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

(11) Publication number: **0 442 549 A2**

(12) EUROPEAN PATENT APPLICATION

(21) Application number: **91200119.5**

(51) Int. Cl.5: **C11D 3/39**

(22) Date of filing: **22.01.91**

(30) Priority: **13.02.90 GB 9003200**

(43) Date of publication of application:
21.08.91 Bulletin 91/34

(84) Designated Contracting States:
CH DE ES FR GB IT LI NL SE

(71) Applicant: **UNILEVER NV**
Burgemeester s'Jacobplein 1 P.O. Box 760
NL-3000 DK Rotterdam(NL)
(84) **CH DE ES FR IT LI NL SE**

Applicant: **UNILEVER PLC**
Unilever House Blackfriars P.O. Box 68
London EC4P 4BQ(GB)

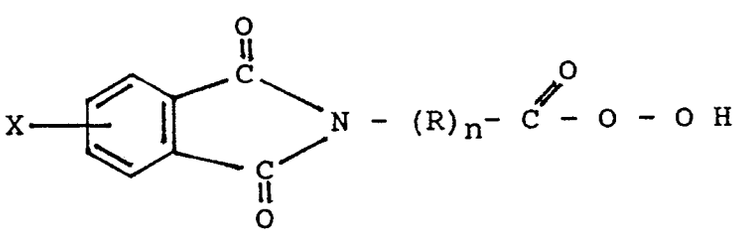
(84) **GB**

(72) Inventor: **Barnes, Stephen George**
Unilever Research Port Sunlight Laboratory
Bebington, Wirral, Merseyside L63 3JW(GB)
Inventor: **Finch, Timothy David**
Unilever Research Port Sunlight Laboratory
Bebington, Wirral, Merseyside L63 3JW(GB)
Inventor: **Thompson, Ian**
Unilever Research Port Sunlight Laboratory
Bebington, Wirral, Merseyside L63 3JW(GB)

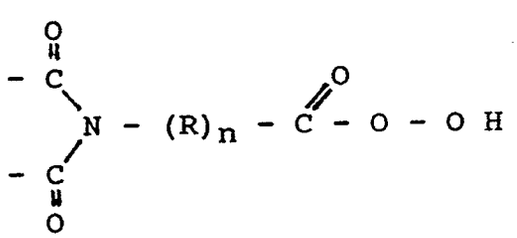
(74) Representative: **Tan, Bian An, Ir. et al**
Unilever N.V. Patent Division P.O. Box 137
NL-3130 AC Vlaardingen(NL)

(54) Aqueous liquid bleach composition.

(57) An aqueous liquid bleaching composition is described having a pH of from 1 to 6.5 and comprising a surfactant, an electrolyte and an organic peroxyacid having the formula:



wherein X is H, alkyl, halogen, a carboxyl group, or the same peroxycarboxylic acid group:



in symmetrical position to the first peroxyacid group on the aromatic ring;
R is a straight or branched chain lower alkylene having 1-4 carbon atoms, preferably $-CH_2-$; and n is an integer

EP 0 442 549 A2

from 1-12, preferably from 3-8. A preferred peroxyacid is phthaloylaminoperoxycaproic acid.

AQUEOUS LIQUID BLEACH COMPOSITION

Background of the invention

1. Field of the invention

The invention relates to an aqueous liquid bleaching composition comprising a selected organic peroxy acid, which composition may be used for the bleaching of fabrics and hard surfaces.

2. The prior art

Quite a number of organic peroxy acids have been reported in the literature. These peroxy materials have begun to assume great commercial importance as bleaches, especially for fabrics. Many of the more effective organic peroxy acids are solid, substantially water-insoluble materials. Much of the published art has been directed at devising means for stably suspending these peroxyacids in water.

One of the early patents in the area is US 3,996,152 disclosing the suspension of substantially water-insoluble peroxyacids by non-starch thickening agents such as Carbopol 94® in an aqueous media at low pH. Suggested as suitable peroxyacid were diperazelaic, diperbrassylic, dipersebacic and diperisophthalic acids. US Patent 4,017,412 reports similar systems except that starch based thickening agents were employed. From later investigations it became evident that the thickener type systems mentioned in the foregoing patents formed gel-like matrices which exhibited instability upon storage at elevated temperatures.

When formulated at high levels, these thickeners-systems became more stable but then caused difficulties with pourability.

US Patent 4,642,198 lists an even more expansive variety of water-insoluble organic peroxy acids intended for suspension in an aqueous, low pH liquid. Herein was first disclosed the use of surfactants, both anionic and nonionic, as suspending agents for the peroxyacid particles.

The preferred peroxy material was identified as 1,12-diperoxydodecanedioic acid (DPDA) and this was employed in almost all the examples.

EP-A-0 176 124 also focusses upon surfactant suspended 1,12-diperoxydodecanedioic acid in a low pH aqueous liquid. This art informs that surfactants other than alkylbenzene sulfonate have a detrimental effect upon chemical stability of the suspensions.

EP-A-0 240 481 seemingly also finds some special significance in the use of alkylbenzene sulfonate, focusses upon DPDA, and further suggests use of magnesium sulfate as a suspension aid and peracid stabiliser.

Other surfactant suspending systems for peroxyacids are disclosed in US Patents 4,824,592 and US 4,828,747. The peroxyacids disclosed herein are of the classes disclosed in the foregoing patents with preference for DPDA.

In US Patent 4,822,510 there is suggested to use 4,4'-sulphonyl-bisperoxybenzoic acid as the solid, water-insoluble peroxyacid.

The aforementioned art has placed great emphasis upon optimizing the suspending systems of the liquid bleach to improve stability.

Evidently, there has been little consideration given to improving both stability and performance altogether.

Consequently it is an object of the present invention to provide an improved aqueous liquid bleach composition based upon a solid, substantially water-insoluble organic peroxy acid having improved stability and performance.

More specifically, it is an object of the present invention to provide an aqueous suspension of a solid, substantially water-insoluble organic peroxy acid, which is chemically and physically stable throughout a wide range of temperatures and which is moreover highly effective for use in the disinfecting and bleaching of substrates, e.g. fabrics and hard surfaces.

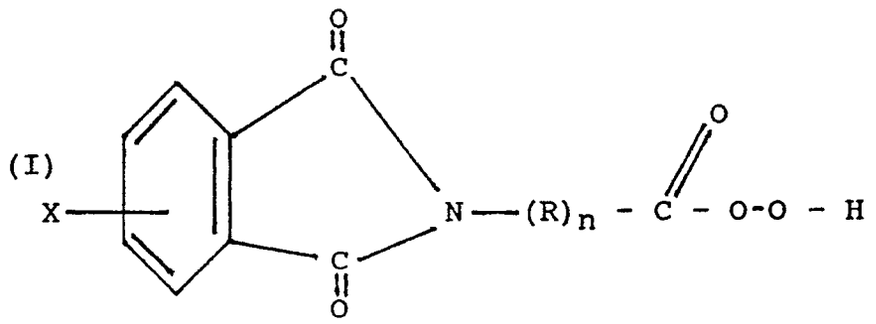
These and other objects of the present invention will become apparent as further details are provided in the subsequent discussion and Examples.

SUMMARY OF THE INVENTION

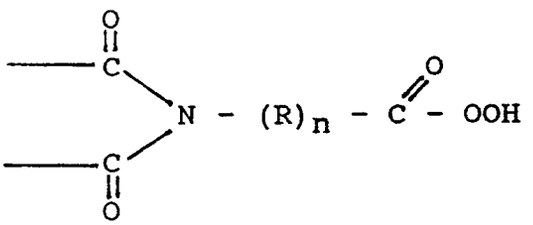
An aqueous liquid bleaching composition having a pH of from 1 to 6.5 is herein provided comprising:

(i) from 1 to 40% by weight of a solid, substantially water-insoluble peroxyacid having the general

formula:



wherein X is H, alkyl chain, a halogen, a carboxyl group in any position on the aromatic ring, or the same peroxycarboxylic acid group.



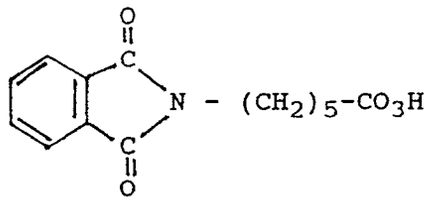
in symmetrical position to the first peroxyacid group on the aromatic ring;
R is a straight or branched chain lower alkylene having 1-4 carbon atoms, preferably - CH_2 -; and
n is between 1-12, preferably 3-8.
(ii) from 2 to 50% by weight of a surfactant; and
(iii) from 1.5 to 30% by weight of an electrolyte.

DETAILED DESCRIPTION OF THE INVENTION

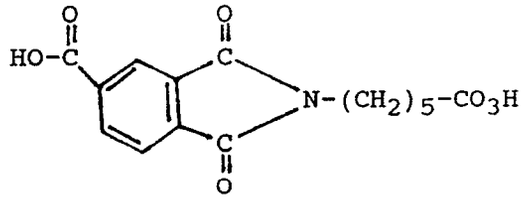
It has now been found that imidoperoxycarboxylic acids of formula (I) above when presented as an aqueous suspension comprising a surfactant and electrolyte as hereinbefore defined at a pH within the range of 1-6.5, preferably from 2-5, are not only extremely stable both physically and chemically, but also show very effective bleaching and disinfecting properties already at low temperatures e.g. from ambient to about 40 ° C, as compared to similar formulations based on DPDA as the peroxyacid.

Preferred examples of imidoperoxycarboxylic acids usable in the present invention are those having the following structures:

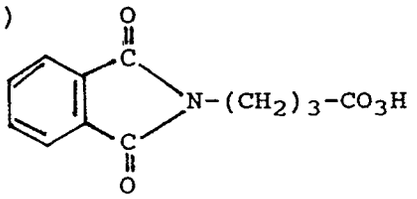
(1)



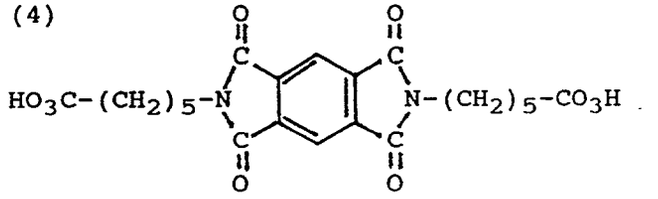
(2)



(3)



(4)



of which phthaloylamino peroxy caproic acid (("PAP") of formula (1) is particularly preferred.

Amounts of this class of peroxyacids to be used in the compositions of this invention range from about 1 to about 40% by weight, preferably from about 2 to 30%, optimally between about 5 and 20% by weight.

The particle size of the peroxy acid used in this invention is of some importance. Particles that are too large have been found to readily separate while very small particle sizes decrease chemical stability. Advantageously the range of particle size should be from about 10 to 1,000 microns, preferably between 20 and 500 microns, optimally between 30 and 250 microns.

Surfactants are required to stably suspend the imidoperoxy carboxylic acid of the present invention. Suitable for this purpose are anionic, nonionic, cationic, zwitterionic surfactants and mixtures thereof. However, the preferred system is a mixed anionic and nonionic detergent combination.

Nonionic surfactants useful for the present invention may be selected from a wide category of materials, many of which are outlined in Schwartz, Perry Vol. II, 1958 "Detergents and Surface Agents" and Schick, vol. I, 1967 "Nonionic Surfactants". For instance, fatty acids, fatty alcohols, fatty amides and alkoxylated derivations thereof may be usefully employed. Within the alkoxylate category, there is recommended ethylene oxide and/or propylene oxide condensation products of C_8-C_{20} linear-or branched-chain aliphatic carboxylic acids, aliphatic alcohols and alkyl phenols. Especially preferred, however, are the C_{12}-C_{18} aliphatic alcohols ethoxylated with an average from about 3 to about 12 moles of ethylene oxide per alcohol molecule. Even more specifically the C_{12}-C_{15} alcohols condensed with either an average of 3 or 9 moles ethylene oxide and the C_{12}-C_{14} aliphatic alcohols condensed with 7 moles ethylene oxide have been found to be highly effective.

Anionic surfactants which may be useful for the present invention can be found listed in Schwartz, Perry, Vol. II, 1958 "Detergents and Surface Active Agents".

Examples of anionic materials are water-soluble salts of alkylbenzene sulfonates, alkyl sulfates, alkyl ether sulfates, diakyl sulfosuccinates, paraffin sulfonates, α-olefin sulfonates, α- sulfocarboxylates and their esters, alkyl glycerol ether sulfonates, alkyl phenol polyethoxy ether sulfates, 2-acyloxy-alkane-1-sulfonates, β-alkoxyalkane sulfonates, secondary alkane sulfonates, and mixtures thereof.

The cationic detergents which can be used in the present invention include quaternary ammonium salts which contain at least one alkyl group having from 12 to 20 carbon atoms.

Although the halide ions are the common anions, other suitable anions include acetate, phosphate, sulfate, nitrate and the like.

Specific cationic detergents include distearyl dimethyl ammonium chloride, stearyl dimethyl benzyl ammonium chloride, stearyl trimethyl ammonium chloride coco dimethyl benzyl ammonium chloride, dicoco dimethyl ammonium chloride, cetyl pyridinium chloride, cetyl trimethyl ammonium bromide, stearyl amine salts that are soluble in water such as stearyl amine acetate and stearyl amine hydrochloride, stearyl dimethyl amine hydrochloride, distearyl amine hydrochloride, alkyl phenoxyethoxyethyl dimethyl ammonium chloride, decyl pyridinium bromide, pyridinium chloride derivative of the acetyl amino ethyl esters of lauric acid, lauryl trimethyl ammonium chloride, decyl amine acetate, lauryl dimethyl ethyl ammonium chloride, the lactic acid and citric acid and other acid salts of stearyl-1-amidoimidazoline with methyl chloride, benzyl chloride, chloroacetic acid and similar compounds, mixtures of the foregoing, and the like.

Zwitterionic detergents include alkyl-β-iminodipropionate, alkyl-β-aminopripionate, fatty imidazolines, betaines, and mixtures thereof. Specific examples of such detergents are 1-coco-5-hydroxyethyl-5-carboxymethyl imidazoline, dodecyl-β-alanine, the inner salt of 2-trimethylamino lauric acid, and N-dodecyl-N,N-dimethyl amino acetic acid.

The total surfactant amount in the liquid bleaching composition of the invention may vary from 2 to 50% by weight, preferably from 5 to 35% by weight, depending on the purpose of use.

In the case of suspending liquids comprising an anionic and a nonionic surfactant, the ratio thereof may vary from about 10:1 to 1:10. The term anionic surfactant used in this context includes the alkali metal soaps of synthetic or natural long-chain fatty acids having normally from 12 to 20 carbon atoms in the chain.

Preferred surfactant mixtures usable in the present invention are mixtures of:

i) sodium C_{10}-C_{18} alkyl benzene sulphonate and an ethyloxylated nonionic surfactant;

ii) Sodium C_{12}-C_{18} secondary alkane sulphonate and an ethoxylated nonionic surfactant,

Mixtures including a fatty acid, especially C_{12}-C_{18} fatty acids, are particularly preferred.

The total level of electrolyte(s) present in the composition to provide structuring may vary from about 1.5 to about 30%, preferably from 2.5 to 25% by weight. Examples of electrolytes include inorganic compounds such as sodium sulfate and sodium nitrate, and mixtures thereof.

Since most commercial surfactants contain metal ion impurities (e.g. iron and copper) that can catalyze peroxy acid decomposition in the liquid bleaching composition of the invention, those surfactants are preferred which contain a minimal amount of these metal ion impurities. The peroxy acid instability results in fact from its limited, though finite, solubility in the suspending liquid base and it is this part of the dissolved peroxy acid which reacts with the dissolved metal ions. It has been found that certain metal ion complexing agents can remove metal ion contaminants from the composition of the invention and so retard the peroxy acid decomposition and markedly increase the lifetime of the composition.

Examples of useful metal ion complexing agents include dipicolinic acid, with or without a synergistic amount of a water-soluble phosphate salt; dipicolinic acid N-oxide; picolinic acid; ethylene diamine tetraacetic acid (EDTA) and its salts; various organic phosphonic acids or phosphonates such as hydroxyethylidenediphosphonic acid (Dequest 2010^{R}), ethylene diamine tetra-(methylene phosphonic acid), -Dequest 2040- and diethylene triamine penta-(methylene phosphonic acid)-Dequest^{R} 2060.

Other metal complexing agents known in the art may also be useful, the effectiveness of which may depend strongly on the pH of the final formulation. Generally, and for most purposes, levels of metal ion complexing agents in the range of from about 10-1000 ppm are already effective to remove the metal ion contaminants.

In addition to the components discussed above, the liquid bleaching compositions of the invention may also contain certain optional ingredients in minor amounts. Typical examples of optional ingredients are suds-controlling agents, such the various silicone oils, fluorescers, perfumes, coloring agents, abrasives, hydrotropes and antioxidants. However, any such optional ingredient should only be incorporated if its presence in the composition does not significantly reduce the chemical and physical stability of the peroxy acid in the suspending system.

A particularly preferred optional ingredient is hydrogen peroxide (H_2O_2). It has been found that hydrogen peroxide, when incorporated in the aqueous liquid bleach composition of the invention is quite compatible with the imido peroxy carboxylic acid. Addition of hydrogen peroxide to the present bleach composition serves to provide an additional benefit of boosting its high temperature (i.e. above 60 °C) bleaching performance.

Usually and in practice an amount of about 2% to 10% by weight, preferably from 4% to 6% by weight of hydrogen peroxide in the composition is adequate to achieve the desired effect.

Aqueous liquid products encompassed by the invention will have a viscosity in the range of from about 50 to 20,000 centipoises (0.05 to 20 Pascal seconds) measured at a shear rate of 21 second^{-1} at 25 °C. In most cases, however, the products of the invention will have a viscosity of from about 0.2 to about 12 PaS, preferably between about 0.5 and 1.5 PaS.

Also of importance is that the aqueous liquid bleaching compositions of this invention have an acid pH in the range of from 1 to 6.5, preferably from 2 to 5, particularly between 3.0 and 4.5.

The following Examples will more fully illustrate the embodiments of this invention. All parts, percentages and proportions referred to herein are by weight of the total composition unless otherwise stated.

Examples I - IV

The following table shows aqueous liquid bleach formulation within the invention which are stable and

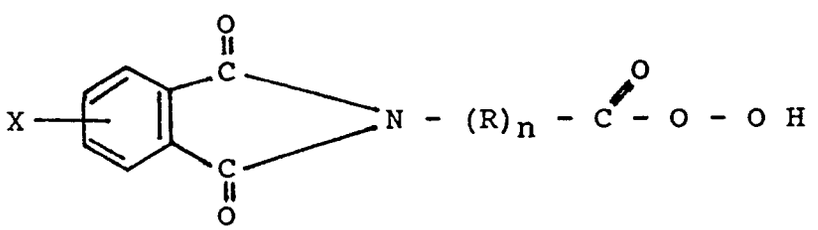
effective.

Table

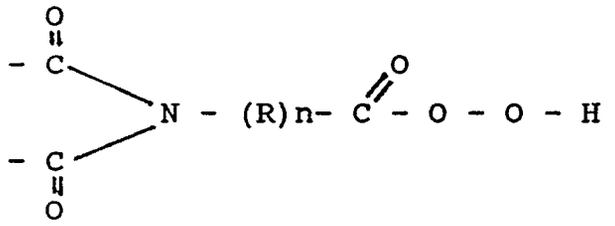
Ingredients	% by weight I	II	III	IV
Sodium C_{12}-alkyl benzene sulphonate	6.65	--	--	--
Secondary C_{13}-C_{17} alkane sulphonate	--	5.1	8.0	6.5
C_{12}-C_{15} primary alcohol/3 ethylene oxide	--	0.9	--	1.5
C_{12}-C_{15} primary alcohol/7 ethylene oxide	2.25	--	--	--
C_{12}-C_{15} primary alcohol/9 ethylene oxide	--	--	1.0	--
C_{12}-C_{16} fatty acid	--	--	2.0	1.0
Anhydrous sodium sulphate	6.65	10.0	3.0	3.8
PAP	5.0	10.0	5.1	5.0
Dequest® 2010 (polyphosphonate)	0.08	0.04	0.07	0.07
H_2O_2	--	--	--	5.0
Water + sulphuric acid to adjust pH to 3.5 - 4.5	Balance			

Claims

1. An aqueous liquid bleaching composition having a pH of from 1 to 6.5, and comprising form 1 to 40% by weight of a solid, particulate, substantially water-insoluble organic peroxyacid, from 2 to 50% by weight of a surfactant and from 1.5 to 30% by weight of an electrolyte, characterized in that said organic peroxyacid is an imidoperoxycarboxylic acid having the formula:

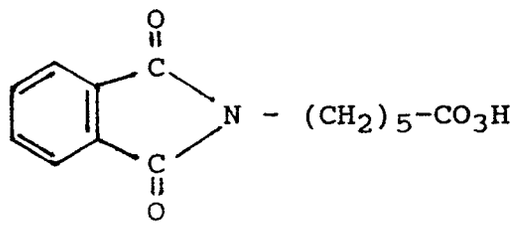


wherein X is H, alkyl chain, a halogen, a carboxyl group in any position in the aromatic ring, or the same peroxycarboxylic acid group



in symmetrical position to the first peroxyacid group on the aromatic ring;
R is a straight or branched chain lower alkylene having 1-4 carbon atoms, preferably - CH_2-; and n is an integer from 1-12, preferably from 3-8.

2. A composition according to claim 1, characterized in that said peroxyacid is phthaloylaminoperoxycaproic acid having the formula:



3. A composition according to claim 1 or 2, characterized in that it comprises a surfactant mixture selected from mixtures of:
   i) sodium C_{10}-C_{18} alkyl benzene sulphonate and an ethoxylated nonionic surfactant; and
   ii) sodium C_{12}-C_{18} secondary alkane sulphonate and an ethoxylated nonionic surfactant.

4. A composition according to claim 3, characterized in that said surfactant mixture further includes a fatty acid.

5. A composition according to any of the above claims 1-4, characterized in that the composition further comprises hydrogen peroxide in an amount of from 2 to 10% by weight.