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(21) International Application Number: PCT/US99/15316 (22) International Filing Date: 8 July 1999 (08.07.99) (30) Priority Data: 60/092,073 8 July 1998 (08.07.98) US (71) Applicant (for all designated States except US): THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): HARTSHORN, Richard, Timothy [GB/GB]; 139 Dene Road, Wylam, Northumberland NE41 8EY (GB). BURNS, Michael, Eugene [US/US]; 7132 Valley Falls Court, Hamilton, OH 45011 (US). BURCKETT-ST. LAURENT, James, Charles, Theophile, Roger [GB/US]; 11477 Gideon Lane, Cincinnati, OH 45239 (US). MIRACLE, Gregory, Scot [US/US]; 3065 Old Oxford Road, Hamilton, OH 45013 (US). (74) Agents: REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217-1087 (US).		(81) Designated States: AE, AL, AM, AT, AT (Utility model), AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, CZ (Utility model), DE, DE (Utility model), DK, DK (Utility model), EE, EE (Utility model), ES, FI, FI (Utility model), GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KR (Utility model), KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SK (Utility model), SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>Without international search report and to be republished upon receipt of that report.</i>
(54) Title: NOVEL DIACYL PEROXIDES AND COMPOSITIONS CONTAINING SAME (57) Abstract The present invention relates to novel diacyl peroxides and compositions containing the activators, and more particularly to bleach and laundry compositions containing same.		

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NOVEL DIACYL PEROXIDES AND COMPOSITIONS CONTAINING SAME

TECHNICAL FIELD

5 The present invention relates to novel diacyl peroxides and compositions containing the activators, and more particularly to bleach and laundry compositions containing same.

BACKGROUND OF THE INVENTION

10 The formulation of bleaching compositions which effectively remove a wide variety of soils and stains from fabrics under wide-ranging usage conditions remains a considerable challenge to the laundry detergent industry. Challenges are also faced by the formulator of automatic dishwashing detergent compositions (ADD's), which are expected to efficiently cleanse and sanitize dishware, often under heavy soil loads. The challenges associated with the formulation of truly effective cleaning and
15 bleaching compositions have been increased by legislation which limits the use of effective ingredients such as phosphate builders in many regions of the world.

 Most conventional cleaning compositions contain mixtures of various deterative surfactants to remove a wide variety of soils and stains from surfaces. In addition, various deterative enzymes, soil suspending agents, non-phosphorus builders, optical
20 brighteners, and the like may be added to boost overall cleaning performance. Many fully-formulated cleaning compositions contain oxygen bleach, which can be a perborate or percarbonate compound. While quite effective at high temperatures, perborates and percarbonates lose much of their bleaching function at the low to moderate temperatures increasingly favored in consumer product use. Accordingly,
25 various bleach activators such as tetraacetythylenediamine (TAED) and nonanoyloxybenzenesulfonate (NOBS) have been developed to potentiate the bleaching action of perborate and percarbonate across a wide temperature range. NOBS is particularly effective on "dingy" fabrics.

 A limitation with activators such as the widely commercialized TAED is that it
30 is effective on hydrophilic soils but is unsatisfactory on hydrophobic soils. While NOBS remains a highly preferred bleach activator, alternative sources of bleaching are desired.

 The search, therefore, continues for more effective activator materials, especially for use in mildly alkaline washing liquors or with decreased levels of
35 perborate or other sources of hydrogen peroxide. Improved activator materials should be safe, effective, and will preferably be designed to interact with troublesome soils and stains. Various activators have been described in the

literature. Many are esoteric and expensive. This need remains, to find a bleach activator which is effective on all soils, can operate in all conditions and is cost effective.

BACKGROUND ART

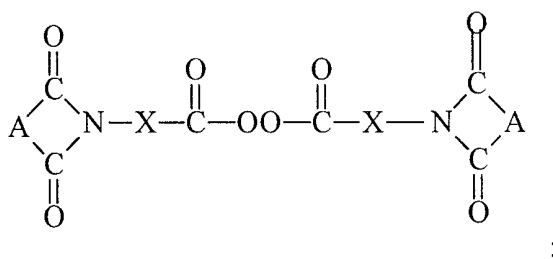
U.S. Patents 5,438,147 , 5,061,807, European Patents 0 325 288 A1, 0 325 289 A1, 0 366 041 A2, German Patent Application DE 3 823 172 A2 and Japanese Patent Application JP 4-28799 all disclose various imidopercarboxylic acid bleach activators. U.S. Patent 5,132,431 discloses a process for the continuous preparation of imidoperoxycarboxylic acids. European Patent 0 484 095 A2 discloses imidoperoxycarboxylic acids in detergent compositions. U.S. Patent 5,419,846 discloses imidoperoxycarboxylic acids encapsulated in granules. European Patent 0 435 379 A2 discloses suspended compositions containing imidoperoxycarboxylic acids.

SUMMARY OF THE INVENTION

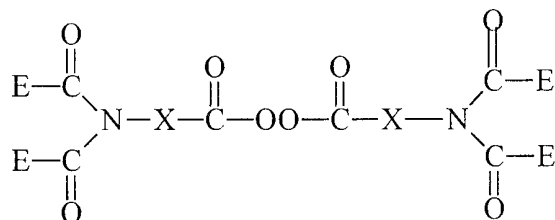
15 It has now been found that certain novel bleach activators are effective in removing soils and stains from fabrics and hard surfaces such as dishes. The activators are designed to function over a wide range of washing or soaking temperatures and are compatible with rubber surfaces, such as those of sump hoses used in some European front-loading washing machines. In short, detergent
20 compositions herein provide a substantial advantage over those known in the art, as will be seen from the disclosures hereinafter.

In accordance with a first aspect of the present invention, novel diacyl peroxides are provided. These novel compounds include those according to the formula:

25 (i)

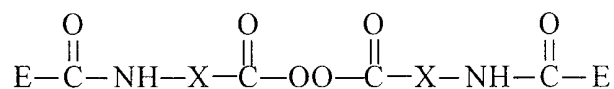


(ii)



; and

(iii)



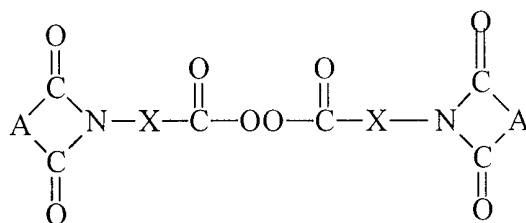
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wherein each of A, E and X comprise a substituted or unsubstituted hydrocarbyl group.

In accordance with the second aspect of this invention, detergent compositions are provided incorporating the novel diacyl peroxides as bleach activators. A detergent composition, comprising a compound selected from the group consisting of:

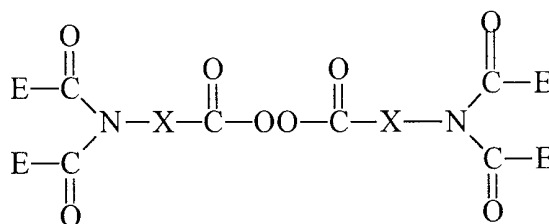
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(i)



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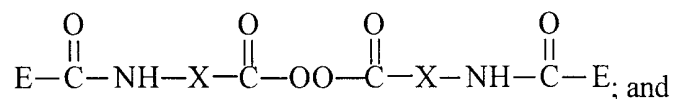
(ii)



;

15

(iii)

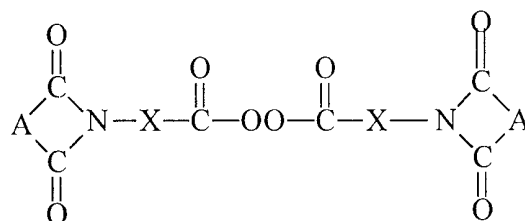


(iv) mixtures thereof;

wherein each of A, E and X comprise a substituted or unsubstituted hydrocarbyl group

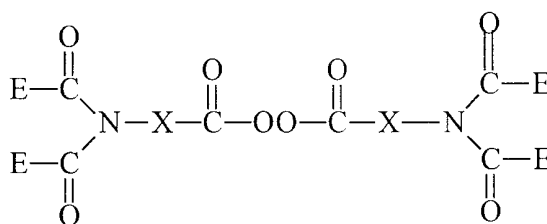
In accordance with the third aspect of this invention bleach additive compositions are provided incorporating the novel diacyl peroxides as bleach
5 activators. A bleach additive composition, comprising a compound selected from the group consisting of:

(i)



;

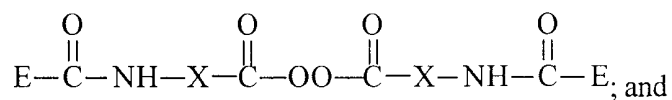
(ii)



;

5

(iii)



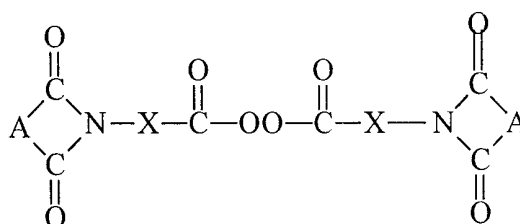
(iv) mixtures thereof;

wherein each of A, E and X comprise a substituted or unsubstituted hydrocarbyl group

10

In accordance with the fourth aspect of this invention bleach compositions are provided incorporating the novel diacyl peroxides as bleach activators. A bleach composition, comprising a compound selected from the group consisting of:

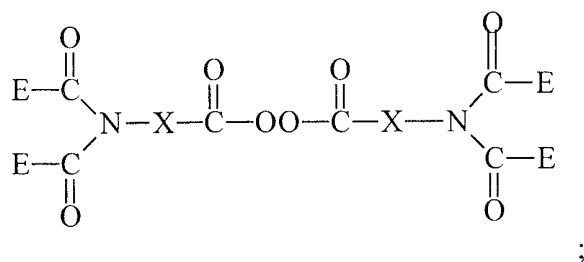
(i)



;

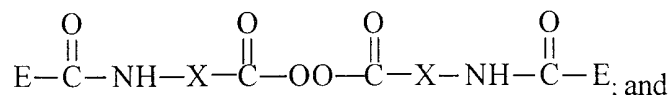
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(ii)



;

(iii)

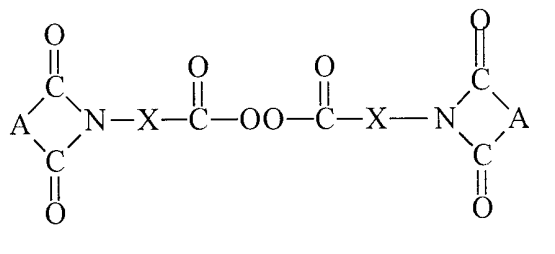


(iv) mixtures thereof;

5 wherein each of A, E and X comprise a substituted or unsubstituted hydrocarbyl group

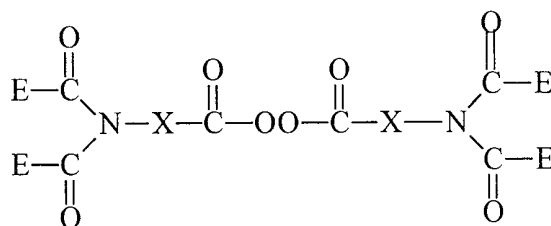
In accordance with the fifth aspect of this invention a method for cleaning soiled fabrics are provided incorporating the novel diacyl peroxides as bleach activators. A method for cleaning soiled fabrics, comprising a step of contacting
 10 said fabrics with an aqueous wash bath comprising a compound selected from the group consisting of:

(i)



;

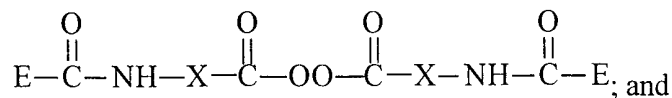
(ii)



;

15

(iii)



(iv) mixtures thereof;

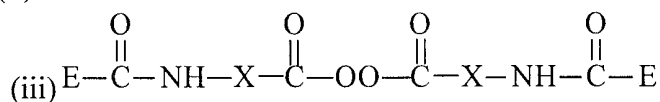
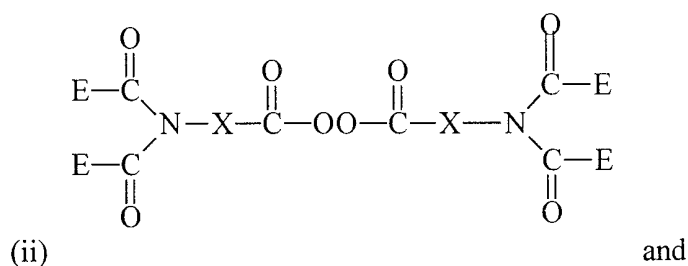
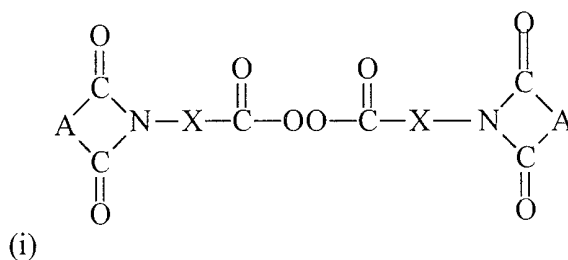
wherein each of A, E and X comprise a substituted or unsubstituted hydrocarbyl
 20 group

Accordingly, it is an aspect of the present invention to provide novel diacyl peroxides. It is another aspect of the present invention to provide bleach additive, bleach and detergent compositions including the diacyl peroxides. It is a further aspect of the invention to provide a method of cleaning soiled fabrics which use the diacyl peroxides. These, and other, aspect, features and advantages will be clear from the following detailed description and the appended claims.

All percentages, ratios and proportions herein are on a weight basis unless otherwise indicated. All documents cited herein are hereby incorporated by reference.

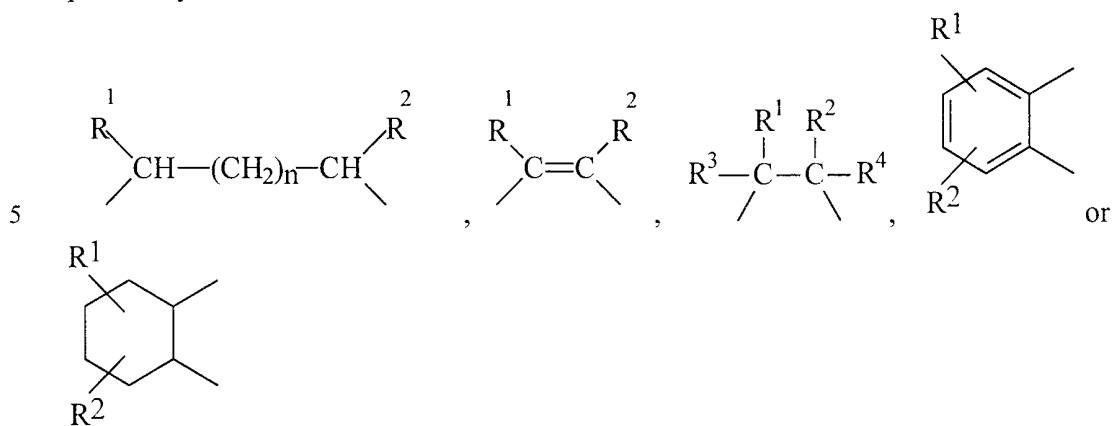
10 DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

In accordance with a first aspect of the present invention, novel diacyl peroxides are provided. These novel compounds include those according to the formula:

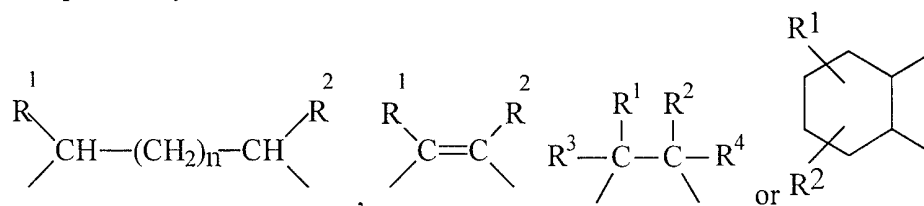


Each of A, E and X comprise a substituted or unsubstituted hydrocarbyl group, and each E, A and X can be the same or different. That is, E and X or A and X can be selected in such a fashion as to produce molecules which are symmetric or asymmetric across any axis. It is preferred that A, E and X are electrically neutral, that is, they are not charged and do not contain any charged moieties. It is preferred that at least one of A, E and X is a substituted or unsubstituted hydrocarbyl group comprising about 4 to about 20 carbon atoms. It is especially preferred that X is selected from substituted or unsubstituted linear or branched C₁-C₂₀ alkyl, substituted or unsubstituted linear or branched C₂-C₂₀ alkylene. It is even more

preferred that X is selected from linear or branched C₁-C₁₂ alkyl or linear or branched C₂-C₁₂ alkylene. It is most preferred that X is a branched or linear C₁-C₈ alkyl, branched or linear C₂-C₈ alkylene, most preferably linear C₁-C₆ alkyl. A is preferably selected from:



More preferably A is selected from:



10 wherein n denotes the number 0, 1, 2 or 3, preferably n is 0 or 1.

R¹ is selected from the group consisting of hydrogen, chloride, bromide, iodide, substituted or unsubstituted branched or linear C₁-C₂₀ alkyl, substituted or unsubstituted branched or linear C₂-C₂₀ alkenyl, substituted or unsubstituted aryl, and substituted or unsubstituted alkylaryl. R¹ is preferably hydrogen, chloride, substituted or unsubstituted branched or linear C₁-C₁₈ alkyl, substituted or unsubstituted branched or linear C₂-C₁₈ alkenyl, substituted or unsubstituted aryl, and substituted or unsubstituted alkylaryl. More preferably, R¹ is hydrogen, unsubstituted branched or linear C₁-C₁₆ alkyl, unsubstituted branched or linear C₂-C₁₆ alkenyl, substituted or unsubstituted phenyl, substituted or unsubstituted naphthyl, substituted or unsubstituted alkylphenyl substituted or unsubstituted alkylphenyl.

R² is selected from the group consisting of hydrogen, chloride, bromide, iodide, substituted or unsubstituted branched or linear C₁-C₂₀ alkyl, substituted or unsubstituted branched or linear C₂-C₂₀ alkenyl, substituted or unsubstituted aryl, and substituted or unsubstituted alkylaryl. R² is preferably hydrogen, chloride, substituted or unsubstituted branched or linear C₁-C₁₈ alkyl, substituted or

unsubstituted branched or linear C₂-C₁₈ alkenyl, substituted or unsubstituted aryl, and substituted or unsubstituted alkylaryl. More preferably, R² is hydrogen, unsubstituted branched or linear C₁-C₁₆ alkyl, unsubstituted branched or linear C₂-C₁₆ alkenyl, substituted or unsubstituted phenyl, substituted or unsubstituted naphthyl, substituted or unsubstituted alkylphenyl and substituted or unsubstituted alkyl naphthyl. It is further preferred that one of R¹ and R² is hydrogen or unsubstituted branched or linear C₁-C₆ alkyl and the other is either an unsubstituted branched or linear C₁-C₁₆ alkyl or an unsubstituted branched or linear C₂-C₁₆ alkenyl.

R³ and R⁴ are independently selected from hydrogen and C₁-C₆ substituted or unsubstituted branched or linear alkyl. Preferably R³ and R⁴ are independently selected from hydrogen and C₁-C₃ substituted or unsubstituted branched or linear alkyl.

E is an substituted or unsubstituted, branched or linear hydrocarbonyl group, and each E can be the same or different. That is, E can be selected in such a fashion as to produce molecules which are symmetric or asymmetric across any axis. Preferably E is selected from the group consisting of substituted or unsubstituted, branched or linear C₁-C₂₀ alkyl, substituted or unsubstituted, branched or linear C₂-C₂₀ alkenyl, substituted or unsubstituted aryl, and substituted or unsubstituted, branched or linear alkylaryl. It is even more preferred that each E has at least 6 carbon atoms.

Preparation of the bleach activator:

The bleach activators of the present application can be made via any of the well known synthesis methods.

Bleach activators of formulas (i) and (ii) can be made by either reacting the corresponding acyl chloride with sodium peroxide or hydrogen peroxide. Alternatively, the acid anhydride may be used in place of the acyl chloride. To form unsymmetrical compounds the acyl chloride or acyl anhydride is reacted with a peroxycarboxylic acid of a different alkyl moiety than the acyl chloride and acyl anhydride. These and other alternative synthesis methods are found in R. Hiatt in Organic Peroxides, (Ed. Dr. D. Swern), Vol. II, Wiley-Interscience, New York-London, 1970; pp. 779-930 and G. Bouillon et al., The Chemistry of Peroxides, (Ed. Saul Patai), John Wiley & sons, Chichester-New York-Brisbane-Toronto-Singapore, 1983; pp. 279-309, both of which are incorporated herein by reference.

Alternative preparations of the bleach activators of formulas (i) and (ii) can be found in European patent applications 484,095, 325,289 and 325,288, all of which are incorporated herein by reference.

Synthesis Examples:Example 1Di- ω -Phthalimidoperoxybutanoic acid

ω -Phthalimidobutanoyl chloride (25.2g, 0.1 mole) is dissolved in 175ml ether and the mixture cooled to 0°C. Hydrogen peroxide (4.25 g of 60% concentration, 0.075 mole) is added to the reaction flask, followed by dropwise addition of pyridine (9.5g, 0.12mole), while the temperature is maintained at 0-5°C. The diacyl peroxide precipitates as it forms. After the pyridine is completely added, the ice bath is removed and stirring of the slurry is continued for one hour. A homogenous solution is obtained by adding ether, which has been previously cooled to 0-2°C, at room temperature. The ether solution is washed with dilute hydrochloric acid, 5% potassium bicarbonate, followed then by water and is then dried over anhydrous sodium sulfate. The desired product is prepared in 98% yield.

Example 215 ω -[2-Dodecylsuccinimido]peroxyhexanoic acid

As per example 1 above but with replacement of ω -[2-dodecylsuccinimido]hexanoyl chloride for ω -Phthalimidobutanoyl chloride.

BLEACH, BLEACH ADDITIVE AND DETERGENT COMPOSITIONS

20 The present invention also relates to bleach additive, bleaching and detergent compositions containing the diacyl peroxides compounds as bleach activators. The amount of bleach activator which can be present in the composition of the present invention is from about 0.1% to about 99.9%, preferably about 1% to about 95%, more preferably about 1% to about 80%. The amount of bleach activator is dependent upon many factors including, the intended use of the composition, desired strength of the bleach activator and the other components present in the composition.

The bleach additive, bleaching and detergent compositions of the present invention can contain cleaning additives. These are any additives which are commonly used in bleaching, bleach additive and detergent compositions. These can be selected from, but not limited to, bleaches, surfactants, builders, enzymes and bleach catalysts. It would be readily apparent to one of ordinary skill in the art what cleaning additives are suitable for inclusion into the compositions. The list provided herein is by no means exhaustive and should be only taken as examples of suitable additives. It will also be readily apparent to one of ordinary skill in the art to only use those additives which are compatible with the diacyl peroxides and other components in the composition, for example, bleach.

Bleaches

Compositions according to the present invention may also include a source of hydrogen peroxide. A source of hydrogen peroxide herein is any convenient compound or mixture which under consumer use conditions provides an effective
5 amount of hydrogen peroxide. Levels may vary widely and are typically from about 0.1% to about 70%, more typically from about 0.2% to about 40% and even more typically from about 0.5% to about 25%, by weight of the compositions herein.

The source of hydrogen peroxide used herein can be any convenient source, including hydrogen peroxide itself. For example, perborate, e.g., sodium perborate
10 (any hydrate but preferably the mono- or tetra-hydrate), sodium carbonate peroxyhydrate or equivalent percarbonate salts, sodium pyrophosphate peroxyhydrate, urea peroxyhydrate, or sodium peroxide can be used herein. Mixtures of any convenient hydrogen peroxide sources can also be used. Organic sources of hydrogen peroxide, such as diacyl peroxides, can also be used. These are
15 extensively illustrated in Kirk Othmer, Encyclopedia of Chemical Technology, Vol. 17, John Wiley and Sons, 1982 at pages 27-90 and especially at pages 63-72, all incorporated herein by reference. Preferred is dibenzoyl peroxide.

A preferred percarbonate bleach comprises dry particles having an average particle size in the range from about 500 micrometers to about 1,000 micrometers,
20 not more than about 10% by weight of said particles being smaller than about 200 micrometers and not more than about 10% by weight of said particles being larger than about 1,250 micrometers. Optionally, the percarbonate can be coated with silicate, borate or water-soluble surfactants. Percarbonate is available from various commercial sources such as FMC, Solvay and Tokai Denka. The source of
25 hydrogen peroxide and diacyl peroxides activator are typically at a ratio of from about 3:1 to about 20:1, as expressed on a basis of peroxide:activator in units of moles H_2O_2 delivered by the hydrogen peroxide source to moles bleach activator.

Fully-formulated bleach additive and bleaching compositions, particularly those for use in laundry and automatic dishwashing, typically will also comprise
30 other adjunct ingredients to improve or modify performance.

Bleach catalysts

If desired, the compositions can contain a bleach catalyst. Preferred are manganese and cobalt-containing bleach catalysts.

One type of metal-containing bleach catalyst is a catalyst system comprising
35 a transition metal cation of defined bleach catalytic activity, such as copper, iron, titanium, ruthenium tungsten, molybdenum, or manganese cations, an auxiliary metal cation having little or no bleach catalytic activity, such as zinc or aluminum

cations, and a sequester having defined stability constants for the catalytic and auxiliary metal cations, particularly ethylenediaminetetraacetic acid, ethylenediaminetetra (methylenephosphonic acid) and water-soluble salts thereof. Such catalysts are disclosed in U.S. Pat. 4,430,243.

5 Other types of bleach catalysts include the manganese-based complexes disclosed in U.S. Pat. 5,246,621 and U.S. Pat. 5,244,594. Preferred examples of these catalysts include $\text{Mn}^{\text{IV}}_2(\text{u-O})_3(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})_2(\text{PF}_6)_2$ ("MnTACN"), $\text{Mn}^{\text{III}}_2(\text{u-O})_1(\text{u-OAc})_2(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})_2(\text{ClO}_4)_2$, $\text{Mn}^{\text{IV}}_4(\text{u-O})_6(1,4,7\text{-triacyclononane})_4(\text{ClO}_4)_2$, $\text{Mn}^{\text{III}}\text{Mn}^{\text{IV}}_4(\text{u-O})_1(\text{u-OAc})_2(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})_2(\text{ClO}_4)_3$, and mixtures thereof. See also European patent application publication no. 549,272. Other ligands suitable for use herein include 1,5,9-trimethyl-1,5,9-triazacyclododecane, 2-methyl-1,4,7-triazacyclononane, 2-methyl-1,4,7-triazacyclononane, and mixtures thereof.

15 The bleach catalysts useful in automatic dishwashing compositions and concentrated powder detergent compositions may also be selected as appropriate for the present invention. For examples of other suitable bleach catalysts herein see U.S. Pat. 4,246,612, U.S. Pat. 5,227,084 and WO 95/34628, December 21, 1995, the latter relating to particular types of iron catalyst.

20 See also U.S. Pat. 5,194,416 which teaches mononuclear manganese (IV) complexes such as $\text{Mn}(1,4,7\text{-trimethyl-1,4,7-triazacyclononane}(\text{OCH}_3)_3)_3(\text{PF}_6)$.

Still another type of bleach catalyst, as disclosed in U.S. Pat. 5,114,606, is a water-soluble complex of manganese (II), (III), and/or (IV) with a ligand which is a non-carboxylate polyhydroxy compound having at least three consecutive C-OH groups. Preferred ligands include sorbitol, iditol, dulcitol, mannitol, xylitol, arabitol, 25 adonitol, meso-erythritol, meso-inositol, lactose, and mixtures thereof.

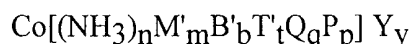
U.S. Pat. 5,114,611 teaches another useful bleach catalyst comprising a complex of transition metals, including Mn, Co, Fe, or Cu, with a non-(macro)-cyclic ligand. Preferred ligands include pyridine, pyridazine, pyrimidine, pyrazine, 30 imidazole, pyrazole, and triazole rings. Optionally, said rings may be substituted with substituents such as alkyl, aryl, alkoxy, halide, and nitro. Particularly preferred is the ligand 2,2'-bispyridylamine. Preferred bleach catalysts include Co-, Cu-, Mn-, or Fe- bispyridylmethane and bispyridylamine complexes. Highly preferred catalysts include $\text{Co}(2,2'\text{-bispyridylamine})\text{Cl}_2$, $\text{Di}(\text{isothiocyanato})\text{bispyridylamine-cobalt (II)}$, $\text{trisdi}(\text{pyridylamine-cobalt(II)}) \text{ perchlorate}$, $\text{Co}(2,2'\text{-bispyridylamine})_2\text{O}_2\text{ClO}_4$, $\text{Bis}(2,2'\text{-bispyridylamine}) \text{ copper(II) perchlorate}$, $\text{tris}(\text{di-2-pyridylamine}) \text{ iron(II) perchlorate}$, and mixtures thereof.

Other bleach catalyst examples include Mn gluconate, $\text{Mn}(\text{CF}_3\text{SO}_3)_2$, $\text{Co}(\text{NH}_3)_5\text{Cl}$, and the binuclear Mn complexed with tetra-N-dentate and bi-N-dentate ligands, including $\text{N}_4\text{Mn}^{\text{III}}(\text{u-O})_2\text{Mn}^{\text{IV}}\text{N}_4)^+$ and $[\text{Bipy}_2\text{Mn}^{\text{III}}(\text{u-O})_2\text{Mn}^{\text{IV}}\text{bipy}_2]-(\text{ClO}_4)_3$.

5 Particularly preferred manganese catalyst for use herein are bridged cyclo Mn catalysts those which are fully disclosed in copending patent applications PCT applications PCT/IB98/00298 (Attorney Docket No. 6527X), PCT/IB98/00299 (Attorney Docket No. 6537), PCT/IB98/00300 (Attorney Docket No. 6525XL&), and PCT/IB98/00302 (Attorney Docket No. 6524L#).

10 Other bleach catalysts are described, for example, in European patent application, publication no. 408,131 (cobalt complex catalysts), European patent applications, publication nos. 384,503, and 306,089 (metallo-porphyrin catalysts), U.S. 4,728,455 (manganese/multidentate ligand catalyst), U.S. 4,711,748 and European patent application, publication no. 224,952, (absorbed manganese on
15 aluminosilicate catalyst), U.S. 4,601,845 (aluminosilicate support with manganese and zinc or magnesium salt), U.S. 4,626,373 (manganese/ligand catalyst), U.S. 4,119,557 (ferric complex catalyst), German Pat. specification 2,054,019 (cobalt chelant catalyst) Canadian 866,191 (transition metal-containing salts), U.S. 4,430,243 (chelants with manganese cations and non-catalytic metal cations), and
20 U.S. 4,728,455 (manganese gluconate catalysts).

Preferred are cobalt (III) catalysts having the formula:



wherein cobalt is in the +3 oxidation state; n is an integer from 0 to 5 (preferably 4 or 5; most preferably 5); M' represents a monodentate ligand; m is an integer from 0
25 to 5 (preferably 1 or 2; most preferably 1); B' represents a bidentate ligand; b is an integer from 0 to 2; T' represents a tridentate ligand; t is 0 or 1; Q is a tetradentate ligand; q is 0 or 1; P is a pentadentate ligand; p is 0 or 1; and $n + m + 2b + 3t + 4q + 5p = 6$; Y is one or more appropriately selected counteranions present in a number y, where y is an integer from 1 to 3 (preferably 2 to 3; most preferably 2 when Y is a -1
30 charged anion), to obtain a charge-balanced salt, preferred Y are selected from the group consisting of chloride, nitrate, nitrite, sulfate, citrate, acetate, carbonate, and combinations thereof; and wherein further at least one of the coordination sites attached to the cobalt is labile under automatic dishwashing use conditions and the remaining coordination sites stabilize the cobalt under automatic dishwashing
35 conditions such that the reduction potential for cobalt (III) to cobalt (II) under alkaline conditions is less than about 0.4 volts (preferably less than about 0.2 volts)

versus a normal hydrogen electrode. Some preferred catalysts are the chloride salts having the formula $[\text{Co}(\text{NH}_3)_5\text{Cl}] \text{Y}_y$, and especially $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$.

More preferred are the present invention compositions which utilize cobalt (III) bleach catalysts having the formula:



wherein cobalt is in the +3 oxidation state; n is 4 or 5 (preferably 5); M is one or more ligands coordinated to the cobalt by one site; m is 0, 1 or 2 (preferably 1); B is a ligand coordinated to the cobalt by two sites; b is 0 or 1 (preferably 0), and when b=0, then m+n = 6, and when b=1, then m=0 and n=4; and T is one or more
10 appropriately selected counteranions present in a number y, where y is an integer to obtain a charge-balanced salt (preferably y is 1 to 3; most preferably 2 when T is a -1 charged anion); and wherein further said catalyst has a base hydrolysis rate constant of less than $0.23 \text{ M}^{-1} \text{ s}^{-1}$ (25°C). As fully disclosed in U.S. Patent application 5,559,261 and copending patent applications U.S. Serial Nos. 08/491,185 (P&G &
15 Case 5726), 08/491,462 (P&G Case 5727) and 08/491,238 (P&G Case 5728) all filed on June 16, 1995, incorporated herein by reference.

As a practical matter, and not by way of limitation, the cleaning compositions and cleaning processes herein can be adjusted to provide on the order of at least one part per hundred million of the active bleach catalyst species in the
20 aqueous washing medium, and will preferably provide from about 0.01 ppm to about 25 ppm, more preferably from about 0.05 ppm to about 10 ppm, and most preferably from about 0.1 ppm to about 5 ppm, of the bleach catalyst species in the wash liquor. In order to obtain such levels in the wash liquor of an automatic dishwashing process, typical automatic dishwashing compositions herein will comprise from
25 about 0.0005% to about 0.2%, more preferably from about 0.004% to about 0.08%, of bleach catalyst by weight of the cleaning compositions.

Conventional Bleach Activators

Compositions of the present invention may also include, in addition to the diacyl peroxides activators, a conventional bleach activator. "Conventional bleach
30 activators" herein are any bleach activators which do not respect the above-identified provisions in defining the diacyl peroxides activators herein. Levels of bleach activators herein may vary widely, e.g., from about 0.1% to about 90%, by weight of the composition, although lower levels, e.g., from about 0.1% to about 30%, or from about 0.1% to about 20% by weight of the composition are more typically used.

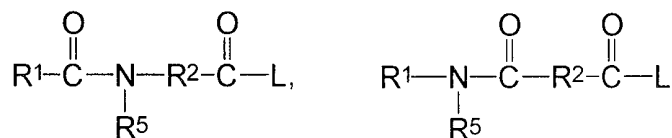
35 Preferred hydrophilic bleach activators include N,N,N',N'-tetraacetyl ethylene diamine (TAED) or any of its close relatives including the triacetyl or other unsymmetrical derivatives. TAED and the acetylated carbohydrates such as glucose

pentaacetate and tetraacetyl xylose are preferred hydrophilic bleach activators. Depending on the application, acetyl triethyl citrate, a liquid, also has some utility, as does phenyl benzoate.

Preferred hydrophobic bleach activators include sodium nonanoyloxybenzene sulfonate (NOBS or SNOBS), substituted amide types described in detail hereinafter, such as activators related to NAPAA, and activators related to certain imidoperacid bleaches, for example as described in U.S. Patent 5,061,807, issued October 29, 1991 and assigned to Hoechst Aktiengesellschaft of Frankfurt, Germany.

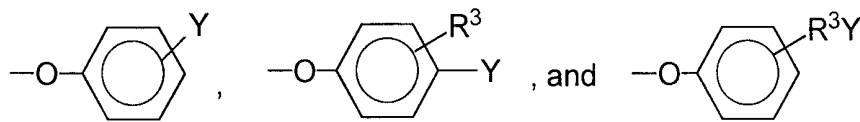
Other suitable bleach activators include sodium-4-benzoyloxy benzene sulfonate (SBOBS); sodium-1-methyl-2-benzoyloxy benzene-4-sulphonate; sodium-4-methyl-3-benzoyloxy benzoate (SPCC); trimethyl ammonium toluoyloxy-benzene sulfonate; or sodium 3,5,5-trimethyl hexanoyloxybenzene sulfonate (STHOBS).

Highly preferred bleach activators useful herein are amide-substituted and have either of the formulae:



or mixtures thereof, wherein R^1 is alkyl, aryl, or alkaryl containing from about 1 to about 14 carbon atoms including both hydrophilic types (short R^1) and hydrophobic types (R^1 is especially from 6, preferably about 8, to about 12), R^2 is alkylene, arylene or alkarylene containing from about 1 to about 14 carbon atoms, R^5 is H, or an alkyl, aryl, or alkaryl containing from about 1 to about 10 carbon atoms, and L is a leaving group.

Preferred bleach activators also include those of the above general formula wherein L is selected from the group consisting of:

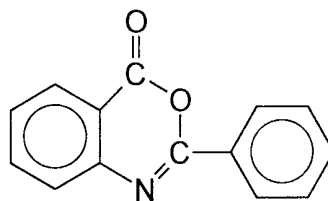


wherein R^3 is as defined above and Y is $-\text{SO}_3^-\text{M}^+$ or $-\text{CO}_2^-\text{M}^+$ wherein M is as defined above.

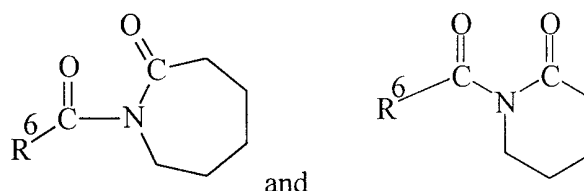
Preferred examples of bleach activators of the above formulae include:

(6-octanamidocaproyl)oxybenzenesulfonate,
 (6-nonanamidocaproyl)oxybenzenesulfonate,
 (6-decanamidocaproyl)oxybenzenesulfonate, and mixtures thereof.

Other useful activators, disclosed in U.S. 4,966,723, are benzoxazin-type, such as a C₆H₄ ring to which is fused in the 1,2-positions a moiety --C(O)OC(R¹)=N-. A highly preferred activator of the benzoxazin-type is:



5 Acyl lactam activators are very useful herein, especially the acyl caprolactams (see for example WO 94-28102 A) and acyl valerolactams (see U.S. 5,503,639) of the formulae:



wherein R⁶ is H, alkyl, aryl, alkoxyaryl, an alkaryl group containing from 1 to
10 about 12 carbon atoms, or substituted phenyl containing from about 6 to about 18
 carbons. See also U.S. 4,545,784 which discloses acyl caprolactams, including
 benzoyl caprolactam adsorbed into sodium perborate.

 Nonlimiting examples of additional activators useful herein are to be found
 in U.S. 4,915,854, U.S. 4,412,934 and 4,634,551. The hydrophobic activator
15 nonanoyloxybenzene sulfonate (NOBS) and the hydrophilic tetraacetyl ethylene
 diamine (TAED) activator are typical, and mixtures thereof can also be used.

 Additional activators useful herein include those of U.S. 5,545,349.
 Examples include esters of an organic acid and ethylene glycol, diethylene glycol or
 glycerin, or the acid imide of an organic acid and ethylenediamine; wherein the
20 organic acid is selected from methoxyacetic acid, 2-methoxypropionic acid, p-
 methoxybenzoic acid, ethoxyacetic acid, 2-ethoxypropionic acid, p-ethoxybenzoic
 acid, propoxyacetic acid, 2-propoxypropionic acid, p-propoxybenzoic acid,
 butoxyacetic acid, 2-butoxypropionic acid, p-butoxybenzoic acid, 2-
 methoxyethoxyacetic acid, 2-methoxy-1-methylethoxyacetic acid, 2-methoxy-2-
25 methylethoxyacetic acid, 2-ethoxyethoxyacetic acid, 2-(2-ethoxyethoxy)propionic
 acid, p-(2-ethoxyethoxy)benzoic acid, 2-ethoxy-1-methylethoxyacetic acid, 2-
 ethoxy-2-methylethoxyacetic acid, 2-propoxyethoxyacetic acid, 2-propoxy-1-
 methylethoxyacetic acid, 2-propoxy-2-methylethoxyacetic acid, 2-
 butoxyethoxyacetic acid, 2-butoxy-1-methylethoxyacetic acid, 2-butoxy-2-

methylethoxyacetic acid, 2-(2-methoxyethoxy)ethoxyacetic acid, 2-(2-methoxy-1-methylethoxy)ethoxyacetic acid, 2-(2-methoxy-2-methylethoxy)ethoxyacetic acid and 2-(2-ethoxyethoxy)ethoxyacetic acid.

Useful herein as oxygen bleaches are the inorganic peroxides such as Na_2O_2 ,
5 superoxides such as KO_2 , organic hydroperoxides such as cumene hydroperoxide and t-butyl hydroperoxide, and the inorganic peroxyacids and their salts such as the peroxosulfuric acid salts, especially the potassium salts of peroxodisulfuric acid and, more preferably, of peroxomonosulfuric acid including the commercial triple-salt form sold as OXONE by DuPont and also any equivalent commercially available
10 forms such as CUROX from Akzo or CAROAT from Degussa. Certain organic peroxides, such as dibenzoyl peroxide, may be useful, especially as additives rather than as primary oxygen bleach.

Mixed oxygen bleach systems are generally useful, as are mixtures of any oxygen bleaches with the known bleach activators, organic catalysts, enzymatic
15 catalysts and mixtures thereof; moreover such mixtures may further include brighteners, photobleaches and dye transfer inhibitors of types well-known in the art.

Other useful peracids and bleach activators herein are in the family of imidoperacids and imido bleach activators. These include phthaloylimidoperoxycaproic acid and related arylimido-substituted and
20 acyloxynitrogen derivatives. For listings of such compounds, preparations and their incorporation into laundry compositions including both granules and liquids, See U.S. 5,487,818; U.S. 5,470,988, U.S. 5,466,825; U.S. 5,419,846; U.S. 5,415,796; U.S. 5,391,324; U.S. 5,328,634; U.S. 5,310,934; U.S. 5,279,757; U.S. 5,246,620; U.S. 5,245,075; U.S. 5,294,362; U.S. 5,423,998; U.S. 5,208,340; U.S.
25 5,132,431 and U.S. 5,087,385.

Additional bleach activators are those described in U.S. Patent 5,130,045, Mitchell et al, and 4,412,934, Chung et al, and copending patent applications U. S. Serial Nos. 08/064,624, 08/064,623, 08/064,621, 08/064,562, 08/064,564, 08/082,270 and copending application to M. Burns, A. D. Willey, R. T. Hartshorn,
30 C. K. Ghosh, entitled "Bleaching Compounds Comprising Peroxyacid Activators Used With Enzymes" and having U.S. Serial No. 08/133,691 (P&G Case 4890R), all of which are incorporated herein by reference.

Quaternary substituted bleach activators may also be included. The present detergent compositions preferably comprise a quaternary substituted bleach activator
35 (QSBA) or a quaternary substituted peracid (QSP); more preferably, the former. Preferred QSBA structures are further described in copending U.S. Patent Nos. 5,460,747, 5,584,888 and 5,578,136, incorporated herein by reference.

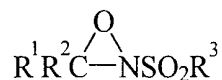
Useful diperoxyacids include, for example, 1,12-diperoxydodecanedioic acid (DPDA); 1,9-diperoxyazelaic acid; diperoxybrassicic acid; diperoxysebasic acid and diperoxyisophthalic acid; 2-decyldiperoxybutane-1,4-dioic acid; and 4,4'-sulphonylbisperoxybenzoic acid. Owing to structures in which two relatively hydrophilic groups are disposed at the ends of the molecule, diperoxyacids have sometimes been classified separately from the hydrophilic and hydrophobic monoperacids, for example as "hydrotropic". Some of the diperacids are hydrophobic in a quite literal sense, especially when they have a long-chain moiety separating the peroxyacid moieties.

10 Enzymatic sources of hydrogen peroxide

On a different track from the oxygen bleaching agents illustrated hereinabove, another suitable hydrogen peroxide generating system is a combination of a C1 -C4 alkanol oxidase and a C1 -C4 alkanol, especially a combination of methanol oxidase (MOX) and ethanol. Such combinations are disclosed in WO 94/03003. Other enzymatic materials related to bleaching, such as peroxidases, haloperoxidases, oxidases, superoxide dismutases, catalases and their enhancers or, more commonly, inhibitors, may be used as optional ingredients in the instant compositions.

Oxygen transfer agents and precursors

Also useful herein are any of the known organic bleach catalysts, oxygen transfer agents or precursors therefor. These include the compounds themselves and/or their precursors, for example any suitable ketone for production of dioxiranes and/or any of the hetero-atom containing analogs of dioxirane precursors or dioxiranes, such as sulfonimines $R^1R^2C=NSO_2R^3$, see EP 446 982 A, published 1991 and sulfonyloxaziridines, for example:



see EP 446,981 A, published 1991. Preferred examples of such materials include hydrophilic or hydrophobic ketones, used especially in conjunction with monoperoxyulfates to produce dioxiranes in situ, and/or the imines described in U.S. 5,576,282 and references described therein. Oxygen bleaches preferably used in conjunction with such oxygen transfer agents or precursors include percarboxylic acids and salts, percarbonic acids and salts, peroxymonosulfuric acid and salts, and mixtures thereof. See also U.S. 5,360,568; U.S. 5,360,569; and U.S. 5,370,826. In a highly preferred embodiment, the invention relates to a detergent composition which incorporates a transition-metal bleach catalyst in accordance with the invention, and organic bleach catalyst such as one named hereinabove, a primary oxidant such as a

hydrogen peroxide source, a hydrophilic bleach activator, and at least one additional detergent, hard-surface cleaner or automatic dishwashing adjunct. Preferred among such compositions are those which further include a precursor for a hydrophobic oxygen bleach, such as NOBS.

5 Deterative Surfactant

The compositions used in the present invention may also additionally include a deterative surfactant. The deterative surfactant may comprise from about 0.1%, to about 99.9%, by weight of the composition depending upon the particular surfactants used and the effects desired. More typical levels comprise from about
10 1% to about 80%, even more preferably from about 5% to about 60%, by weight of the composition. Examples of suitable surfactants can be found in McCutcheon's EMULSIFIERS AND DETERGENTS, North American Edition, 1997, McCutcheon Division, MC Publishing Company, in U.S. 3,929,678, Dec. 30, 1975 Laughlin, et al, and U.S. 4,259,217, March 31, 1981, Murphy; in the series "Surfactant Science",
15 Marcel Dekker, Inc., New York and Basel; in "Handbook of Surfactants", M.R. Porter, Chapman and Hall, 2nd Ed., 1994; in "Surfactants in Consumer Products", Ed. J. Falbe, Springer-Verlag, 1987 and "Surface Active Agents and Detergents" (Vol. I and II by Schwartz, Perry and Berch) all of which are incorporated hereinbefore by reference.

20 The deterative surfactant can be nonionic, anionic, ampholytic, zwitterionic, or cationic. Mixtures of these surfactants can also be used. Preferred deterative surfactants comprise anionic surfactants or mixtures of anionic surfactants with other surfactants, especially nonionic surfactants. Methods for use in conventional front loading washing machines and automatic dishwashing compositions typically
25 employ low sudsing deterative surfactants, such as mixed ethyleneoxy/propyleneoxy nonionics.

Those deterative surfactants which can act as a pH-reducing ionic nonsoap deterative surfactant include anionic surfactants in at least partially acidic form, semipolar surfactants, zwitterionic surfactants and mixtures of all three. Nonlimiting
30 examples of pH reducing surfactants include the conventional C₁₁-C₁₈ alkylbenzene sulfonates ("LAS") and primary, branched-chain and random C₁₀-C₂₀ alkyl sulfates ("AS"), the C₁₀-C₁₈ secondary (2,3) alkyl sulfates of the formula CH₃(CH₂)_x(CHOSO₃-M⁺)CH₃ and CH₃(CH₂)_y(CHOSO₃-M⁺)CH₂CH₃ where x and (y + 1) are integers of at least about 7, preferably at least about 9, and M is a
35 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), and C₁₂-C₁₈ alpha-sulfonated fatty acid esters.

Nonlimiting examples of surfactants useful herein include such as the conventional C₁₀-C₁₈ alkyl polyglycosides and their corresponding sulfated polyglycosides, C₁₂-C₁₈ alkyl and alkyl phenol alkoxylates (especially ethoxylates and mixed ethoxy/propoxy), C₁₂-C₁₈ betaines and sulfobetaines ("sultaines"), C₁₀-C₁₈ amine oxides, and the like. Another possible surfactant are the so-called Dianionics. These are surfactants which have at least two anionic groups present on the surfactant molecule. Some suitable dianionic surfactants are further described in copending U.S. Serial No. 60/020,503 (Docket No. 6160P), 60/020,772 (Docket No. 6161P), 60/020,928 (Docket No. 6158P), 60/020,832 (Docket No. 6159P) and 60/020,773 (Docket No. 6162P) all filed on June 28, 1996, and 60/023,539 (Docket No. 6192P), 60/023,493 (Docket No. 6194P), 60/023,540 (Docket No. 6193P) and 60/023,527 (Docket No. 6195P) filed on August 8th, 1996, the disclosures of which are incorporated herein by reference. Other conventional useful surfactants are listed in standard texts.

Additionally, the surfactant may be a branched alkyl sulfate, branched alkyl alkoxylate, branched alkyl alkoxylate sulfate or mid chain branched alkyl aryl sulfonate. These Surfactants are further described in copending U.S. Patent applications No. 60/053,319 Attorney docket No 6766P filed on July 21st, 1997, No. 60/053,318, Attorney docket No 6767P filed on July 21st, 1997, No. 60/053,321, Attorney docket No 6768P filed on July 21st, 1997, No. 60/053,209, Attorney docket No 6769P filed on July 21st, 1997, No. 60/053,328, Attorney docket No 6770P filed on July 21st, 1997, No. 60/053,186, Attorney docket No 6771P filed on July 21st, 1997, No. 60/061,971, Attorney docket No 6881P October 14, 1997, No. 60/061,975, Attorney docket No 6882P October 14, 1997, No. 60/062,086, Attorney docket No 6883P October 14, 1997, No. 60/061,916, Attorney docket No 6884P October 14, 1997, No. 60/061,970, Attorney docket No 6885P October 14, 1997, No. 60/062,407, Attorney docket No 6886P October 14, 1997,. Other suitable mid-chain branched surfactants can be found in U.S. Patent applications Serial Nos. 60/032,035 (Docket No. 6401P), 60/031,845 (Docket No. 6402P), 60/031,916 (Docket No. 6403P), 60/031,917 (Docket No. 6404P), 60/031,761 (Docket No. 6405P), 60/031,762 (Docket No. 6406P) and 60/031,844 (Docket No. 6409P). Mixtures of these branched surfactants with conventional linear surfactants are also suitable for use in the present compositions.

One class of nonionic surfactant particularly useful in detergent compositions of the present invention is condensates of ethylene oxide with a hydrophobic moiety.

The hydrophobic (lipophilic) moiety may be aliphatic or aromatic in nature. The length of the polyoxyethylene group which is condensed with any particular hydrophobic group can be readily adjusted to yield a water-soluble compound having the desired degree of balance between hydrophilic and hydrophobic elements.

Especially preferred nonionic surfactants of this type are the C₉-C₁₅ primary alcohol ethoxylates containing 3-8 moles of ethylene oxide per mole of alcohol, particularly the C₁₄-C₁₅ primary alcohols containing 6-8 moles of ethylene oxide per mole of alcohol, the C₁₂-C₁₅ primary alcohols containing 3-5 moles of ethylene oxide per mole of alcohol, and mixtures thereof.

Another suitable class of nonionic surfactants comprises sugar derived surfactants such as the polyhydroxy fatty acid amides of the formula:



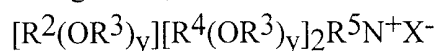
wherein: R¹ is H, C₁-C₈ hydrocarbyl, 2-hydroxyethyl, 2-hydroxypropyl, or a mixture thereof, preferably C₁-C₄ alkyl, more preferably C₁ or C₂ alkyl, most preferably C₁ alkyl (i.e., methyl); and R² is a C₅-C₃₂ hydrocarbyl moiety, preferably straight chain C₇-C₁₉ alkyl or alkenyl, more preferably straight chain C₉-C₁₇ alkyl or alkenyl, most preferably straight chain C₁₁-C₁₉ alkyl or alkenyl, or mixture thereof; and Z is a polyhydroxyhydrocarbyl moiety having a linear hydrocarbyl chain with at least 2 (in the case of glyceraldehyde) or at least 3 hydroxyls (in the case of other reducing sugars) directly connected to the chain, or an alkoxylated derivative (preferably ethoxylated or propoxylated) thereof. Z preferably will be derived from a reducing sugar in a reductive amination reaction; more preferably Z is a glycityl moiety. Suitable reducing sugars include glucose, fructose, maltose, lactose, galactose, mannose, and xylose, as well as glyceraldehyde. As raw materials, high dextrose corn syrup, high fructose corn syrup, and high maltose corn syrup can be utilized as well as the individual sugars listed above. These corn syrups may yield a mix of sugar components for Z. It should be understood that it is by no means intended to exclude other suitable raw materials. Z preferably will be selected from the group consisting of -CH₂-(CHOH)_n-CH₂OH, -CH(CH₂OH)-(CHOH)_{n-1}-CH₂OH, -CH₂-(CHOH)₂(CHOR')(CHOH)-CH₂OH, where n is an integer from 1 to 5, inclusive, and R' is H or a cyclic mono- or poly- saccharide, and alkoxylated derivatives thereof. Most preferred are glycityls wherein n is 4, particularly -CH₂-(CHOH)₄-CH₂OH.

R¹ can be, for example, N-methyl, N-ethyl, N-propyl, N-isopropyl, N-butyl, N-isobutyl, N-2-hydroxy ethyl, or N-2-hydroxy propyl. For highest sudsing, R¹ is preferably methyl or hydroxyalkyl. If lower sudsing is desired, R¹ is preferably C₂-

C₈ alkyl, especially n-propyl, iso-propyl, n-butyl, iso-butyl, pentyl, hexyl and 2-ethyl hexyl.

R²-CO-N< can be, for example, cocamide, stearamide, oleamide, lauramide, myristamide, capricamide, palmitamide, tallowamide, etc.

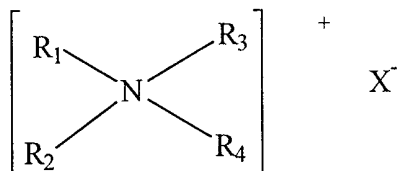
- 5 Cationic surfactants suitable for use in the compositions of the present invention include those having a long-chain hydrocarbyl group. Examples of such cationic co-surfactants include the ammonium co-surfactants such as alkyldimethylammonium halogenides, and those co-surfactants having the formula:



- 10 wherein R² is an alkyl or alkyl benzyl group having from 8 to 18 carbon atoms in the alkyl chain, each R³ is selected from the group consisting of -CH₂CH₂-, -CH₂CH(CH₃)-, -CH₂CH(CH₂OH)-, -CH₂CH₂CH₂-, and mixtures thereof; each R⁴ is selected from the group consisting of C₁-C₄ alkyl, C₁-C₄ hydroxyalkyl, benzyl ring structures formed by joining the two R⁴ groups, -CH₂CHOH-
15 CHOHCOR⁶CHOHCH₂OH wherein R⁶ is any hexose or hexose polymer having a molecular weight less than about 1000, and hydrogen when y is not 0; R⁵ is the same as R⁴ or is an alkyl chain wherein the total number of carbon atoms of R² plus R⁵ is not more than about 18; each y is from 0 to about 10 and the sum of the y values is from 0 to about 15; and X is any compatible anion.

- 20 Examples of other suitable cationic surfactants are described in following documents, all of which are incorporated by reference herein in their entirety: M.C. Publishing Co., McCutcheon's, Detergents & Emulsifiers, (North American edition 1997); Schwartz, et al., Surface Active Agents, Their Chemistry and Technology, New York: Interscience Publishers, 1949; U.S. Patent 3,155,591; U. S. Patent
25 3,929,678; U. S. Patent 3,959,461 U. S. Patent 4,387,090 and U.S. Patent 4,228,044.

Examples of suitable cationic surfactants are those corresponding to the general formula:



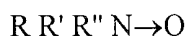
- 30 wherein R₁, R₂, R₃, and R₄ are independently selected from an aliphatic group of from 1 to about 22 carbon atoms or an aromatic, alkoxy, polyoxyalkylene, alkylamido, hydroxyalkyl, aryl or alkylaryl group having up to about 22 carbon atoms; and X is a salt-forming anion such as those selected from halogen, (e.g. chloride, bromide), acetate, citrate, lactate, glycolate, phosphate nitrate, sulfate, and alkylsulfate radicals. The aliphatic groups can contain, in addition to carbon and

hydrogen atoms, ether linkages, and other groups such as amino groups. The longer chain aliphatic groups, e.g., those of about 12 carbons, or higher, can be saturated or unsaturated. Preferred is when R₁, R₂, R₃, and R₄ are independently selected from C1 to about C22 alkyl. Especially preferred are cationic materials containing two long alkyl chains and two short alkyl chains or those containing one long alkyl chain and three short alkyl chains. The long alkyl chains in the compounds described in the previous sentence have from about 12 to about 22 carbon atoms, preferably from about 16 to about 22 carbon atoms, and the short alkyl chains in the compounds described in the previous sentence have from 1 to about 3 carbon atoms, preferably from 1 to about 2 carbon atoms.

Suitable levels of cationic deterative surfactant herein are from about 0.1% to about 20%, preferably from about 1% to about 15%, although much higher levels, e.g., up to about 30% or more, may be useful especially in nonionic : cationic (i.e., limited or anionic-free) formulations.

Amphoteric or zwitterionic deterative surfactants when present are usually useful at levels in the range from about 0.1% to about 20% by weight of the detergent composition. Often levels will be limited to about 5% or less, especially when the amphoteric is costly.

Suitable amphoteric surfactants include the amine oxides corresponding to the formula:



wherein R is a primary alkyl group containing 6-24 carbons, preferably 10-18 carbons, and wherein R' and R'' are, each, independently, an alkyl group containing 1 to 6 carbon atoms. The arrow in the formula is a conventional representation of a semi-polar bond.

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 automatic dishwashing and 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 about 1% builder. High performance compositions typically comprise from about 10% to about 80%, more typically from about 15% to about 50% by weight, of the detergent builder. Lower or higher levels of builder, however, are not excluded.

Inorganic or P-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 metaphosphates), phosphonates, phytic acid, silicates, carbonates (including bicarbonates and sesquicarbonates), sulphates, and aluminosilicates. However, non-phosphate builders are required in some locales. 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. See U.S. Pat. 4,605,509 for examples of preferred aluminosilicates.

Examples of silicate builders are the 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 layered silicates, such as the layered sodium silicates described in U.S. Patent 4,664,839, issued May 12, 1987 to H. P. Rieck. NaSKS-6[®] is 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 aluminum. NaSKS-6 is the $\delta\text{-Na}_2\text{SiO}_5$ morphology form of layered silicate and 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 α -, β - and γ - forms. Other silicates may also be useful, such as for example magnesium silicate, which can serve as a crispening agent in granular formulations, as a stabilizing agent for oxygen bleaches, and as a component of suds control systems.

Silicates useful in automatic dishwashing (ADD) applications include granular hydrous 2-ratio silicates such as BRITESIL[®] H20 from PQ Corp., and the commonly sourced BRITESIL[®] H24 though liquid grades of various silicates can be used when the ADD composition has liquid form. Within safe limits, sodium metasilicate or sodium hydroxide alone or in combination with other silicates may be used in an ADD context to boost wash pH to a desired level.

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. Various grades and types of sodium carbonate and sodium sesquicarbonate may be used, certain of which are particularly useful as carriers for other ingredients, especially deterative surfactants.

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
5 formula: $[M_z(zAlO_2)_y] \cdot xH_2O$ 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 about 0.5, and x is an integer from about 15 to about 264.

Useful aluminosilicate ion exchange materials are commercially available. These aluminosilicates can be crystalline or amorphous in structure and can be
10 naturally-occurring aluminosilicates or synthetically derived. A method for producing aluminosilicate ion exchange materials is disclosed in U.S. Patent 3,985,669, Krummel, et al, issued October 12, 1976. 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
15 preferred embodiment, the crystalline aluminosilicate ion exchange material has the formula: $Na_{12}[(AlO_2)_{12}(SiO_2)_{12}] \cdot xH_2O$ wherein x is from about 20 to about 30, especially about 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 about 0.1-10 microns in diameter. As with other builders such as carbonates, it may
20 be desirable to use zeolites in any physical or morphological form adapted to promote surfactant carrier function, and appropriate particle sizes may be freely selected by the formulator.

Organic detergent builders suitable for the purposes of the present invention include, but are not restricted to, a wide variety of polycarboxylate compounds. As
25 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 neutralized salt or "overbased". When utilized in salt form, alkali metals, such as sodium, potassium, and lithium, or alkanolammonium salts are preferred.

30 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 Berg, U.S. Patent 3,128,287, issued April 7, 1964, and Lamberti et al, U.S. Patent 3,635,830, issued January 18, 1972. See also "TMS/TDS" builders of U.S. Patent 4,663,071,
35 issued to Bush et al, on May 5, 1987. 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, 1, 3, 5-trihydroxy benzene-2, 4, 6-trisulphonic acid, and carboxymethyloxysuccinic acid, the various alkali metal, ammonium and substituted ammonium salts of polyacetic
5 acids such as ethylenediaminetetraacetic 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
10 salt), are polycarboxylate builders of particular importance for heavy duty laundry detergent formulations due to their availability from renewable resources and their biodegradability. Citrates can also be used in combination with zeolite and/or layered silicate builders. Oxydisuccinates are also especially useful in such compositions and combinations.

Also suitable in the detergent compositions of the present invention are the
15 3,3-dicarboxy-4-oxa-1,6-hexanedioates and the related compounds disclosed in U.S. Patent 4,566,984, Bush, issued January 28, 1986. 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
20 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 European Patent Application 86200690.5/0,200,263, published November 5, 1986.

Other suitable polycarboxylates are disclosed in U.S. Patent 4,144,226,
25 Crutchfield et al, issued March 13, 1979 and in U.S. Patent 3,308,067, Diehl, issued March 7, 1967. See also U.S. Patent 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
30 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-laundering operations, the various alkali metal phosphates such as the well-known sodium tripolyphosphates, sodium
35 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. However, in general, phosphorous-based builders are not desired.

Chelating Agents

The compositions herein may also optionally contain one or more heavy
5 metal chelating agents, such as diethylenetriaminepentaacetic acid (DTPA). More generally, chelating agents suitable for use herein can be selected from the group consisting of aminocarboxylates, aminophosphonates, polyfunctionally-substituted aromatic chelating agents and mixtures thereof. Without intending to be bound by theory, it is believed that the benefit of these materials is due in part to their
10 exceptional ability to remove heavy metal ions from washing solutions by formation of soluble chelates; other benefits include inorganic film or scale prevention. Other suitable chelating agents for use herein are the commercial DEQUEST® series, and chelants from Monsanto, DuPont, and Nalco, Inc.

Aminocarboxylates useful as optional chelating agents include
15 ethylenediaminetetracetates, N-hydroxyethylethylenediaminetriacetates, nitrilotriacetates, ethylenediamine tetrapropionates, triethylenetetraaminehexacetates, diethylenetriamine-pentaacetates, and ethanoldiglycines, alkali metal, ammonium, and substituted ammonium salts therein and mixtures therein.

20 Aminophosphonates 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). Preferably, these aminophosphonates do not contain alkyl or alkenyl groups with more than about 6 carbon atoms.

25 Polyfunctionally-substituted aromatic chelating agents are also useful in the compositions herein. See U.S. Patent 3,812,044, issued May 21, 1974, to Connor et al. Preferred compounds of this type in acid form are dihydroxydisulfobenzenes such as 1,2-dihydroxy-3,5-disulfobenzene.

A highly preferred biodegradable chelator for use herein is ethylenediamine
30 disuccinate ("EDDS"), especially (but not limited to) the [S,S] isomer as described in U.S. Patent 4,704,233, November 3, 1987, to Hartman and Perkins. The trisodium salt is preferred though other forms, such as magnesium salts, may also be useful.

If utilized, especially in ADD compositions, these chelating agents or
35 transition-metal-selective sequestrants will preferably comprise from about 0.001% to about 10%, more preferably from about 0.05% to about 1% by weight of the bleaching compositions herein.

Dispersant Polymers

The compositions of the present invention may also include from about 0.1% to about 20%, more preferably from about 0.5% to about 10% by weight of the composition of a dispersant polymer. Dispersant polymers are compounds which act
5 as soil suspending agents in the aqueous wash liquor. That is, they act to suspend the soils in solution and prevent the soils from re-depositing on the surfaces of fabrics or dishes. This allows soils to be removed with the wash liquor. Dispersant polymers are well-known and conventional and are available from BASF Corp. and Rohm & Haas. Typical examples include polyethoxylated amines and acrylic
10 acid/maleic acid copolymers.

Soil Release Agents

The compositions according to the present invention may optionally comprise one or more soil release agents. Polymeric soil release agents are characterized by having both hydrophilic segments, to hydrophilize the surface of
15 hydrophobic fibers, such as polyester and nylon, and hydrophobic segments, to deposit upon hydrophobic fibers and remain adhered thereto through completion of the laundry cycle 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.

20 If utilized, soil release agents will generally comprise from about 0.01% to about 10% preferably from about 0.1% to about 5%, more preferably from about 0.2% to about 3% by weight, of the composition.

The following, all included herein by reference, describe soil release polymers suitable for use in the present invention. U.S. 5,691,298 Gosselink et al.,
25 issued November 25, 1997; U.S. 5,599,782 Pan et al., issued February 4, 1997; U.S. 5,415,807 Gosselink et al., issued May 16, 1995; U.S. 5,182,043 Morrall et al., issued January 26, 1993; U.S. 4,956,447 Gosselink et al., issued September 11, 1990; U.S. 4,976,879 Maldonado et al. issued December 11, 1990; U.S. 4,968,451 Scheibel et al., issued November 6, 1990; U.S. 4,925,577 Borchert, Sr. et al., issued
30 May 15, 1990; U.S. 4,861,512 Gosselink, issued August 29, 1989; U.S. 4,877,896 Maldonado et al., issued October 31, 1989; U.S. 4,771,730 Gosselink et al., issued October 27, 1987; U.S. 711,730 Gosselink et al., issued December 8, 1987; U.S. 4,721,580 Gosselink issued January 26, 1988; U.S. 4,000,093 Nicol et al., issued December 28, 1976; U.S. 3,959,230 Hayes, issued May 25, 1976; U.S. 3,893,929
35 Basadur, issued July 8, 1975; and European Patent Application 0 219 048, published April 22, 1987 by Kud et al.

Further suitable soil release agents are described in U.S. 4,201,824 Voilland et al.; U.S. 4,240,918 Lagasse et al.; U.S. 4,525,524 Tung et al.; U.S. 4,579,681 Ruppert et al.; U.S. 4,220,918; U.S. 4,787,989; EP 279,134 A, 1988 to Rhone-Poulenc Chemie; EP 457,205 A to BASF (1991); and DE 2,335,044 to Unilever N.V., 1974; all incorporated herein by reference.

Deterstive Enzymes

The compositions of the present invention may also include the presence of at least one deterstive enzyme. "Deterstive enzyme", as used herein, means any enzyme having a cleaning, stain removing or otherwise beneficial effect in a composition. Suitable optional enzymes include cellulases, hemicellulases, peroxidases, proteases, gluco-amylases, amylases, lipases, cutinases, pectinases, xylanases, reductases, oxidases, phenoloxidases, lipoxygenases, ligninases, pullulanases, tannases, pentosanases, malanases, β -glucanases, arabinosidases and mixtures thereof of any suitable origin, such as vegetable, animal, bacterial, fungal and yeast origin. Preferred deterstive enzymes are hydrolases such as proteases, amylases and lipases. Highly preferred for automatic dishwashing are amylases and/or proteases, including both current commercially available types and improved types which, though more bleach compatible, have a remaining degree of bleach deactivation susceptibility.

In general, as noted, preferred compositions herein comprise one or more deterstive enzymes. If only one enzyme is used, it is preferably an amyolytic enzyme when the composition is for automatic dishwashing use. Highly preferred for automatic dishwashing is a mixture of proteolytic enzymes and amyolytic enzymes. More generally, 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, stability versus active detergents, builders, etc. In this respect bacterial or fungal enzymes are preferred, such as bacterial amylases and proteases, and fungal cellulases.

Enzymes are normally incorporated in the instant detergent compositions at levels sufficient to provide a "cleaning-effective amount". The term "cleaning-effective amount" refers to any amount capable of producing a cleaning, stain removal or soil removal effect on substrates such as fabrics, dishware and the like. Since enzymes are catalytic materials, such amounts may be very small. In practical terms for current commercial preparations, typical amounts are up to about 5 mg by weight, more typically about 0.01 mg to about 3 mg, of active enzyme per gram of

the composition. Stated otherwise, the compositions herein will typically comprise from about 0.001% to about 6%, preferably 0.01%-1% by weight of a commercial enzyme preparation. Protease enzymes are usually present in such commercial preparations at levels sufficient to provide from 0.005 to 0.1 Anson units (AU) of activity per gram of composition. For automatic dishwashing purposes, it may be desirable to increase the active enzyme content of the commercial preparations, in order to minimize the total amount of non-catalytically active materials delivered and thereby improve spotting/filming results.

Suitable examples of proteases are the subtilisins which are obtained from particular strains of *B. subtilis* and *B. licheniformis*. 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 as ESPERASE®. The preparation of this enzyme and analogous enzymes is described in British Patent Specification No. 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 European Patent Application 130,756, published January 9, 1985) and Protease B (see European Patent Application Serial No. 87303761.8, filed April 28, 1987, and European Patent Application 130,756, Bott et al, published January 9, 1985).

An especially preferred protease, referred to as "Protease D" is a carbonyl hydrolase variant having an amino acid sequence not found in nature, which is derived from a precursor carbonyl hydrolase by substituting a different amino acid for a plurality of amino acid residues at a position in said carbonyl hydrolase equivalent to position +76, preferably also in combination with one or more amino acid residue positions equivalent to those selected from the group consisting of +99, +101, +103, +104, +107, +123, +27, +105, +109, +126, +128, +135, +156, +166, +195, +197, +204, +206, +210, +216, +217, +218, +222, +260, +265, and/or +274 according to the numbering of *Bacillus amyloliquefaciens* subtilisin, as described in WO 95/10615 published April 20, 1995 by Genencor International.

Other preferred protease enzymes include protease enzymes which are a carbonyl hydrolase variant having an amino acid sequence not found in nature, which is derived by replacement of a plurality of amino acid residues of a precursor carbonyl hydrolase with different amino acids, wherein said plurality of amino acid residues replaced in the precursor enzyme correspond to position +210 in combination with one or more of the following residues: +33, +62, +67, +76, +100,

+101, +103, +104, +107, +128, +129, +130, +132, +135, +156, +158, +164, +166, +167, +170, +209, +215, +217, +218 and +222, where the numbered positions correspond to naturally-occurring subtilisin from Bacillus amyloliquefaciens or to equivalent amino acid residues in other carbonyl hydrolases or subtilisins (such as Bacillus lentus subtilisin). Preferred enzymes according include those having position changes +210, +76, +103, +104, +156, and +166.

Useful proteases are also described in PCT publications: WO 95/30010 published November 9, 1995 by The Procter & Gamble Company; WO 95/30011 published November 9, 1995 by The Procter & Gamble Company; WO 95/29979 published November 9, 1995 by The Procter & Gamble Company.

Amylases suitable herein include, for example, α -amylases described in British Patent Specification No. 1,296,839 (Novo), RAPIDASE®, International Bio-Synthetics, Inc. and TERMAMYL®, Novo Industries.

Preferred amylases herein have the commonality of being derived using site-directed mutagenesis from one or more of the *Bacillus* amylases, especially the *Bacillus* alpha-amylases, regardless of whether one, two or multiple amylase strains are the immediate precursors.

As noted, "oxidative stability-enhanced" amylases are preferred for use herein despite the fact that the invention makes them "optional but preferred" materials rather than essential. Such amylases are non-limitingly illustrated by the following:

(a) An amylase according to the hereinbefore incorporated WO/94/02597, Novo Nordisk A/S, published Feb. 3, 1994, as further illustrated by a mutant in which substitution is made, using alanine or threonine (preferably threonine), of the methionine residue located in position 197 of the *B.licheniformis* alpha-amylase, known as TERMAMYL®, or the homologous position variation of a similar parent amylase, such as *B. amyloliquefaciens*, *B.subtilis*, or *B.stearothermophilus*;

(b) Stability-enhanced amylases as described by Genencor International in a paper entitled "Oxidatively Resistant alpha-Amylases" presented at the 207th American Chemical Society National Meeting, March 13-17 1994, by C. Mitchinson. Therein it was noted that bleaches in automatic dishwashing detergents inactivate alpha-amylases but that improved oxidative stability amylases have been made by Genencor from *B.licheniformis* NCIB8061. Methionine (Met) was identified as the most likely residue to be modified. Met was substituted, one at a time, in positions 8,15,197,256,304,366 and 438 leading to specific mutants, particularly important being M197L and M197T with the M197T variant being the

most stable expressed variant. Stability was measured in CASCADE® and SUNLIGHT®;

(c) Also preferred herein are amylase variants having additional modification in the immediate parent available from Novo Nordisk A/S and are those referred to
5 by the supplier under the tradename DURMAMYL®;

(d) Particularly preferred are amylase variants as disclosed in WO95/26397 and in the co-pending application to Novo Nordisk PCT/DK96/00056 and characterized by having a specific activity at least 25% higher than the specific activity of Termamyl® at a temperature range of 25°C to 55°C and at a pH value in
10 the range of 8 to 10, measured by the Phadebas® α -amylase activity assay and is obtained from an alkalophilic *Bacillus* species (such as the strains NCIB 12289, NCIB 12512, NCIB 12513 and DSM 935) comprising the following amino acid sequence in the N-terminal: His-His-Asn-Gly-Thr-Asn-Gly-Thr-Met-Met-Gln-Tyr-Phe-Glu-Trp-Tyr-Leu-Pro-Asn-Asp

15 Cellulases usable in, but not preferred, for the present invention include both bacterial or fungal cellulases. Typically, they will have a pH optimum of between 5 and 9.5. Suitable cellulases are disclosed in U.S. Patent 4,435,307, Barbesgaard et al, issued March 6, 1984, which discloses fungal cellulase produced from *Humicola insolens* and *Humicola* strain DSM1800 or a cellulase 212-producing fungus
20 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. CAREZYME® (Novo) is especially useful.

Suitable lipase enzymes for detergent use include those produced by
25 microorganisms of the *Pseudomonas* group, such as *Pseudomonas stutzeri* ATCC 19.154, as disclosed in British Patent 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
30 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 Disoynt Co., The Netherlands, and lipases ex *Pseudomonas gladioli*. The LIPOLASE® enzyme derived from *Humicola*
35 *lanuginosa* and commercially available from Novo (see also EPO 341,947) is a preferred lipase for use herein. Another preferred lipase enzyme is the D96L variant of the native *Humicola lanuginosa* lipase, as described in WO 92/05249 and

Research Disclosure No. 35944, March 10, 1994, both published by Novo. In general, lipolytic enzymes are less preferred than amylases and/or proteases for automatic dishwashing embodiments of the present invention.

Peroxidase enzymes can be used in combination with oxygen sources, e.g.,
5 percarbonate, perborate, persulfate, hydrogen peroxide, etc. They are typically 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.
10 Peroxidase-containing detergent compositions are disclosed, for example, in PCT International Application WO 89/099813, published October 19, 1989, by O. Kirk, assigned to Novo Industries A/S. The present invention encompasses peroxidase-free automatic dishwashing composition embodiments.

A wide range of enzyme materials and means for their incorporation into
15 synthetic detergent compositions are also disclosed in U.S. Patent 3,553,139, issued January 5, 1971 to McCarty et al. Enzymes are further disclosed in U.S. Patent 4,101,457, Place et al, issued July 18, 1978, and in U.S. Patent 4,507,219, Hughes, issued March 26, 1985. Enzymes for use in detergents can be stabilized by various techniques. Enzyme stabilization techniques are disclosed and exemplified in U.S.
20 Patent 3,600,319, issued August 17, 1971 to Gedge, et al, and European Patent Application Publication No. 0 199 405, Application No. 86200586.5, published October 29, 1986, Venegas. Enzyme stabilization systems are also described, for example, in U.S. Patent 3,519,570.

Brightener

25 Any optical brighteners or other brightening or whitening agents known in the art can be incorporated at levels typically from about 0.05% to about 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,
30 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).

35 Specific examples of optical brighteners which are useful in the present compositions are those identified in U.S. Patent 4,790,856, issued to Wixon on December 13, 1988. 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-stryl-phenyl)-2H-naphthol[1,2-d]triazoles; 4,4'-bis- (1,2,3-triazol-2-yl)-stil-
benes; 4,4'-bis(stryl)bisphenyls; 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-stryl-naphth-[1,2-d]oxazole; and 2-(stilbene-4-yl)-2H-naphtho- [1,2-
d]triazole. See also U.S. Patent 3,646,015, issued February 29, 1972 to Hamilton.
Anionic brighteners are preferred herein.

Other additives

Usual ingredients can include one or more materials for assisting or enhancing cleaning performance, treatment of the substrate to be cleaned, or to modify the aesthetics of the composition. Usual deterative adjuncts of detergent
compositions include the ingredients set forth in U.S. Pat. No. 3,936,537, Baskerville et al. Adjuncts which can also be included in detergent compositions employed in the present invention, in their conventional art-established levels for use (generally from 0% to about 20% of the detergent ingredients, preferably from about 0.5% to about 10%), include other active ingredients such as enzyme stabilizers,
color speckles, anti-tarnish and/or anti-corrosion agents, dyes, fillers, optical brighteners, germicides, alkalinity sources, hydrotropes, anti-oxidants, enzyme stabilizing agents, perfumes, dyes, solubilizing agents, clay soil removal/anti-redeposition agents, carriers, processing aids, pigments, solvents for liquid formulations, fabric softeners, static control agents, solid fillers for bar
compositions, etc. Dye transfer inhibiting agents, including polyamine N-oxides such as polyvinylpyridine N-oxide can be used. Dye-transfer-inhibiting agents are further illustrated by polyvinylpyrrolidone and copolymers of N-vinyl imidazole and N-vinyl pyrrolidone. 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 detergent ingredient is admixed with a surfactant before being absorbed into the porous substrate. In use, the detergent ingredient is released from the substrate into the aqueous washing liquor, where it performs its intended
5 detergent 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.
10 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
15 hydrolyzable surfactants can be "protected" for use in detergents, including liquid laundry detergent compositions.

Form of composition

The compositions of the present invention can be in any of the conventional forms. This includes, but is not limited to, solids, bars, powders, granules, both high
20 bulk density 550g/l or higher and the so-called "fluffy" granules with a bulk density of 400 g/l or less, tablets, liquids, both aqueous and non-aqueous, liquid-gels and flakes.

Liquid Compositions

The present invention can be formulated as a liquid including the
25 aforementioned ingredients. Liquid compositions, including gels, typically contain some water and other fluids 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 about 6 carbon atoms and from 2 to about 6 hydroxy
30 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. Liquid compositions according to the present invention are formulated acidic to deliver an in-use alkaline pH. Formulation pH is generally from about 2 to about 5 and preferably from about 2.5 to about 4.5. In-use pH is
35 generally from about 7 to about 9.5, preferably from about 7.5 to about 8.5. The use of lower formulation pH provides for more stability of the diacyl peroxides activator

in solution. Furthermore, when formulating liquid compositions, the source of hydrogen peroxide, if any, is preferably, hydrogen peroxide itself.

Coating

Various deterative ingredients employed in the compositions of the present invention optionally can be further stabilized by absorbing the ingredients onto a porous hydrophobic substrate, then coating the substrate with a hydrophobic coating. Preferably, the deterative ingredient is admixed with a surfactant before being adsorbed 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 2.5X 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.

Granular Compositions

Various means and equipment are available to prepare high density (i.e., greater than about 550, preferably greater than about 650, grams/liter or "g/l"), high solubility, free-flowing, granular detergent compositions according to the present invention. Current commercial practice in the field employs spray-drying towers to manufacture granular laundry detergents which often have a density less than about 500 g/l. In this procedure, an aqueous slurry of various heat-stable ingredients in the final detergent composition are formed into homogeneous granules by passage through a spray-drying tower, using conventional techniques, at temperatures of about 175°C to about 225°C. However, if spray drying is used as part of the overall process herein, additional process steps as described hereinafter must be used to obtain the level of density (i.e., > 650 g/l) required by modern compact, low dosage detergent products.

For example, spray-dried granules from a tower can be densified further by loading a liquid such as water or a nonionic surfactant into the pores of the granules and/or subjecting them to one or more high speed mixer/densifiers. A suitable high speed mixer/densifier for this process is a device marketed under the tradename

"Lödige CB 30" or "Lödige CB 30 Recycler" which comprises a static cylindrical mixing drum having a central rotating shaft with mixing/cutting blades mounted thereon. In use, the ingredients for the detergent composition are introduced into the drum and the shaft/blade assembly is rotated at speeds in the range of 100-2500 rpm to provide thorough mixing/densification. See Jacobs et al, U.S. Patent 5,149,455, issued September 22, 1992. The preferred residence time in the high speed mixer/densifier is from about 1 to 60 seconds. Other such apparatus includes the devices marketed under the tradename "Shugi Granulator" and under the tradename "Drais K-TTP 80).

Another process step which can be used to densify further spray-dried granules involves grinding and agglomerating or deforming the spray-dried granules in a moderate speed mixer/densifier so as to obtain particles having lower intraparticle porosity. Equipment such as that marketed under the tradename "Lödige KM" (Series 300 or 600) or "Lödige Ploughshare" mixer/densifiers are suitable for this process step. Such equipment is typically operated at 40-160 rpm. The residence time of the detergent ingredients in the moderate speed mixer/densifier is from about 0.1 to 12 minutes conveniently measured by dividing the steady state mixer/densifier weight by the throughput (e.g., Kg/hr). Other useful equipment includes the device which is available under the tradename "Drais K-T 160". This process step which employs a moderate speed mixer/densifier (e.g. Lödige KM) can be used by itself or sequentially with the aforementioned high speed mixer/densifier (e.g. Lödige CB) to achieve the desired density. Other types of granules manufacturing apparatus useful herein include the apparatus disclosed in U.S. Patent 2,306,898, to G. L. Heller, December 29, 1942.

While it may be more suitable to use the high speed mixer/densifier followed by the low speed mixer/densifier, the reverse sequential mixer/densifier configuration is also contemplated by the invention. One or a combination of various parameters including residence times in the mixer/densifiers, operating temperatures of the equipment, temperature and/or composition of the granules, the use of adjunct ingredients such as liquid binders and flow aids, can be used to optimize densification of the spray-dried granules in the process of the invention. By way of example, see the processes in Appel et al, U.S. Patent 5,133,924, issued July 28, 1992 (granules are brought into a deformable state prior to densification); Delwel et al, U.S. Patent 4,637,891, issued January 20, 1987 (granulating spray-dried granules with a liquid binder and aluminosilicate); Kruse et al, U.S. Patent 4,726,908, issued February 23, 1988 (granulating spray-dried granules with a liquid binder and aluminosilicate); and, Bortolotti et al, U.S. Patent 5,160,657, issued

November 3, 1992 (coating densified granules with a liquid binder and aluminosilicate).

In those situations in which particularly heat sensitive or highly volatile detergent ingredients are to be incorporated into the final detergent composition, processes which do not include spray drying towers are preferred. The formulator can eliminate the spray-drying step by feeding, in either a continuous or batch mode, starting detergent ingredients directly into mixing/densifying equipment that is commercially available. One particularly preferred embodiment involves charging a surfactant paste and an anhydrous builder material into a high speed mixer/densifier (e.g. Lödige CB) followed by a moderate speed mixer/densifier (e.g. Lödige KM) to form high density detergent agglomerates. See Capeci et al, U.S. Patent 5,366,652, issued November 22, 1994 and Capeci et al, U.S. Patent 5,486,303, issued January 23, 1996. Optionally, the liquid/solids ratio of the starting detergent ingredients in such a process can be selected to obtain high density agglomerates that are more free flowing and crisp.

Optionally, the process may include one or more recycle streams of undersized particles produced by the process which are fed back to the mixer/densifiers for further agglomeration or build-up. The oversized particles produced by this process can be sent to grinding apparatus and then fed back to the mixing/densifying equipment. These additional recycle process steps facilitate build-up agglomeration of the starting detergent ingredients resulting in a finished composition having a uniform distribution of the desired particle size (400-700 microns) and density (> 550 g/l). See Capeci et al, U.S. Patent 5,516,448, issued May 14, 1996 and Capeci et al, U.S. Patent 5,489,392, issued February 6, 1996. Other suitable processes which do not call for the use of spray-drying towers are described by Bollier et al, U.S. Patent 4,828,721, issued May 9, 1989; Beerse et al, U.S. Patent 5,108,646, issued April 28, 1992; and, Jolicoeur, U.S. Patent 5,178,798, issued January 12, 1993.

In yet another embodiment, the high density detergent composition of the invention can be produced using a fluidized bed mixer. In this process, the various ingredients of the finished composition are combined in an aqueous slurry (typically 80% solids content) and sprayed into a fluidized bed to provide the finished detergent granules. Prior to the fluidized bed, this process can optionally include the step of mixing the slurry using the aforementioned Lödige CB mixer/densifier or a "Flexomix 160" mixer/densifier, available from Shugi. Fluidized bed or moving beds of the type available under the tradename "Escher Wyss" can be used in such processes.

Another suitable process which can be used herein involves feeding a liquid acid precursor of an anionic surfactant, an alkaline inorganic material (e.g. sodium carbonate) and optionally other detergent ingredients into a high speed mixer/densifier (residence time 5-30 seconds) so as to form agglomerates containing a partially or totally neutralized anionic surfactant salt and the other starting detergent ingredients. Optionally, the contents in the high speed mixer/densifier can be sent to a moderate speed mixer/densifier (e.g. Lödige KM) for further agglomeration resulting in the finished high density detergent composition. See Appel et al, U.S. Patent 5,164,108, issued November 17, 1992.

Optionally, high density detergent compositions according to the invention can be produced by blending conventional or densified spray-dried detergent granules with detergent agglomerates in various proportions (e.g. a 60:40 weight ratio of granules to agglomerates) produced by one or a combination of the processes discussed herein. Additional adjunct ingredients such as enzymes, perfumes, brighteners and the like can be sprayed or admixed with the agglomerates, granules or mixtures thereof produced by the processes discussed herein.

Another process for the manufacture of granules containing the novel bleach activator comprises the steps of:

- (i) preparing a mix of solids, and optionally liquids, comprising the bleach activator;
- (ii) extruding the mix through a die under pressure to form an extrudate;
- (iii) breaking the extrudate to form a spheronised extrudate; and
- (iv) optionally coating the particles to improve friability and flow characteristics.

The mixing step (i) is carried out using any conventional powder/liquid mixer, e.g. a Loedige KM mixer. The extruding step (ii) can be achieved using any conventional extruder which can be axial, radial or more preferably dome-type, e.g. Fuji Paudal Model DGL-1, most preferably having a die with <0.1mm orifices and extruded at pressures of about 20 bar. Step (iii) is preferably carried out using a rotating disc spheroniser such as a Fuji Paudal QJ-1000 where the extrudates are broken down into short lengths and formed into substantially spherical particles.

Additionally, the extrudates may then be dried in a vibrating fluid bed drier, e.g. Niro, to result in crisp, free-flowing particles with a particle size range of from 0.25mm to 20mm and a Heubach dust measurement of less than 100mg/g.

The optional coating step (iv) could involve materials such as film forming polymers or preferably a liquid fixative, e.g. nonionic surfactant and an inert powder

such as Zeolite A. See WO9800504, published January 8, 1998 and WO 97277280, published July 31, 1997.

Granular Compositions

The compositions of the present invention are ideally suited for use in laundry applications and automatic dishwashing compositions. Bleach additive compositions are intended to be employed in conjunction with a source of hydrogen peroxide such as a bleaching composition or a bleaching composition including a detergent, e.g. TIDE® WITH BLEACH. Accordingly, the present invention includes a method for laundering a soiled fabric. The method includes contacting a fabric to be laundered with an aqueous laundry liquor. The fabric may comprise most any fabric capable of being laundered in normal consumer use conditions. The laundry liquor includes the added bleach additive or bleaching composition containing a diacyl peroxides activator as fully described above. The laundry liquor may also include any of the above described additives to the compositions such as hydrogen peroxide source, deterative surfactants, chelates, and deterative enzymes. The solution preferably has a pH of from about 7 to about 9.5. The compositions are preferably employed at concentrations of at least about 50 ppm and typically from about 1,000 to about 10,000 ppm in solution. The water temperatures preferably range from about 25°C to about 50°C. The water to fabric ratio is preferably from about 1:1 to about 15:1

Methods for washing soiled dishes such as tableware, also involve contacting the soiled dishes with an aqueous dishwashing liquor. The dishwashing liquor includes the added bleach additive or bleaching composition containing a diacyl peroxides activator as fully described above. The dishwashing liquor may also include any of the above described additives to the compositions such as hydrogen peroxide source, deterative surfactants, chelates, and deterative enzymes. The solution preferably has a pH of from about 7 to about 9.5. The compositions are preferably employed at concentrations of at least about 50 ppm and typically from about 1,000 to about 10,000 ppm in solution. The water temperatures preferably range from about 25°C to about 50°C.

The present invention will now be described by reference to the following examples. Of course, one of ordinary skill in the art will recognize that the present invention is not limited to the specific examples herein described or the ingredients and steps contained therein, but rather, may be practiced according to the broader aspects of the disclosure.

EXAMPLE 3

Bleaching compositions having the form of granular laundry detergents are exemplified by the following formulations.

	A	B	C	D	E
INGREDIENT	%	%	%	%	%
Bleach Activator*	5	5	3	3	8
Sodium Percarbonate	0	0	19	21	0
Sodium Perborate monohydrate	21	0	0	0	20
Sodium Perborate tetrahydrate	12	21	0	0	0
Tetraacetythylenediamine	0	0	0	1	0
Nonanoyloxybenzenesulfonate	0	0	3	0	0
Linear alkylbenzenesulfonate	7	11	19	12	8
Alkyl ethoxylate (C45E7)	4	0	3	4	6
Zeolite A	20	20	7	17	21
SKS-6 [®] silicate (Hoechst)	0	0	11	11	0
Trisodium citrate	5	5	2	3	3
Acrylic Acid/Maleic Acid copolymer	4	0	4	5	0
Sodium polyacrylate	0	3	0	0	3
Diethylenetriamine penta(methylene phosphonic acid)	0.4	0	0.4	0	0
DTPA	0	0.4	0	0	0.4
EDDS	0	0	0	0.3	0
Carboxymethylcellulose	0.3	0	0	0.4	0
Protease	1.4	0.3	1.5	2.4	0.3
Lipolase	0.4	0	0	0.2	0
Cellulase	0.1	0	0	0.2	0
Anionic soil release polymer	0.3	0	0	0.4	0.5
Dye transfer inhibiting polymer	0	0	0.3	0.2	0
Carbonate	16	14	24	6	23
Silicate	3.0	0.6	12.5	0	0.6
Sulfate, Water, Perfume, Colorants	to 100	to 100	to 100	to 100	to 100

*Bleach activator according to any of Examples 1 or 2

EXAMPLE 4

This Example illustrates bleaching compositions, more particularly, liquid bleach additive compositions in accordance with the invention.

	A	B	C	D
Ingredients	wt %	wt %	wt %	wt %
NEODOL 91-10 ¹	6	5	7	4
NEODOL 45-7 ¹	6	5	5	8
NEODOL 23-2 ¹	3	5	3	3
DEQUEST 2060 ²	0.5	0.5	1.0	1.0
Bleach Activator ³	6	6	4	7
Citric Acid	0.5	0.5	0.5	0.5
NaOH	to pH 4	to pH 4	to pH 4	to pH 4
Hydrogen Peroxide	7	3	2	7
Water	Balance to 100%	Balance to 100%	Balance to 100%	Balance to 100%

¹ Alkyl ethoxylate available from The Shell Oil Company.

5 ² Commercially available from Monsanto Co.

³ Bleach Activator according to any of Examples 1 or 2.

	E	F	G
Ingredients	wt %	wt %	wt %
Water	to 100%	to 100%	to 100%
NEODOL 91-10 ¹	10	10	10
NEODOL 23-2 ¹	5	5	5
DEQUEST 2010 ²	0.5	0.5	1.0
Bleach Activator ³	4	4	8
Citric Acid	0.5	0.5	0.5
NaOH	to pH 4	to pH 4	to pH 4
Hydrogen Peroxide	7	5	5

¹ Alkyl ethoxylate available from The Shell Oil Company.

² Commercially available from Monsanto Co.

10 ³ Bleach activator according to any of Examples 1 or 2.

The compositions are used as bleach boosting additive (to be used in ADDITION to a bleach OR non-bleach detergent such as TIDE®). The additive is used at 1000 ppm.

EXAMPLE 5

This Example illustrates cleaning compositions having bleach additive form, more particularly, liquid bleach additive compositions without a hydrogen peroxide source in accordance with the invention.

	A	B	C	D
Ingredients	wt %	wt %	wt %	wt %
NEODOL 91-10 ¹	6	5	7	10
NEODOL 45-7 ¹	6	5	5	0
NEODOL 23-2 ¹	3	5	3	5
DEQUEST 2060 ²	0.5	0.5	1.0	1.0
Bleach Activator ³	6	6	4	7
Citric Acid	0.5	0.5	0.5	0.5
NaOH	to pH 4	to pH 4	to pH 4	to pH 4
Water	Balance to 100%	Balance to 100%	Balance to 100%	Balance to 100%

5 ¹ Alkyl ethoxylate available from The Shell Oil Company.

2 Commercially available from Monsanto Co.

3 Bleach Activator according to any of Examples 1 or 2.

10 The compositions are used as bleach boosting additive (to be used in ADDITION to a bleach detergent such as TIDE® WITH BLEACH). The additive is used at 1000 ppm.

EXAMPLE 6

Bleaching compositions having the form of granular laundry detergents are exemplified by the following formulations.

	A	B	C	D	E
INGREDIENT	%	%	%	%	%
Bleach Activator*	5	5	3	3	8
Sodium Percarbonate	0	5	15	0	0
Sodium Perborate monohydrate	5	0	0	10	20
Brightener 49	0.4	0.4	0	0	0
NaOH	2	2	2	0	2
Linear alkylbenzenesulfonate, partially neutralized	9	9	9	9	9
Alkyl ethoxylate (C25E9)	7	7	5	4	6
Zeolite A	32	20	7	17	21

Acrylic Acid/Maleic Acid copolymer	0	0	4	5	8
Sodium polyacrylate	0.6	0.6	0.6	0	0
Diethylenetriamine penta(methylene phosphonic acid)	0.5	0	0.5	0	1
EDDS	0	0.5	0	0.5	0
Protease	1	1	1.5	2.4	0.3
Lipolase	0	0	0	0.2	0
Cellulase	0	0	0	0.2	0
Anionic soil release polymer	0	0	0.5	0.4	0.5
Dye transfer inhibiting polymer	0	0	0.3	0.2	0
Soda Ash	22	22	22	22	22
Silicate (2r)	7.0	7.0	7.0	7.0	7.0
Sulfate, Water, Perfume, Colorants	to 100	to 100	to 100	to 100	to 100

*Bleach activator according to any of Examples 1 or 2

Any of the above compositions is used to launder fabrics under mildly alkaline conditions (pH 7 - 8). The pH can be adjusted by altering the proportion of acid to Na- salt form of alkylbenzenesulfonate.

5

EXAMPLE 7

A granular automatic dishwashing detergent composition comprising the following.

	A	B	C	D
INGREDIENT	wt %	wt %	wt %	wt %
Bleach Activator (See Note 1)	3	4.5	2.5	4.5
Sodium Perborate Monohydrate (See Note 2)	1.5	0	1.5	0
Sodium Percarbonate (See Note 2)	0	1.2	0	1.2
Amylase (TERMAMYL [®] from NOVO)	1.5	2	2	2
Dibenzoyl Peroxide	0	0	0.8	0
Transition Metal Bleach Catalyst (See Note 3)	0	0.1	0.1	0
Protease (SAVINASE [®] 12 T, NOVO, 3.6% active protein)	2.5	2.5	2.5	2.5
Trisodium Citrate Dihydrate (anhydrous basis)	7	15	15	15
Citric Acid	14	0	0	0
Sodium Bicarbonate	15	0	0	0
Sodium Carbonate, anhydrous	20	20	20	20

BRITESIL H2O [®] , PQ Corp. (as SiO ₂)	7	8	7	5
Diethylenetriaminepenta(methylenephosphonic acid), Na	0	0	0	0.2
Hydroxyethyldiphosphonate (HEDP), Sodium Salt	0	0.5	0	0.5
Ethylenediaminedisuccinate, Trisodium Salt	0.1	0.3	0	0
Dispersant Polymer (Accusol 480N)	6	5	8	10
Nonionic Surfactant (LF404, BASF)	2.5	1.5	1.5	1.5
Paraffin (Winog 70 [®])	1	1	1	0
Benzotriazole	0.1	0.1	0.1	0
Sodium Sulfate, water, minors BALANCE TO:	100%	100%	100%	100%

Note 1: Bleach Activator according to any of Examples 1 or 2.

Note 2: These hydrogen peroxide sources are expressed on a weight % available oxygen basis. To convert to a basis of percentage of the total composition, divide by about 0.15.

- 5 Note 3: Transition Metal Bleach Catalyst: Pentamaineacetatocobalt (III) nitrate; may be replaced MnTACN.

EXAMPLE 8

A granular automatic dishwashing detergent composition comprising the following.

	A	B	C	D
INGREDIENT	wt %	wt %	wt %	wt %
Bleach Activator (See Note 1)	3	4.5	2.5	4.5
Sodium Perborate Monohydrate (See Note 2)	1.5	0	1.5	0
STPP (anhydrous)(See Note 4)	31	26	45	50
Sodium Percarbonate (See Note 2)	0	1.5	0	1.5
Amylase (See Note 5)	1.5	1.5	1.62	1.62
Transition Metal Bleach Catalyst (See Note 3)	0	0	0.016	0.008
Protease (See Note 6)	2.2	1.26	0	1.5
Sodium Carbonate, anhydrous	32	22	5	14
BRITESIL H2O [®] , PQ Corp. (as SiO ₂)	9	7	8	8
Nonionic Surfactant (LF404, BASF)	1	0.5	1.5	2
Sodium Sulfate, water, minors BALANCE TO:	100%	100%	100%	100%

- 10 Note 1: Bleach Activator according to any of Examples 1 or 2.

Note 2: These hydrogen peroxide sources are expressed on a weight % available oxygen basis. To convert to a basis of percentage of the total composition, divide by about 0.15.

Note 3: Transition Metal Bleach Catalyst: Pentamaineacetatocobalt (III) nitrate; may be replaced MnTACN.

Note 4: Sodium tripolyphosphate.

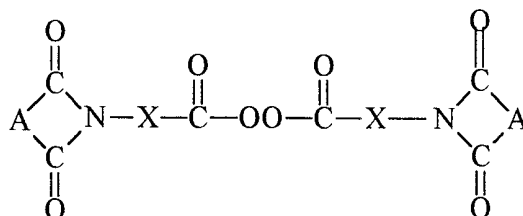
Note 5: The amylase is selected from: Termamyl®, Fungamyl®, Duramyl®, BAN®,
5 and the amylases as described in WO95/26397 and in co-pending application by
Novo Nordisk PCT/DK/96/00056.

Note 6: The protease is selected from: Savinase®; Maxatase®; Maxacal®;
Maxapem 15®; subtilisin BPN and BPN'; Protease B; Protease A; Protease C,
Protease D; Primase®; Durazym®; Opticlean®; and Optimase®; and Alcalase ®.

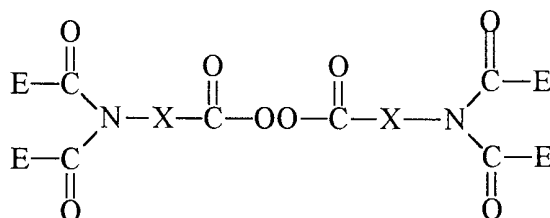
What is claimed is:

1. A compound having formula selected from the group consisting of :

(i)

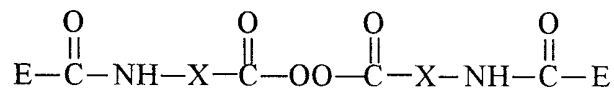


(ii)



; and

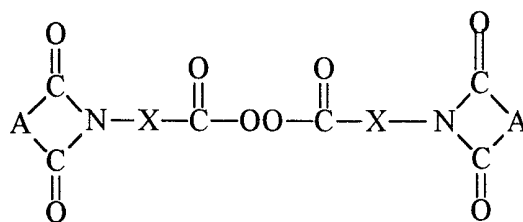
(iii)



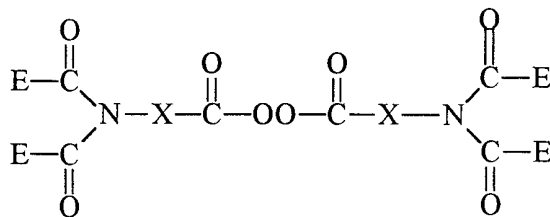
wherein each of A, E and X comprise a substituted or unsubstituted hydrocarbyl group

2. A detergent composition comprising a compound selected from the group consisting of:

(i)

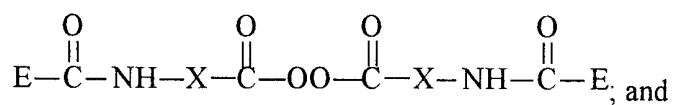


(ii)



;

(iii)

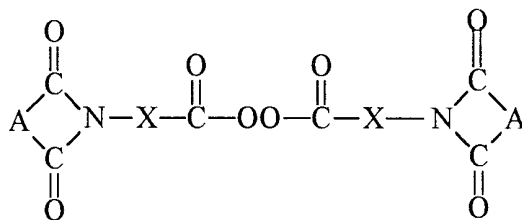


(iv) mixtures thereof;

wherein each of A, E and X comprise a substituted or unsubstituted hydrocarbyl group

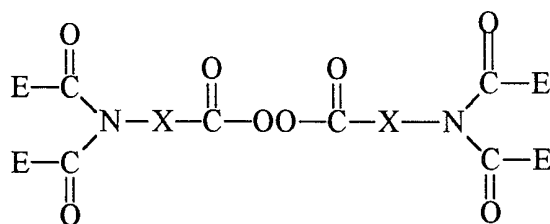
3. A bleach additive composition comprising a compound selected from the group consisting of:

(i)



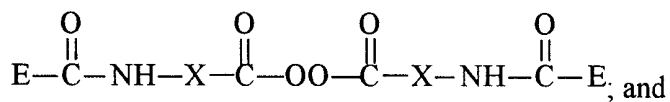
;

(ii)



;

(iii)

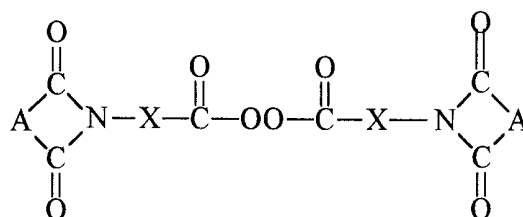


(iv) mixtures thereof;

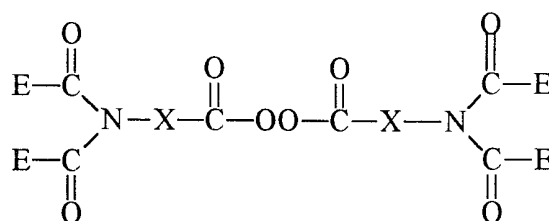
wherein each of A, E and X comprise a substituted or unsubstituted hydrocarbyl group

4. A bleach composition comprising a compound selected from the group consisting of:

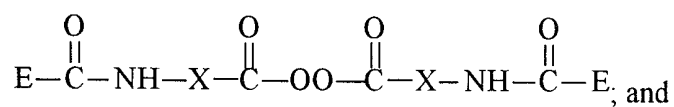
(i)



(ii)



(iii)

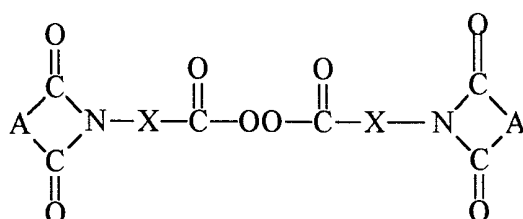


(iv) mixtures thereof;

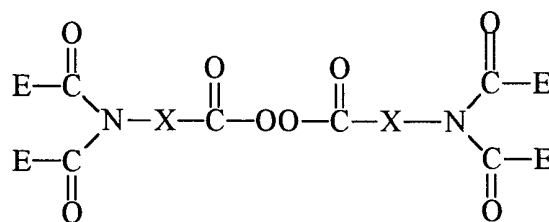
wherein each of A, E and X comprise a substituted or unsubstituted hydrocarbyl group

5. A method for cleaning soiled fabrics, comprising a step of contacting said fabrics with an aqueous wash bath comprising a compound selected from the group consisting of:

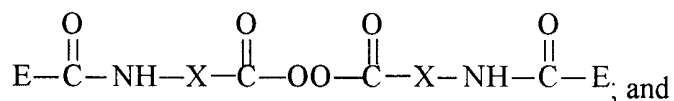
(i)



(ii)



(iii)



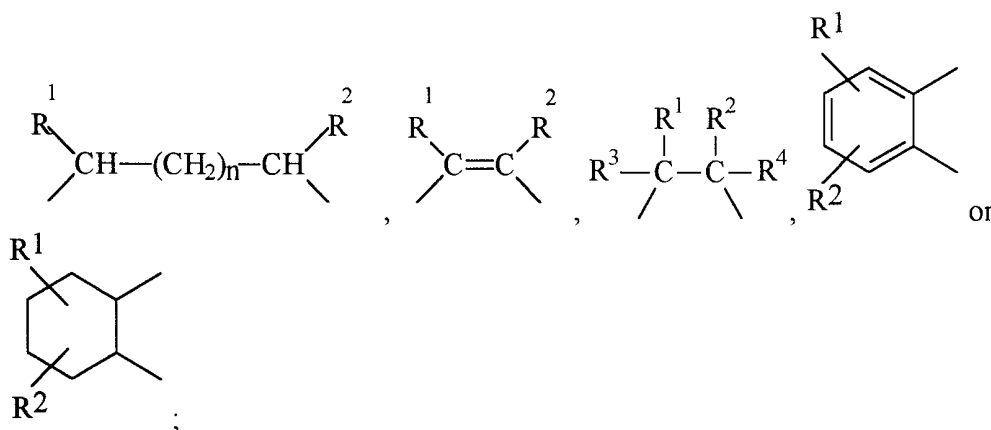
(iv) mixtures thereof;

wherein each of A, E and X comprise a substituted or unsubstituted hydrocarbyl group

6. A composition according to any one of Claims 1 to 5 wherein said moieties A, E and X are electrically neutral.

7. A composition according to any one of Claims 1 to 5 wherein at least one of said hydrocarbyl groups comprises from about 4 to about 20 carbon atoms.

8. A composition according to any one of Claims 1 to 5 wherein, X is selected from C₁ - C₂₀ alkyl, C₂-C₂₀ alkenylene, A is selected from:



wherein n denotes the number 0, 1, 2 or 3, R¹ is selected from the group consisting of hydrogen, chloride, bromide, iodide, substituted or unsubstituted branched or linear C₁-C₂₀ alkyl, substituted or unsubstituted branched or linear C₂-C₂₀ alkenyl, substituted or unsubstituted aryl, and substituted or unsubstituted alkylaryl, R² is selected from the group consisting of hydrogen, chloride, bromide, iodide, substituted or unsubstituted branched or linear C₁-C₂₀ alkyl, substituted or unsubstituted branched or linear C₂-C₂₀ alkenyl, substituted or unsubstituted aryl, and substituted or unsubstituted alkylaryl, R³ and R⁴ are independently selected from hydrogen and C₁-C₆ substituted or unsubstituted branched or linear alkyl; and E is selected from the group consisting of substituted or unsubstituted, branched or linear C₁-C₂₀ alkyl, substituted or unsubstituted, branched or linear C₂-C₂₀ alkenyl, substituted or unsubstituted aryl, and substituted or unsubstituted, branched or linear alkylaryl.