

Europäisches Patentamt  
European Patent Office  
Office européen des brevets



Publication number: **0 443 640 A2**

**EUROPEAN PATENT APPLICATION**

Application number: **91200071.8**

Int. Cl.<sup>5</sup>: **C11D 3/39, C11D 1/62**

Date of filing: **16.01.91**

Priority: **23.01.90 GB 9001491**

Date of publication of application:  
**28.08.91 Bulletin 91/35**

Designated Contracting States:  
**CH DE ES FR GB IT LI NL SE**

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

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

Inventor: **Francis, Keith Charles**  
**Unilever Res. Port Sunlight, Lab. Quarry**  
**Road East**  
**Bebington, Wirral, Merseyside L63 3JW(GB)**  
Inventor: **Oakes, John**  
**Unilever Res. Port Sunlight, Lab. Quarry**  
**Road East**  
**Bebington, Wirral, Merseyside L63 3JW(GB)**

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

**Bleaching process and bleach compositions.**

Use is disclosed of low levels of a quaternary ammonium compound as a bleach booster for organic mono-peroxyacid compounds not containing an additional negative charge in bleach solutions and in bleach (detergent) compositions comprising said peroxyacid bleach compound.

Process for bleaching substrates is also disclosed by treating the substrate with a bleach solution comprising said mono-peroxyacid and a quaternary ammonium compound as bleach booster.

**EP 0 443 640 A2**

## BLEACHING PROCESS AND BLEACH COMPOSITIONS

This invention relates to an improved process for bleaching substrates using a peroxyacid bleach compound and to improved bleach compositions comprising a peroxyacid bleach compound. The term "substrates" used herein includes fibres, textiles and fabrics of both animal and vegetable origins, synthetics and mixtures thereof, such as cottons, cellulotics, wool and other protein fibres, bast fibres, acrylic and other synthetic fibres, fabrics, and textiles.

An important trend in washing and bleaching practices in household and industry has been the move towards lower wash and bleaching temperatures, i.e. at about 40° C and below. In turn, this trend towards lower temperature bleaching has necessitated improvement in the bleaching performance of bleach (detergent) compositions, particularly with respect to the stain removal of bleachable stains and soiling, such as tea, wine, coffee, etc. and the so-called dingy soils.

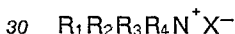
It is known that organic peroxyacids incorporated as such or in the form of their precursors generating the peroxyacid in situ in bleach formulations are effective bleaches at temperatures significantly below the boil-wash temperatures, e.g. from above 40 to 60° C. Their effect at about 40° C and below, however, is still far from ideal.

US Patent no. 3,749,674 proposes the use of a quaternary ammonium salt as so-called micelle catalyst for the bleaching reaction of organic peroxyacids containing an additional anionic group capable of forming bi-anionic dimers in solution. Formation of these indispensable transition complexes of the bleaching reaction is said to be facilitated by positively charged micelles formed by the quaternary ammonium salts in solution.

GB-A-1,557,568 discloses granular laundry compositions comprising an agglomerate of an organic peroxyacid precursor and a quaternary ammonium surfactant. The agglomerated quaternary ammonium compound present in the same granular particles together with the peroxyacid precursor is said to reduce the tendency of "pin-point" spotting.

It has now been found, surprisingly, that the bleaching performance of organic peroxyacid bleach compounds not containing an additional negative charge can be boosted to an unexpectedly substantial degree by the use of specified low levels of a quaternary ammonium compound.

The quaternary ammonium compounds suitable in the present invention are the mono-long chain type quaternary ammonium compounds having the formula :



wherein R<sub>1</sub> is a C<sub>8</sub>-C<sub>18</sub> alkyl, alkenyl or alkaryl group, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> are each C<sub>1</sub>-C<sub>3</sub> alkyl groups, wherein the total number of carbon atoms of R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> is from 15 to 21; and X<sup>-</sup> is a counter-ion, including Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup> or CH<sub>3</sub>SO<sub>4</sub><sup>-</sup>; and the poly-long chain type quaternary ammonium compounds having the formula:

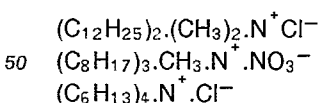


wherein at least two R's are C<sub>4</sub>-C<sub>12</sub> alkyl, alkenyl or alkaryl groups and the remaining R or R's are C<sub>1</sub>-C<sub>12</sub> alkyl, alkenyl or alkaryl groups, wherein the total number of carbon atoms of all four R's is from 12 to 28, preferably from 14 to 26; and X<sup>-</sup> is a counter-ion, including Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup> or CH<sub>3</sub>SO<sub>4</sub><sup>-</sup>.

Preferred mono-long chain quaternary ammonium compounds are those wherein R<sub>1</sub> is an alkyl group having from 12-16 carbon atoms, preferably from 14-16 carbon atoms; R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> are each methyl or ethyl, preferably methyl; and the carbon atoms of R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> total 17-19.

Specific examples of such compounds are tetradecyl-trimethyl ammonium nitrate; tetradecyl-trimethyl ammonium methosulphate and hexadecyl-trimethyl ammonium chloride.

Specific examples of suitable poly-long chain quaternary ammonium compounds are:



Quaternary ammonium compounds are, of course, known in the art as belonging to the class of cationic surface-active agents. They are referred to in the prior art for use as, among other things, emulsifiers, fabric softeners, antistatics and disinfectants, or for use in a conventional detergent functionality. They have also

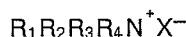
been used, as claimed in US-A-3,749,674, to improve the bleaching action of monopersulphates and certain types of organic peroxyacids having an extra charged group e.g.  $\text{CO}_2^-$ ,  $\text{CO}_3^-$  and  $\text{SO}_3^-$ , in addition to the peroxy carboxylic group. It is said that this is due to the quaternary ammonium compounds forming micelles in solution which facilitate formation of bi-anionic complexes typical for the afore-mentioned peroxyacid compounds.

There has apparently been no realisation or appreciation in the art of the beneficial effect that low levels of quaternary ammonium compounds can have upon the performance of organic peroxyacid bleach compounds which in solution do not form bi-anionic dimers.

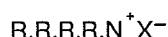
The present invention is based on the discovery that the bleach performance of the more effective mono-peroxyacid compounds not containing an additional charge can be boosted still to a significant degree with mono- or poly-long chain quaternary ammonium compounds as defined hereinabove already at a level of as low as  $1 \times 10^{-4}$  Molar (M) in the bleach solution, improving steeply with increasing levels up to about  $12 \times 10^{-4}$  Molar (M). Below  $1 \times 10^{-4}$  Molar the effect is too insignificant and above  $12 \times 10^{-4}$  Molar the effect generally plateaus or decreases quickly. Preferred use levels are from 2 to  $10 \times 10^{-4}$  M, particularly from 5 to  $10 \times 10^{-4}$  M.

The pH of the bleaching solution is not critical and improvements of the bleaching and stain-removal effect can be achieved under acid as well as under alkaline conditions, e.g. at pH 4 to about 10.5, though a bleaching pH of from about 7 to about 10 is generally preferred.

Accordingly, in its broadest aspect the invention provides in the use of a quaternary ammonium compound having the formula :

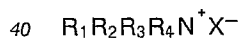


wherein  $\text{R}_1$  is a  $\text{C}_8$ - $\text{C}_{18}$  alkyl, alkenyl or alkaryl group;  $\text{R}_2$ ,  $\text{R}_3$  and  $\text{R}_4$  are each  $\text{C}_1$ - $\text{C}_3$  alkyl groups, wherein the total number of carbon atoms of  $\text{R}_1$ ,  $\text{R}_2$ ,  $\text{R}_3$  and  $\text{R}_4$  is from 15 to 21; and  $\text{X}^-$  is a counter-ion, including  $\text{Cl}^-$ ,  $\text{NO}_3^-$  or  $\text{CH}_3\text{SO}_4^-$ ; or a quaternary ammonium compound having the formula :

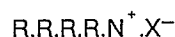


wherein at least two R's are  $\text{C}_4$ - $\text{C}_{12}$  alkyl, alkenyl or alkaryl groups and the remaining R or R's are  $\text{C}_1$ - $\text{C}_{12}$  alkyl, alkenyl or alkaryl groups, wherein the total number of carbon atoms of all four R's is from 12 to 28, preferably from 14 to 26; and  $\text{X}^-$  is a counter-ion, including  $\text{Cl}^-$ ,  $\text{NO}_3^-$  or  $\text{CH}_3\text{SO}_4^-$ , as a bleach booster for organic mono-peroxyacid compounds not containing an additional negative charge, in bleach solutions or bleaching (detergent) compositions comprising said peroxyacid bleach compound.

In another aspect, the invention provides a process for bleaching substrates by treating the substrate with a bleach solution comprising essentially a peroxyacid bleach compound, characterized in that said bleach solution comprises an organic mono-peroxyacid not containing an additional negative charge and a quaternary ammonium compound having the formula :



wherein  $\text{R}_1$  is a  $\text{C}_8$ - $\text{C}_{10}$  alkyl, alkenyl or alkaryl group,  $\text{R}_2$ ,  $\text{R}_3$  and  $\text{R}_4$  are each  $\text{C}_1$ - $\text{C}_3$  alkyl groups wherein the total number of carbon atoms of  $\text{R}_1$ ,  $\text{R}_2$ ,  $\text{R}_3$  and  $\text{R}_4$  is from 15 to 21; and  $\text{X}^-$  is a counter-ion, including  $\text{Cl}^-$ ,  $\text{NO}_3^-$  or  $\text{CH}_3\text{SO}_4^-$ ; or a quaternary ammonium compound having the formula:



wherein at least two R's are  $\text{C}_4$ - $\text{C}_{12}$  alkyl, alkenyl or alkaryl groups and the remaining R or R's are  $\text{C}_1$ - $\text{C}_{12}$  alkyl, alkenyl or alkaryl groups, wherein the total number of carbon atoms of all four R's is from 12 to 28, preferably from 14 to 26, and  $\text{X}^-$  is a counter-ion, including  $\text{Cl}^-$ ,  $\text{NO}_3^-$  or  $\text{CH}_3\text{SO}_4^-$ ; as bleach booster for said mono-peroxyacid, said quaternary ammonium compound being present at a level of from  $1 \times 10^{-4}$  to  $12 \times 10^{-4}$  Molar, preferably from  $2 \times 10^{-4}$  to  $10 \times 10^{-4}$  Molar.

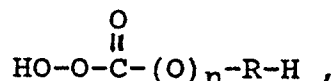
Bleaching processes incorporating said low levels of quaternary ammonium compounds can be carried out using the mono-peroxyacid compound at the usual active oxygen concentration in solution of about  $0.3 \times 10^{-3}$  Molar to about  $3 \times 10^{-3}$  Molar, preferably from 0.3 to  $1.5 \times 10^{-3}$  Molar.

Advantageously, the organic mono-peroxyacid bleach compound as defined above and the quaternary ammonium compound as defined above are present in a molar ratio of peroxyacid bleach compound to quaternary ammonium compound of from about 50:1 to about 1:2.5, preferably from about 25:1 to 1:2.

Compositions comprising the aforesaid mono-peroxyacid compound bleach and the aforesaid quaternary ammonium compound are effective over a wide pH range of between 4 and about 10.5, with optimal pH range lying between 7 and 9.5.

The peroxyacid bleach compounds utilized in the present invention are the organic mono-peroxyacids and their salts, having no other anionic moiety than the peroxycarboxyl group.

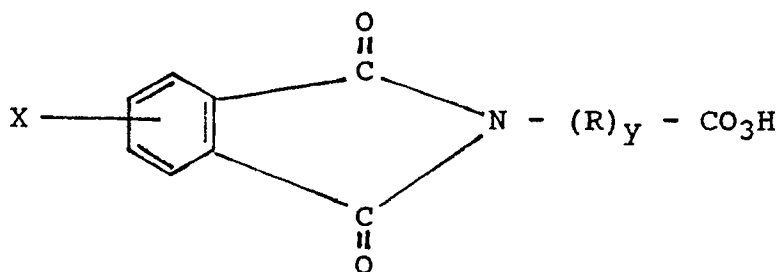
A suitable class of organic peroxyacids can be represented by compounds of the general formula :



wherein R is an alkylene or substituted alkylene group containing 1 to 20 carbon atoms or an arylene group containing from 6 to 8 carbon atoms, n is 0 or 1.

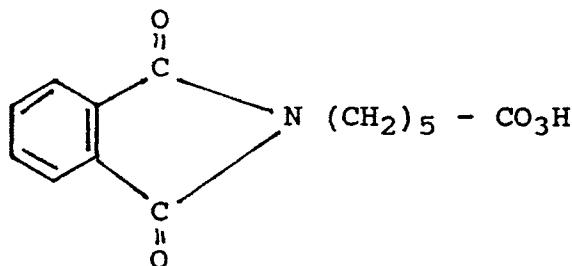
Specific examples of compounds of this type are peracetic acid, peroxyauric acid, peroxy-nonanoic acid, peroxybenzoic acid, m-chloroperoxybenzoic acid, and p-nitro-peroxybenzoic acid.

Another class of peroxyacids usable herein are those as described in EP-A-0 325 288 which can be represented by the general formula:



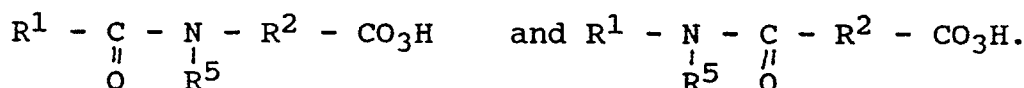
wherein X is H, alkyl chain, a halogen or nitro-group in any position of the aromatic ring; R is a straight or branched chain lower C<sub>1</sub>-C<sub>4</sub>-alkylene, preferably -CH<sub>2</sub>-; and y is between 1 and 12, preferably 3-8.

A preferred compound within this class is one having the formula:



phthaloylaminoperoxyheptanoic acid.

Still another class of peroxyacids usable herein is for example the class of fatty peroxyacids and salts thereof having amide moieties in the fatty chain as described in EP-A-0 170 386 and EP-A-0 290,292, of the following general formulae:



wherein R<sup>1</sup> and R<sup>2</sup> are alkyl(ene), aryl(ene) or alkaryl(ene) groups containing from about 1 to about 14 carbon atoms and R<sup>5</sup> is H or an alkyl, aryl or alkaryl group containing from about 1 to about 10 carbon atoms.

Still further classes of organic mono-peroxyacids not containing an additional anionic moiety are known, such as the imidoperoxy-carboxylic acids of EP-A-0 366 041.

Suitable peroxy acid salts for use herein are for example the alkalimetal and magnesium salts thereof.

In systems wherein the peroxyacid is formed **in situ** from its precursor or precursors, the peroxyacid can be formed from the combination of an organic peroxyacid precursor and hydrogen peroxide or a persalt of the peroxyhydrate type, e.g. sodium perborate, by perhydrolysis, or from a precursor which generates peroxyacid by hydrolysis. Hence, various peroxyacid precursors will fall within the scope of use in the compositions of the invention. These include, for example, benzoyl peroxide, which is capable of generating peroxybenzoic acid.

Typical examples of peroxyacid precursors generating peroxyacids by perhydrolysis are disclosed in e.g. US Patent 3,256,198; US Patent 3,272,750; GB Patent 836,988; GB Patent 864,798; US Patent 4,283,301; US Patent 4,486,327; US Patent 4,536,314; US Patent 3,686,127; US Patent 4,397,757; US Patent 4,751,015; and EP-A-0 120 591.

Preferred peroxyacid precursors include sodium-4-benzoyloxy benzene sulphonate; N,N,N',N'-tetraacetyl ethylene diamine; sodium-1-methyl-2-benzoyloxy benzene-4-sulphonate; and sodium-4-methyl-3-benzoyloxy benzoate, and also those precursors as described in EP-A 0 170 386 and EP-A 0 290 292. These precursors are utilized in the presence of an alkaline source of hydrogen peroxide to generate the corresponding peracids **in situ**.

Any of the hydrogen peroxide sources known in the art, including  $H_2O_2$ , can be utilized together with peracid precursors to generate peracids by a reaction, known as perhydrolysis. Examples of hydrogen peroxide sources utilizable herein include the alkali metal peroxides, organic peroxides, such as urea peroxide, and the inorganic "persalts" such as the alkali metal perborates, percarbonates, perphosphates and persulfates. Preferred compounds for use in the process of the invention are hydrogen peroxide, sodium percarbonate and sodium perborate tetra- or monohydrate.

The peroxyacid bleach compounds, the performance of which can be boosted by the use of the quaternary ammonium compounds as defined herein according to the invention, therefore include the peroxyacids or peroxyacid salts **per se**, as well as the above-described peroxyacid precursor systems generating the peroxyacid bleach **in situ**, the peroxyacids and salts thereof being preferred.

The process of the invention is effective at low temperatures, e.g. at 40° C and below, and can be advantageously used in both household practice for the effective bleaching and stain removal from textiles and fabrics, as well as in industrial practice for various purposes whereby the results are substantially improved such as in the following areas:

- 1) The bleaching of cotton, cotton blends and cellulosics by discontinuous methods whereby temperatures can be reduced to significantly below the boil;
- 2) Cold pad batch cotton or cellulosic bleaching in shorter times than normal;
- 3) Continuous bleaching where steaming temperatures and times lower than normal can be used;
- 4) Oxidative de-sizing;
- 5) Bleaching of wool and other protein fibres;
- 6) Bleaching bast fibres; and
- 7) The preparation of wool for the subsequent exhaustion of shrink-resisting polymers.

The compositions of the invention having improved bleaching effect, particularly at the lower temperature region, can be used as a true bleaching composition, as a bleach additive to a wash liquor- or for admixing with a cleaning composition.

In the case of a true bleaching composition and a bleach additive, the composition will essentially comprise a peroxyacid bleach compound, which may be an organic peroxyacid or a peroxyacid salt or a precursor thereof, as herein before described, and a quaternary ammonium compound as defined hereinbefore.

When admixed to cleaning compositions forming effective low temperature detergent bleach compositions, the compositions are usable for washing and bleaching of textiles, fabrics and fibres at low temperatures. In such a case, the formulation will normally contain, apart from the above essential ingredients, a surface-active material, detergency builders and other known ingredients of such formulations.

In that case, the bleaching composition is incorporated therein in an amount such that, upon use, the detergent bleach composition at a dosage of from 1-6 g/l will have the peroxyacid and the quaternary ammonium compound in the washing and bleaching solution at molar concentrations within the ranges as advantageously described hereinbefore. The lower dosage is normally used under US washing conditions, whereas the higher dosage is normal in European washing practice.

The surface-active material should preferably be non-anionic in nature, since anionic surfactants may neutralize the effect of the cationic quaternary ammonium compound.

Suitable surface-active agents which can be utilized herein are nonionic, zwitterionic and/or amphoteric in nature, the total level of which may range from 0% up to about 50% by weight, preferably from about 2% to 40% by weight of the composition, most preferably 4 to 25% by weight.

Examples of suitable nonionic surface-active compounds which may be used include in particular the reaction products of alkylene oxides, usually ethylene oxide, with alkyl ( $C_6$ - $C_{22}$ ) phenols, generally 5-25 EO, i.e. 5-25 units of ethylene oxides per molecule; the condensation products of aliphatic ( $C_8$ - $C_{18}$ ) primary or secondary linear or branched alcohols with ethylene oxide, generally 6-30 EO, and products made by  
 5 condensation of ethylene oxide with the reaction products of propylene oxide and ethylene diamine. Other so-called nonionic surface-actives include alkyl polyglycosides, long chain tertiary amine oxides, long chain tertiary phosphine oxides and dialkyl sulfoxides.

Amounts of amphoteric or zwitterionic surface-active compounds can also be used in the compositions of the invention but this is not normally desired owing to their relatively high cost. If any amphoteric or  
 10 zwitterionic detergent compounds are used, it is generally in small amounts in compositions based on the much more commonly used nonionic actives.

A further description of surface-active compounds of the aforementioned classes can be found in Schwartz, Perry Vol. II, 1958, "Detergents and Surface Active Agents" and Schick, Vol. I, 1967, "Nonionic Surfactants".

15 The bleaching and cleaning compositions utilizing the bleach composition of the invention will normally also contain a detergency builder. Builder materials may be selected from (1) calcium sequestrant materials, (2) precipitating materials, (3) calcium ion-exchange materials and (4) mixtures thereof.

Examples of calcium sequestrant builder materials include alkali metal polyphosphates, such as sodium tripolyphosphate, nitrilotriacetic acid and its water-soluble salts; the alkali metal salts of carboxymethoxy  
 20 succinic acid, ethylene diamine tetraacetic acid, oxydisuccinic acid, mellitic acid, benzene polycarboxylic acids, citric acid; and polyacetalcarboxylates as disclosed US Patents 4,144,225 and 4,146,495.

Examples of precipitating builder materials include sodium orthophosphate, sodium carbonate and long-chain fatty acid soaps.

Examples of calcium ion-exchange builder materials include the various types of water-insoluble  
 25 crystalline or amorphous aluminosilicates, of which zeolites are the best-known representatives.

In particular, the compositions of the invention may contain any one of the organic or inorganic builder materials, such as sodium or potassium tripolyphosphate, sodium or potassium pyrophosphate, sodium or potassium orthophosphate, sodium carbonate, the sodium salt of nitrilotriacetic acid, sodium citrate, carboxymethyl malonate, carboxymethyl succinate and the water-insoluble crystalline or amorphous aluminosilicate builder materials, or mixtures thereof.  
 30

These builder materials may be present at a level of, for example, from 5 to 80% by weight, preferably from 10 to 60% by weight.

Apart from the components already mentioned, a fully formulated bleaching and cleaning composition of the invention can contain any of the conventional additives in the amounts in which such materials are  
 35 normally employed in fabric-washing detergent compositions. Examples of these additives include lather boosters, such as alkanolamides, particularly the monoethanolamides derived from palmkernel fatty acids and coconut fatty acids, lather depressants such as alkyl phosphates and silicones, anti-redeposition agents such as sodium carboxymethyl cellulose and alkyl or substituted alkyl cellulose ethers, stabilizers such as ethylene diamine tetraacetic acid, fabric-softening agents, inorganic salts such as sodium sulphate, and,  
 40 usually present in very small amounts, fluorescent agents, perfumes, enzymes such as proteases, cellulases, lipases and amylases, germicides and colorants.

The peroxyacid compounds usable in the bleach or bleach and detergent compositions of the invention may be present in an amount of from 0.5-65% by weight of the total composition, preferably from 1-50%, particularly from 1-25% by weight.

45 The higher side of the range is usually applied to true bleaching compositions which can be used as such for bleaching fabrics or as a bleach adjunct to detergent compositions. The lower side of the range applies to fully formulated heavy duty bleaching detergent compositions. In such compositions the peroxyacid compound is usually present at a level within the range of 0.5-15% by weight, preferably from 1-10% by weight.

50 The invention will now be further illustrated by way of the following examples.

#### EXAMPLE 1

Bleaching experiments were carried out on tea-stained test cloths. The tea-stained test cloths were  
 55 treated with bleaching solution at 40° C containing p-nitro peroxybenzoic acid in a concentration of  $1.2 \times 10^{-3}$  Molar for 30 minutes, at pH 4, pH 7.1 and pH 10 with and without tetradecyl-trimethyl ammonium nitrate (TDTAN) added at a concentration of  $5 \times 10^{-4}$  Molar.

The bleaching performances of each test were measured using a reflectophotometer and the results

expressed as difference in reflectance ( $\Delta R$ ) are tabulated below:

**TABLE 1** $\Delta R_{460}^*$ 

TD TAN	pH=4	pH=7.1	pH=10
(-)	15.0	17.0	4.0
(+)	27.3	29.7	20.8

**EXAMPLE II**

In this Example the effect of TD TAN on the bleaching performance of various peroxyacids is demonstrated. The bleaching experiments were carried out with bleaching solutions, again at 40 °C and for 30 minutes, using tea-stained test pieces. The peroxyacids used were m-chloroperoxybenzoic acid (MCPBA), peroxy-nonanoic acid (PNA) and peroxybenzoic acid (PBA), incorporated therein at a concentration of  $1.2 \times 10^{-3}M$  and the bleaching solutions were adjusted to pH 10.

The following results were obtained:

**TABLE 2**

<u>TD TAN concentration</u> ( $\times 10^{-4}M$ )	<u><math>\Delta R_{460}^*</math></u>		
	<u>MCPBA</u>	<u>PNA</u>	<u>PBA</u>
0	4.5	6.8	4.5
5	22.4	12.9	16.7

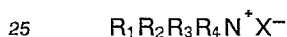
**EXAMPLE III**

When the bleaching experiments of Examples I and II were repeated in a Tergotometer together with a detergent base powder composition, dosed at 5 g/l, of the following formulation, the same significant bleach boosting effects were observed.

	<u>Base powder composition</u>	<u>% by weight</u>
	Nonionic fatty alcohol-7 ethoxylate	7.0
5	Maleic acid/acrylic acid copolymer (Sokolan CP5 ex BASF)	4.0
	Zeolite 4A	30.0
	Sodium triphosphate	15.0
10	Sodium sulphate	35.0
	Sodium ethylene diamine tetraacetate	0.3
	Sodium carboxymethyl cellulose	0.6
15	Ethylene diamine tetra(methylene phosphonate) (Dequest <sup>(R)</sup> 2047)	0.6
	Water + fluorescer	7.5

## 20 Claims

1. Use of a quaternary ammonium compound having the formula :

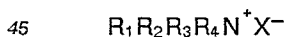


wherein  $R_1$  is a  $C_8$ - $C_{18}$  alkyl, alkenyl or alkaryl group;  $R_2$ ,  $R_3$  and  $R_4$  are each  $C_1$ - $C_3$  alkyl groups, wherein the total number of carbon atoms of  $R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$  is from 15 to 21; and  $X^-$  is a counter-ion, including  $Cl^-$ ,  $NO_3^-$  or  $CH_3SO_4^-$ ; or a quaternary ammonium compound having the formula :

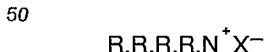


wherein at least two R's are  $C_4$ - $C_{12}$  alkyl, alkenyl or alkaryl groups and the remaining R or R's are  $C_1$ - $C_{12}$  alkyl, alkenyl or alkaryl groups, wherein the total number of carbon atoms of all four R's is from 12 to 28, preferably from 14 to 26; and  $X^-$  is a counter-ion, including  $Cl^-$ ,  $NO_3^-$  or  $CH_3SO_4^-$ , as a bleach booster for organic mono-peroxyacid compounds not containing an additional negative charge, in bleach solutions or bleaching (detergent) compositions comprising said peroxyacid bleach compound.

- 40 2. Process for bleaching substrates by treating the substrate with a bleach solution comprising essentially a peroxyacid bleach compound, characterized in that said bleach solution comprises an organic mono-peroxyacid not containing an additional negative charge and a quaternary ammonium compound having the formula :



wherein  $R_1$  is a  $C_8$ - $C_{18}$  alkyl, alkenyl or alkaryl group;  $R_2$ ,  $R_3$  and  $R_4$  are each  $C_1$ - $C_3$  alkyl groups, wherein the total number of carbon atoms of  $R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$  is from 15 to 21; and  $X^-$  is a counter-ion, including  $Cl^-$ ,  $NO_3^-$  or  $CH_3SO_4^-$ ; or a quaternary ammonium compound having the formula :



wherein at least two R's are  $C_4$ - $C_{12}$  alkyl, alkenyl or alkaryl groups and the remaining R or R's are  $C_1$ - $C_{12}$  alkyl, alkenyl or alkaryl groups, wherein the total number of carbon atoms of all four R's is from 12 to 28, preferably from 14 to 26; and  $X^-$  is a counter-ion, including  $Cl^-$ ,  $NO_3^-$  or  $CH_3SO_4^-$ , as bleach booster for said mono-peroxyacid; said quaternary ammonium compound being present at a level of from  $1 \times 10^{-4}$  to  $12 \times 10^{-4}$  Molar, preferably from  $2 \times 10^{-4}$  to  $10 \times 10^{-4}$  Molar.



3. Process according to Claim 2, characterized in that the mono-peroxyacid compound is present in the bleach solution at an active oxygen concentration of about  $0.3 \times 10^{-3}$  Molar to about  $3 \times 10^{-3}$  Molar.
- 5 4. Process according to Claim 3, characterized in that said active oxygen concentration is from 0.3 to  $1.5 \times 10^{-3}$  Molar.
5. Process according to Claims 2-4, characterized in that the organic mono-peroxyacid and the quaternary ammonium compound are present in a molar ratio of from about 50:1 to about 1:2.5, preferably from 25:1 to 1:2.
- 10 6. Process according to any of the above Claims 2-5, characterized in that said peroxyacid is selected from the group consisting of peroxybenzoic acid, p-nitroperoxybenzoic acid, m-chloroperoxybenzoic acid and peroxynonanoic acid.
- 15 7. Process according to Claim 2 or 6, characterized in that said peroxyacid is generated **in situ** via a peroxyacid bleach precursor.
8. Process according to any of the above Claims 2-7, characterized in that the quaternary ammonium compound is selected from the group of tetradecyl-trimethyl ammonium nitrate; tetradecyl-trimethyl ammonium methosulphate and hexadecyl-trimethyl ammonium chloride.
- 20 9. Use according to Claim 1, characterized in that in said bleach solution or bleaching composition the organic mono-peroxyacid and the quaternary ammonium compound are present in a molar ratio of from about 50:1 to 1:2.5, preferably from 25:1 to 1:2.
- 25 10. Use according to Claim 9, characterized in that said quaternary ammonium compound is selected from the group consisting of tetradecyl-trimethyl ammonium nitrate; tetradecyl-trimethyl ammonium methosulphate and hexadecyl-trimethyl ammonium chloride.
- 30 11. Use according to Claim 9 or 10, characterized in that said peroxyacid is selected from the group consisting of peroxybenzoic acid, p-nitro-peroxybenzoic acid, m-chloroperoxybenzoic acid and peroxynonanoic acid.
- 35 12. Use according to Claim 1 or 11, characterized in that said peroxyacid is generated **in situ** via a peroxyacid bleach precursor.

40

45

50

55