⑲ Europäisches Patentamt
European Patent Office
Office européen des brevets

⑪ Publication number: **0 384 911 A2**

⑫ **EUROPEAN PATENT APPLICATION**

㉑ Application number: **90870027.1**

(51) Int. Cl.5: **C11D 3/39, C08G 65/00**

㉒ Date of filing: **20.02.90**

㉚ Priority: **21.02.89 US 313001**

㊸ Date of publication of application:
29.08.90 Bulletin 90/35

(84) Designated Contracting States:
AT BE CH DE DK ES FR GB GR IT LI LU NL SE

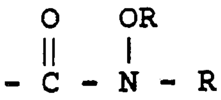
(71) Applicant: **MONSANTO COMPANY**
Patent Department 800 North Lindbergh
Boulevard
St. Louis, Missouri 63167(US)

(72) Inventor: **May, Bronislav Henri**
Courtensdreef 5
B-1900 Overijse(BE)
Inventor: **Zutterman, Fredy Gustaaf**
58 Rue Trous Minières
B-5140 Naninne(BE)
Inventor: **Nijs, Hubert Hendrik**
10 Crown Hill
St. Louis, Missouri 63005(BE)
Inventor: **Coleman, James Patrick**
2374 Wescreek Drive
Maryland Heights, Missouri 63043(US)
Inventor: **Monzyk, Bruce Francis**
2066 Pheasant Run
Maryland Heights, Missouri 63043(US)

(74) Representative: **Ernst, Hubert et al**
Monsanto Services International S.A.
Avenue de Tervuren 270/272
B-1150 Brussels(BE)

(54) Stabilized compositions containing peroxygen compounds.

(57) Stabilized bleach compositions are disclosed comprising peroxygen compounds or a precursor thereof and a stabilizing amount of a polyhydroxamic acid or salt thereof wherein a polymer has a plurality of hydroxamato groups of the formula:



$$-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle OR}{|}}{N}-R$$

where R represents hydrogen or an optionally substituted alkyl group having from 1 to 6 carbon atoms in the alkyl group.

EP 0 384 911 A2

STABILIZED COMPOSITIONS CONTAINING PEROXYGEN COMPOUNDS

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

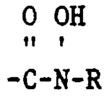
Peroxygen compounds, both organic and inorganic, are widely used as bleaching agents. Major applications include the bleaching of paper pulp, where hydrogen peroxide itself can be used, and the washing of textiles. In products in powder or granular form that are sold as domestic detergents, solid peroxygen 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 stabilise 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 auto-decomposition.

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

Poly(hydroxamic acids) have been investigated as ion exchange resins or resins useful for metal extraction. The resins which are useful for ion exchange are cross-linked and water insoluble. FR-A-2 536 383 and FR-A-2 538 717 describe water-soluble polyacrylamide polymers in which a significant proportion of the amide groups are replaced by hydroxamic acid groups. The polymers thus obtained are said to be useful in preventing the deposition of calcium and magnesium scale and in inhibiting the sedimentation of clay.

As indicated above, the present invention is based on observations that certain poly(hydroxamic acids) and poly (hydroxamates) are effective stabilizers for peroxygen-containing systems. Accordingly, the invention provides compositions comprising a peroxygen compound or a precursor thereof and a poly(hydroxamic acid) or a salt thereof, the poly(hydroxamic acid) being a polymer having a plurality of hydroxamato groups of the formula

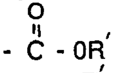


$$-\overset{O}{\overset{\|}{C}}-\overset{OH}{\overset{|}{N}}-R$$

as or in groups pendant from the polymer chain, where R represents hydrogen or an optionally-substituted straight- or branched chain C_{1-6} alkyl group.

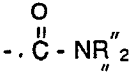
Embodiments of the invention include a solution of hydrogen peroxide that is stabilized by the presence of a poly(hydroxamic acid) or salt; and a detergent composition including surface active components and a peroxygen bleaching agent, together with a poly(hydroxamic acid) or salt as defined above.

Poly(hydroxamic) acids can be made by the reaction of hydroxylamines of the formula RNHOH with polycarboxylate polymers, preferably polycarboxylic esters, or polycarboxylic anhydrides or polycarboxylic amides or polycarboxylic chlorides. Conversion of carboxylate groups of the polycarboxylate polymer may be complete or partial. In the latter case, a polymer useful in the invention will contain, in addition to hydroxamato groups, groups of the formula



$$-\overset{O}{\overset{\|}{C}}-OR'$$

where R' represents hydrogen, an esterifying group, for example a C_{1-6} alkyl group, or a cation where the original polycarboxylate polymer is an ester or anhydride, and carboxamide groups, for example carboxamide groups of the formula



$$-\overset{O}{\overset{\|}{C}}-NR''_2$$

where R'' is hydrogen or a C_{1-6} alkyl group, the two R'''s being the same or different, where the original polycarboxylate polymer is a polycarboxylic amide.

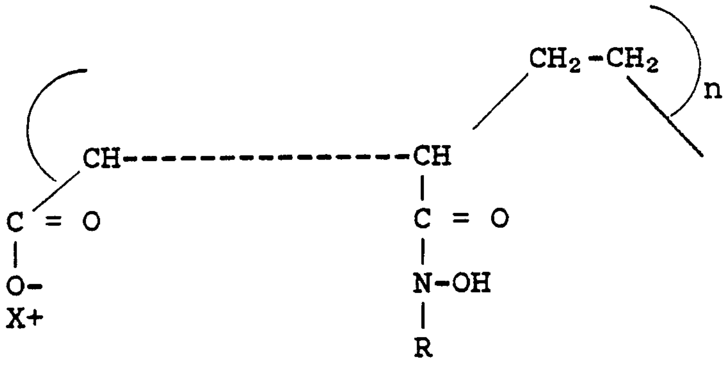
Preferably at least 30% of the total number of hydroxamato, carboxylic acid, carboxylate salt, carboxylate ester and/or carboxylic amide groups in the poly(hydroxamic acids) are the said hydroxamato groups.

Examples of polycarboxylate polymers useful as starting materials for the production of the poly-

(hydroxamic acids) include homopolymers of acrylic acid and methacrylic acid, and copolymers of either or both of these acids with comonomers such as olefinic hydrocarbons, for example ethylene, propylene or styrene, or alkyl vinyl ethers, for example methyl vinyl ether. Polyacrylamides are further examples of starting materials which can be used.

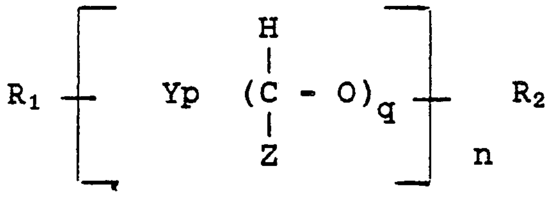
Other examples of polycarboxylate polymers are those derived from ethylenically unsaturated di-or polycarboxylic acids or their anhydrides, for example maleic acid, fumaric acid, itaconic acid, mesaconic acid, aconitic, methylenemalonic acid, and citraconic acid. These can be homopolymers or copolymers with other acids of the same class or with other ethylenically unsaturated monomers, for example acrylic and methacrylic acids, ethylene, propylene or methyl vinyl ether (See US-A-3 308 067).

A particularly preferred polyhydroxamate of this invention is derived from the ethylene maleic anhydride copolymer to provide novel polymers represented by the formula:



wherein R is as defined above; X is a cation and n is an integer of from 10 to 200. Substitution of the polymer by hydroxamate groups is desirably in the range of from about 10 percent to about 100 percent of the available carboxyl groups. More preferably the polymer is substituted by hydroxamate groups to the extent of from about 25 to about 50 percent. These novel polymers of this invention are strong chelants for heavy metals.

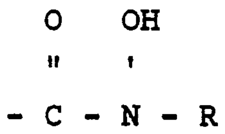
A further class of polycarboxylate polymers comprises the polymeric acetal carboxylates described in EP-A-O 001 004. These are polymers made by the polymerisation or copolymerisation of an ester of glyoxylic acid, and stabilising an intermediate polymer or copolymer against depolymerisation by addition to the termini of the intermediate polymer or copolymer of chemically stable end groups. Examples of monomers which can be copolymerised with the glyoxylic ester are ethylene oxide, propylene oxide, epichlorohydrin, formaldehyde and acetaldehyde. Suitable end groups include alkyl, alkoxy, and carboxyalkyl. Poly(hydroxamic acids) and their salts derived from the polymeric acetal carboxylates are novel polymers and may be represented by the formula:



$$R_1 \left[Y_p \left(\overset{H}{\underset{Z}{C}} - O \right)_q \right]_n R_2$$

wherein Y is one or more comonomers randomly distributed in the polymer; n averages at least 4; p is an integer from 0 to an average of about 5; q is an integer of at least 1; R_1 and R_2 are individually any chemically stable group which stabilizes the polymer such that in an aqueous solution of .5 molar sodium hydroxide containing 10 grams per liter of the polymer, the average chain length of the polymer is reduced by not more than 50 percent as determined by Proton Magnetic Resonance after 1 hour at 20° C. and Z is

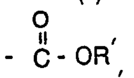
(i) a hydroxamato group represented by the formula:



$$-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle OH}{|}}{N}-R$$

where R represents hydrogen or an optionally-substituted straight- or branched-chain C_{1-6} alkyl group,

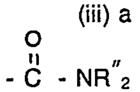
(ii) a carboxylate group having the formula



$$-\overset{\overset{\displaystyle O}{\|}}{C}-OR'$$

wherein R′ represents hydrogen, a C_{1-4} alkyl group or a cation selected from alkali metal, ammonium, tetra (C_{1-4} alkyl) ammonium, and (C_{1-4} alkanol) ammonium cations, or

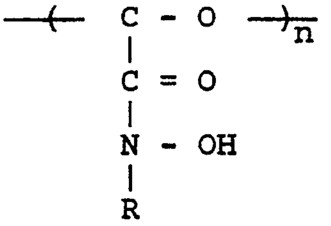
(iii) a carboxamide group having the formula



$$-\overset{\overset{\displaystyle O}{\|}}{C}-NR''_2$$

where R″ is hydrogen or a C_{1-6} alkyl group, the two R″'s being the same or different; provided that at least 30% of the total number of groups Z are the said hydroxamato groups.

In a preferred embodiment the novel polymers of this invention are derived from polyacetal carboxylate homopolymers to provide polyhydroxamates represented by the formula:



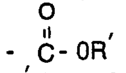
wherein R and n are as defined above.

In salts of poly(hydroxamic acids), the hydroxyl hydrogen of the hydroxamato group 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, or an ammonium ion.

When R in the above formula of the hydroxamato group represents an unsubstituted alkyl group, preferred groups are methyl, ethyl, n-propyl and isopropyl, especially methyl.

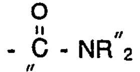
Optional substituents in the group R include halogen atoms, for instance chlorine or bromine, and substituent groups selected from hydroxy, alkoxy, carboxy, and hydroxamato groups. R can, for example, be a hydroxymethyl, 2-hydroxyethyl, 2-carboxyethyl, 1,2-dicarboxyethyl, 2-hydroxamatoethyl or 1,2 di-(hydroxamato)ethyl group.

In poly(hydroxamic acids) which contain carboxylate groups of the formula



$$-\overset{\overset{\displaystyle O}{\|}}{C}-OR'$$

R′ is preferably hydrogen, an alkali metal cation, for example sodium, or a C_{1-4} alkyl group, especially a methyl or ethyl group. In poly(hydroxamic acids) which contain carboxamide groups



$$-\overset{\overset{\displaystyle O}{\|}}{C}-NR''_2$$

R″ is preferably hydrogen or a C_{1-4} alkyl group, for example methyl or ethyl.

The poly(hydroxamic acids) and their salts can be used according to the invention to stabilise 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.

A particular application of the stabilization of hydrogen peroxide solutions according to the invention is the use of the poly(hydroxamic acids) to enhance the bleaching action of hydrogen peroxide in the bleaching of cellulose pulp. The pulp typically has a pulp concentration (expressed as the dry weight of the fibers as a percentage of the actual weight of the pulp) of from 10 to 30%, for example from 15 to 25%.

The alkalinity of the pulp is usually provided by the addition of sodium hydroxide, but other water-soluble alkaline substances can be used as partial or complete replacements for the sodium hydroxide, for example sodium carbonate. The amount of sodium hydroxide or other alkaline substance used can, for example, be from 0.5% to 5% of the dry weight of the pulp, and is preferably from 1% to 3% of this weight. The initial concentration of hydrogen peroxide in the bleach bath can be, for example, from 1% to 3% relative to the dry weight of the pulp, depending on the quality of the original pulp.

The temperature at which bleaching of the pulp is effected may, for example, be within the range 40 to 100° C, and is preferably within the range 50 to 80° C, while the duration of treatment can vary, depending, for example, on the quality of the origial pulp, the amounts of peroxide and stabilizers and the temperature employed. The optimum can readily be determined by simple experimentation, and will usually not be less than 30 minutes or more than 3 hours.

Amounts of stabilizer within the range 0.1 to 0.3% relative to the dry weight of the pulp have been found to be very effective in promoting the effectiveness of the bleach, but smaller or larger amounts can be used, for example from 0.05 to 1% relative to the dry weight of the pulp.

In a preferred procedure, the pulp to be bleached is subjected to a pre-treatment in which stabilizer in an amount of from 0.05 to 1%, preferably 0.1 to 0.2%, is added to the pulp at substantially ambient temperature, for example from 10 to 35° C. The fiber concentration at the pretreatment stage is preferably relatively low, for example from 1 to 5% by weight of the pulp. The pulp can be stirred or otherwise agitated for a short period, for example from 5 to 20 minutes, and then concentrated by filtration prior to bleaching.

The poly(hydroxamic acids) and poly(hydroxamates) can be used as components of formulations, particularly detergent formulations, containing solid peroxygen compounds or precursors of peroxygen compounds. Addition of such a formulation to water provides a peroxygen bleaching agent in solution, and the function of the poly (hydroxamic acid) or poly(hydroxamate) is to inhibit the decomposition of the peroxygen compound and thereby prolong its bleaching action. 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 tetrahydrates, 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, diperoxydodecanedioic acid, peroxylauric acid, 2-lauryl diperoxysuccinic acid, peroxybenzoic acid and diperoxyphthalic acid.

Detergent formulations containing an inorganic peroxygen salt as exemplified above, preferably also contain a bleach activator. In solution, the bleach activator reacts with the inorganic peroxygen salt to generate an organic peroxygen compound such as peracetic acid, which is effective as a bleach at lower temperatures than the original inorganic peroxygen salt.

Many types of compounds have been reported to be useful as bleach activators in detergent formulations containing an inorganic peroxygen salt. 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 C_{14-15} 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 (C_{10-16} 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 (C_{10-16} 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

Preparation of a poly(hydroxamic acid) from an ethylene-maleic anhydride copolymer.

Sodium hydroxide (16 g, 0.4 mole) and N-methylhydroxylamine hydrochloride (16.8 g, 0.2 mole) were added with stirring to water (288 ml) in a 500 ml reactor under nitrogen blanketing. The reactor was surrounded by an ice bath. A solid ethylene-maleic anhydride copolymer having a molecular weight of approximately 2×10^5 (25.2 g containing 0.2 mole of maleic anhydride units) was added with stirring to the solution at 0-5° C. Most of the polymer dissolved in the first 30 minutes. Stirring was continued for about 60 hours during which time the polymer dissolved completely to give a slightly turbid solution containing 10% of a copolymer of ethylene with N-hydroxy-N-methyl maleamic acid, sodium salt.

Example 2

Preparation of a partial hydroxamic acid from a poly(methyl glyoxylate).

Triethylamine (10.5 g, 0.104 mole) was added slowly with stirring to a solution of N-methylhydroxylamine hydrochloride (8.4 g, 0.1 mole) in methylene chloride (75.0 g). The precipitate was filtered off and the filtrate solution was analysed by ^{1}H nmr showing: methylene chloride 88 wt.%, N-methylhydroxylamine 5.0 wt.% and triethylamine hydrochloride 7.0 wt.%.

The filtrate solution containing 0.078 mole of N-methylhydroxyl amine was added in one portion to a stirred solution of poly (methyl glyoxylate) (9.12 g, 75% in methylene chloride, 0.1 mole). Samples were removed at intervals to determine the extent of conversion. A 64% conversion was obtained after 6 hours, and a conversion of 68% after 25 hours. This did not increase during a further 47 hours, after which the mixture was evaporated to dryness to remove methylene chloride and methanol, leaving a pale yellow solid residue (11.46 g). The ^{1}H nmr spectrum of the solid was consistent with the conversion of about 67% of the original methoxycarbonyl groups of the poly(methyl glyoxylates) to N-hydroxy-N-methyl-carbamido groups.

Example 3

This Example demonstrates the effectiveness of a poly (hydroxamic acids) as bleach stabilizers in a typical laundry detergent formulation.

Tests were carried out using a standard launderometer apparatus of 500 ml capacity containing 125 ml of detergent solution. The detergent formulation used to prepare the solution had the following composition:

TABLE 1

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 ethylenediaminetetraacete	1.2%
Sodium sulphate	22.0%
Sodium perborate tetrahydrate	17%
TAED[1]	3%
Sodium carbonate	10%
Sodium aluminosilicate	20%
Test detergent	100%

(1) tetra-acetyl ethylenediamine

The concentration of the detergent formulation in the solution was 7 g/l. The solution also contained an additive for evaluation or comparison as a peroxide stabilizer as shown in Table 1 below. The water used to prepare the solution had a German Hardness of 20 and contained 2 ppm of iron.

A 2 cm x 2 cm square sample of EMPA 114, a standard commercial wine-stain test swatch, was placed in the detergent solution and subjected to agitation at 40° C for 30 minutes. At the end of this time, the sample was removed, rinsed, dried and lightly ironed. Stain removal efficiency was assessed by brightness measurements on the swatch defined as the reflectance (Rd) of stimulus Z ("blue" light) relative to a standard white reference using an IEC three stimulus colorimeter. The reflectance of both sides of the swatch was measured and the reflectance values averaged. The results obtained with various solutions are shown in Table 2 below.

Table 2

Test No.	Additive in Detergent Solution	% Stain Removal[1]
1	None	35.7
2	100 ppm TAED	51.3
3	100 ppm TAED + 20 ppm EDTMPA(1)	56.4
4	100 ppm TAED + poly(hydroxamic acid) of Example 1 (20 ppm active)	60.4
5	100 ppm TAED + poly(hydroxamic acid) of Example 2 (20 ppm active)	58.3

[1]. $$\% \text{ Stain Removal} = 100 \times \frac{\text{Rd washed swatch} - \text{Rd unwashed swatch}}{\text{Rd unsoiled fabric} - \text{Rd unwashed swatch}}$$

The results demonstrate that peroxide stabilization, as shown by percentage stain removal, is improved by using the polyhydroxamate of the invention relative to EDTMPA, one of the most effective peroxide stabilizers currently used in detergent formulations.

Example 4

This Example illustrates the specificity of the poly(hydroxamic acids) relative to polycarboxylate polymers or other derivatives of polycarboxylate polymers. Test conditions were the same as in Example 3, except that 250 ml detergent solution was used, TAED concentration was increased to 200 ppm and two swatches were used per container. The Stain Removal in Table 3 below is the average for the two swatches.

Table 3

Test No.	Additive in Detergent Solution	% Stain Removal
1	None	40
2	30 ppm TAED	42
3	100 ppm Poly(hydroxamic acid) of Example 2	51
4	100 ppm Poly(hydroxamic acid)(1)	48
5	100 ppm polymeric glyoxylate, sodium salt(2)	40
6	100 ppm commercial sodium polyacrylate(3)	40
7	100 ppm polymeric acetal sodium polycarboxylate with 40% of the acid groups converted in corresponding amide from glycine	40
8	same as 7 with amides from ethanolamine	40

(1) Derivative of poly(methyl glyoxylate) with 43% of methoxycarbonyl groups replaced by N-hydroxy-N-methylcarbamido groups.
(2) Product of hydrolysing poly(methyl glyoxylate) with sodium hydroxide.
(3) A commercial product sold by BASF under the trade name Sokalan CP5.

Experimental results demonstrate the specificity of the polyhydroxamic groups in terms of peroxygen compounds stabilization. The higher the degree of substitution, the better the stabilization.

Example 5

This example illustrates the effectiveness of the poly(hydroxamic acids) of Examples 1 and 2 as peroxide stabilizers in the bleaching of cellulose pulp. In comparative experiments, sodium diethylenetriaminepenta(methylenephosphonate), (NaDTPMP) which is among the most effective of the prior art peroxide stabilizers, was used.

In a prebleaching stage, a sample of Pinus Radiata pulp containing approximately 5 g dry weight of fibers was diluted to 1.5% by weight consistency and then defibrated in a pulper for 9 minutes. A solution of the poly(hydroxamic acid) or of NaDTPMP was added with stirring at room temperature to the fiber suspension to provide 0.12% of the active ingredient relative to the dry weight of fiber, and stirring was continued for 10 minutes at 20°C. The suspension was then concentrated by filtration to about 20% consistency.

This suspension was then added to an alkaline hydrogen peroxide solution to give a bleach bath containing 12% by weight of fiber and (relative to the dry weight of fiber) 2% of hydrogen peroxide, 1.5% of sodium hydroxide and the amounts of stabilizer shown in Table 4 below. In a control test no stabilizer was added. The bath was maintained at 60°C for 4 hours.

To prepare paper sheets, the pulp at the end of the bleach was dispersed in 950 ml of water and the pH of the liquid was adjusted to 5 by the addition of 1N sulphuric acid. 450 ml of this suspension were filtered on to a stainless steel mesh (approx. 0.1 mm aperture) in the base of a Buchner funnel having a diameter of 110 mm. The filter cake was then placed between two filter papers and dried on a heated photographic glazing plate for 80 minutes. The filter papers were removed. To determine the brightness of the sheet, the reflectance of the "cold side" was measured at at least five points on stimulus Z of a tristimulus Neotec 240 colorimeter (filter 455 mm). The average value of the reflectance was recorded. The instrument was calibrated with a white standard relative to an Elrepho spectophotometer.

Results are shown in Table 4 below wherein (A) indicates the poly(hydroxamic acid) of Example 2.

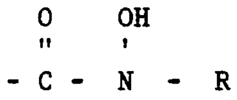
TABLE 4

Pretreatment Additive	Stabiliser in bleach liquor	Brightness
	%	
NaDTPMP	-	67.6
NaDTPMP	0.1 (A)	68.6
NaDTPMP	0.2 (A)	69.3
NaDTPMP	0.2 NaDTPMP	68.8
(A)	0.18 (A)	69.5
(A)	0.18 (A)	70.2

Comparison of the result obtained using 0.2% NaDTPMP as stabilizer with 0.2% poly(hydroxamic acid) as stabilizer, each following pretreatment with NaDTPMP, shows that the poly (hydroxamic acid) gives a superior brightness. Highest brightness is obtained by using the poly(hydroxamic acid) both as pretreatment additive and as peroxide stabilizer.

Claims

1. A composition comprising a peroxygen compound or a precursor thereof and a poly(hydroxamic acid) or a salt thereof, the poly(hydroxamic acid) being a polymer having a plurality of hydroxamato groups of the formula



$$-\overset{\overset{O}{\|}}{C}-\overset{\overset{OH}{|}}{N}-R$$

as or in groups pendant from the polymer chain where R represents hydrogen or an optionally substituted C_{1-6} alkyl group.

2. A composition according to Claim 1 wherein, in the formula of the hydroxamato group, R represents hydrogen or an unsubstituted C_{1-3} alkyl group.

3. A composition according to either of Claims 1 and 2 wherein the poly(hydroxamic acid) is a derivative of a polycarboxylate polymer selected from polycarboxylic esters, polycarboxylic anhydrides and polycarboxylic amides.

4. A composition according to Claim 3 wherein at least 30% of the total number of hydroxamato, carboxylic acid, carboxylate salt, carboxylate ester and/or carboxylic amide groups in the poly(hydroxamic acid) are hydroxamato groups.

5. A composition according to Claim 4 wherein the poly(hydroxamic acid) is a derivative of a polymer or copolymer of acrylic acid, methacrylic acid, acrylamide or methacrylamide, a derivative of a polymer or copolymer of an ethylenically unsaturated di- or polycarboxylic acid or anhydride, or a derivative of a polymeric acetal carboxylate.

6. A composition according to Claim 4 wherein the poly (hydroxamic acid) is the product of reacting an ethylene/maleic anhydride copolymer or a poly(alkyl glyoxylate) with hydroxylamine or an N-alkylhydroxylamine.

7. A composition according to any of Claims 1 to 6 wherein a salt of a poly(hydroxamic acid), if present, is an alkali metal salt.

8. A composition according to any of Claims 1 to 7 which is an aqueous solution of hydrogen peroxide.

9. A composition according to Claim 8 in which the aqueous solution of hydrogen peroxide is an alkaline solution containing bleachable cellulose fibers.

10. A composition according to any of Claims 1 to 7 which is a detergent formulation including surface active components, a bleaching agent that comprises an organic peroxy acid, a combination of an inorganic peroxy compound and a bleach activator, or a mixture of said organic peroxy acid and said combination.

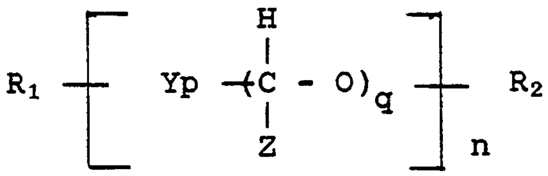
11. A composition acccording to Claim 10 wherein the bleaching agent is an organic peroxy acid selected from aromatic and aliphatic mono-and di-peroxy carboxylic acids.

12. A composition according to Claim 10 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.

13. A composition according to Claim 12 wherein the bleaching agent is sodium perborate mono-or tetra-hydrate and the bleach activator is N,N,N′,N′-tetraacetyl ethylenediamine.

14. A composition according to any of Claims 10 to 14 wherein the amount of the poly(hydroxamic acid) or salt is from 0.1 to 10% relative to the weight of surface active components in the composition.

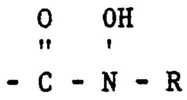
15. A polymer having the formula:



$$R_1 - \left[Y_p \left(\overset{H}{\underset{Z}{\overset{|}{\underset{|}{C}}}} - O \right)_q \right]_n - R_2$$

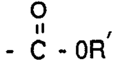
wherein Y is one or more comonomers randomly distributed in the polymer; n averages at least 4; p is 0 to an average of about 5; q is at least 1; R_1 and R_2 are individually any chemically stable group which stabilizes the polymer such that in an aqueous solution of 0.5 molar sodium hydroxide containing 10 grams per litre of the polymer, the average chain length of the polymer is reduced by not more than 50 percent as determined by Proton Magnetic Resonance after one hour at 20° C; and Z represents

(i) a hydroxamato group having the formula



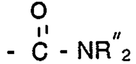
$$-\overset{O}{\overset{\|}{C}}-\overset{OH}{\overset{|}{N}}-R$$

where R represents hydrogen or an optionally-substituted straight- or branched-chain C_{1-6} alkyl group,
(ii) a carboxylate group having the formula



$$-\overset{O}{\overset{\|}{C}}-OR'$$

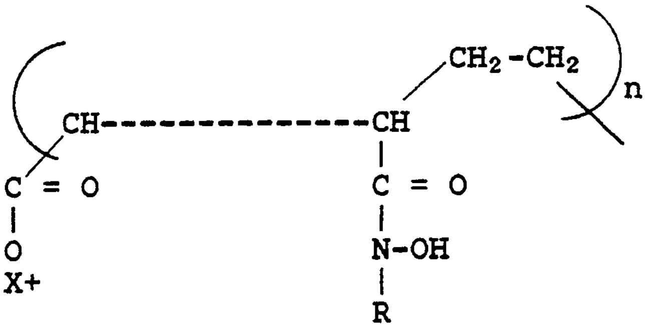
where R′ represents hydrogen, a C_{1-4} alkyl group or a cation selected from alkali metal, ammonium, tetra-(C_{1-4} alkyl) ammonium, and (C_{1-4} alkanol)ammonium cations, or
(iii) a carboxamide group having the formula



$$-\overset{O}{\overset{\|}{C}}-NR''_2$$

where R″ is hydrogen or a C_{1-6} alkyl group, the two R″'s being the same or different;
provided that at least 30% of the total number of groups Z are the said hydroxamato groups.

16. A polymer represented by the formula:



wherein R is selected from the group consisting of hydrogen or an optionally substituted straight or branched chain alkyl gropu having from 1 to 6 carbon atoms, X is a cation, n is an integer of from 10 to 200 and wherein the -NR-OH group is present in the range of from about 10 to 100 percent of the available carboxylate groups.