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(54) Title: HYDROPHOBIC PEROXYACID BLEACH PRECURSOR COMPOSITIONS STABILISED WITH A WATER SOLUBLE CARBOXYLIC ACID (57) Abstract There is provided a peroxyacid bleach precursor composition, and detergent composition containing it, comprising: a) a particulate peroxyacid bleach precursor of a size less than 100µm and selected from precursors which produce under perhydrolysis hydrophobic peroxyacid whose parent carboxylic acid has a critical micelle concentration less than 0.5 moles/litre; and b) a water-soluble organic acid compound; wherein said precursor and said organic acid are in close physical proximity. The compositions of the invention show enhanced storage stability as well as an enhanced perhydrolysis rate.		

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HYDROPHOBIC PEROXYACID BLEACH PRECURSOR COMPOSITIONS STABILISED WITH A WATER SOLUBLE CARBOXYLIC ACID

Technical field

The present invention relates to peroxyacid bleach precursor compositions and to detergent compositions containing them, which have improved perhydrolysis rate as well as improved storage stability. More particularly, it relates to bleach activators which in aqueous media produce hydrophobic peroxyacids.

Background to the invention

Under alkaline conditions, bleach activators are susceptible to hydrolysis under alkaline conditions, which thus reduces the storage stability as well as the perhydrolysis rate when in aqueous wash liquor.

The prior art contains numerous examples of organic peroxyacid bleach precursors coated or agglomerated so as to increase their stability on storage in detergent compositions and/or to influence their solution behaviour.

EP-A-0070474 discloses granulate organic peroxyacid bleach precursors prepared by spray drying an aqueous pumpable dispersion containing an N-acyl or O-acyl compound together with at least one water soluble cellulose ether, starch or starch derivative in a weight ratio of activator to coating of from 98:2 to 90:10.

GB-A-1507312 discloses the coating of organic peroxyacid bleach precursors with a mixture of alkali metal C₈ - C₂₂ fatty acid salts in admixture with the corresponding fatty acids. GB-A-1381121 employs a molten coating of inter alia C₁₄ - C₁₈ fatty acid mixtures to protect solid organic peroxyacid bleach precursors. GB-A-1441416 discloses a similar process employing a mixture of C₁₂ - C₁₄ fatty acids and C₁₀ - C₂₀ aliphatic alcohols. EP-A-0375241 describes stabilised organic peroxyacid bleach precursor extrudates in which C₅- C₁₈ alkyl peroxy carboxylic acid precursors are mixed with a binder selected from anionic

and nonionic surfactants, film forming polymers fatty acids or mixtures of such binders.

EP-A-0356700 discloses compositions comprising a organic peroxyacid bleach precursor, a water soluble film forming polymer and 2-15% of a C₃-C₆ polyvalent carboxylic acid or hydroxycarboxylic acid for enhanced stability and ease of dispersion/solubility. The carboxylic acid, of which a preferred example is citric acid, is dry mixed with the organic peroxyacid bleach precursor and then granulated with the film forming polymer. Specifically disclosed is a granule comprising 88.1% of TAED of mean particle size of 0.01 to 0.8mm, 10.4% of citric acid, 0.5% polyacrylate and 1.0% of water. The citric acid is asserted to provide an enhanced rate of dissolution of the organic peroxyacid bleach precursor granules.

EP-A-0382464 concerns a process for coating or encapsulation of solid particles including bleaching compounds and organic peroxyacid bleach precursors in which a melt is formed of coating material in which the particles form a disperse phase, the melt is destabilised and then caused to crumble to a particulate material in which the disperse phase particles are embedded in the continuous (coating) phase. A variety of coating materials are disclosed and certain materials such as polyacrylic acid and cellulose acetate phthalate are taught as being useful where release of the coated material is dependent on pH.

Notwithstanding the advances in the art represented by the above disclosures, difficulties have still been encountered in providing peroxyacid precursor particles having acceptable physical characteristics for bulk storage and perhydrolysis rate, where the peroxyacid precursor is selected from those producing hydrophobic peroxyacid in aqueous wash liquor.

Furthermore, when hydrophobic cleaning of dingy, yellow stains is needed, the use of precursors which are hydrophobic in nature is necessary for providing excellent performance on dingy stains. Examples of such precursors are 3,5,5-tri-methyl hexanoyl oxybenzene sulfonate, nonanoyl oxybenzene sulfonate and derivatives of caproyl oxybenzene

sulfonate. However, due to their hydrophobic character, a solubility problem is encountered with the use of such activators.

Moreover, when derivatives of caproyl oxybenzene sulfonate such as (6-octanamido-caproyl)oxybenzenesulfonate, (6-nonanamidocaproyl)oxybenzene sulfonate, (6-decanamido-caproyl)oxybenzenesulfonate, and mixtures thereof are used, the Applicants have found that these problems were exacerbated.

The applicants have found that the above mentioned problems can be particularly troublesome when said peroxyacid bleach precursor is used under high hardness conditions, resulting upon dissolution in the formation of insoluble calcium salts.

The Applicants have now found that these problems can be overcome by the provision of a peroxyacid bleach precursor of a specific maximum size together with a water-soluble organic acid compound, where the peroxyacid bleach precursor is selected from those producing upon perhydrolysis hydrophobic peroxyacid.

Summary

According to the invention, there is provided a peroxyacid bleach precursor composition comprising:

- a)-a particulate peroxyacid bleach precursor of a size less than 100 μ m and selected from precursors which produce under perhydrolysis hydrophobic peroxyacid whose parent carboxylic acid has a critical micelle concentration less than 0.5 moles/litre, and
- b)-a water-soluble organic acid compound;
wherein said precursor and said organic acid are in close physical proximity.

For the purpose of the present invention, the term close physical proximity means one of the following:

- i) an agglomerate or extrudate in which said precursor and said organic acid are in intimate admixture;

- ii) a bleach precursor particulate coated with one or more layers wherein at least one layer contains the organic acid;
- iii) an organic acid compound coated with one or more layers wherein at least one layer contains the bleach activator.

It has to be understood by close physical proximity that the precursor and the organic acid are not two separate discrete particles in the detergent composition.

Detailed description of the invention

An essential feature of the invention is a peroxyacid bleach precursor which produces upon perhydrolysis hydrophobic peroxyacid whose parent carboxylic acid has a critical micelle concentration less than 0.5 moles/litre and wherein said critical micelle concentration is measured in aqueous solution at 20°-50°C. Preferably, the peroxyacid backbone chain contains at least 7 carbons which may be partly or totally branched, chained or cyclic and any mixtures thereof.

Peroxyacid bleach precursor

Peroxyacid bleach precursor compounds typically contain one or more N- or O-acyl groups, which precursors can be selected from a wide range of classes.

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

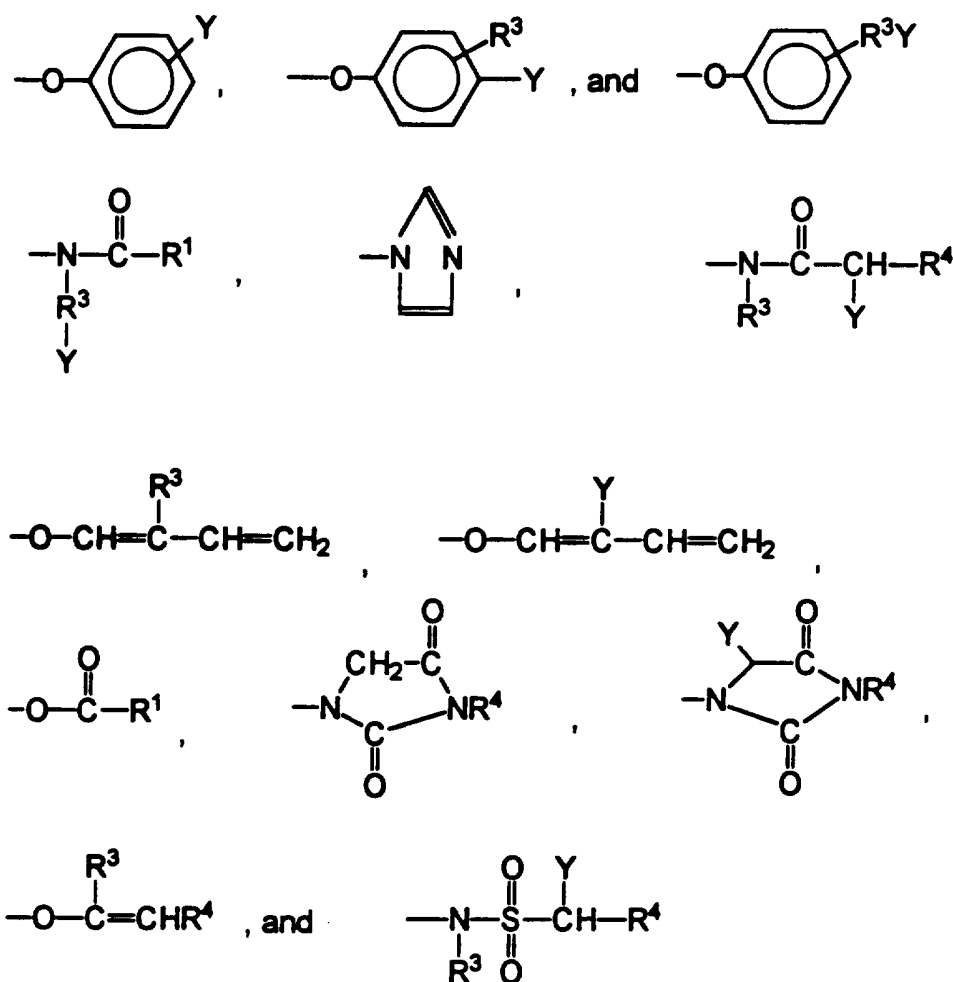


wherein R^1 is an aryl or alkaryl group with from about 1 to about 14 carbon atoms, R^2 is an alkylene, arylene, and alkarylene group containing from about 1 to 14 carbon atoms, and R^5 is H or an alkyl, aryl, or alkaryl group containing 1 to 10 carbon atoms and L can be essentially any leaving group. R^1 preferably contains from about 6 to 12 carbon atoms. R^2 preferably contains from about 4 to 8 carbon atoms. R^1 may be straight chain or branched alkyl, substituted aryl or alkaryl 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 R^2 . R^2 can include alkyl, aryl, wherein said R^2 may also contain halogen, nitrogen, sulphur and other typical substituent groups or organic compounds. R^5 is preferably H or methyl. R^1 and R^5 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 the group consisting of:



and mixtures thereof, wherein R^1 is an alkyl, aryl, or alkaryl group containing from 1 to 14 carbon atoms, R^3 is an alkyl chain containing from 1 to 8 carbon atoms, R^4 is H or R^3 , and Y is H or a solubilizing group. Any of R^1 , R^3 and R^4 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 $-\text{SO}_3^- \text{M}^+$, $-\text{CO}_2^- \text{M}^+$, $-\text{SO}_4^- \text{M}^+$, $-\text{N}^+(\text{R}^3)_4 \text{X}^-$ and $\text{O} < -\text{N}(\text{R}^3)_3$ and most preferably $-\text{SO}_3^- \text{M}^+$ and $-\text{CO}_2^- \text{M}^+$ wherein R^3 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 activators of the above formulae include derivatives of caproyl oxybenzene sulfonate selected from (6-octanamido-caproyl)oxybenzenesulfonate, (6-nonanamidocaproyl)oxy benzene sulfonate, (6-decanamido-caproyl)oxybenzenesulfonate, and mixtures thereof as described in EP-A-0170386.

Still another preferred class of bleach activator is the class of alkyl percarboxylic acid bleach precursors.

Preferred alkyl percarboxylic acid precursors include nonanoyl oxy benzene sulphonate (NOBS described in US 4,412,934) and 3,5,5-trimethyl hexanoyl oxybenzene sulfonate (ISONOBS described in EP120,591) and salts thereof.

Mixture of any of the peroxyacid bleach precursor, herein before described, may also be used.

The peroxyacid bleach precursors are normally incorporated at a level of from 20% to 95% by weight of the bleach precursor composition, preferably at least 50% and most preferably at least 60% by weight thereof.

In absolute terms the peroxyacid bleach precursor is typically from 1 % to 20% by weight, more preferably from 1 % to 10% by weight, most preferably from 1 % to 7% by weight of the detergent compositions.

Water-soluble organic acid compound

The composition of the invention contains as another essential component a water-soluble organic acid compound.

Organic acids compounds suitable for incorporation as agglomerating agents of the particles of the invention comprise aliphatic or aromatic carboxylates. The carboxylates may be monomeric, oligomeric or polymeric in nature and preferably comprise aliphatic carboxylic acids. Examples of monomeric aliphatic acid compounds are glycolic, glutamic, citraconic, succinic, 1-lactic, malonic, glutaric, adipic, maleic, malic, tartaric, citric, diglycolic and carboxymethyl succinic acids. Examples of polymeric acid compounds include poly(meth)acrylic acids and copolymeric derivatives with maleic anhydride. Preferably, the organic acid is a monomeric or oligomeric carboxylate and more preferably a monomeric aliphatic carboxylic acid. Preferred monomeric aliphatic acids are 1-lactic, citric and glycolic acids while preferred polymeric acids include polyacrylic acids of MWt 3000-5000, especially about 4500 and acrylic acid maleic anhydride copolymers of MWt 40,000-90,000. A preferred organic acid is citric acid.

The organic acid is incorporated at levels of from 5% to 50% by weight of the particulate to be agglomerated, more preferably from 5% to 25% by weight and most preferably from 7% to 20% by weight.

The incorporation of other ingredients additional to the organic peroxyacid bleach precursor compound and organic acid compound can be advantageous particularly in the processing of the bleach precursor particulates and also in enhancing the stability of detergent compositions in which the particulates are included. In particular, certain types of agglomerates may require the addition of one or more binder agents in order to assist in binding the organic peroxyacid bleach precursor compound and organic acid compound so as to produce particulates with acceptable physical characteristics. The binder agents may be present at a level of from 0% to 40% by weight of the particulate. Preferably, the

binder agents will be in intimate admixture with the organic peroxyacid bleach precursor compound and organic acid compound. Preferred binder agents have a melting point between 30°C-70°C. The binder agents are preferably present in amounts from 1-30% by weight of the particulate and most preferably from 2-20% by weight of the particulate.

Preferred binder agents include the C₁₀-C₂₀ alcohol ethoxylates containing from 5-100 moles of ethylene oxide per mole of alcohol and more preferably the C₁₅-C₂₀ primary alcohol ethoxylates containing from 20-100 moles of ethylene oxide per mole of alcohol. Of these tallow alcohol ethoxylated with 25 moles of ethylene oxide per mole of alcohol (TAE25) or 50 moles of ethylene oxide per mole of alcohol (TAE50) are preferred.

Other preferred binder agents include certain polymeric materials. Polyvinylpyrrolidones with an average molecular weight of from 12,000 to 700,000 and polyethylene glycols with an average weight of from 600 to 10,000 are examples of such polymeric materials. Copolymers of maleic anhydride with ethylene, methylvinyl ether, methacrylic acid or acrylic acid are further examples of polymeric materials useful as binder agents. Of these, copolymers of maleic anhydride with acrylic acid are preferred. These polymeric materials may be used as such or in combination with solvents such as water, propylene glycol and the above mentioned C₁₀-C₂₀ alcohol ethoxylates containing from 5-100 moles of ethylene oxide per mole. Further examples of binder agents include the C₁₀-C₂₀ mono- and diglycerol ethers and also the C₁₀-C₂₀ fatty acids. Solutions of certain inorganic salts including sodium silicate are also of use for this purpose.

Cellulose derivatives such as carboxymethylcellulose, and homo- or copolymeric polycarboxylic acid or their salts are other examples of suitable binder agents.

Other additives that are compatible with the peroxyacid precursors may also be included in detergent additive compositions in accordance with the invention. Examples of such additives include surfactants, fluorescers, enzymes, suds suppressors, dye transfer inhibition agents, soil suspending

agents, water soluble builders and chelating agents. Specific embodiments of such additives and their levels of incorporation are described hereinafter but the total level of the additives normally lies in the range of from 5% to 50% by weight of the additive composition. The peroxyacid precursor(s) should substantially form the major component of the precursor composition, ie. from 20% to 95% by weight of the agglomerate, preferably at least 50% by weight and most preferably at least 60% by weight thereof.

In preferred agglomerate embodiments of the invention the diameter of the pores forming the spaces between the agglomerated particles is selected by controlling the levels of compaction and shear applied during the agglomeration process. Too large a pore size results in an agglomerate of inadequate strength and a tendency to disintegrate during handling. Too small a pore size results in an agglomerate having a slow rate of dissolution. It has been found that a satisfactory agglomerate has a % of porosity of at least 12 corresponding to a mean pore diameter of at least 0.5 μ m and preferably in the range of from 0.6 to 5 micrometers. The porosity is measured according to the following technique, using a Micromeritics Poresizer 9320.

This equipment is manufactured by Micromeritics Instrument Corporation, One Micromeritics Drive, Norcross GA 30093-1877, USA and comprises a Penetrometer, Analyser and printer.

For this analysis the Penetrometer bulb is filled with a known weight (to 4dp) of particulate material. The Penetrometer is then fully assembled with the insulator seal, spring and retaining collar. This is then fitted into the low pressure port of the porosity analyser. The Penetrometer is then evacuated and the sample analysed under the following set point conditions:

Maximum measurable volume	0.387 ml
Total stem volume	0.412 ml
Maximum head pressure	4.68 psi (porosity pressure readings)
Penetrometer constant	10.79 l/pf (litres/pico farad)

at the following pressures: 2, 3, 4, 5.5, 7, 8.5, 10.5, 13, 16, 20, 23, 25 psia.

After this analysis the Penetrometer bulb is installed in the high pressure chamber and analysed under the same set point conditions and the printer then gives the median pore diameter and pore intrusion volumes for the sample. For the preferred pore diameter of at least 0.5 micrometers, the pore intrusion volume is at least 0.2 ml/g

Detergent compositions incorporating the peroxy acid bleach precursor particulates will normally contain from 1% to 20% of the precursor, more frequently from 1% to 10% and most preferably from 1% to 7%, on a composition weight basis.

Such detergent compositions will, of course, contain a source of alkaline hydrogen peroxide necessary to form a peroxyacid bleaching species in the wash solution and preferably will also contain other components conventional in detergent compositions. The precise nature of these additional components and levels of incorporation thereof will depend on the physical form of the composition, and the nature of the cleaning operation for which it is to be used.

The compositions of the invention may, for example, be formulated as hand and machine laundry detergent compositions, including laundry additive compositions and compositions suitable for use in the pretreatment of stained fabrics and machine dishwashing compositions. When incorporated in compositions suitable for use in a machine washing method, eg: machine laundry and machine dishwashing methods, the compositions of the invention preferably contain one or more additional deterative components.

Thus preferred detergent compositions will incorporate one or more of surfactants, organic and inorganic builders, soil suspending and anti-redeposition agents, suds suppressors, enzymes, fluorescent whitening agents photo activated bleaches, perfumes and colours.

Detergent compositions incorporating the particulate peroxyacid precursors 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 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 $2\text{Na}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}_2$, 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 variety of coatings can be used including borate, boric acid and citrate or 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. 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.

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 USP 3,929,678 issued to Laughlin and Heuring on December, 30, 1975. A list of suitable cationic

surfactants is given in USP 4,259,217 issued to Murphy on March 31, 1981.

Nonlimiting examples of surfactants useful herein typically at levels from 1% to 55%, by weight, include the conventional C₁₁-C₁₈ alkyl benzene sulfonates ("LAS") and primary, branched-chain and random C₁₀-C₂₀ alkyl sulfates ("AS"), the C₁₀-C₁₈ secondary (2,3) alkyl sulfates of the formula $\text{CH}_3(\text{CH}_2)_x(\text{CHOSO}_3^-\text{M}^+)\text{CH}_3$ and $\text{CH}_3(\text{CH}_2)_y(\text{CHOSO}_3^-\text{M}^+)\text{CH}_2\text{CH}_3$ 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 C₁₀-C₁₈ alkyl alkoxy sulfates ("AE_xS"; especially EO 1-7 ethoxy sulfates), C₁₀-C₁₈ alkyl alkoxy carboxylates (especially the EO 1-5 ethoxycarboxylates), the C₁₀-18 glycerol ethers, the C₁₀-C₁₈ alkyl polyglycosides and their corresponding sulfated polyglycosides, and C₁₂-C₁₈ alpha-sulfonated fatty acid esters. If desired, the conventional nonionic and amphoteric surfactants such as the C₁₂-C₁₈ alkyl ethoxylates ("AE") including the so-called narrow peaked alkyl ethoxylates and C₆-C₁₂ alkyl phenol alkoxyates (especially ethoxylates and mixed ethoxy/propoxy), C₁₂-C₁₈ betaines and sulfobetaines ("sultaines"), C₁₀-C₁₈ amine oxides, and the like, can also be included in the overall compositions. The C₁₀-C₁₈ N-alkyl polyhydroxy fatty acid amides can also be used. Typical examples include the C₁₂-C₁₈ N-methylglucamides. See WO 9,206,154. Other sugar-derived surfactants include the N-alkoxy polyhydroxy fatty acid amides, such as C₁₀-C₁₈ N-(3-methoxypropyl) glucamide. The N-propyl through N-hexyl C₁₂-C₁₈ glucamides can be used for low sudsing. C₁₀-C₂₀ conventional soaps may also be used. If high sudsing is desired, the branched-chain C₁₀-C₁₆ soaps may be used. Other suitable surfactants suitable for the purpose of the invention are the anionic alkali metal sarcosinates of formula:



wherein R is a C₉-C₁₇ linear or branched alkyl or alkenyl group, R¹ is a C₁-C₄ alkyl group and N 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. Mixtures of anionic and nonionic

surfactants are especially useful. Other conventional useful surfactants are listed in standard texts.

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

Builders - Detergent builders can 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. Liquid formulations typically comprise from 5% to 50%, more typically 5% to 30%, by weight, of detergent builder. Granular formulations typically comprise from 10% to 80%, more typically from 15% to 50% 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, 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). Importantly, the compositions herein function surprisingly well even in the presence of the so-called "weak" builders (as compared with phosphates) such as citrate, or in the so-called "underbuilt" situation that may occur with zeolite or layered silicate builders.

Examples of silicate builders are the so called 'amorphous' alkali metal silicates, particularly those having a $\text{SiO}_2\text{:Na}_2\text{O}$ ratio in the range 1.6:1 to 3.2:1 and crystalline layered silicates, such as the layered sodium silicates described in U.S. Patent 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- $\text{Na}_2\text{Si}_2\text{O}_5$ morphology form of layered silicate. It can be prepared by methods such as those described in German 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 $\text{NaMSi}_x\text{O}_{2x+1}\cdot y\text{H}_2\text{O}$ 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- $\text{Na}_2\text{Si}_2\text{O}_5$ (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 bleaches, and as a component of suds control systems.

Examples of carbonate builders are the alkaline earth and alkali metal carbonates as disclosed in German Patent Application No. 2,321,001 published on November 15, 1973.

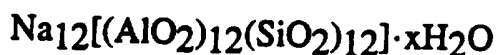
Aluminosilicate builders are useful in the present invention. Aluminosilicate builders are of great importance in most currently marketed heavy duty granular detergent compositions, and can also be a significant builder ingredient in liquid detergent formulations. Aluminosilicate builders include those having the empirical formula:



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. Patent 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:



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.

Organic detergent builders suitable for the purposes of the present invention 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. Patent 3,128,287 and U.S. Patent 3,635,830. See also "TMS/TDS" builders of U.S. Patent 4,663,071. Suitable ether polycarboxylates also include cyclic compounds, particularly alicyclic compounds, such as those described in U.S. Patents 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 of particular importance for heavy duty liquid detergent formulations due to their availability from renewable resources and their biodegradability. Citrates

can also 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 containing the present invention are the 3,3-dicarboxy-4-oxa-1,6-hexanedioates and the related compounds disclosed in U.S. Patent 4,566,984. Useful succinic acid builders include the C₅-C₂₀ 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. Patent 4,144,226 and in U.S. Patent 3,308,067. See also U.S. Pat. 3,723,322.

Fatty acids, e.g., C₁₂-C₁₈ 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.

In situations where phosphorus-based builders can be used, and especially in the formulation of bars used for hand-laundrying operations, the various alkali metal phosphates such as the well-known sodium tripolyphosphates, sodium pyrophosphate and sodium orthophosphate can be used. Phosphonate builders such as ethane-1-hydroxy-1,1-diphosphonate and other known phosphonates (see, for example, U.S. Patents 3,159,581; 3,213,030; 3,422,021; 3,400,148 and 3,422,137) can also be used.

Chelating Agents - The detergent compositions herein may also optionally contain one or more iron and/or manganese chelating agents. Such chelating agents can be selected from the group consisting of amino carboxylates, amino phosphonates, polyfunctionally-substituted aromatic chelating agents and mixtures therein, all as hereinafter defined. Without intending to be bound by theory, it is believed that the benefit of these materials is due in part to their exceptional ability to remove iron and manganese ions from washing solutions by formation of soluble chelates.

Amino carboxylates useful as optional chelating agents include ethylenediaminetetracetates, N-hydroxyethylethylenediaminetriacetates, nitrilotriacetates, ethylenediamine tetrapropionates, triethylenetetra-aminehexacetates, diethylenetriaminepentaacetates, and ethanoldiglycines, alkali metal, ammonium, and substituted ammonium salts therein and mixtures therein.

Amino phosphonates are also suitable for use as chelating agents in the compositions of the invention when at least low levels of total phosphorus are permitted in detergent compositions, and include ethylenediaminetetrakis (methylenephosphonates) available under the trademark DEQUEST from Monsanto. Preferably, these amino phosphonates do not contain alkyl or alkenyl groups with more than 6 carbon atoms.

Polyfunctionally-substituted aromatic chelating agents are also useful in the compositions herein. See U.S. Patent 3,812,044. Preferred compounds of this type in acid form are dihydroxydisulfobenzenes such as 1,2-dihydroxy-3,5-disulfobenzene.

Preferred biodegradable non-phosphorus chelants for use herein are ethylenediamine disuccinate ("EDDS"), especially the [S,S] isomer as described in U.S. Patent 4,704,233, ethylenediamine-N,N'-diglutamate (EDDG) and 2-hydroxypropylene-diamine-N,N'-disuccinate (HPDDS) compounds.

If utilized, these chelating agents will generally comprise from 0.1% to 10% by weight of the detergent compositions herein. More preferably, if utilized, the chelating agents will comprise from 0.1% to 3.0% by weight of such compositions.

Clay Soil Removal/Anti-redeposition Agents - The compositions according to the present invention can also optionally contain water-soluble ethoxylated amines having clay soil removal and antiredeposition properties. Granular detergent compositions which contain these compounds typically contain from 0.01% to 10.0% by weight of the water-soluble ethoxylated amines; liquid detergent compositions typically contain 0.01% to 5%.

The most preferred soil release and anti-redeposition agent is ethoxylated tetraethylenepentamine. Exemplary ethoxylated amines are further described in U.S. Patent 4,597,898, VanderMeer, issued July 1,

1986. 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. Patent 4,548,744. Other clay soil removal and/or anti redeposition agents known in the art can also be utilized in the compositions herein. Another type of preferred antiredeposition agent includes the carboxy methyl cellulose (CMC) materials. These materials are well known in the art.

Polymeric Soil Release Agent - Any polymeric soil release agent known to those skilled in the art can optionally be employed in the compositions and processes of this invention. 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.

Soil release agents characterised by poly(vinyl ester) hydrophobe segments include graft copolymers of poly(vinyl ester), e.g., C₁-C₆ 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. Patent 3,959,230 to Hays and U.S. Patent 3,893,929.

Another preferred polymeric soil release agent is a polyester with repeat units of ethylene terephthalate units 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. Patent 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 fully in U.S. Patent 4,968,451. Other suitable polymeric soil release agents include the terephthalate polyesters of U.S. Patent 4,711,730, the anionic end-capped oligomeric esters of U.S. Patent 4,721,580 and the block polyester oligomeric compounds of U.S. Patent 4,702,857.

Preferred polymeric soil release agents also include the soil release agents of U.S. Patent 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 detergent compositions herein, typically from 0.1 % to 5 %, preferably from 0.2 % to 3.0 %.

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.

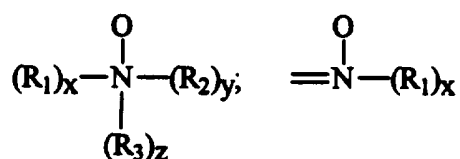
Dye Transfer Inhibiting Agents

The compositions according to the present invention may also include one or more materials effective for inhibiting the transfer of dyes from one fabric to another during the cleaning process. 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:



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 $pK_a < 10$, preferably $pK_a < 7$, more preferred $pK_a < 6$.

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".

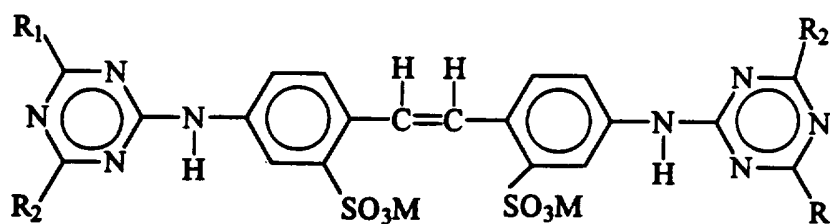
The most preferred polyamine N-oxide useful in the detergent compositions herein is poly(4-vinylpyridine-N-oxide) which has an average molecular weight of 50,000 and an amine to amine N-oxide ratio of 1:4.

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 polyvinylpyrrolidone ("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 detergent 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% 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. Tinopal-UNPA-GX is the preferred hydrophilic optical brightener useful in the detergent compositions herein.

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 specific optical brightener species which may be used in the present invention provide especially effective dye transfer inhibition performance benefits when used in combination with the selected polymeric dye transfer inhibiting agents hereinbefore described. The combination of such selected polymeric materials (e.g., PVNO and/or PVPVI) with such selected optical brighteners (e.g., Tinopal UNPA-GX, Tinopal 5BM-GX and/or Tinopal AMS-GX) provides significantly better dye transfer inhibition in aqueous wash solutions than does either of these two detergent composition components when used alone. Without being

bound by theory, it is believed that such brighteners work this way because they have high affinity for fabrics in the wash solution and therefore deposit relatively quick on these fabrics. The extent to which brighteners deposit on fabrics in the wash solution can be defined by a parameter called the "exhaustion coefficient". The exhaustion coefficient is in general as the ratio of a) the brightener material deposited on fabric to b) the initial brightener concentration in the wash liquor. Brighteners with relatively high exhaustion coefficients are the most suitable for inhibiting dye transfer in the context of the present invention.

Of course, it will be appreciated that 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 0.05% to 1.2%, by weight, into the detergent compositions herein. Commercial optical brighteners which may be useful in the present invention can be classified into subgroups, which include, but are not necessarily limited to, derivatives of stilbene, pyrazoline, coumarin, carboxylic acid, methinecyanines, dibenzothiphen-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).

Specific examples of optical brighteners which are useful in the present compositions are those identified in U.S. Patent 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, available from Hilton-Davis, located in Italy; the 2-(4-styryl-phenyl)-2H-naphthol[1,2-d]triazoles; 4,4'-bis-(1,2,3-triazol-2-yl)-stil-benes; 4,4'-bis(styryl)biphenyls; and the aminocoumarins. Specific examples of these brighteners include 4-methyl-7-diethyl- amino coumarin; 1,2-bis(-venzimidazol-2-yl)ethylene; 1,3-diphenyl-phrazolines; 2,5-bis(benzoxazol-2-yl)thiophene; 2-styryl-

naph-[1,2-d]oxazole; and 2-(stilbene-4-yl)-2H-naphtho-[1,2-d]triazole. See also U.S. Patent 3,646,015. Anionic brighteners are preferred herein.

Suds Suppressors - Compounds for reducing or suppressing the formation of suds can be incorporated into the compositions of the present invention. Suds suppression can be of particular importance in the so-called "high concentration cleaning process" and in front-loading European-style washing machines.

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., 1979). One category of suds suppressor of particular interest encompasses monocarboxylic fatty acid and soluble salts therein. See U.S. Patent 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 detergent 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 C₁₈-C₄₀ 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 di-alkali metal (e.g., K, Na, and Li) phosphates and phosphate esters. The hydrocarbons such as paraffin and haloparaffin can be utilized in liquid form. The liquid hydrocarbons will be liquid at room temperature and atmospheric pressure, and will have a pour point in the range of -40°C and 50°C, and a minimum boiling point not less than 110°C (atmospheric pressure). It is also known to utilise 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. Patent 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. Patent 4,265,779 and EP 354016.

Other silicone suds suppressors are disclosed in U.S. Patent 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. Patent 3,933,672 and in U.S. Patent 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 $(\text{CH}_3)_3\text{SiO}_{1/2}$ units of SiO_2 units in a ratio of from $(\text{CH}_3)_3\text{SiO}_{1/2}$ 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.

To illustrate this point further, typical liquid laundry detergent compositions with controlled suds will optionally comprise from 0.001 to 1, preferably from 0.01 to 0.7, most preferably from 0.05 to 0.5, weight % of said silicone suds suppressor, which comprises (1) a nonaqueous emulsion of a primary antifoam agent which is a mixture of (a) a polyorganosiloxane, (b) a resinous siloxane or a silicone resin-producing silicone compound, (c) a finely divided filler material, and (d) a catalyst to promote the reaction of mixture components (a), (b) and (c), to form silanolates; (2) at least one nonionic silicone surfactant; and (3) polyethylene glycol or a copolymer of polyethylene-polypropylene glycol having a solubility in water at room temperature of more than 2 weight %; and without polypropylene glycol. Similar amounts can be used in granular compositions, gels, etc. See also U.S. Patents 4,978,471 and 4,983,316; 5,288,431 and U.S. Patents 4,639,489 and 4,749,740, Aizawa et al at column 1, line 46 through column 4, line 35.

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 C₆-C₁₆ alkyl alcohols having a C₁-C₁₆ 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 detergent 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 detergent 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.

Enzymes

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, peroxidases, esterases and cellulases conventionally incorporated into detergent compositions. Suitable proteolytic enzymes are described in GB-A-1243784, EP-A-0130756 and USP 5185250 and 5204015. Suitable amylases are disclosed in GB-A-1296839 while cellulases are disclosed in USP 4435307, GB-A-2075028 and 2095275. Lipases for use in detergent compositions are disclosed in GB-A-1372034 and EP-A-0341947. A suitable peroxidase is disclosed by WO89/099813. A wide range of enzyme materials and means for their incorporation into synthetic detergent granules is also discussed in US Patents 3,519,570 and 3,533,139.

Fabric Softeners - Various through-the-wash fabric softeners, especially the impalpable smectite clays of U.S. Patent 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% 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. Patent 4,375,416 and U.S. Patent 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, solvents for liquid formulations, solid fillers for bar compositions, etc. If high sudsing is desired, suds boosters such as the C₁₀-C₁₆ alkanolamides can be incorporated into the compositions, typically at 1%-10% levels. The C₁₀-C₁₄ monoethanol and diethanol amides illustrate a typical class of such suds boosters. Use of such suds boosters with high sudsing adjunct surfactants such as the amine oxides, betaines and sultaines noted above is also advantageous. If desired, soluble magnesium salts such as MgCl₂, MgSO₄, and the like, can be added at levels of, typically, 0.1%-2%, to provide additional suds and to enhance grease removal performance.

Various deterative ingredients employed in the present compositions optionally can be further stabilized by absorbing said ingredients onto a porous hydrophobic substrate, then coating said substrate with a hydrophobic coating. Preferably, the deterative ingredient is admixed with a surfactant before being absorbed into the porous substrate. In use, the deterative ingredient is released from the substrate into the aqueous washing liquor, where it performs its intended deterative function.

To illustrate this technique in more detail, a porous hydrophobic silica (trademark SIPERNAT D10, DeGussa) is admixed with a proteolytic enzyme solution containing 3%-5% of C₁₃₋₁₅ ethoxylated alcohol (EO 7) nonionic surfactant. Typically, the enzyme/surfactant solution is 2.5 X the weight of silica. The resulting powder is dispersed with stirring in silicone oil (various silicone oil viscosities in the range of 500-12,500 can be used). The resulting silicone oil dispersion is emulsified or otherwise added to the final detergent matrix. By this means, ingredients such as the aforementioned enzymes, bleaches, bleach activators, bleach catalysts, photoactivators, dyes, fluorescers, fabric conditioners and hydrolyzable surfactants can be "protected" for use in detergents, including liquid laundry detergent compositions.

Liquid detergent compositions can contain water and other solvents as carriers. Low molecular weight primary or secondary alcohols exemplified by methanol, ethanol, propanol, and isopropanol are suitable. Monohydric alcohols are preferred for solubilizing surfactant, but polyols such as those containing from 2 to 6 carbon atoms and from 2 to 6 hydroxy groups (e.g., 1,3-propanediol, ethylene glycol, glycerine, and 1,2-propanediol) can also be used. The compositions may contain from 5% to 90%, typically 10% to 50% of such carriers.

The detergent 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. Liquid dishwashing product formulations preferably have a pH between 6.8 and 9.0. 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. The bulk density of granular detergent compositions is typically at least 450 g/litre, more usually at least 600 g/litre and more preferably from 650 g/litre to 1000 g/litre.

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

In the detergent compositions, the abbreviated component identifications have the following meanings:

XYAS	:	Sodium C _{1X} - C _{1Y} alkyl sulfate
25EY	:	A C ₁₂₋₁₅ predominantly linear primary alcohol condensed with an average of Y moles of ethylene oxide
C ₁₂ LAS	:	Sodium linear C ₁₂ alkyl benzene sulphonate
TAS	:	Sodium tallow alcohol sulphate
TAE _n	:	Tallow alcohol ethoxylated with n moles of ethylene oxide per mole of alcohol
C ₂₅ E ₃ S	:	Sodium C _{12-C15} branched alkyl sulphate condensed with three moles of ethylene oxide
45E7	:	A C ₁₄₋₁₅ predominantly linear primary alcohol condensed with an average of 7 moles of ethylene oxide
TFAA	:	C _{16-C18} alkyl N-methyl glucamide
Silicate	:	Amorphous Sodium Silicate (SiO ₂ :Na ₂ O ratio normally follows)
NaSKS-6	:	Crystalline layered silicate of formula -Na ₂ Si ₂ O ₅
Carbonate	:	Anhydrous sodium carbonate
CMC	:	Sodium carboxymethyl cellulose
Zeolite A	:	Hydrated Sodium Aluminosilicate of formula Na ₁₂ (Al ₁₀ Si ₂ O ₂) ₁₂ . 27H ₂ O having a primary particle size in the range from 1 to 10 micrometers

Polyacrylate	:	Homopolymer of acrylic acid of MWt 4000
Citrate	:	Tri-sodium citrate dihydrate
MA/AA	:	Copolymer of 1:4 maleic/acrylic acid, average molecular weight about 70,000.
Perborate	:	Sodium perborate tetrahydrate of nominal formula $\text{NaBO}_2 \cdot 3\text{H}_2\text{O} \cdot \text{H}_2\text{O}_2$
Perborate Monohydrate	:	Anhydrous sodium perborate bleach empirical formula $\text{NaBO}_2 \cdot \text{H}_2\text{O}_2$
Percarbonate	:	Sodium Percarbonate of nominal formula $2\text{Na}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}_2$
Savinase	:	proteolytic enzyme activity 4KNPU/g
Alcalase 3T	:	proteolytic enzyme activity 3AU/g
Cellulase IT	:	cellulytic enzyme activity 1000 SCEVU/g
Lipalase	:	Lipolytic enzyme activity 100kLU/g all sold by NOVO Industries AS
DETPMP	:	Diethylene triamine penta (Methylene phosphonic acid), marketed by Monsanto under the Trade name Dequest 2060
EDDS	:	Ethylenediamine disuccinate
PVNO	:	Poly (4-vinylpyridine)-N-oxide copolymer of vinylimidazole and vinylpyrrolidone having an average molecular weight of 10,000
Mixed Suds Suppressor	:	25% paraffin wax Mpt 50°C, 17% hydrophobic silica, 58% paraffin oil.

Example 1

An agglomerate having the following formulation was made in a Kenwood food mixer

	wt%
(6-octanamido-caproyl) oxybenzenesulfonate/ (6-decanamido-caproyl) oxybenzenesulfonate	60
citric acid	25
TAE 25	15
	100

A blend of (6-octanamido-caproyl) oxybenzenesulfonate/ (6-decanamido-caproyl) oxybenzenesulfonate in fine powder form (particle size less than 100 micrometers) and citric acid were added to the Kenwood food mixer and pre-mixed. The temperature of the powders was 25°C. The molten nonionic binder TAE25 was added to the powder mix over a period of 2 minutes. The resulting mass was further mixed for 30 seconds. The mixing was then stopped and the agglomerate removed from the Kenwood food mixer and cooled to ambient temperature.

The product was then sieved and materials that were greater than 1180 micrometers and smaller than 250 micrometers were removed.

Example 2

The same procedure as above was repeated with the exception of the blend of (6-octanamido-caproyl) oxybenzenesulfonate/ (6-decanamido-caproyl) oxybenzenesulfonate being replaced in the same amounts with a benzoyl caprolactam.

Example 3

Further experiment was carried out with the peroxyacid bleach precursor of example 1 and 2 taken respectively in their raw material form.

Example 4

For the purpose of the present invention, unrestrained dissolution conditions are defined as those existing in the Beaker Perhydrolysis Test as carried out using a Sotax Dissolution Tester Model AT6 supplied by Sotax AG CH-4008 BASEL Switzerland. This Apparatus comprises an array of polycarbonate beakers, each capable of holding 1 litre of water, supported in a thermostatically controlled water bath. Each beaker is provided with a paddle stirrer whose speed can be controlled.

Two beakers in the Sotax Tester are employed in the perhydrolysis procedure using the following method:

- 1- Set water bath to required temperature (40°C).
- 2- Add 1litre of water (12° Clark) to each Sotax beaker and allow to equilibrate to required temperature.
- 3- Sample accurately 2 x 10g samples of detergent and precursor.
- 4- Prepare a number of titration beakers by adding:
25ml 3:2 glacial acetic acid distilled water solution together with 2 ice cubes
- 5- Set the stirring speed of the Sotax to 150 rpm.
- 6- Add the first sample to Sotax beaker No.1 and start the clock (t=0 minutes). Add 5ml potassium iodide solution to the first titration beaker.
- 7- Take a 10ml aliquot from Sotax beaker No. 1 and discharge into the first titration beaker at t=1 minute.
- 8- Add the second sample to Sotax beaker No.2 at t= 1 minute and add 5 ml potassium iodide to a second titration beaker.
- 9- Titrate the first aliquot against 0.005 M sodium thiosulphate solution until the solution is first decolourised (The colour is slowly regenerated as the solution warms and the perhydrate reacts with the iodide).
- 10- Take a 10 ml aliquot from Sotax beaker No.2 at t= 2 minutes and discharge into the second titration beaker and repeat step .
- 11- Take further aliquots at the following times (t= minutes)

<u>Beaker No. 1</u>	<u>Beaker No.2</u>
(t)	(t)
1	2
3	4
5	6
10	11

The aliquots from Beaker No. 1 at 1 minute and from Beaker No. 2 at 2 minutes constitutes replicates and the results are averaged to give a figure from which the % perhydrolysis is calculated.

Material from each example was then incorporated into a model detergent formulation having the composition in % by weight.

45AS/25AS (3:1)	9.1
35AE3S	2.3
24E5	4.5
TFAA	2.0
Zeolite A	10.2
Na SKS-6/citric acid (79:21)	10.6
Carbonate	7.6
Peroxyacid bleach precursor composition	4.16
Percarbonate	22.5
EDDS	0.5
Protease	0.55
Lipase	0.15
Cellulase	0.28
Amylase	0.27
MA/AA	3.1
CMC	0.4
PVNO	0.03
Granular suds suppressor	1.5
Minors/misc to 100%	

The four formulations were then subjected to a Beaker Perhydrolysis Test as hereinbefore described and gave the peroxyacid yields shown in Table 1. Results are given for 1, 3, 5 & 10 minutes elapsed time and are expressed in percent of the theoretically available weight of peracid.

Table I (Temperature = 40°C) minutes from start of perhydrolysis				
Product with peroxyacid fraction of example	1	3	5	10
3 (C8:C10 oxybenzenesulfonate)	43	42	34	32
1	45	58	66	62
3 (benzoyl caprolactam)	14	37	52	71
2	20	31	40	55

It can be seen that the perhydrolysis rate of the blend of (6-octanamido-caproyl) oxybenzenesulfonate/ (6-decanamido-caproyl) oxybenzenesulfonate is significantly enhanced by the agglomeration with citric acid. No such enhancement can be seen when benzoyl caprolactam is similarly agglomerated.

Example 5

The same experiment as above was carried out but in a hard water environment (25° Clarck) at 60°C with only product with peroxyacid fraction of example 3(C8:C10 oxybenzenesulfonate) and 1.

The two formulations were then subjected to a Beaker Perhydrolysis Test as hereinbefore described and gave the peroxyacid yields shown in Table II. Results are given for 1, 3, 5 & 10 minutes elapsed time and are expressed in percent of the theoretically available weight of peracid.

Table II (Temperature = 60°C) minutes from start of perhydrolysis				
Product with peroxyacid fraction of example	1	3	5	10
3 (C8:C10 oxybenzenesulfonate)	58	66	71	53
1	86	88	87	66

It can be seen that the enhancement in perhydrolysis of the blend of (6-octanamido-caproyl) oxybenzenesulfonate/ (6-decanamido-caproyl) oxybenzenesulfonate is consistent over the temperature range and also in very hard water.

Example 6

The same experiment as in example 5 was conducted in a hard water environment (25° Clarck) at 30°C with the exception of the peroxyacid bleach precursor being replaced by (6-decanamido-caproyl) oxybenzenesulfonate with different % of porosity and different mean pore diameter.

The two formulations were then subjected to a Beaker Perhydrolysis Test as hereinbefore described and gave the peroxyacid yields shown in Table III. Results are given for 3, 5 & 10 minutes elapsed time and are expressed in percent of the theoretically available weight of peracid.

Table III (Temperature = 30°C)					
Product with	% of porosity	mean pore diameter (μm)	minutes from start of perhydrolysis		
			3	5	10
C10 oxybenzenesulfonate (raw material)*	-	-	25	31	34
C10 oxybenzenesulfonate (agglomerate)**	15.2	0.8	45	70	75
C10 oxybenzenesulfonate (agglomerate)**	11.9	0.4	36	38	42
C10 oxybenzenesulfonate (extrudate)	11.8	0.3	12	15	19

* according to Example 3

** as made according to Example 1

It can be seen that (6-decanamido-caproyl) oxybenzenesulfonate in agglomerate form affords a way of improving the perhydrolysis versus (6-decanamido-caproyl) oxybenzenesulfonate in raw material form.

Furthermore, it can also be seen that (6-decanamido-caproyl) oxybenzenesulfonate particles having a % of porosity > 12 and a mean pore diameter > 0.5μm show enhanced perhydrolysis.

Example 7

The following detergent compositions are in accordance with the invention.

	A	B	C	D
C ₁₂ LAS	6.5	6.5	7.6	6.9
TAS	3.0	3.0	1.3	2.0
C ₂₅ E ₃ S	0.15	0.15	0.15	0.15
C ₄₅ E ₇	4.0	5.0	1.3	4.0
Zeolite	18.0	17.0	17.0	20
Citrate	-	-	1.5	5.5
Citric Acid	2.3	1.8	2.6	-
SKS-6	8.7	6.5	9.5	-
Carbonate	16.0	15.5	7.0	15.4
Silicate (2.0 ratio)	0.5	0.5	0.5	3.0
Bicarbonate	4.5	7.5	1.5	-
MA/AA Copolymer:	4.0	4.5	3.2	4.0
CMC	0.3	0.3	0.2	0.3
Savinase	0.4	-	0.4	1.4
Lipolase	0.2	0.1	0.1	0.3
Cellulase	0.15	0.15	-	0.1
Alcalase	-	0.3	-	-
Perborate	-	-	9.0	11.6
Perborate Monohydrate	-	-	5.0	8.7
Percarbonate	17.5	16.5	-	-
DETPMP	0.4	0.4	0.4	0.4
MgSO ₄	0.4	0.4	0.4	0.4
Fluorescer	0.19	0.19	0.15	0.19
Suds Suppressor	0.8	0.8	0.8	0.8
Perfume	0.35	0.4	0.35	0.4
Peroxyacid precursor composition (1)	4.5	-	3.4	-
Peroxyacid precursor composition (2)	-	2.5	-	5.0

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Sulphate**Minors etc. to : 100 100 100 100****(1) as in Example 1****(2) as in Example 6 (6-decanamido-caproyl) oxybenzenesulfonate
agglomerate having a % of porosity = 15.2 and a mean pore diameter =
0.8 μ m)**

WHAT IS CLAIMED IS:

1-A peroxyacid bleach precursor composition comprising:

- a)-a particulate peroxyacid bleach precursor of a size less than 100 μ m and selected from precursors which produce under perhydrolysis hydrophobic peroxyacid whose parent carboxylic acid has a critical micelle concentration less than 0.5 moles/litre; and**
 - b)-a water-soluble organic acid compound;**
- wherein said precursor and said organic acid are in close physical proximity.**

2-A peroxyacid bleach precursor composition according to Claim 1, wherein the backbone chain of the peroxyacid contains more than 7 carbons.

3-A peroxyacid bleach precursor composition according to either one of Claims 1 or 2, wherein said organic acid compound is present in amount of from 5% to 50% by weight of the peroxyacid bleach precursor composition.

4-A peroxyacid bleach precursor composition according to any one of Claims 1-3, wherein said bleach precursor is selected from those containing one or more N-or O-acyl group.

5-A peroxyacid bleach precursor composition according to any one of Claims 1-4, wherein said bleach precursor is selected from 3,5,5-trimethyl hexanoyl oxybenzene sulfonate, nonanoyl oxybenzene sulfonate, derivatives of caproyl oxybenzene sulfonate and any mixtures thereof.

6-A peroxyacid bleach precursor composition according to any one of Claims 1-5, wherein said bleach activator is a derivative of caproyl oxybenzene sulfonate selected from (6-octanamido-caproyl)oxybenzenesulfonate, (6-nonanamidocaproyl)oxy benzene sulfonate, (6-decanamido-caproyl)oxybenzenesulfonate, and mixtures thereof.

7-A peroxyacid bleach precursor composition according to any one of Claims 1-6, wherein said organic acid compound is monomeric or oligomeric carboxylate.

8-A peroxyacid bleach precursor composition according to any one of Claims 1-7, wherein said organic acid compound is a monomeric aliphatic carboxylic acid selected from glycolic, 1-lactic and citric acids, preferably citric acid.

9-A peroxyacid bleach precursor composition according to any one of Claims 1-8, wherein said bleach precursor composition is an agglomerate further bound with a binder.

10-A peroxyacid bleach precursor composition according to any one of Claims 1-9, wherein said bleach precursor composition is an agglomerate having a mean pore diameter of at least 0.5 micrometers.

11-A detergent composition comprising a surfactant material, a source of alkaline hydrogen peroxide and further comprising a peroxyacid bleach precursor composition according to any one of Claims 1-10.

12-A detergent composition according to Claim 11, wherein said source of alkaline hydrogen peroxide is an inorganic perhydrate salt, preferably sodium perborate or sodium percarbonate.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US95/15494

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :C11D 3/20, 3/32,3/34,3/39, 3/395, 7/26, 7/38, 7/54,17/06

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. : 8/111; 252/90, 91, 95, 100, 102, 174, 174.13, 174.14, 174.19, 174.24, 186.27, 186.31, 186.38

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
NONE

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 5,002,691 [BOLKAN et al] 26 March 1991, See Col. 4, lines 1-65; Col. 12, lines 1-67; Col. 15, lines 10-12; TABLE VI; TABLE VII and the claims.	1-3
X,P	US, A, 5,411,673 [AGAR et al] 02 May 1995, See Col. 3, lines 1-67; Col. 4, lines 19-51; the Abstract and the claims.	1-4
Y	EP, A, 0 318 470 [GRADWELL et al] 31 May 1989, See the claims.	1-3
Y	EP, A, 0 598 170 [MARTINO et al] 25 May 1994, See the Examples.	1-3

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

* "A"	Special categories of cited documents: document defining the general state of the art which is not considered to be of particular relevance	"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
"E"	earlier document published on or after the international filing date	"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
"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)	"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
"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	"A"	document member of the same patent family

Date of the actual completion of the international search

16 FEBRUARY 1996

Date of mailing of the international search report

07 MAR 1996

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US95/15494

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.: 4-12
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.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US95/15494

A. CLASSIFICATION OF SUBJECT MATTER:

US CL :

8/111; 252/90, 91, 95, 100, 102, 174, 174.13, 174.14, 174.19, 174.24, 186.27, 186.31, 186.38