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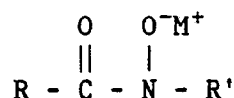
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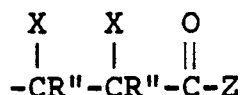
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(54) Hydroxamate bleach stabilizer.

(57) There are disclosed compositions comprising peroxygen containing bleach systems containing a bleach stabilizing amount of compound represented by the formula



wherein R is selected from the group consisting of optionally substituted straight and branched chained alkyl C₁₋₂₁, alkenyl C₁₋₂₁, hydrogen, and optionally substituted phenyl groups, and



wherein each R'' is independently selected from groups consisting of hydrogen, alkyl C₁₋₂₁ and alkenyl C₁₋₂₁, provided that the total number of carbons in both R'' groups is not greater than 21, each X is independently selected from hydrogen and SO₃ and Z is selected from the group consisting of hydroxy, alkoxy C₁₋₅ and alkenoxy C₁₋₅, -O⁻M⁺, -NR₂''' wherein each R''' is independently selected from the group consisting of hydrogen, alkyl C₁₋₅ or alkenyl C₁₋₅, and R' is selected from the group consisting of hydrogen, optionally substituted straight and branched chained alkyl C₁₋₂₁, alkenyl C₁₋₂₁ and an optionally substituted phenyl group, provided only one of R and R' is hydrogen said stabilizer having a hydrophile-lipophile (HLB) balance within the same range as the HLB of said compounds wherein R is an unsubstituted C₁₋₂₁ alkyl group and R' is hydrogen or an unsubstituted C₁₋₆ alkyl group, M is selected from hydrogen

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and a non-interfering cation, and further provided that when M^+ represents hydrogen and the composition contains a detergent active agent, the bleaching agent is selected from an inorganic peroxy compounds and bleach activator combination or an organic peroxy acid.

HYDROXAMATE BLEACH STABILIZER

This invention relates to the use of hydroxamic acids and their derivatives as stabilizers for peroxygen compounds.

Peroxygen compounds, both organic and inorganic, are widely used as bleaching agents. Major applications include the bleaching of paper pulp, where hydrogen peroxide itself can be used, and the washing of textiles. In products in powder or granular form that are sold as domestic detergents, solid peroxygen compounds such as perborates, percarbonates or percarboxylic acids are used. In order to improve the bleaching performance of such compounds at temperatures below 60° C, it is usual also to include in the detergent formulation one or more compounds that are referred to as bleach activators.

It is also known that peroxygen compounds are relatively unstable, so that, for example, commercial solutions of hydrogen peroxide normally include substances that stabilize the solution, i.e. reduce the rate at which the hydrogen peroxide decomposes on storage. Similarly, it is desirable to include components in detergent formulations that will prolong the bleaching efficiency of the peroxygen compound by reducing its rate of decomposition.

We have now found that certain hydroxamic acids and hydroxamates are very effective as stabilizers for hydrogen peroxide and other peroxygen compounds.

Hydroxamic acids have been proposed as extractants for metals. For example, according to U.S. Patent 3,900, 551, neo-alkylhydroxamic acids can be employed as ion-exchange agents in processes for liquid-liquid extraction with the aim of separating or purifying dissolved metals and of converting a metal salt solution into a solution of a salt of the same metal but with a different anion.

U.S. Patent 3,707,502 discloses detergent compositions containing sodium nitrilotriacetate, peroxy compounds and alkali metal salts of mono- and di-hydroxamic acids. In the compositions of U.S. Patent 3,707,502, the purpose of the hydroxamates is to reduce the corrosivity to copper shown by aqueous solutions of similar detergent compositions not containing the hydroxamates.

As indicated above, the present invention comprises hydroxamic acids and hydroxamates effective as stabilizers for peroxygen-containing systems. Accordingly, the invention provides compositions comprising a peroxygen containing bleach system and a bleach stabilizing amount of a bleach stabilizer represented by the formula



wherein R is selected from the group consisting of optionally substituted straight and branched chained alkyl C₁₋₂₁, alkenyl C₁₋₂₁, hydrogen, and optionally substituted phenyl groups, and



wherein each R'' is independently selected from groups consisting of hydrogen, alkyl C₁₋₂₁ and alkenyl C₁₋₂₁, provided that the total number of carbons in both R'' groups is not greater than 21, each X is independently selected from hydrogen and SO₃ and Z is selected from the group consisting of hydroxy, alkoxy C₁₋₅ and alkenoxy C₁₋₅, -O⁻M⁺, -NR₂''' wherein each R''' is independently selected from the group consisting of hydrogen, alkyl C₁₋₅ or alkenyl C₁₋₅, R' is selected from the group consisting of hydrogen, optionally substituted straight and branched chained alkyl C₁₋₂₁, alkenyl C₁₋₂₁ and an optionally substituted phenyl group, provided only one of R and R' is hydrogen said stabilizer having a hydrophile-lipophile (HLB) balance within the same range as the HLB of said compounds wherein R is an unsubstituted C₅₋₂₁ alkyl group and R' is hydrogen or an unsubstituted C₁₋₆ alkyl group, M is selected from hydrogen and a non-interfering cation, and further provided that when R' represents hydrogen and the composition contains a detergent active agent, the bleaching agent comprises an inorganic peroxy compound and bleach activator combination or an organic peroxy acid.

Embodiments of the invention include a solution of hydrogen peroxide that is stabilized by the presence

of a hydroxamic acid or salt; and a detergent composition including surface active (detergent active) components and a bleaching agent that comprises an organic peroxy acid, a combination of an inorganic peroxy compound and a bleach activator, or a mixture thereof, together with a hydroxamic acid or salt as defined above.

5 Some of the hydroxamic acids and their salts useful in the present invention are known compounds. They can be made from esters or acid halides of the corresponding carboxylic acids, RCOOH , by reaction with hydroxylamine or an alkyl hydroxylamine $\text{HNR}'\text{OH}$. When R represents an unsubstituted alkyl or alkenyl group, the preferred compounds are those wherein R is a straight-chain alkyl or alkenyl group of from 9 to 15 carbon atoms. R' (when an unsubstituted alkyl group) preferably contains 1 to 4 carbon atoms.

10 Examples of unsubstituted alkyl and alkenyl groups R are nonyl, undecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, 8-undecenyl, 4-tridecenyl, 8-pentadecenyl, and 8-heptadecenyl. Preferred examples of unsubstituted alkyl groups R' are methyl, ethyl and n-propyl, especially methyl.

In salts of hydroxamic acids, the hydroxyl hydrogen is replaced by a neutralising cation. This will usually be an alkali metal ion, for example sodium or potassium, but it may be an alkaline earth metal cation such as calcium, a quaternary ammonium ion or an ammonium ion.

15 Specific examples of hydroxamic acids and their salts useful in the present invention are nonanohydroxamic acid, N-methyl nonanohydroxamic acid, N-isopropyl nonanohydroxamic acid, dodecanohydroxamic acid, N-methyl dodecanohydroxamic acid, N-ethyl dodecanohydroxamic acid, tetradecanohydroxamic acid, hexadecanohydroxamic acid, octadecanohydroxamic acid, and the sodium and potassium salts of these acids, N-methyl succinomonohydroxamic acid, sodium N-methyl succinomonohydroxamate, N-methyl- β -n-decylsuccinomonohydroxamic acid, N-methyl- α -dodecylsuccinomonohydroxamic acid.

Mixtures of compounds wherein the number of carbon atoms in the group R and R' extends over a range can be used. Where R or R' are unsubstituted alkyl or alkenyl groups, such mixtures are often preferred for economic reasons, because the corresponding mixtures of carboxylic acids or nitroparaffins which serve as starting materials for the production of the hydroxamic acids are less expensive than the pure acids.

Optional substituents in the groups R and R' include halogen atoms, for instance chlorine or bromine, and substituent groups selected from hydroxy, alkoxy, phenyl, phenoxy, carboxy, and hydroxamido groups -CONR'OH. An example of a hydroxy-substituted alkenyl group R occurs in the hydroxamic acid derived from ricinoleic (12-hydroxy-9-octadecenoic) acid, while R' can be, for example, a hydroxymethyl or 2-hydroxyethyl group. When R or R' represents a substituted phenyl group, substituents can, for example, be selected from the optional substituents mentioned above. However, possible substituents in a phenyl group also include alkyl groups, for example C_{1-3} alkyl groups, so that R or R' can be, for instance, a tolyl, xylyl or isopropylphenyl group. In other hydroxamic acids, such alkyl groups can have longer chains, so that R or R' can be, for instance a (C_{5-21} alkyl)phenyl group. Examples of hydroxamic acids where R represents a phenyl or alkyl phenyl group are N-methyl benzohydroxamic acid, N-methyl p-isopropylbenzohydroxamic acid and the various isomeric (C_{14-18} alkyl) benzohydroxamic acids.

The occurrence of one carboxyl group as a substituent in the group R represents a mono-hydroxamic acid derivative of a dicarboxylic acid. For example, compounds having a carboxyl group in the α - or β - position of an alkyl group R in the above formula are derivatives respectively of alkyl or alkenyl malonic or succinic acids. Other examples are monohydroxamic derivatives of azelaic and of suberic acids. It is of course possible for a group R to contain more than one carboxyl substituent. Similarly R' can be a group containing one or more, normally one or two, carboxyl groups as substituents. Thus it can be, for example, a 2-carboxyethyl- or 1,2-dicarboxyethyl-group.

45 A compound having one hydroxamato group as a substituent in the group R is a dihydroxamic acid. Dihydroxamic acids which are derivatives of malonic and succinic acids are exemplified in U.S. Patent 3,704,502 and include dodecane-1,1-dihydroxamic acid and hexadecane-1,1-dihydroxamic acid. Other examples of dihydroxamic acids are octane-1,8-dihydroxamic acid (from sebacic acid) and undecane-1,11-dihydroxamic acid (from brassylic acid).

50 The hydroxamato group may also occur as a substituent in the group R'. Examples of such R' groups are 2-hydroxamidoethyl and 1,2-di(hydroxamido) ethyl.

A characteristic of any hydroxamic acid suitable for use in a composition of the invention is that it should have an HLB within the same range as the range of HLB's of the hydroxamic acids wherein R is an unsubstituted C_{5-21} alkyl group and R' is hydrogen or an unsubstituted C_{1-6} alkyl group. Of the latter hydroxamic acids, the most lipophilic will be hydroxamic acids wherein R contains 21 carbon atoms and R' contains 12 carbon atoms. The most hydrophilic will be hydroxamic acids wherein either R or R' contains fewer than 12 carbon atoms and the other is hydrogen. In general, the optional substituents are groups, for example hydroxy or carboxy, which increase hydrophilicity. As a result, compounds within the required HLB

range and containing such substituents will usually be those where the number of carbon atoms in R lies towards the upper end of the C₅₋₂₁ range, for example, within the C₁₂₋₁₂ range.

The hydroxamic acids and hydroxamates can be used according to the invention to stabilize solutions of hydrogen peroxide having, for example, from 0.5 to 70% of available oxygen, but they are particularly useful in the stabilization of dilute alkaline solutions. Such solutions may have pH's in the range 8 to 12 and initial concentrations of hydrogen peroxide of, for example, from 0.5 to 5% by weight. The amount of hydroxamic acid or derivative employed can vary. Under most conditions, a useful degree of stabilization can be achieved with as little as 50 parts by weight of hydroxamic acid or derivative per million parts by weight of solution (50 ppm). Larger amounts than this, for example up to 500 ppm, can, however, be employed.

The hydroxamic acids and hydroxamates can be used to stabilize solid peroxy compounds. In a stabilized composition containing a solid peroxygen compound, such a compound can be, for example, an inorganic persalt, for instance an alkali metal perborate, perphosphate or percarbonate, or an organic peroxide, for instance urea peroxide, a percarboxylic acid or an alkali metal percarboxylate.

Preferred inorganic salts include sodium perborate, which is available in the form of mono- and tetra-hydrates, sodium carbonate peroxyhydrate and sodium pyrophosphate peroxyhydrate. Examples of percarboxylic acids include aliphatic and aromatic mono- and di-peroxy carboxylic acids, as described, for example in EP-A-0 068 547. These include mono- and di-peroxyadipic acid, diperoxylodecanedioic acid, peroxyauric acid, 2-lauryl diperoxy succinic acid, peroxybenzoic acid and diperoxyphthalic acid.

Many types of compound have been reported to be useful as bleach activators in detergent formulations containing an inorganic peroxygen bleach. A summary is found in EP-A-0 051 987, which mentions various esters, imides, imidazoles, oximes and carbonates. Included in the imide class are the tetra-acetylated derivatives of alkylene diamines, for instance of ethylenediamine and hexamethylenediamine. N,N,N',N'-tetraacetyl ethylenediamine is a preferred bleach activator of this class.

More recent publications referring to bleach activators include EP-A-0 106 634, which discloses bleach activators having the general formula R-CO-L wherein R is an alkyl group containing from 5 to 18 carbon atoms wherein the longest linear alkyl chain extending from and including the carbonyl carbon contains from 6 to 10 carbon atoms and L is a leaving group containing an anionic moiety, such that the conjugate acid of the anion formed on L has a pK_a in the range of from 4 to 13. The most preferred bleach activators are compounds where L represents a para-oxybenzenesulphonate group, for example sodium linear octanoyloxybenzenesulphonate.

Other bleach activators and the corresponding peracids are disclosed in EP-A-0 166 571. These include compounds such as a C₁₄₋₁₅ alkyloxycarbonyloxybenzenesulphonic acid or salt, sodium 2-ethylhexylsuccinyl oxybenzenesulphonate and sodium isopropyl octylsuccinyl oxybenzenesulphonate.

Further bleach activators which are p-sulphophenyl alkyl carbonates, are shown in EP-A-0202 698. Examples given include sodium p-sulphophenyl n-hexyl carbonate and sodium p-sulphophenyl n-octyl carbonate.

Any of these bleach activators can be used in the compositions of the present invention.

Surface active components that can be used in detergent formulations according to the invention include anionic surfactants, or a mixture of one or more anionic surfactants with one or more nonionic surfactants. Examples of suitable anionic surfactants include soaps such as the salts of fatty acids containing about 9 to 20 carbon atoms, e.g. salts of fatty acids derived from coconut oil and tallow; alkyl benzene sulphonates, particularly linear alkyl benzene sulphonates; alkyl sulphates and sulphonates; monoglyceride sulphates, and acid condensates of fatty acid chlorides with hydroxy alkyl sulphonates.

Examples of suitable nonionic surfactants include condensates of alkylene oxides (e.g., ethylene oxide), with mono- or poly- hydroxy alcohols, alkyl phenols, fatty acid amides or with fatty amines; sugar derivatives such as sucrose monopalmitate; or fatty acid amines.

In certain instances, the surfactant may include compounds having at least one tertiary amine oxide group, for example dimethyl dodecylamine oxide.

Preferably the surfactant component contains (C₁₀₋₁₆ alkyl) benzene sulphonate, in an amount exceeding that of any other surfactant, and particularly good detergency performance has been obtained with surfactant components which are blends containing 40-60% weight of one or more (C₁₀₋₁₆ alkyl)benzene sulphonates, 15-30% of condensates of fatty alcohols with 10-18 ethylene oxide units, and 15-30% of soaps.

It will be understood that many more examples of surfactants are known to those skilled in the art, and the compositions of the invention may contain other compounds having surfactant activity, for example zwitterionic and amphoteric surfactants.

The proportions of surfactant component, peroxy bleach compounds and bleach activator in a detergent

composition of the invention are those conventionally employed in such formulations. Thus the amount of surfactant component may be from 5% to 50% by weight of the composition while the bleach activator may be present in amount of from 10% to 100% of the molar equivalent of the hydrogen peroxide generated or generatable from the peroxy compound. The amount of the hydroxamic acid or derivative incorporated in the composition will depend on a number of factors, including the amount of active bleaching agents expected to be generated in washing solutions, wash temperature, water quality etc. Usefully, the amount may be such as to provide from 20 to 500 ppm, preferably from 50 to 200 ppm of hydroxamic acid or hydroxamate derivate in the wash solution. Relative to the surfactant, this amount may represent from about 0.1 to 10% by weight, more usually from about 0.5 to 2.5 % by weight of the surfactant.

A detergent composition of the invention will also normally contain other conventional additives, especially detergency builders such as phosphates, nitrilotriacetates, polycarboxylates, zeolites and mixtures thereof.

The invention is illustrated by the following Examples.

Example 1

This Example shows the effect of hydroxamic acids in improving the bleaching performance of a detergent composition containing sodium perborate bleach with tetraacetyl ethylenediamine (TAED) as the bleach activator.

A detergent powder having the following composition was added to water of 20° German hardness and an iron contamination of 2 ppm to give a detergent concentration of 0.6%.

Sodium alkyl benzene sulphonate	8.6%
Ethoxylated tallow alcohol	3.1%
Sodium soap	3.8%
Sodium silicate	8.0%
Magnesium silicate	2.0%
Carboxymethylcellulose	1.3%
Sodium ethylenediaminetetraacetate	1.2%
Sodium sulphate	22.0%
Sodium perborate tetrahydrate	17%
TAED	3%
Sodium carbonate	10%
Sodium aluminosilicate	20%
Test detergent	100%

In a control test, the solution was used in a tergotometer at 40° C to wash a standard commercial wine-stained swatch with a wash cycle of 30 minutes. In the evaluation of the hydroxamic acid, further wine-stained swatches were washed under the same conditions in a solution containing in addition to the above components, 100 ppm of hydroxamic acid.

After the washing cycle was completed, the swatches were dried and lightly ironed. Washing efficiency was assessed by brightness measurements on the swatches defined as the reflectance of stimulus Z ("blue" light) relative to a standard white reference with an IEC three stimulus colorimeter. The reflectance of both sides of the swatches was measured and the reflectance values averaged.

The average reflectance was 3.2 units higher for the swatches washed in the presence of dodecanohydroxamic acid than for the control swatches washed in its absence. Similar results were obtained with N-methyl dodecanohydroxamic acid and with N-isopropyl nonanohydroxamic acid.

Example 2

This Example shows the effect of various hydroxamic acids on the stabilities of solutions of peracetic acid. The peracetic acid was generated in situ in aqueous solution in the same way as it would be by the

addition of a detergent formulation of the invention containing an inorganic peroxygen compound and an appropriate bleach activator.

Tetraacetyl ethylenediamine (TAED) was added to a dilute aqueous hydrogen peroxide solution containing twice the molar equivalent of H_2O_2 relative to the TAED added. The solution, which contained 130 ppm of peracetic acid and 1 ppm of iron contamination, was buffered to pH 10 with sodium carbonate. Hydroxamates were added to portions of this solution. These test solutions were then stored at 60 °C, together with a further portion of the solution without hydroxamate as a control, and the active oxygen levels were measured after 1 hour. The results are expressed below as available oxygen after 1 hour as a percentage of the available oxygen at time zero.

Hydroxamate	% Active Oxygen
None	21
Sodium Octadecanohydroxamate	34
Sodium N-methyl dodecanohydroxamate	93

Example 3

This Example illustrates the stabilization of hydrogen peroxide solution.

Solutions of hydroxamates were prepared by dissolving hydroxamic acids in aqueous carbonate buffer solutions containing 2 ppm of iron at pH 10, and were then warmed to 60 °C. Hydrogen peroxide (70%) was added to give an initial concentration of 1% H_2O_2 , and the solutions, together with a control containing no hydroxamate, were held at 60 °C. After 30 minutes, the solutions were sampled and the remaining hydrogen peroxide was determined by the thiosulphate titration method. The results are shown in the table below wherein the peroxide remaining is shown as percent of the initial amount.

Hydroxamic Acid concentration (ppm)		Peroxide Remaining
None	-	1
N-methylnonano hydroxamic acid	400	91
N-methyldodecano hydroxamic acid	100	97

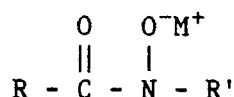
Example 4

The efficacy of N-methyl n-decylsuccinomonohydroxamic acid (NMDS) as a bleach stabilizer was demonstrated by a launderometer test with swatches stained with wine and tea. The test was performed as described in Example 1 above. The amount of NMDS and results as reflectance measurements are shown below. Such data indicated improvement in bleaching performance when NMDS is present in the wash liquid.

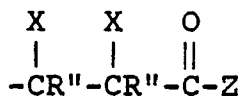
Stain	NMDS (ppm)	Reflectance
wine	0	56.6
	40	58.0
	80	61.9
tea	0	78.3
	40	86.9
	80	89.0

Claims

1. A composition comprising a peroxygen containing bleach system and a bleach stabilizing amount of a bleach stabilizer represented by the formula:



wherein R is selected from the group consisting of optionally substituted straight and branched chained alkyl C₁₋₂₁, alkenyl C₁₋₂₁, hydrogen, and optionally substituted phenyl groups, and



wherein each R'' is independently selected from groups consisting of hydrogen, alkyl C₁₋₂₁ and alkenyl C₁₋₂₁, provided that the total number of carbons in both R'' groups is not greater than 21, each X is independently selected from hydrogen and SO₃ and Z is selected from the group consisting of hydroxy, alkoxy C₁₋₅ and alkenoxy C₁₋₅, -O⁻M⁺, -NR₂'' wherein each R'' is independently selected from the group consisting of hydrogen, alkyl C₁₋₅ or alkenyl C₁₋₅, R' is selected from the group consisting of hydrogen, optionally substituted straight and branched chained alkyl C₁₋₂₁, alkenyl C₁₋₂₁ and an optionally substituted phenyl group, provided only one of R and R' is hydrogen said stabilizer having a hydrophile-lipophile (HLB) balance within the same range as the HLB of said compounds wherein R is an unsubstituted C₅₋₂₁ alkyl group and R' is hydrogen or a non-interfering cation, and further provided that when M⁺ represents hydrogen and the composition contains a detergent active agent, the bleaching system is selected from an inorganic peroxy compound and bleach activator combination or an organic peroxy compound.

2. A composition according to Claim 1 wherein R represents an unsubstituted C₉₋₁₅ alkyl or alkenyl group and R' represents hydrogen or an unsubstituted C₁₋₄ alkyl group.

3. A composition of Claim 2 wherein the stabilizer is selected from dodecanohydroxamic acid and N-methyl dodecanohydroxamic acid.

4. A composition of Claim 1 wherein the stabilizer is a salt of a hydroxamic acid.

5. A composition of Claim 4 wherein the salt is an alkali metal salt.

6. A composition of Claim 1 which is an aqueous solution of hydrogen peroxide.

7. A composition of Claim 1 which is a detergent formulation including surface active components, a bleaching agent selected from the group consisting of a combination of an inorganic peroxy compound and a bleach activator, an organic peroxy acid and mixtures thereof.

8. A composition of Claim 7 wherein the bleaching agent is an organic peroxy acid selected from aromatic and aliphatic mono- and di-peroxy carboxylic acids.

9. A composition of Claim 7 wherein the bleaching agent is an inorganic peroxy compound selected from alkali metal perborates, perphosphates and percarbonates, and the bleach activator is a tetra-acetylated alkylene diamine.

10. A composition of Claim 9 wherein the bleaching agent is sodium perborate mono- or tetra-hydrate

and the bleach activator is N,N,N',N'-tetraacetyl ethylenediamine.

11. A composition of Claim 1 wherein the amount of stabilizer is from 0.1 to 10% relative to the weight of surface active components in the composition.

12. A composition of Claim 1 wherein the stabilizer is N-methyl-n-decylsuccinomonohydroxamic acid.

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