90-80% by weight of polyoxyethylene terephthalate units, derived from a polyoxyethylene glycol of average molecular weight 300-5,000. Examples of this polymer include the commercially available material ZELCON 5126 (from Dupont) and MILEASE T (from ICI). See also U.S. 4,702,857.

Another preferred polymeric soil release agent is a sulfonated product of a substantially linear ester oligomer comprised of an oligomeric ester backbone of terephthaloyl and oxyalkyleneoxy repeat units and terminal moieties covalently attached to the backbone. These soil release agents are described in U.S. 4,968,451. Other suitable polymeric soil release agents include the terephthalate polyesters of U.S. 4,711,730, the anionic end-capped oligomeric esters of U.S. 4,721,580 and the block polyester oligomeric compounds of U.S. 4,702,857.

Still another preferred soil release agent is an oligomer with repeat units of terephthaloyl units, sulfoisoterephthaloyl units, oxyethyleneoxy and oxy-1,2-propylene units. The repeat units form the backbone of the oligomer and are preferably terminated with modified isethionate end-caps. A particularly preferred soil release agent of this type comprises one sulfoisophthaloyl unit, 5 terephthaloyl units, oxyethyleneoxy and oxy-1,2-propyleneoxy units in a ratio of from 1.7 to 1.8, and two end-cap units of sodium 2-(2-hydroxyethoxy)ethanesulfonate. Said soil release agent also comprises from 0.5% to 20%, by weight of the oligomer, of a crystalline-reducing stabilizer, preferably selected from xylene sulfonate, cumene sulfonate, toluene sulfonate and mixtures thereof.

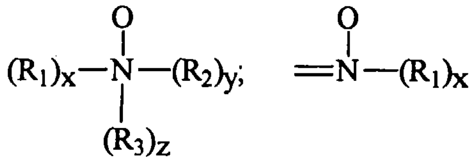
Preferred polymeric soil release agents also include the soil release agents of U.S. 4,877,896, which discloses anionic, especially sulfoaroyl, end-capped terephthalate esters.

If utilized, soil release agents will generally comprise from 0.01% to 10.0%, by weight, of the compositions herein, typically from 0.1% to 5%, preferably from 0.2% to 3.0%.

Dye Transfer Inhibiting Agents

Generally, such dye transfer inhibiting agents include polyvinyl pyrrolidone polymers, polyamine N-oxide polymers, copolymers of N-vinylpyrrolidone and N-vinylimidazole, manganese phthalocyanine, peroxidases, and mixtures thereof. If used, these agents typically comprise from 0.01% to 10% by weight of the composition, preferably from 0.01% to 5%, and more preferably from 0.05% to 2%.

More specifically, the polyamine N-oxide polymers preferred for use herein contain units having the following structural formula: R-A_x-P; wherein P is a polymerizable unit to which an N-O group can be attached or the N-O group can form part of the polymerizable unit or the N-O group can be attached to both units; A is one of the following structures: -NC(O)-, -C(O)O-, -S-, -O-, -N=; x is 0 or 1; and R is aliphatic, ethoxylated aliphatics, aromatics, heterocyclic or alicyclic groups or any combination thereof to which the nitrogen of the N-O group can be attached or the N-O group is part of these groups. Preferred polyamine N-oxides are those wherein R is a heterocyclic group such as pyridine, pyrrole, imidazole, pyrrolidine, piperidine and derivatives thereof. The N-O group can be represented by the following general structures:



$$(R_1)_x-\overset{\overset{\large O}{|}}{\underset{\underset{(R_3)_z}{|}}{N}}-(R_2)_y; \qquad =\overset{\overset{\large O}{|}}{N}-(R_1)_x$$

wherein R_1, R_2, R_3 are aliphatic, aromatic, heterocyclic or alicyclic groups or combinations thereof; x, y and z are 0 or 1; and the nitrogen of the N-O group can be attached or form part of any of the aforementioned groups. The amine oxide unit of the polyamine N-oxides has a pKa <10, preferably pKa <7, more preferred pKa <6.

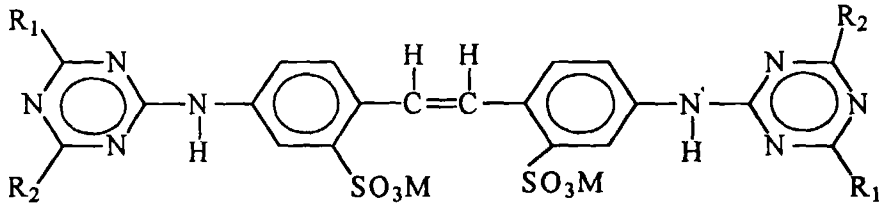
Any polymer backbone can be used as long as the amine oxide polymer formed is water-soluble and has dye transfer inhibiting properties. Examples of suitable polymeric backbones are polyvinyls, polyalkylenes, polyesters, polyethers, polyamide, polyimides, polyacrylates and mixtures thereof. These polymers include random or block copolymers where one monomer type is an amine N-oxide and the other monomer type is an N-oxide. The amine N-oxide polymers typically have a ratio of amine to the amine N-oxide of 10:1 to 1:1,000,000. However, the number of amine oxide groups present in the polyamine oxide polymer can be varied by appropriate copolymerization or by an appropriate degree of N-oxidation. The polyamine oxides can be obtained in almost any degree of polymerization. Typically, the average molecular weight is within the range of 500 to 1,000,000; more preferred 1,000 to 500,000; most preferred 5,000 to 100,000. This preferred class of materials can be referred to as "PVNO".

The most preferred polyamine N-oxide useful in the compositions herein is poly(4-vinylpyridine-N-oxide) which as an average molecular weight of 50,000 and an amine to amine N-oxide ratio of 1:4.

Copolymers of N-vinylpyrrolidone and N-vinylimidazole polymers (referred to as a class as "PVPVI") are also preferred for use herein. Preferably the PVPVI has an average molecular weight range from 5,000 to 1,000,000, more preferably from 5,000 to 200,000, and most preferably from 10,000 to 20,000. (The average molecular weight range is determined by light scattering as described in Barth, et al., Chemical Analysis, Vol 113. "Modern Methods of Polymer Characterization".) The PVPVI copolymers typically have a molar ratio of N-vinylimidazole to N-vinylpyrrolidone from 1:1 to 0.2:1, more preferably from 0.8:1 to 0.3:1, most preferably from 0.6:1 to 0.4:1. These copolymers can be either linear or branched.

The present invention compositions also may employ a polyvinyl pyrrolidone ("PVP") having an average molecular weight of from 5,000 to 400,000, preferably from 5,000 to 200,000, and more preferably from 5,000 to 50,000. PVP's are known to persons skilled in the detergent field; see, for example, EP-A-262,897 and EP-A-256,696. Compositions containing PVP can also contain polyethylene glycol ("PEG") having an average molecular weight from 500 to 100,000, preferably from 1,000 to 10,000. Preferably, the ratio of PEG to PVP on a ppm basis delivered in wash solutions is from 2:1 to 50:1, and more preferably from 3:1 to 10:1.

The bleaching compositions herein may also optionally contain from 0.005% to 5% by weight of certain types of hydrophilic optical brighteners which also provide a dye transfer inhibition action. If used, the compositions herein will preferably comprise from 0.01% to 1.2% by weight of such optical brighteners. The hydrophilic optical brighteners useful in the present invention are those having the structural formula:



wherein R_1 is selected from anilino, N-2-bis-hydroxyethyl and NH-2-hydroxyethyl; R_2 is selected from N-2-bis-hydroxyethyl, N-2-hydroxyethyl-N-methylamino, morphilino, chloro and amino; and M is a salt-forming cation such as sodium or potassium.

When in the above formula, R_1 is anilino, R_2 is N-2-bis-hydroxyethyl and M is a cation such as sodium, the brightener is 4,4',-bis[(4-anilino-6-(N-2-bis-hydroxyethyl)-s-triazine-2-yl)amino]-2,2'-stilbenedisulfonic acid and disodium salt. This particular brightener species is commercially marketed under the tradename Tinopal-UNPA-GX by Ciba-Geigy Corporation.

When in the above formula, R_1 is anilino, R_2 is N-2-hydroxyethyl-N-2-methylamino and M is a cation such as sodium, the brightener is 4,4'-bis[(4-anilino-6-(N-2-hydroxyethyl-N-methylamino)-s-triazine-2-yl)amino]2,2'-stilbenedisulfonic acid disodium salt. This particular brightener species is commercially marketed under the tradename Tinopal 5BM-GX by Ciba-Geigy Corporation.

When in the above formula, R_1 is anilino, R_2 is morphilino and M is a cation such as sodium, the brightener is 4,4'-bis[(4-anilino-6-morphilino-s-triazine-2-yl)amino]2,2'-stilbenedisulfonic acid, sodium salt. This particular brightener species is commercially marketed under the tradename Tinopal AMS-GX by Ciba Geigy Corporation.

Other conventional optical brightener types of compounds can optionally be used in the present compositions to provide conventional fabric "brightness" benefits, rather than a true dye transfer inhibiting effect. Such usage is conventional and well-known to detergent formulations.

Conventional optical brighteners or other brightening or whitening agents known in the art can be incorporated at levels typically from 0.005% to 5%, preferably from 0.01% to 1.2% and most preferably from 0.05% to 1.2%, by weight, into the compositions herein. Commercial optical brighteners which may be useful can be classified into subgroups, which include, but are not necessarily limited to, derivatives of stilbene, pyrazoline, coumarin, carboxylic acid, methinecyanines, dibenzothiophene-5,5-dioxide, azoles, 5- and 6-membered-ring heterocycles, and other miscellaneous agents. Examples of such brighteners are disclosed in "The Production and Application of Fluorescent Brightening Agents", M. Zahradnik, Published by John Wiley & Sons, New York (1982). Further optical brightener which may also be used include naphthalimide, benzoxazole, benzofuran, benzimidazole and any mixtures thereof.

Specific examples of optical brighteners which are useful in the present compositions are those identified in U.S. 4,790,856. These brighteners include the PHORWHITE series of brighteners from Verona. Other brighteners disclosed in this reference include: Tinopal UNPA, Tinopal CBS and Tinopal 5BM; available from Ciba-Geigy; Artic White CC and Artic White CWD; the 2-(4-styryl-phenyl)-2H-naptho[1,2-d]triazoles; 4,4'-bis(1,2,3-triazol-2-yl)-stilbenes; 4,4'-bis(styryl)bisphenyls; and the aminocoumarins. Specific examples of these brighteners include 4-methyl-7-diethyl- amino coumarin; 1,2-bis(-benzimidazol-2-yl)ethylene; 1,3-diphenyl-pyrazolines; 2,5-bis(benzoxazol-2-yl)thiophene; 2-styryl-naptho-[1,2-d]oxazole; and 2-(stilbene-4-yl)-2H-naphtho[1,2-d]triazole. See also U.S. 3,646,015.

Suds Suppressors

A wide variety of materials may be used as suds suppressors, and suds suppressors are well known to those skilled in the art. See, for example, Kirk Othmer Encyclopedia of Chemical Technology, Third Edition, Volume 7, pages 430-447 (John Wiley & Sons, Inc., 979). One category of suds suppressor of particular interest encompasses monocarboxylic fatty acid and soluble salts therein. See U.S. 2,954,347. The monocarboxylic fatty acids and salts thereof used as suds suppressor typically have hydrocarbyl chains of 10 to 24 carbon atoms, preferably 12 to 18 carbon atoms. Suitable salts include the alkali metal salts such as sodium, potassium, and lithium salts, and ammonium and alkanolammonium salts.

The compositions herein may also contain non-surfactant suds suppressors. These include, for example: high molecular weight hydrocarbons such as paraffin, fatty acid esters (e.g., fatty acid triglycerides), fatty acid esters of monovalent alcohols, aliphatic C_{18}-C_{40} ketones (e.g., stearone), etc. Other suds inhibitors include N-alkylated amino triazines such as tri- to hexa-alkylmelamines or di- to tetra-alkyldiamine chlortriazines formed as products of cyanuric chloride with two or three moles of a primary or secondary amine containing 1 to 24 carbon atoms, propylene oxide, and monostearyl phosphates such as monostearyl alcohol phosphate ester and monostearyl dialkali metal (e.g., K, Na, and Li) phosphates and phosphate esters. The hydrocarbons such as paraffin and haloparaffin can be utilized in liquid form. It is also known to utilize waxy hydrocarbons, preferably having a melting point below 100°C. The hydrocarbons constitute a preferred category of suds suppressor for detergent compositions. Hydrocarbon suds suppressors are described, for example, in U.S. 4,265,779. The hydrocarbons, thus, include aliphatic, alicyclic, aromatic, and heterocyclic saturated or unsaturated hydrocarbons having from 12 to 70 carbon atoms. The term "paraffin," as used in this suds suppressor discussion, is intended to include mixtures of true paraffins and cyclic hydrocarbons.

Another preferred category of non-surfactant suds suppressors comprises silicone suds suppressors. This category includes the use of polyorganosiloxane oils, such as polydimethylsiloxane, dispersions or emulsions of polyorganosiloxane oils or resins, and combinations of polyorganosiloxane with silica particles wherein the polyorganosiloxane is chemisorbed or fused onto the silica. Silicone suds suppressors are well known in the art and are, for example, disclosed in U.S. 4,265,779 and EP 354016. Other silicone suds suppressors are disclosed in U.S. 3,455,839 which relates to compositions and processes for defoaming aqueous solutions by incorporating therein small amounts of polydimethylsiloxane fluids.

Mixtures of silicone and silanated silica are described, for instance, in German Patent Application DOS 2,124,526. Silicone defoamers and suds controlling agents in granular detergent compositions are disclosed in U.S. 3,933,672 and in U.S. 4,652,392.

An exemplary silicone based suds suppressor for use herein is a suds suppressing amount of a suds controlling agent consisting essentially of:

(i) polydimethylsiloxane fluid having a viscosity of from 20 cs. to 1,500 cs. at 25°C;
(ii) from 5 to 50 parts per 100 parts by weight of (i) of siloxane resin composed of $(CH_3)_3SiO_{1/2}$ units of SiO_2 units in a ratio of from $(CH_3)_3$ $SiO_{1/2}$ units and to SiO_2 units of from 0.6:1 to 1.2:1; and
(iii) from 1 to 20 parts per 100 parts by weight of (i) of a solid silica gel.

In the preferred silicone suds suppressor used herein, the solvent for a continuous phase is made up of certain polyethylene glycols or polyethylene-polypropylene glycol copolymers or mixtures thereof (preferred), or polypropylene glycol. The primary silicone suds suppressor is branched/crosslinked and preferably not linear.

The silicone suds suppressor herein preferably comprises polyethylene glycol and a copolymer of polyethylene glycol/polypropylene glycol, all having an average molecular weight of less than 1,000, preferably between 100 and 800. The polyethylene glycol and polyethylene/polypropylene copolymers herein have a solubility in water at room temperature of more than 2 weight %, preferably more than 5 weight %.

The preferred solvent herein is polyethylene glycol having an average molecular weight of less than 1,000, more preferably between 100 and 800, most preferably between 200 and 400, and a copolymer of polyethylene glycol/polypropylene glycol, preferably PPG 200/PEG 300. Preferred is a weight ratio of between 1:1 and 1:10, most preferably between 1:3 and 1:6, of polyethylene glycol:copolymer of polyethylene-polypropylene glycol.

The preferred silicone suds suppressors used herein do not contain polypropylene glycol, particularly of 4,000 molecular weight. They also preferably do not contain block copolymers of ethylene oxide and propylene oxide, like PLURONIC L101.

Other suds suppressors useful herein comprise the secondary alcohols (e.g., 2-alkyl alkanols) and mixtures of such alcohols with silicone oils, such as the silicones disclosed in U.S. 4,798,679, 4,075,118 and EP 150,872. The secondary alcohols include the C_6-C_{16} alkyl alcohols having a C_1-C_{16} chain. A preferred alcohol is 2-butyl octanol, which is available from Condea under the trademark ISOFOL 12. Mixtures of secondary alcohols are available under the trademark ISALCHEM 123 from Enichem. Mixed suds suppressors typically comprise mixtures of alcohol + silicone at a weight ratio of 1:5 to 5:1.

For any detergent compositions to be used in automatic laundry washing machines, suds should not form to the extent that they overflow the washing machine. Suds suppressors, when utilized, are preferably present in a "suds suppressing amount". By "suds suppressing amount" is meant that the formulator of the composition can select an amount of this suds controlling agent that will sufficiently control the suds to result in a low-sudsing laundry detergent for use in automatic laundry washing machines.

The compositions herein will generally comprise from 0% to 5% of suds suppressor. When utilized as suds suppressors, monocarboxylic fatty acids, and salts therein, will be present typically in amounts up to 5%, by weight, of the composition. Preferably, from 0.5% to 3% of fatty monocarboxylate suds suppressor is utilized. Silicone suds suppressors are typically utilized in amounts up to 2.0%, by weight, of the composition, although higher amounts may be used. This upper limit is practical in nature, due primarily to concern with keeping costs minimized and effectiveness of lower amounts for effectively controlling sudsing. Preferably from 0.01% to 1% of silicone suds suppressor is used, more preferably from 0.25% to 0.5%. As used herein, these weight percentage values include any silica that may be utilized in combination with polyorganosiloxane, as well as any adjunct materials that may be utilized. Monostearyl phosphate suds suppressors are generally utilized in amounts ranging from 0.1% to 2%, by weight, of the composition. Hydrocarbon suds suppressors are typically utilized in amounts ranging from 0.01% to 5.0%, although higher levels can be used. The alcohol suds suppressors are typically used at 0.2%-3% by weight of the finished compositions.

Fabric Softeners

Various through-the-wash fabric softeners, especially the impalpable smectite clays of U.S. 4,062,647, as well as other softener clays known in the art, can optionally be used typically at levels of from 0.5% to 10%, preferably from 0.5% to 2% by weight in the present compositions to provide fabric softener benefits concurrently with fabric cleaning. Clay softeners can be used in combination with amine and cationic softeners as disclosed, for example, in U.S. 4,375,416 and U.S. 4,291,071.

Other Ingredients

A wide variety of other functional ingredients useful in detergent compositions can be included in the compositions herein, including other active ingredients, carriers, hydrotropes, processing aids, dyes or pigments, solid fillers for bar compositions. The compositions herein will preferably be formulated such that, during use in aqueous cleaning operations, the wash water will have a pH of between 6.5 and 11, preferably between 7.5 and 10.5. Laundry products are typically at pH 9-11. Techniques for controlling pH at recommended usage levels include the use of buffers, alkalis, acids, etc., and are well known to those skilled in the art.

Mean particle size of the components of granular compositions

Preferably, the mean particle size of the components of granular compositions in accordance with the invention should be such that no more than 5% of particles are greater than 1.4mm in diameter and not more than 5% of particles are less than 0.15mm in diameter.

The term "mean particle size" as defined herein is determined 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.

The bulk density of granular detergent compositions in accordance with the present invention is particularly useful in concentrated granular detergent compositions that are characterised by a relatively high density in comparison with conventional laundry detergent compositions. Such high density compositions typically have a bulk density of at least 400 g/litre, more preferably from 650 g/litre to 1200 g/litre, most preferably from 800g/litre to 1000g/litre.

Manufacturing processes - granular compositions

In general, granular detergent compositions in accordance with the present invention can be made via a variety of methods including dry mixing, spray drying, agglomeration and granulation.

In another aspect of the invention a method of washing laundry is provided which comprises the step of contacting the fabrics with an aqueous liquor of the above defined granular detergent composition. By the present method, effective perhydrolysis of the bleach precursor is obtained.

By effective perhydrolysis is meant that the use of a composition comprising an alcohol alkoxylate nonionic surfactant and a bleach precursor having a Krafft point of at least 10°C as described above exhibits a better bleach precursor perhydrolysis than the use of the same composition without the alcohol alkoxylate nonionic surfactant or than the same composition without the molar ratio requirement.

The invention is illustrated in the following non-limiting examples, in which all percentages are on a weight basis unless otherwise stated.

In the compositions of the invention, the abbreviated component identifications have the following meanings:

LAS : Sodium linear C_{12} alkyl benzene sulphonate
TAS : Sodium tallow alcohol sulphate
C45AS : Sodium C_{14}-C_{15} linear alkyl sulphate
C45E7 : A C_{14-15} predominantly linear primary alcohol condensed with an average of 7 moles of ethylene oxide
C25 E3 : A C_{12-15} branched primary alcohol condensed with an average of 3 moles of ethylene oxide
C25E5 : A C_{12-15} branched primary alcohol condensed with an average of 5 moles of ethylene oxide
Soap : Sodium linear alkyl carboxylate derived from an 80/20 mixture of tallow and a coconut oils.

STPP	: Anhydrous sodium tripolyphosphate
Zeolite A	: Hydrated Sodium Aluminosilicate of formula $Na_{12}(A10_2SiO_2)_{12}.27H_2O$ having a primary particle size in the range from 0.1 to 10 micrometers
NaSKS-6	: Crystalline layered silicate of formula δ-$Na_2Si_2O_5$
Carbonate	: Anhydrous sodium carbonate with a particle size between 200μm and 900μm
Silicate	: Amorphous Sodium Silicate (SiO_2:Na_2O; 2.0 ratio)
Sulphate	: Anhydrous sodium sulphate
Citrate	: Tri-sodium citrate dihydrate of activity 86.4% with a particle size distribution between 425μm and 850μm
MA/AA	: Copolymer of 1:4 maleic/acrylic acid, average molecular weight about 70,000. CMC : Sodium carboxymethyl cellulose
Savinase	: Proteolytic enzyme of activity 4KNPU/g
Carezyme	. Cellulytic enzyme of activity 1000 CEVU/g
Termamyl	: Amylolytic enzyme of activity 60KNU/g
Lipolase	: Lipolytic enzyme of activity 100kLU/g all sold by NOVO Industries A/S and of activity mentioned above unless otherwise specified
PB4	: Sodium perborate tetrahydrate of nominal formula $NaBO_2.3H_2O.H_2O_2$
PB1	: Anhydrous sodium perborate bleach of nominal formula $NaBO_2.H_2O_2$
Percarbonate	: Sodium Percarbonate of nominal formula $2Na_2CO_3.3H_2O_2$
TAED	: Tetraacetyl ethylene diamine
NACA-OBS	: (6-nonanamidocaproyl)oxy benzene sulfonate
DTPMP	: Diethylene triamine penta (methylene phosphonate), marketed by Monsanto under the Trade name Dequest 2060
Photoactivated bleach	: Sulphonated Zinc Phthalocyanin encapsulated in dextrin soluble polymer
Brightener 1	: Disodium 4,4'-bis(2-sulphostyryl)biphenyl
Brightener 2	: Disodium 4,4'-bis(4-anilino-6-morpholino-1.3.5-triazin-2-yl)amino) stilbene-2:2'-disulphonate.
HEDP	: 1,1-hydroxyethane diphosphonic acid
SRP	: Sulfobenzoyl end capped esters with oxyethylene oxy and terephtaloyl backbone
Silicone antifoam	: Polydimethyldiloxane foam controller with Siloxane-oxyalkylene copolymer as dispersing agent with a ratio of said foam controller to said dispersing agent of 10:1 to 100:1.

Example 1

The following detergent formulations, according to the present invention were prepared, where formulation A is a phosphorus-containing detergent composition, formulation B is a zeolite-containing detergent composition and formulation C is a compact detergent composition:

	A	B	C
Blown Powder			
STPP	24	-	24.0
Zeolite A	-	24.0	-
Sulphate	9.0	6.0	13.0
MA/AA	2.0	4.0	2.0
LAS	6.0	8.0	11.0
TAS	2.0	-	-
Silicate	7.0	3.0	3.0
CMC	1.0	1.0	0.5
Brightener 2	0.2	0.2	0.2
Soap	1.0	1.0	1.0
DTPMP	0.4	0.4	0.2
Spray On			
C45E7	2.5	2.5	2.0
C25E3	2.5	2.5	2.0
Silicone antifoam	0.3	0.3	0.3
Perfume	0.3	0.3	0.3
Dry additives			
Carbonate	6.0	13.0	15.0
PB4	18.0	18.0	10.0
PB1	4.0	4.0	-
TAED	3.0	3.0	1.0
Photoactivated bleach	0.02	0.02	0.02
Savinase	1.0	1.0	1.0
Lipolase	0.4	0.4	0.4
Termamyl	0.25	0.30	0.15
Sulphate	3.0	3.0	5.0
NACA-OBS	1.0	1.0	0.8
Balance (Moisture & Miscellaneous)	100.0	100.0	100.0
Density (g/litre)	630	670	670

Example 2

The following high density detergent formulations D and E, according to the present invention were prepared:

	D	E
Agglomerate		
C45AS	11.0	14.0
Zeolite A	15.0	6.0
Carbonate	4.0	8.0
MA/AA	4.0	2.0
CMC	0.5	0.5
DTPMP	0.4	0.4
Spray On		
C25E5	5.0	5.0
Perfume	0.5	0.5
Dry Additives		
HEDP	0.5	0.3
NaSKS 6	13.0	10.0
Citrate	3.0	1.0
TAED	3.0	3.5
NACA-OBS	1.6	1.4
Percarbonate	20.0	20.0
SRP	0.3	0.3
Savinase	1.4	1.4
Lipolase	0.4	0.4
Carezyme	0.6	0.6
Termamyl	0.6	0.6
Silicone antifoam particle	5.0	5.0
Brightener 1	0.2	0.2
Brightener 2	0.2	-
Balance (Moisture and Miscellaneous)	100	100
Density (g/litre)	850	850

Claims

1. A granular bleaching composition comprising an alcohol alkoxylate nonionic surfactant, a hydrogen peroxide source and a bleach precursor having a Krafft point of at least 10°C, said surfactant and said precursor being present in a molar ratio of alcohol alkoxylate nonionic surfactant to bleach precursor of at least 3:1.

2. A composition according to Claim 2, wherein said surfactant is selected from polyethylene, polypropylene, and polybutylene oxide condensates of alkyl phenols, condensation products of aliphatic alcohols with from 1 to 25 moles of ethylene oxide, condensation products of ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol, condensation products of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylenediamine and mixtures thereof.

3. A composition according to either one of Claim 1 or 2, wherein said bleach precursor has a Krafft point of at least 50°C, preferably 60°C.

4. A composition according to any one of Claims 1-3, wherein said bleach precursor is an anionic bleach precursor.

5. A composition according to Claim 4, wherein said bleach precursor is an anionic bleach precursor of the amido peroxy class.

6. A composition according to Claim 5, wherein said bleach precursor is selected from the group consisting of monovalent, divalent, trivalent metal salts of amide substituted peroxyacid precursor compounds and mixtures thereof, preferably monovalent salt of amide substituted peroxyacid precursor compounds.

7. A composition according to Claim 6, wherein said bleach precursor is selected from the group consisting of (6-octanamidocaproyl)oxybenzenesulfonate, (6-nonanamidocaproyl)oxy benzene sulfonate, (6-decanamidocaproyl)oxybenzenesulfonate, and mixtures thereof.

8. A composition according to any one of Claims 1-6, wherein said composition further comprises a bleach co-precursor.

9. A composition according to Claim 8, wherein said bleach co-precursor is tetraacetyl ethylene diamine.

10. A method of washing laundry which comprises the step of contacting the fabrics with an aqueous liquor of a composition as defined in any one of Claims 1-9.

European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 96 87 0084

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)
Y	EP-A-0 402 971 (UNILEVER NV ET AL.) * page 6, line 27 - line 40 * * page 6, line 47 - line 58 * * claims 1,9-20 * ---	1-10	C11D3/39 C11D1/72
Y	FR-A-2 329 747 (UNILEVER NV) * page 5, line 37 - line 40 * * page 6 - page 7 * * claims * ---	1-10	
D,A	EP-A-0 170 386 (PROCTER & GAMBLE) * page 11, line 34 - line 37 * * page 12, line 1 - line 19 * * claims * ---	1-10	
A	GB-A-2 178 075 (COLGATE PALMOLIVE CO) * page 1, line 5 - line 9 * * page 3, line 32 - line 65 * * page 4, line 1 - line 19 * * claims * ---	1-3,10	
A	EP-A-0 106 634 (PROCTER & GAMBLE) * claims 1,3 * ---	1	
A	EP-A-0 006 655 (PROCTER & GAMBLE ET AL.) * page 3, line 31 - line 37 * * page 5, line 22 - line 37 * * page 6 * -----	1-3,10	

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	2 December 1996	Pelli Wablat, B

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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A : technological background
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