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

(11) Publication number: **0 512 533 A2**

(12) EUROPEAN PATENT APPLICATION

(21) Application number: **92107693.1**

(22) Date of filing: **07.05.92**

(51) Int. Cl.5: **C11D 3/39**, C11D 1/62, C11D 1/52

(30) Priority: **09.05.91 JP 104216/91**

(43) Date of publication of application:
11.11.92 Bulletin 92/46

(84) Designated Contracting States:
DE ES FR GB IT

(71) Applicant: **KAO CORPORATION**
14-10, Nihonbashi, Kayabacho 1-chome
Chuo-ku, Tokyo(JP)

(72) Inventor: **Sotoya, Kohshiro**
446-26, Nakaguro, Iwadecho
Naga-gun, Wakayama(JP)
Inventor: **Aoyagi, Muneo**
217-13, Tsurutacho
Utsunomiya-shi, Tochigi(JP)
Inventor: **Ogura, Nobuyuki**
2-4, Genzobaba
Wakayama-shi, Wakayama(JP)
Inventor: **Kaneko, Youhei**
1450, Nishihama
Wakayama-shi, Wakayama(JP)
Inventor: **Mino, Konomi**
5-28, Nishitakamatsu 1-chome
Wakayama-shi, Wakayama(JP)

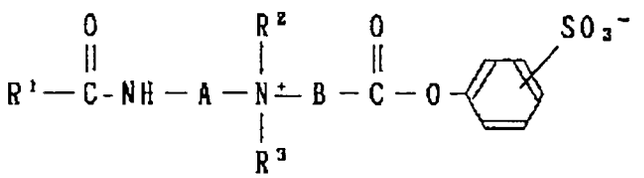
(74) Representative: **Hansen, Bernd, Dr.rer.nat. et al**
Hoffmann, Eitle & Partner Patentanwälte
Arabellastrasse 4 Postfach 81 04 20
W-8000 München 81(DE)

(54) Bleach or bleaching detergent composition.

(57) A bleach or bleaching detergent composition which can be applied to colored or patterned soft goods, materials, cloths, fabrics and the like with the discoloration of the soft goods, etc. being inhibited sufficiently comprising:

(a) hydrogen peroxide or a peroxide which liberates hydrogen peroxide in an aqueous solution thereof,

(b) a quaternary ammonium compound having the general formula (I);

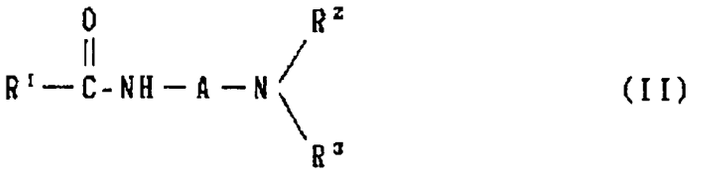


(I)

in which R^1 is, either a straight- or branched-chain, substituted or unsubstituted, alkyl having 1 to 20 carbon atoms or alkenyl having 2 to 20 carbon atoms, R^2 and R^3 are, each independently an alkyl having 1 to 3 carbon atoms, and A and B are, each independently, either a straight- or branched-chain, substituted or unsubstituted, alkylene having 2 to 20 carbon atoms; and

(c) an amide derivative having the general formula (II);

EP 0 512 533 A2



(II)

in which R^1, R^2, R^3 and A are defined above, and wherein the weight ratio of (b)/(c) is in the range of from 100/0.01 to 100/5.

Background of the Invention

Field of the Invention

The present invention relates to a bleach or bleaching detergent composition containing a bleach activator having a cationic group.

Description of the Related Art

A chlorinated bleaching agent has disadvantages in that the fibers to which it is applicable are limited, i.e., it is not applicable to colored or patterned soft goods, materials, cloths, fabrics and the like, and that it has a peculiar odor, so that an oxygenic bleaching agent free from these disadvantages has recently been used widely.

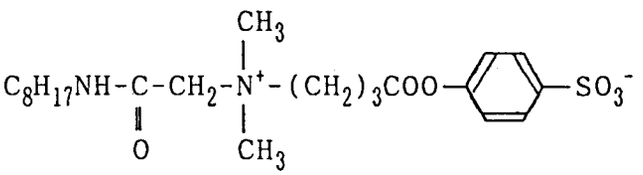
As such an oxygenic bleaching agent, sodium percarbonate and sodium perborate are particularly utilized from the standpoint of bleaching performance and stability.

However, the bleaching power of the oxygenic bleaching agent is poorer than that of a chlorinated bleaching agent, so that various bleach activators have been used together therewith.

Although tetraacetyl ethylene diamine (TAED), acetoxybenzene sulfonic acid salts, tetraacetyl glycoluril and glucose pentaacetate have been representatively used as the bleach activator, they are still insufficient in bleach activating effects.

The present inventors previously found that a compound which reacts with hydrogen peroxide to form an organic peracid having a cationic group is excellent as a bleach activator (see U. S. Patent Nos. 4,933,103 and 5,059,344, and European Patent Publication-A Nos. 371809 and 403152).

For instance, European Patent Publication-A No. 403152 mentions a bleach activator represented by the following formula:



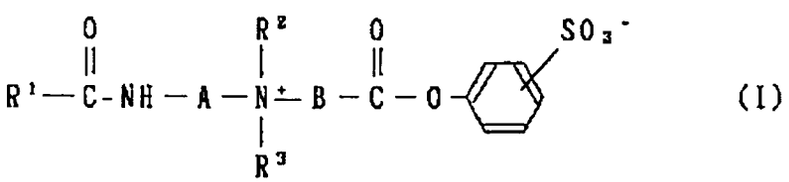
However, when a bleach or bleaching detergent composition containing such a compound which can form an organic peracid having a cationic group is applied to colored or patterned soft goods, materials, cloths, fabrics and the like, the discoloration of the soft goods, etc. cannot be acceptably inhibited, though the compound is excellent in bleach activating performance.

Disclosure of the Invention

Summary of the Invention

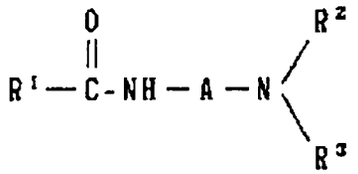
Under these circumstances, the object of the present invention is to provide a bleach or bleaching detergent composition which is excellent in bleach activating performance and which hardly discolors colored or patterned soft goods, materials, cloths, fabrics and the like.

The present inventors have extensively studied to solve the above-mentioned problems and have found that a composition which comprises hydrogen peroxide or a peroxide which liberates hydrogen peroxide in an aqueous solution thereof and compounds represented respectively by the following general formulae (I) and (II) at a specified ratio solves the aforementioned problems:



(I)

in which R^1 is, either a straight- or branched-chain, substituted or unsubstituted, alkyl having 1 to 20 carbon atoms or alkenyl having 2 to 20 carbon atoms, R^2 and R^3 are, each independently, an alkyl having 1 to 3 carbon atoms and A and B are, each independently, either a straight- or branched-chain, substituted or unsubstituted, alkylene having 2 to 20 carbon atoms, and



(II)

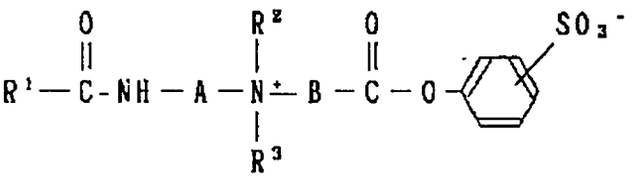
in which R^1, R^2, R^3 and A are defined above.

The present invention has been accomplished on the basis of this finding.

Namely, the present invention provides a bleach or bleaching detergent composition which comprises or essentially consists of:

(a) hydrogen peroxide or a peroxide which liberates hydrogen peroxide in an aqueous solution thereof,

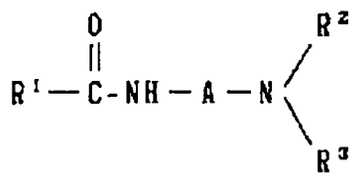
(b) a quaternary ammonium compound having the general formula (I);



(I)

in which R^1 is, either a straight- or branched-chain, substituted or unsubstituted, alkyl having 1 to 20 carbon atoms or alkenyl having 2 to 20 carbon atoms, R^2 and R^3 are, each independently, an alkyl having 1 to 3 carbon atoms and A and B are, each independently, either a straight- or branched-chain, substituted or unsubstituted, alkylene having 2 to 20 carbon atoms, and

(c) an amide derivative having the general formula (II);



(II)

in which R^1, R^2, R^3 and A are defined above, wherein the weight ratio of (b)/(c) is in the range of from 100/0.01 to 100/5.

R^1 in the formulae (I) and (II) is, preferably, either a straight- or branched-chain, alkyl having 1 to 20 carbon atoms and having at least one substituent selected from the group consisting of a hydroxyl group and a halogen atom or alkenyl having 2 to 20 carbon atoms and having at least one substituent selected from the group consisting of a hydroxyl group and a halogen atom.

When R^1 in the formulae (I) and (II) is alkyl, it is preferably, either a straight- or branched-chain, alkyl having 1 to 9 carbon atoms.

When R^1 in the formulae (I) and (II) is alkenyl, it is preferably a straight-chain alkenyl having 2 to 17 carbon atoms.

A and B in the formulae (I) and (II) are preferably, each independently, a straight-chain alkylene having 2 to 10 carbon atoms.

The molar ratio of component (a)/component (b) is in the range of preferably from 99.9/0.1 to 20/80, and more preferably from 99/1 to 50/50.

The weight ratio of component (b)/component (c) is in the range of preferably from 100/0.1 to 100/4.

The composition may further comprise at least one component selected from the group consisting of a

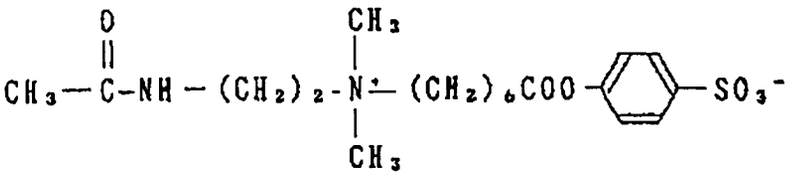
bleach activator other than component (b), a surfactant, a divalent metal ion-sequestering agent, an alkaline agent, an inorganic electrolyte, an antiredeposition agent, an enzyme, a fluorescent dye, a stabilizer for the peroxide, a perfume and a coloring matter in their respective effective amounts.

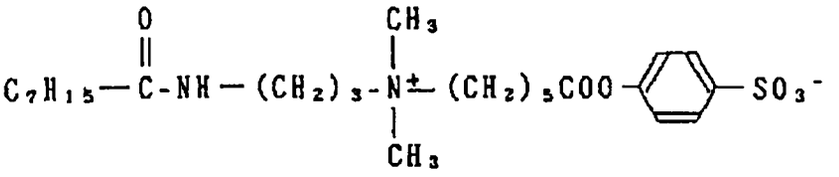
Further scope and the applicability of the present invention will become apparent from the detailed description given hereinafter. However, it should be understood that the detailed description and specific examples, while indicating preferred embodiments of the invention, are given by way of illustration only, since various changes and modifications within the spirit and scope of the invention will become apparent to those skilled in the art from this detailed description.

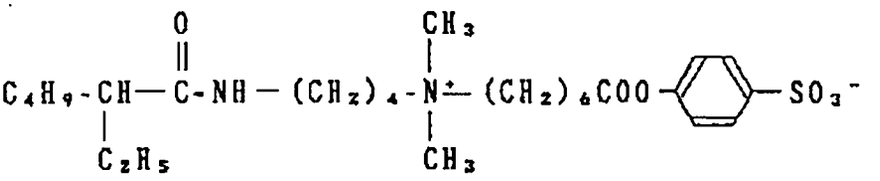
Detailed Description of the Invention

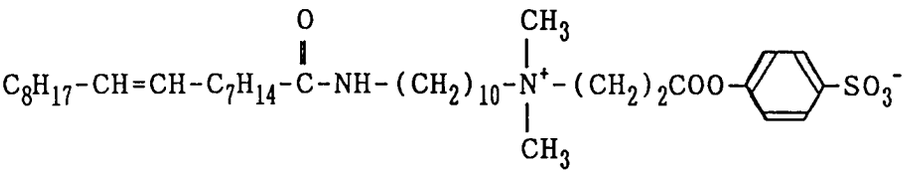
Component (a) according to the present invention is either hydrogen peroxide or a peroxide which can generate hydrogen peroxide in an aqueous solution thereof. Examples of the latter include sodium percarbonate, sodium tripolyphosphate/hydrogen peroxide adduct, sodium pyrophosphate/hydrogen peroxide adduct, urea/hydrogen peroxide adduct, $4Na_2SO_4 \cdot 2H_2O_2 \cdot NaCl$, sodium perborate monohydrate, sodium perborate tetrahydrate, sodium peroxide and potassium peroxide, among which sodium percarbonate, sodium perborate monohydrate and sodium perborate tetrahydrate are preferable.

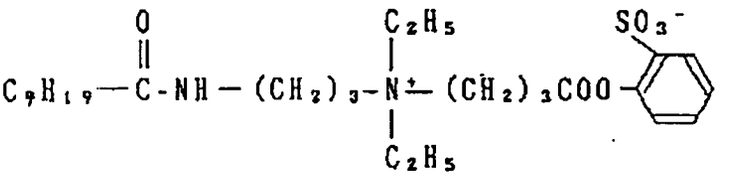
Component (b) according to the present invention is a quaternary ammonium compound represented by the general formula (I) and examples thereof include the following compounds:

(a) 

(b) 

(c) 

(d) 

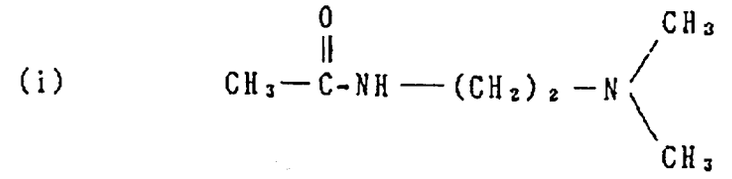
(e) 

When these compounds, that is, compounds (a) to (e), for example, are synthesized, an inorganic salt such as an alkali metal halide and an ammonium halide or an organic salt such as a quaternary ammonium halide is generally formed as a by-product. The bleach or bleaching detergent composition of the present invention may contain at least one of the above-mentioned inorganic salt and the above-mentioned organic salt in such an amount that it does not hinder the object of the present invention.

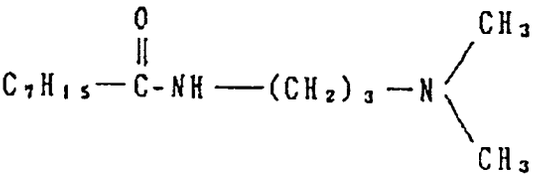
The molar ratio of component (a) to component (b) is preferably in the range of from 99.9 : 0.1 to 20 : 80, and still more preferably from 99 : 1 to 50 : 50.

Component (c) according to the present invention is an amide derivative represented by the general formula (II) and examples thereof include the following compounds:

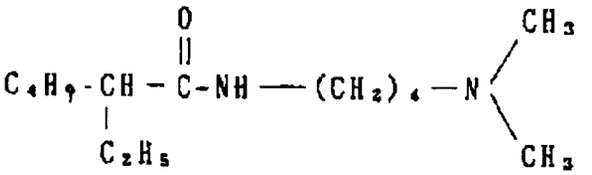
(i)



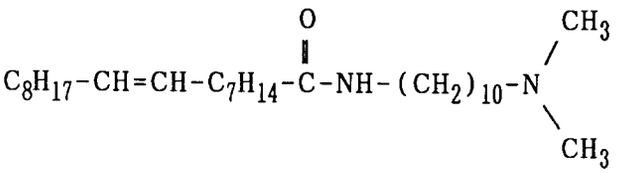
(ii)



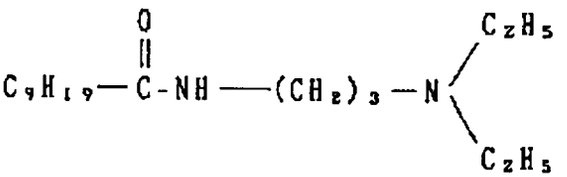
(iii)



(iv)



(v)



In the present invention, it is necessary that component (c) is used in an amount of from 0.01 to 5 parts by weight, preferably from 0.1 to 4 parts per 100 parts by weight of component (b). This range is critical, because when the amount of component (c) used is less than 0.01 part by weight per 100 parts by weight of the component (b), the discoloration of colored or patterned soft goods, materials, cloths, fabrics and the like in bleaching will not be sufficiently inhibited, while when it exceeds 5 parts by weight, bleaching performance will be hindered.

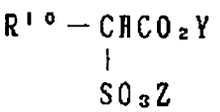
The bleach or bleaching detergent composition of the present invention may contain a bleach activator other than component (b) and additives which are ordinarily added to a bleach or bleaching detergent composition, in addition to the above essential components (a), (b) and (c). Examples of such additives are as follows:

[1] bleach activators other than component (b)

tetraacetyl ethylene diamine (TAED), acetoxybenzene sulfonic acid salts, tetraacetyl glycolyl uril, glucose pentaacetate and a compound which reacts with hydrogen peroxide to form an organic peracid having a cationic group (see Japanese Patent Laid-Open Nos. 315666/1988, 147698/1990 and 17196/1991).

[2] surfactants

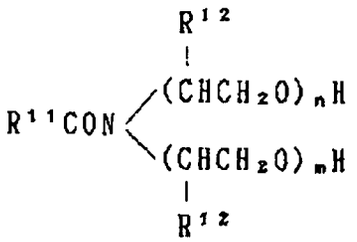
(1) salts of alkyl (a straight chain or branched) benzenesulfonic acids or alkyl (a straight chain or branched) benzenesulfonates wherein the alkyl group has 10 to 16 carbon atoms on average.
(2) ethylene oxide, propylene oxide or butylene oxide adducts of salts of alkyl or alkenyl ether sulfates, or, ethylene oxide and propylene oxide or butylene oxide adducts, at a molar ratio of ethylene oxide : propylene oxide or butylene oxide ranging 0.1 : 9.9 to 9.9 : 0.1, of salts of alkyl or alkenyl ether sulfates, wherein the adducts have 0.5 to 8 the above-described alkylene oxide units per molecule on average and the alkyl or alkenyl group is a straight chain or branched and has 10 to 20 carbon atoms on average.
(3) salts of alkyl- or alkenyl-sulfuric acids, or, alkyl- or alkenyl-sulfates wherein the alkyl or alkenyl group has 10 to 20 carbon atoms on average.
(4) salts of olefin (or alkene) sulfonic acids or olefin sulfonates wherein 10 to 20 carbon atoms are contained per molecule on average.
(5) salts of alkanesulfonic acids or alkanesulfonates wherein 10 to 20 carbon atoms are contained per molecule on average.
(6) salts of saturated or unsaturated fatty acids wherein 10 to 24 carbon atoms are contained per molecule on average.
(7) ethylene oxide, propylene oxide or butylene oxide adducts of alkyl or alkenyl ether carboxylic acid salts, or, ethylene oxide and propylene oxide or butylene oxide adducts, at a molar ratio of ethylene oxide : propylene oxide or butylene oxide ranging 0.1 : 9.9 to 9.9 : 0.1, of alkyl or alkenyl ether carboxylic acid salts, wherein the adducts have 0.5 to 8 the above-described alkylene oxide units per molecule on average and the alkyl or alkenyl group has 10 to 20 carbon atoms on average.
(8) salts and esters of α-sulfo fatty acids represented by the following formula:



wherein Y represents an alkyl group having 1 to 3 carbon atoms or a counter ion; Z represents a counter ion; and R^{10} represents an alkyl or alkenyl group having 10 to 20 carbon atoms.

The counter ion constituting the above anionic surfactant includes ions of alkali metals such as sodium and potassium.

(9) polyoxyethylene alkyl or alkenyl ethers wherein the alkyl or alkenyl group has 10 to 20 carbon atoms on average and the polyoxyethylene moiety is derived from 1 to 30 ethylene oxide molecules on average.
(10) polyoxyethylene alkylphenyl ethers wherein the alkyl group has 6 to 12 carbon atoms on average and the polyoxyethylene moiety is derived from 1 to 25 ethylene oxide molecules on average.
(11) polyoxypropylene alkyl or alkenyl ethers wherein the alkyl or alkenyl group has 10 to 20 carbon atoms on average and the polyoxypropylene moiety is derived from 1 to 20 propylene oxide molecules on average.
(12) polyoxybutylene alkyl or alkenyl ethers wherein the alkyl or alkenyl group has 10 to 20 carbon atoms on average and the polyoxybutylene moiety is derived from 1 to 20 butylene oxide molecules on average.
(13) ethylene oxide and propylene oxide or butylene oxide adducts, at a molar ratio of ethylene oxide : propylene oxide or butylene oxide ranging 0.1 : 9.9 to 9.9 : 0.1, of alkyl or alkenyl ethers, wherein the adducts have 1 to 30 the above-described alkylene oxide units per molecule on average and the alkyl or alkenyl group has 10 to 20 carbon atoms on average.
(14) higher fatty acid alkanolamides and adducts thereof with alkylene oxide represented by the following general formula:

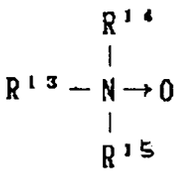


wherein R^{11} represents an alkyl or alkenyl group having 10 to 20 carbon atoms; R^{12} represents a hydrogen atom or a methyl group; n is an integer of 1 to 3; and m is 0 or an integer of 1 to 3.

(15) esters of sucrose with fatty acids having 10 to 20 carbon atoms on average.

(16) monoesters of glycerol with fatty acids having 10 to 20 carbon atoms on average.

(17) alkylamine oxides represented by the following general formula:

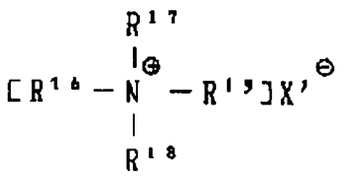


wherein R^{13} represents an alkyl or alkenyl group having 10 to 20 carbon atoms; and R^{14} and R^{15} each represent an alkyl group having 1 to 3 carbon atoms.

(18) nonionic surfactants commercially available under the trade name of "Pluronic" which is prepared by the condensation of ethylene oxide.

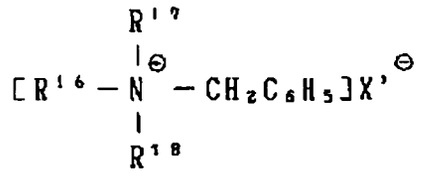
(19) cationic surfactants represented by the following general formulae:

No. 1



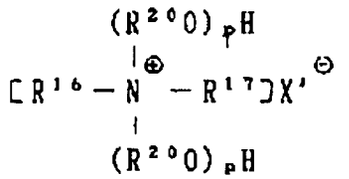
wherein at least one of R^{16}, R^{17}, R^{18} and R^{19} represents an alkyl or alkenyl group having 8 to 24 carbon atoms and the others each represent an alkyl group having 1 to 5 carbon atoms; and X' represents a halogen atom or a methylsulfate;

No. 2



wherein R^{16}, R^{17}, R^{18} and X' are each as defined above; and

No. 3



wherein R^{16}, R^{17} and X' are each as defined above; R^{20} represents an alkylene group having 2 to 3 carbon atoms; and p is an integer of 1 to 20.

[3] divalent metal ion-sequestering agents

One or more builder components selected from among the following compounds, for example, alkali metal salts and alkanolamine salts which may be present in an amount of 0 to 50% by weight per the bleach or bleaching detergent composition of the present invention:

(1) alkali metal salts and alkanolamine salts of phosphoric acids such as orthophosphoric acid, pyrophosphoric acid, triphosphoric acid, metaphosphoric acid, hexametaphosphoric acid and phytic acid.

(2) alkali metal salts and alkanolamine salts of phosphonic acids such as ethane-1,1-diphosphonic acid, ethane-1,1,2-triphosphonic acid, ethane-1-hydroxy-1,1-diphosphonic acid and their derivatives, ethane-hydroxy-1,1,2-triphosphonic acid, ethane-1,2-dicarboxy-1,2-diphosphonic acid and methanehydroxyphosphonic acid.

(3) alkali metal salts and alkanolamine salts of phosphono carboxylic acids such as 2-phosphonobutane-1,2-dicarboxylic acid, 1-phosphonobutane-2,3,4-tricarboxylic acid and α-methylphosphonosuccinic acid.

(4) alkali metal salts and alkanolamine salts of amino acids such as aspartic acid, glutamic acid and glycine.

(5) alkali metal salts and alkanolamine salts of aminopolyacetic acids such as nitrilotriacetic acid, iminodiacetic acid, ethylenediaminetetraacetic acid, diethylenetriaminepentaacetic acid, glycoletherdiaminetetraacetic acid, hydroxyethyliminodiacetic acid, triethylenetetraminehexaacetic acid and djenkolic acid.

(6) polyelectrolytes such as polyacrylic acid, polyfumaric acid, polymaleic acid, poly-α-hydroxyacrylic acid and polyacetalcarboxylic acid and alkali metal salts and alkanolamine salts thereof.

(7) alkali metal salts and alkanolamine salts of organic acids such as diglycolic acid, oxydisuccinic acid, carboxymethyloxysuccinic acid, citric acid, lactic acid, tartaric acid, oxalic acid, malic acid, oxydisuccinic acid, gluconic acid, carboxymethylsuccinic acid and carboxymethyltartaric acid, among which alkali metal salts are preferable.

(8) aluminosilicates represented by zeolite A.

[4] alkaline agents and inorganic electrolytes

silicates, carbonates and sulfates, among which alkali metal salts, for example, Glauber's salt are preferable.

[5] antiredeposition agents

polyethylene glycol, polyvinyl alcohol, polyvinylpyrrolidone and carboxymethylcellulose.

[6] enzymes

protease, lipase, amylase and cellulase.

[7] fluorescent dyes

salts of 4,4'-bis(2-sulfostyryl)-biphenyl, salts of 4,4'-bis(4-chloro-3-sulfostyryl)-biphenyl, 2-(stylphenyl)-naphthothiazole derivatives, 4,4'-bis(triazol-2-yl)stilbene derivatives and bis(triazinylamino)stilbene disulfonic acid derivatives.

[8] stabilizers for peroxides

magnesium salts such as magnesium sulfate, magnesium silicate, magnesium chloride, magnesium silicofluoride, magnesium oxide and magnesium hydroxide; and silicates such as sodium silicate.

[9] perfumes and dyestuffs or coloring matters

The bleach or bleaching detergent composition according to the present invention exhibits not only an excellent bleaching effect but also an excellent detergency against sebum and mud dirts. Further, even when it is applied to colored or patterned soft goods, materials, cloths, fabrics and the like, it does not cause the discoloration of the soft goods, etc.. Furthermore, the bleach activator used in the bleach or bleaching detergent composition according to the present invention is biodegradable, being extremely safe for the human bodies.

Examples

The present invention will now be described by referring to the following Examples, though the present invention is not limited to it.

Example 1

Bleach compositions were prepared according to the formulations specified in Table 1 and subjected to the following bleaching test and discoloration test:

(1) Bleaching Test

Preparation of tea-stained cloth:

80 g of Nitto black tea (yellow package) was dipped in 3 ℓ of deionized water, and was boiled for about 15 minutes and filtered through a desized bleached cotton cloth. A cotton shirting cloth # 2003 was dipped in the obtained filtrate, followed by boiling for about 15 minutes. The boiled liquid was taken off the fire and allowed to stand for about 2 hours. The cloth was dried spontaneously, washed with water until the washings became colorless, dehydrated, pressed and cut into a test piece of 10 cm × 10 cm. This test piece was used in the following determination.

Determination of rate of bleaching:

Each bleaching composition specified in Table 1 was added to 300 ml of water at 20 °C so as to give an available oxygen content of 0.04%. The tea-stained cloth prepared above was dipped in the solution for 30 minutes, washed with water and dried. The rate of bleaching of the resulting cloth was determined according to the following formula:

Rate of bleaching of tea-stained cloth:

$$\text{rate of bleaching (\%)} = \frac{(\text{reflectance after bleaching}) - (\text{reflectance before bleaching})}{(\text{reflectance of white cloth}) - (\text{reflectance before bleaching})} \times 100$$

Each reflectance was determined with a reflectometer NDR-101 DP (mfd. by Nippon Denshoku Kogyo) with a filter of 460 nm. The results are given in Table 1.

(2) Discoloration Test

Each bleach composition specified in Table 1 was dissolved in tap water at 40 °C so as to give an available oxygen content of 0.04%. A cotton cloth dyed with a direct dye (Sumilight Supra Blue FBGL) was

dipped in the solution prepared above, dried and examined for discoloration with a gray scale for discoloration according to JIS L 0804. Cases wherein the grade was 4.5 or above is shown by "◎"; cases wherein the grade was 4 or above but below 4.5 is shown by "○"; cases wherein the grade was 3 or above but below 4 is shown by "△"; and cases wherein the grade was below 3 is shown by "x". The results are set forth in Table 1.

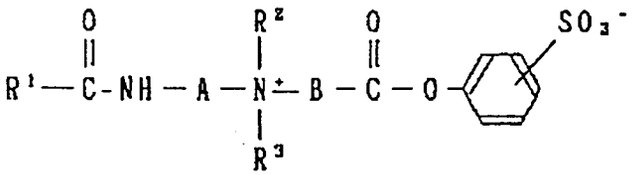
Table 1

		Invention					Comp.						
		1	2	3	4	5	6	7	8	9	10	11	12
Bleach composition (% by weight)	sodium percarbonate	60	60	60	60	60	60	60	60	60	60	60	60
	compound (a)*1	13	–	–	–	–	13	13	–	–	–	–	–
	compound (b)*1	–	16	–	–	–	–	–	16	16	–	–	–
	compound (c)*1	–	–	17	–	–	–	–	–	–	17	17	–
	compound (d)*1	–	–	–	26	–	–	–	–	–	–	–	–
	compound (e)*1	–	–	–	–	17	–	–	–	–	–	–	–
	compound (i)*2	0.2	–	–	–	–	–	1.2	–	–	–	–	–
	compound (ii)*2	–	0.3	–	–	–	–	–	–	1.6	–	–	–
	compound (iii)*2	–	–	0.3	–	–	–	–	–	–	–	3.0	–
	compound (iv)*2	–	–	–	1.0	–	–	–	–	–	–	–	–
	compound (v)*2	–	–	–	–	0.02	–	–	–	–	–	–	–
	TAED (tetraacetyl ethylene diamine)	–	–	–	–	–	–	–	–	–	–	–	3.6
	Glauber's salt	B*3	B*3	B*3	B*3	B*3	B*3	B*3	B*3	B*3	B*3	B*3	B*3
Results	rate of bleaching (%)	45	44	43	41	43	44	34	43	33	43	29	22
	discoloration	◎	◎	◎	◎	◎	△	◎	△	◎	△	◎	△

note) *1) These compounds are described previously as component (b).
The amount of these compounds (bleach activators) is one-sixteenth by equivalent as much as sodium percarbonate (available oxygen content: 13.5%).
*2) These compounds are described previously as component (c).
*3) B is an abbreviation of balance.

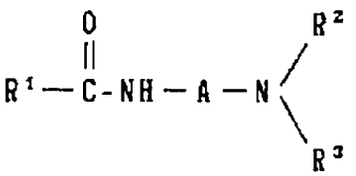
Claims

1. A bleach or bleaching detergent composition comprising:
(a) hydrogen peroxide or a peroxide which generates hydrogen peroxide in an aqueous solution thereof,
(b) a quaternary ammonium compound having the general formula (I);



(I)

in which R^1 is, either a straight- or branched-chain, substituted or unsubstituted, alkyl having 1 to 20 carbon atoms or alkenyl having 2 to 20 carbon atoms, R^2 and R^3 are, each independently an alkyl having 1 to 3 carbon atoms, and A and B are, each independently, either a straight- or branched-chain, substituted or unsubstituted, an alkylene having 2 to 20 carbon atoms, and
(c) an amide derivative having the general formula (II);



(II)

in which R^1, R^2, R^3 and A are defined above; and wherein the weight ratio of (b)/(c) is in the range of from 100/0.01 to 100/5.

2. The composition as claimed in claim 1, wherein R^1 in the formulae (I) and (II) is, either a straight- or branched-chain, alkyl having 1 to 20 carbon atoms and having at least one substituent selected from the group consisting of a hydroxyl group and a halogen atom or alkenyl having 2 to 20 carbon atoms and having at least one substituent selected from the group consisting of a hydroxyl group and a halogen atom.

3. The composition as claimed in claim 1, wherein R^1 in the formulae (I) and (II) is, either a straight- or branched-chain, alkyl having 1 to 9 carbon atoms.

4. The composition as claimed in claim 1, wherein R^1 in the formulae (I) and (II) is a straight-chain alkenyl having 2 to 17 carbon atoms.

5. The composition as claimed in claim 1, wherein A and B in the formulae (I) and (II) are, each independently, a straight-chain alkylene having 2 to 10 carbon atoms.

6. The composition as claimed in claim 1, wherein the molar ratio of component (a)/component (b) is in the range of from 99.9/0.1 to 20/80.

7. The composition as claimed in claim 1, wherein a molar ratio of component (a)/component (b) is in the range of from 99/1 to 50/50.

8. The composition as claimed in claim 1, wherein the weight ratio of component (b)/component (c) is in the range of from 100/0.1 to 100/4.

9. The composition as claimed in claim 1, which further comprises at least one component selected from the group consisting of a bleach activator other than component (b), a surfactant, a divalent metal ion-

sequestering agent, an alkaline agent, an inorganic electrolyte, an antiredeposition agent, an enzyme, a fluorescent dye, a stabilizer for the peroxide, a perfume and a coloring matter in an effective amount thereof.