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## Description

This invention relates to activation of bleaches employing peroxy compounds, including hydrogen peroxide or a hydrogen peroxide adduct, which liberate hydrogen peroxide in aqueous solution, as well as peroxy acids; to compounds that activate or catalyse peroxy compounds; to bleach compositions including detergent bleach compositions which contain a catalyst for peroxy compounds; and to processes for bleaching and/or washing of substrates employing the aforementioned types of compositions.

In particular, the present invention is concerned with the effective use of transition metal compounds as catalyst for the bleach activation of peroxy compound bleaches.

Peroxide bleaching agents for use in laundering have been known for many years. Such agents are effective in removing stains, such as tea, fruit and wine stains, from clothing at or near boiling temperatures. The efficacy of peroxide bleaching agents drops off sharply at temperatures below 60 °C.

It is known that many transition metal ions catalyse the decomposition of H<sub>2</sub>O<sub>2</sub> and H<sub>2</sub>O<sub>2</sub>-liberating percompounds, such as sodium perborate. It has also been suggested that transition metal salts together with a chelating agent can be used to activate peroxide compounds so as to make them usable for satisfactory bleaching at lower temperatures. Not all combinations of transition metals with chelating agents appeared to be suitable for improving the bleaching performance of peroxide compound bleaches. Many combinations indeed show no effect, or even a worsening effect, on the bleaching performance; no proper rule seems to exist by which the effect of metal ion/chelating agent combinations on the bleaching performance of peroxide compound bleaches can be predicted.

Various attempts have been made to select suitable metal/chelating agent combinations for said purpose and to correlate bleach-catalysing effect with some physical constants of the combination; so far without much success and of no practical value.

US Patent N° 3,156,654 suggested particularly cobalt and copper salts in conjunction with pyridine-2-carboxylic acid or pyridine-2,6-dicarboxylic acid, preferably as a pre-formed complex, as being a suitable combination. Another suggestion is made in US Patent N° 3,532,634 to use a transition metal, especially cobalt, manganese and copper salts, together with a chelating agent in combination with a persalt and an organic bleach activator. It is said here that the chelating agent should have a first complex formation constant with the transition metal ion of log 2 to about log 10 at 20 °C. Preferred options include (di)-picolinic acid, pyrrolidine-carboxylic acids and 1,10-phenanthroline, whereas well-known chelating agents, such as ethylene diamine tetraacetic acid - found usable according to US Patent N° 3,156,654 - are unsuitable. These catalysts, as shows in the Examples, have very little or no effect on persalts alone.

Other patent documents discussing the use of chelating agents are, for example, GB Patents 984,459 and 1,192,524, which suggested the use of copper salts in combination with other specific chelating agents of the class of amino acetic acids, and US Patent N° 4,119,557, which suggested the use of pre-formed ferric ion complexes with a polycarboxy amine-type chelating agent. All these prior art suggestions are based on systems in which free metal ion is the catalytically active species and consequently produce results in practice that are often very inconsistent and/or unsatisfactory, especially when used for washing at low temperatures. The ferric ion complexes of US Patent N° 4,119,557 are furthermore not effective at low temperatures.

For a transition metal to be useful as a bleach catalyst in a detergent bleach composition, the transition metal compound must not unduly promote peroxide decomposition by non-bleaching pathways and must be hydrolytically and oxidatively stable. US Patent N° 4,728,455 discusses the use of Mn(III)-gluconate as peroxide bleach catalyst and EP-A-0272030 discloses the use of cobalt(III)amine complexes, e.g. [Co(NH<sub>3</sub>)<sub>5</sub>Cl]Cl<sub>2</sub>, as peroxide bleach catalysts. Still, the performance of these systems is inadequate when used for bleaching in the low-temperature region of about 20-40 °C. They are furthermore restricted in their efficacy to remove a wide class of stains.

It is an object of the present invention to provide an improved transition metal catalyst for the bleach activation of hydrogen peroxide and hydrogen peroxide-liberating compounds, as well as peroxyacid compounds, including peroxyacid precursors, over a wide class of stains at lower temperatures.

Another object of the invention is to provide an improved bleaching composition for use in detergent formulations which are effective at low to medium temperatures of e.g. 20-40 °C.

Still another object of the invention is to provide new, improved detergent bleach formulations.

Yet another object of the invention is to provide aqueous laundry wash media containing new, improved detergent bleach formulations.

A further object of the invention is to provide an improved bleaching system comprising a peroxy compound bleach and a transition metal catalyst for the effective use in the textile and paper industries and other related industries.

These and other objects of the invention, as well as further understandings of the features and advantages thereof, can be had from the following description and claims.

The improved transition metal bleach catalyst according to the invention is a cobalt complex of the following general formula (A) :

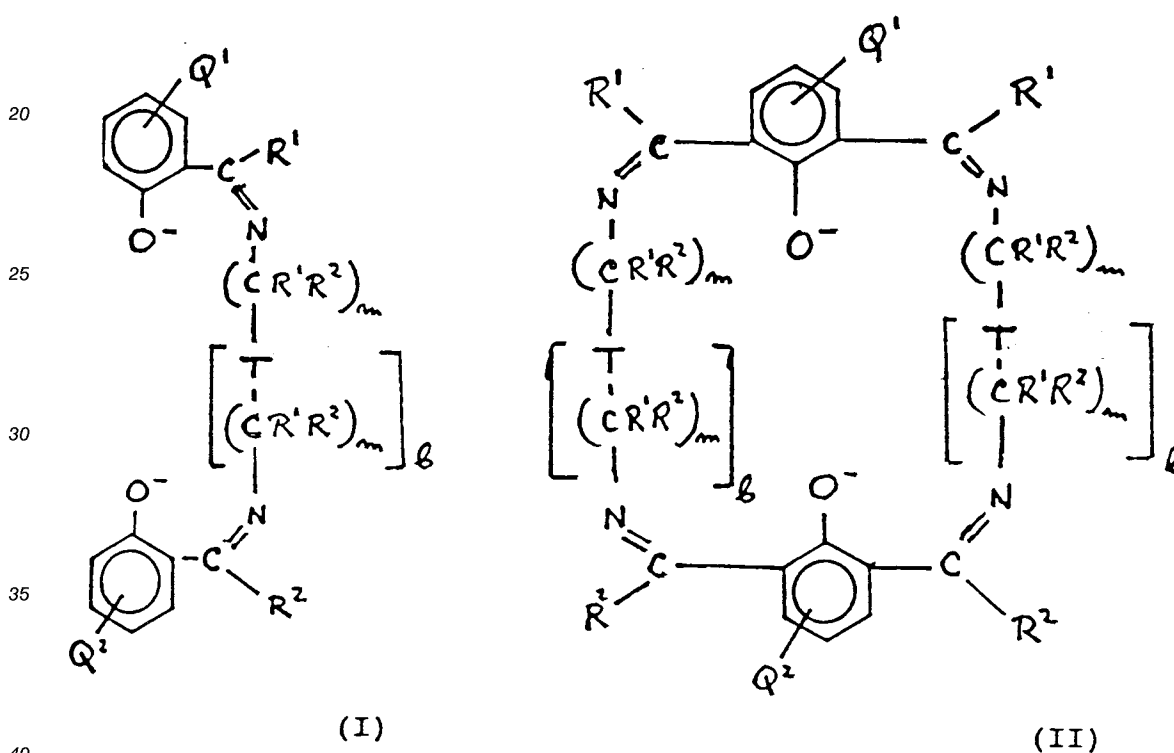
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wherein M is a metal ion selected from Co and Cu; a is 0 or 1; X is a common anion such as  $Cl^-$ ,  $Br^-$ ,  $I^-$ ,  $NO_3^-$ ,  $ClO_4^-$ ,  $NCS^-$  and  $OH^-$ , or a small co-ordinating ligand such as  $H_2O$ ,  $NH_3$  and pyridine, or a species selected from  $O_2^{2-}$ ,  $O_2^-$ ,  $HO_2^-$  and  $H_2O_2$ ; p is an integer from 0 to 4; Y is a counter ion, the type of which is dependent upon the charge z of the complex; z denotes the charge of the complex and is an integer which can be positive or negative, whereby, if z is positive, Y is a common anion as denoted for X and, if z is negative, Y is a common cation selected from alkali metal, alkaline earth metal or an alkyl ammonium cation;  $n = z/[charge\ Y]$ ; and L is a ligand being an organic molecule of the general formula I if  $a = 0$ , and of the general formula II if  $a = 1$ .

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wherein m is 2-6, preferably 2-3;  $R^1$ ,  $R^2$  are each a substituent selected from H, alkyl, aryl, optionally substituted;  $Q^1$  and  $Q^2$  are each a substituent selected from H, optionally substituted alkyl or aryl,  $NO_2$ ,  $NR_2$ ,  $NR_3^+$ , O-alkyl, O-aryl, halogen,  $SO_3^-$ , alkyl  $SO_3^-$  and aryl  $SO_3^-$ , T is either NR, O, PR or S, wherein  $R = R^1$  or  $R^2$  and b is 0-1.

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Preferred ligands are those wherein  $T = NR$ ,  $m = 3$  and  $R$ ,  $R^1$  and  $R^2$  are H; more preferably wherein  $b = 0$ . Examples of the ligands in their simplest forms are thus:

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I (a)

and

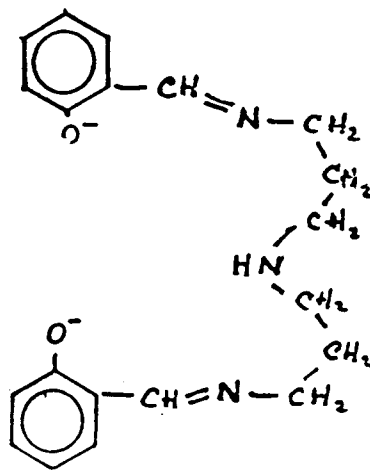
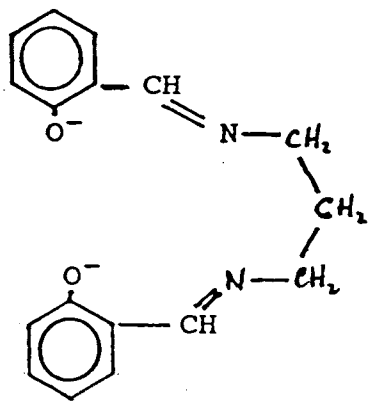
I (b)

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II (a)

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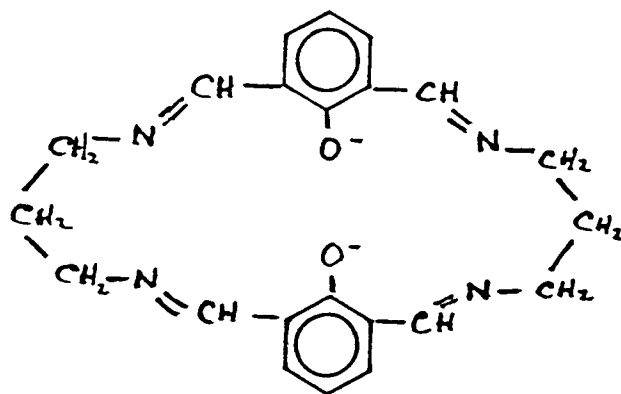
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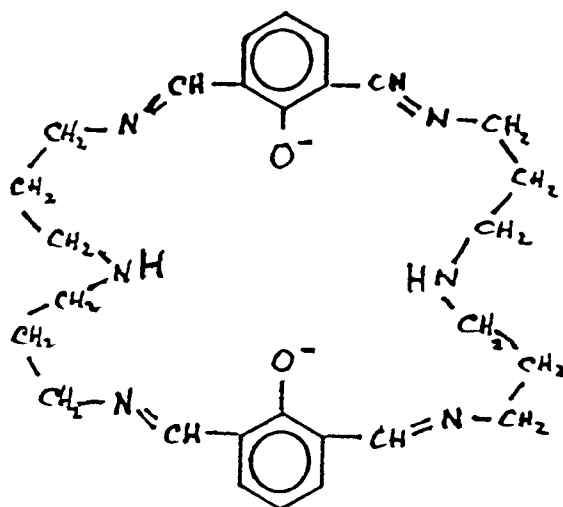


and II(b)

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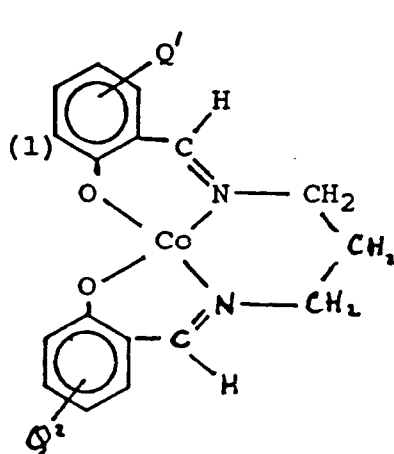
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Being a Co-complex, ligand (I) will form a mono-nuclear Co-complex and ligand (II) will form a bi-nuclear Co-Co- or Co-Cu-complex. Examples of some catalyst complexes are:

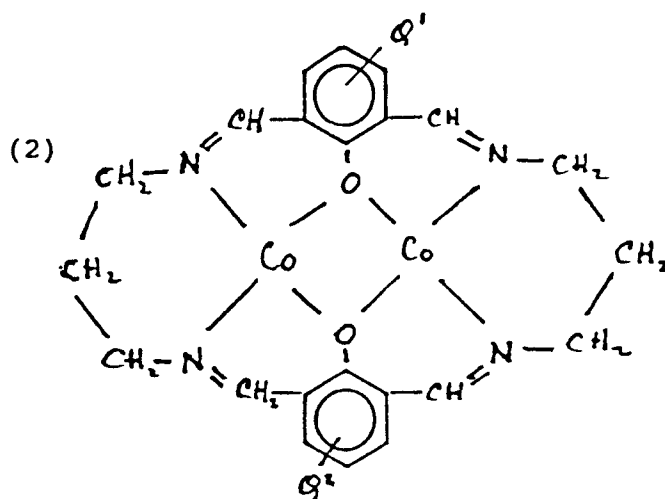
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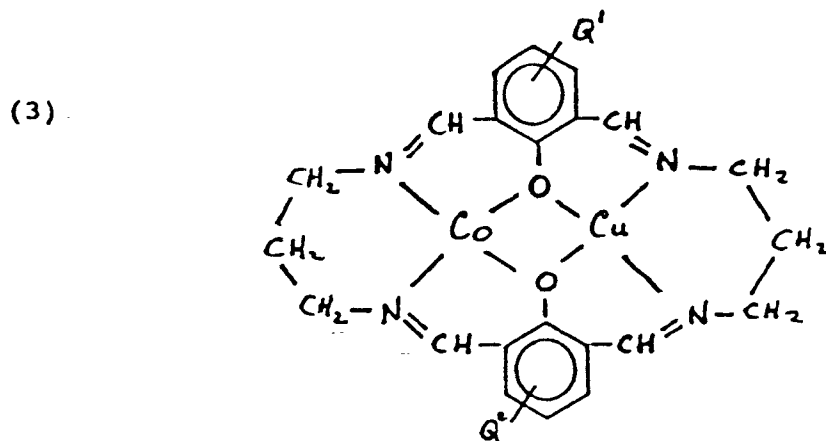
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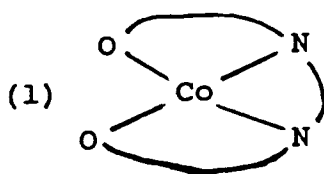
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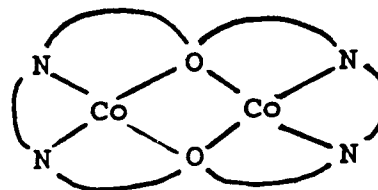


which can be, and are normally, written in simplified form :

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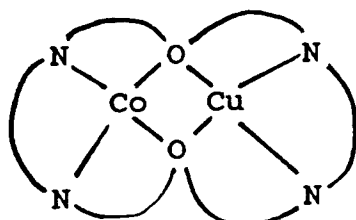


(2)



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(3)



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In the further description of the invention, the mono-nuclear Co-complexes are denoted as Co-SALEN's (m=2) or Co-SALPD's (m=3) and the bi-nuclear complexes are denoted as bi-nuclear Co-Co- or Co-Cu-complexes. They can be present as simple complexes or with substituents and containing further co-ordinating ligands, anions and cations.

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Examples thereof are :

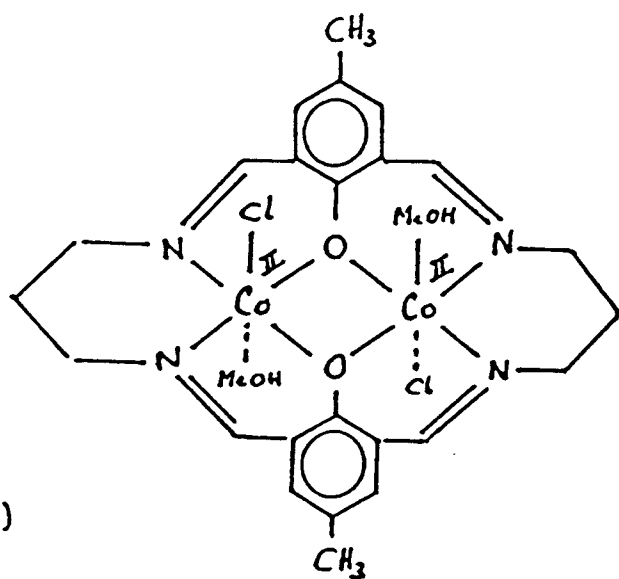
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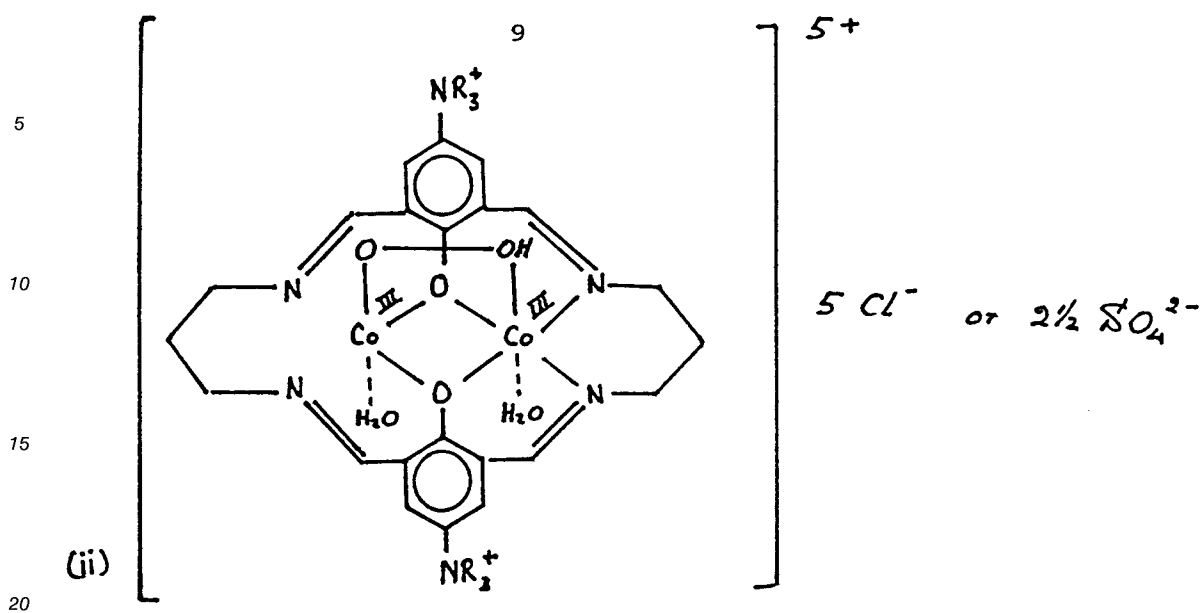
(i)



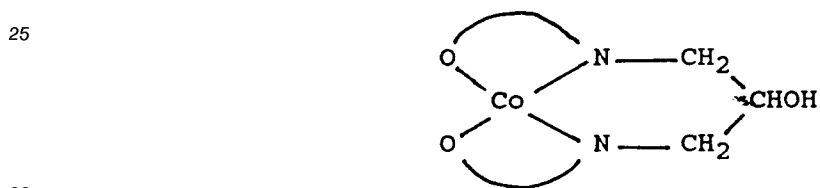
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An example of a complex wherein R<sup>1</sup> or R<sup>2</sup> is substituted is :



Any of these complexes are useful catalysts for the bleach activation of peroxy compounds over a wide class of stains at lower temperatures, in a much more effective way than the metal catalysts of the art hitherto known. Preferred complexes are those of formulae (2) and (3), wherein Q<sup>1</sup> and Q<sup>2</sup> = -CH<sub>3</sub>. These compounds will be referred to in the further description of the invention as "Co-Co", and "Co-Cu", respectively.

Several of the complexes usable herein have been prepared previously as scientific and laboratory curiosities without any practical function being in mind. Preparative routes for some complexes and the ligands are described in scientific literature such as Bull. Chem. Soc. of Japan, 1938, 13, 252; Journ. Am. Chem. Soc. 1947, 69, 1886; J. Chem. Soc., 1985, 107, 2903 and Austr. Journ. Chemistry 1970, 23, 2225/36.

It should be appreciated that the [Co.M<sub>a</sub>L]-core complex is the determining factor of its catalytic action and that the presence of X and Y in the formula, which may be inherent to the methods of preparation, has hardly any effect on the catalytic action of the instant complexes. It is also essential that the catalyst complex of the invention should contain at least one cobalt atom, since otherwise no, or hardly any, catalyzing effect is observed, e.g. Cu-SALEN or a bi-nuclear Cu-Cu-complex is hardly catalytically active. These non-cobalt-containing complexes are thus outside the purview of the present invention.

An advantage of the bleach catalysts of the invention is that they are hydrolytically and oxidatively stable, and that the complexes themselves are catalytically active, insensitive to builder variations in the composition. Another advantage is that the instant catalysts appear to be better than similar complexes proposed in the art.

The instant bleach catalysts have furthermore the surprising feature in that they activate not only hydrogen peroxide or hydrogen peroxide-liberating compounds but also peroxyacids and peroxyacid bleach systems, such as a persalt/peroxyacid precursor mixture.

A further surprising feature of the bleach systems according to the invention is that they are effective on a wide range of stains including both hydrophilic and hydrophobic stains, which is very unusual for hydrogen peroxide-based bleach systems.

Accordingly, in one aspect, the invention provides a bleaching or cleaning process employing a peroxy compound bleaching agent selected from the group of hydrogen peroxide, hydrogen peroxide-liberating



compounds, peroxyacids and their salts, and peroxyacid bleach precursors and mixtures thereof, which process is characterized in that said bleaching agent is activated by a catalytic amount of a cobalt complex of general formula (A) as defined hereinbefore.

5 The catalytic component is a novel feature of the invention. The effective level of the cobalt complex catalyst, expressed in terms of parts per million (ppm) of transition metal in the aqueous bleaching solution, will normally range from 0.01 ppm to 1000 ppm, preferably from 0.1 ppm to 100 ppm, most preferably from 0.1 ppm to 10 ppm. Higher levels may be desired and applied in industrial bleaching processes, such as textile and paper pulp-bleaching. The lower range levels are primarily destined and preferably used in domestic laundry operations.

10 In another aspect, the invention provides an improved bleaching composition comprising a peroxy compound bleach as defined above and a catalyst for the bleaching action of the peroxy compound bleach, said catalyst comprising the aforesaid Co-complex of general formulae (A). As indicated above, the improved bleaching composition has particular application in detergent formulations to form a new and improved detergent bleach composition within the purview of the invention, comprising said peroxy  
15 compound bleach, the aforesaid cobalt complex catalyst, a surface-active material, and usually also detergency builders and other known ingredients of such formulations, as well as in the industrial bleaching of yarns, textiles, paper and the like.

Compositions comprising a peroxy compound bleach and the aforesaid bleach catalyst are effective over a wide pH range of between 7 and 13, with optimal pH range lying between 8 and 11.

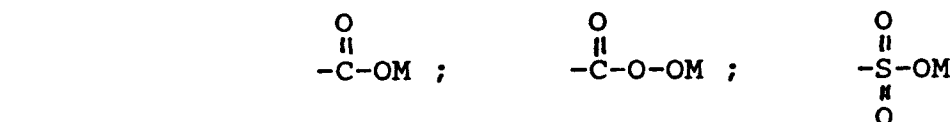
20 The peroxy compound bleaches which can be utilized in the present invention include hydrogen peroxide, hydrogen peroxide-liberating compounds, peroxyacids and their salts, and peroxyacid bleach precursors and mixtures thereof.

Hydrogen peroxide sources are well known in the art. They include the alkali metal peroxides, organic peroxide bleaching compounds such as urea peroxide, and inorganic persalt bleaching compounds, such as  
25 the alkali metal perborates, percarbonates, perphosphates and persulphates. Mixtures of two or more such compounds may also be suitable. Particularly preferred are sodium percarbonate and sodium perborate and, especially, sodium perborate monohydrate. Sodium perborate monohydrate is preferred to tetrahydrate because of its excellent storage stability while also dissolving very quickly in aqueous bleaching solutions.

30 Peroxyacid compounds include the organic peroxyacids and their salts and the inorganic peroxyacid salts. One 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, and Y is hydrogen, halogen, alkyl, aryl or any group which provides an anionic or cationic moiety in aqueous solution. Such groups can include, for example,  
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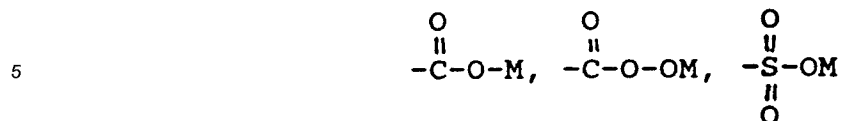


and  $-\text{N}^+\text{R}_3$  wherein M is H or a water-soluble, salt-forming cation.

50 The organic peroxyacids and salts thereof can contain either one, two or more peroxy groups and can be either aliphatic or aromatic. When the organic peroxyacid is aliphatic, the unsubstituted acid may have the general formula :



wherein Y can be H, -CH<sub>3</sub>, -CH<sub>2</sub>Cl,



or -N<sup>+</sup>R<sub>3</sub>

10 and m can be an integer from 1 to 20.

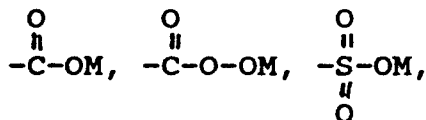
Specific examples of compounds of this type are diperoxyazelaic acid, peroxyauric acid and diperoxydodecanedioic acid, and the magnesium salts thereof.

When the organic peroxyacid is aromatic, the unsubstituted acid may have the general formula:



wherein Y is, for example, hydrogen, halogen, alkyl,

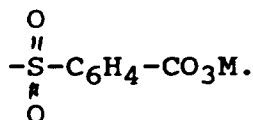
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-(CH<sub>2</sub>)<sub>n</sub>N<sup>+</sup>R<sub>3</sub> or

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35 The percarboxy or percarbonic and Y groupings can be in any relative position around the aromatic ring. The ring and/or Y group (if alkyl) can contain any non-interfering substituents, such as halogen or sulphonate groups.

Specific examples of such aromatic peroxyacids and salts thereof include peroxybenzoic acid, m-chloro-peroxybenzoic acid, p-nitro-peroxybenzoic acid, p-sulphonato-peroxybenzoic acid, diperoxyisophthalic acid, peroxy- $\alpha$ -naphthoic acid, and 4,4'-sulphonyl-diperoxybenzoic acid and magnesium salts thereof.

A specific example of inorganic peroxyacid salts is potassium monopersulphate. A product comprising this compound is the triple salt, K<sub>2</sub>SO<sub>4</sub>.KHSO<sub>4</sub>.2KHSO<sub>5</sub>, available commercially under the trade-name Oxone ® from E.I. Dupont de Nemours and Company and Caroat ® from Degussa.

45 Preferred peroxyacids are peracetic acid and potassium monopersulphate.

Peroxyacid bleach precursors are known and amply described in literature, such as in the GB-Patents 836,988; 864,798; 907,356; 1,003,310 and 1,519,351; German Patent 3,337,921; EP-A-0185522; EP-A-0174132; EP-A-0120591; and U.S. Patents 1,246,339; 3,332,882; 4,128,494; 4,412,934 and 4,675,393.

50 Another useful class of peroxyacid bleach precursors is that of the quaternary ammonium substituted peroxyacid precursors as disclosed in U.S. Patents 4,751,015 and 4,397,757, in EP-A-284292 and in our pending unpublished European Patent Application 89200385.6. Examples of peroxyacid bleach precursors of this class are:

2-(N,N,N-trimethyl ammonium) ethyl sodium-4-sulphophenyl carbonate chloride - (SPCC);

N-octyl,N,N-dimethyl-N10-carbophenoxy decyl ammonium chloride - (ODC);

55 3-(N,N,N-trimethyl ammonium) propyl sodium-4-sulphophenyl carboxylate; and

N,N,N-trimethyl ammonium toluoyloxy benzene sulphonate.

Of the above classes of bleach precursors, the preferred classes are the esters, including acyl phenol sulphonates and acyl alkyl phenol sulphonates; amides, including TAED; and the quaternary ammonium

substituted peroxyacid precursors.

Highly preferred activators include sodium-4-benzoyloxy benzene sulphonate; N,N,N',N'-tetraacetyl ethylene diamine; sodium-1-methyl-2-benzoyloxy benzene-4-sulphonate; sodium-4-methyl-3-benzoyloxy benzoate; SPCC and trimethyl ammonium toluoyloxy benzene sulphonate.

5 A detergent bleach composition of the invention can be formulated by combining effective amounts of the components. The term "effective amounts" as used herein means that the ingredients are present in quantities such that each of them is operative for its intended purpose when the resulting mixture is combined with water to form an aqueous medium which can be used to wash clothes, fabrics and other articles.

10 In particular, the detergent bleach composition can be formulated to contain, for example, 5% to 30% by weight, preferably from 10 to 25% by weight, of a peroxide compound. Peroxyacids may be utilized in somewhat lower amounts, for example from 1% to 15% by weight, preferably from 2% to 10% by weight.

Peroxyacid precursors may be utilized in combination with a peroxide compound in approximately the same level as peroxyacids, i.e. 1% to 15%, preferably from 2% to 10% by weight.

15 The cobalt complex catalyst will be present in such formulations in amounts so as to provide the required level of cobalt in the wash liquor. Normally, an amount of cobalt complex catalyst is incorporated in the formulation which corresponds to a transition metal content of from 0.0002% to 10.0% by weight, preferably 0.002% to 1.0% by weight.

20 The bleach catalyst of the invention is compatible with substantially any known and common surface-active agents and detergency builder materials.

The surface-active material may be naturally derived or a synthetic material selected from anionic, nonionic, amphoteric, zwitterionic, cationic actives and mixtures thereof. Many suitable actives are commercially available and are fully described in literature, for example in "Surface Active Agents and Detergents", Volumes I and II, by Schwartz, Perry and Berch. The total level of the surface-active material may range up to 50% by weight, preferably being from 1% to 40% by weight of the composition, most preferably 4 to 25%.

Synthetic anionic surface-actives are usually water-soluble alkali metal salts of organic sulphates and sulphonates having alkyl groups containing from 8 to 22 carbon atoms, the term alkyl being used to include the alkyl portion of higher aryl radicals.

30 Examples of suitable synthetic anionic detergent compounds are sodium and ammonium alkyl sulphates, especially those obtained by sulphating higher (C<sub>8</sub>-C<sub>18</sub>) alcohols produced, for example, from tallow or coconut oil; sodium and ammonium alkyl (C<sub>9</sub>-C<sub>20</sub>) benzene sulphonates, particularly sodium linear secondary alkyl, (C<sub>10</sub>-C<sub>15</sub>) benzene sulphonates; sodium alkyl glyceryl ether sulphates, especially those esters of the higher alcohols derived from tallow or coconut oil and synthetic alcohols derived from petroleum; sodium coconut oil fatty acid monoglyceride sulphates and sulphonates; sodium and ammonium salts of sulphuric acid esters of higher (C<sub>9</sub>-C<sub>18</sub>) fatty alcohol alkylene oxides particularly ethylene oxide, reaction products; the reaction products of fatty acids such as coconut fatty acids esterified with isethionic acid and neutralized with sodium hydroxide; sodium and ammonium salts of fatty acid amides of methyl taurine; alkane monosulphonates such as those derived by reacting alpha-olefins (C<sub>8</sub>-C<sub>20</sub>) with sodium bisulphite and those derived by reacting paraffins with SO<sub>2</sub> and Cl<sub>2</sub> and then hydrolyzing with a base to produce a random sulphonate; sodium and ammonium C<sub>7</sub>-C<sub>12</sub> dialkyl sulfosuccinates; and olefin sulphonates, which term is used to describe the material made by reacting olefins, particularly C<sub>10</sub>-C<sub>20</sub> alpha-olefins, with SO<sub>3</sub> and then neutralizing and hydrolyzing the reaction product. The preferred anionic detergent compounds are sodium (C<sub>11</sub>-C<sub>15</sub>) alkylbenzene sulphonates, sodium (C<sub>16</sub>-C<sub>18</sub>) alkyl sulphates and sodium (C<sub>16</sub>-C<sub>18</sub>) alkyl ether sulphates.

45 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<sub>6</sub>-C<sub>22</sub>) phenols, generally 5-25 EO, i.e. 5-25 units of ethylene oxides per molecule; the condensation products of aliphatic (C<sub>8</sub>-C<sub>18</sub>) primary or secondary linear or branched alcohols with ethylene oxide, generally 3-30 EO, and products made by 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.

55 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 zwitterionic detergent compounds are used, it is generally in small amounts in compositions based on the much more commonly used synthetic anionic and nonionic actives.

The detergent compositions 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 succinic acid, ethylene diamine tetraacetic acid, oxydisuccinic acid, mellitic acid, benzene polycarboxylic acids, citric acid; and polyacetal carboxylates as disclosed in US patents 4,144,226 and 4,146,495.

Examples of precipitating builder materials include sodium orthophosphate, sodium carbonate and sodium carbonate/calcite.

Examples of calcium ion-exchange builder materials include the various types of water-insoluble 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 or sodium carbonate/calcite mixtures, the sodium salt of nitrilotriacetic acid, sodium citrate, carboxymethyl malonate, carboxymethoxy succinate and the water-insoluble crystalline or amorphous aluminosilicate builder materials, or mixtures thereof.

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, the detergent compositions of the invention can contain any of the conventional additives in the amounts in which such materials are normally employed in fabric washing detergent compositions. Examples of these additives include lather boosters, such as alkanolamides, particularly the monoethanol amides 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, other stabilizers, such as ethylene diamine tetraacetic acid and the phosphonic acid derivatives (i.e. Dequest ® types), fabric softening agents, inorganic salts, such as sodium sulphate, and, usually present in very small amounts, fluorescent agents, perfumes, enzymes, such as proteases, cellulases, lipases and amylases, germicides and colourants.

Another optional but highly desirable additive ingredient with multi-functional characteristics in detergent compositions is from 0.1% to about 3% by weight of a polymeric material having a molecular weight of from 1,000 to 2,000,000 and which can be a homo- or co-polymer of acrylic acid, maleic acid, or salt or anhydride thereof, vinyl pyrrolidone, methyl- or ethyl-vinyl ethers, and other polymerizable vinyl monomers. Preferred examples of such polymeric materials are polyacrylic acid or polyacrylate; polymaleic acid/acrylic acid copolymer; 70:30 acrylic acid/hydroxyethyl maleate copolymer; 1:1 styrene/maleic acid copolymer; isobutylene/maleic acid and diisobutylene/maleic acid copolymers; methyl- and ethyl-vinylether/maleic acid copolymers; ethylene/maleic acid copolymer; polyvinyl pyrrolidone; and vinyl pyrrolidone/maleic acid copolymer.

Detergent bleach compositions of the invention formulated as free-flowing particles, e.g. in powdered or granulated form, can be produced by any of the conventional techniques employed in the manufacture of detergent compositions, but preferably by slurry-making and spray-drying processes to form a detergent base powder to which the heat-sensitive ingredients including the peroxy compound bleach and optionally some other ingredients as desired, and the bleach catalyst, can be added as dry substances. Alternatively, the bleach catalyst can be added separately to a wash/bleach water containing the peroxy compound bleaching agent.

The instant bleach catalyst can also be formulated in detergent bleach compositions of other product forms, such as flakes, tablets, bars and liquids, particularly non-aqueous liquid detergent compositions.

Such non-aqueous liquid detergent compositions in which the instant bleach catalyst can be incorporated are known in the art and various formulations have been proposed, e.g. in US Patents 2,864,770; 3,368,977; 4,772,412; GB Patents 1,205,711; 1,370,377; 2,194,536; DE-A-2,233,771 and EP-A-0,028,849.

The following Examples are given to further illustrate the invention.

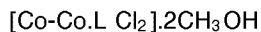
#### EXAMPLE I

Preparation of  $[\text{Co-Co L Cl}_2] \cdot 2\text{CH}_3\text{OH}$ . (Compound (i))

$[\text{Cu-Cu L Cl}_2] \cdot 6\text{H}_2\text{O}$ .

A solution of 5-methyl isophthalaldehyde (5.3 g) in the minimum volume of boiling methanol was added to the pale-blue suspension formed by mixing 1,3-diaminopropane (2.4 g) with a saturated solution of cupric chloride dihydrate (5.5 g) in methanol. The mixture was heated under reflux, whereupon the initial pale-blue suspended solid first turned pea-green and then eventually dissolved. Methanol was removed by boiling at

atmospheric pressure until precipitation had just commenced and the dark-green precipitate was collected, dried at the pump, and then recrystallized from hot water, yielding  $L Cu_2Cl_6 \cdot 6 H_2O$  as dark-green platelets, which were dried over calcium chloride at room temperature and atmospheric pressure. Drying at  $80^\circ C$  under vacuum over phosphorus pentoxide yielded  $Cu-Cu L \cdot Cl_2 \cdot H_2O$  and pale-green powder. Prolonged heating in vacuo at  $160^\circ C$  was required for removal of the final molecule of water.



This compound was prepared by a procedure analogous to that described for  $Cu-Cu L \cdot Cl_2 \cdot 6H_2O$ , except that the reaction was carried out under an atmosphere of oxygen-free nitrogen to avoid possible aerial oxidation and the crude product was obtained simply by cooling the reaction mixture. The precaution of excluding oxygen during the reaction was probably unnecessary, for the solid product was stable to air. The crude solid was recrystallized from hot methanol and dried under vacuum over calcium chloride at room temperature. The ligand L in these complexes is that of formula II(a) having a  $CH_3$  substituent on each aromatic ring and the Co-Co-complex is that of formula (2) as hereinbefore described with Q being methyl. [N.H. Pilkington et al., Austr. Journ. Chemistry (1970), 23, pages 2225/36].

#### EXAMPLE II

This Example shows that "Co-Co" is a superior catalyst for  $H_2O_2$  on tea-stained test cloths compared with  $Mn^{2+}$ ,  $Co^{2+}$  or cobalt-bipyridine complex.  $(Co-bipy)_3$ .

Test conditions : Isothermal wash at  $40^\circ C$  and pH 10.5 for one hour,  $H_2O_2$  concentration :  $8.6 \cdot 10^{-3}$  Mol/l, using demineralized water.

and results :  $[Co-Co] = 10^{-5}$  Mol/l.  $\Delta R_{460} = 26.3$   
 $[Mn] = 10^{-5}$  Mol/l.  $\Delta R_{460} = 21.4$   
 $[Co] = 10^{-5}$  Mol/l.  $\Delta R_{460} = 6.1$   
 $[Co-(bipy)_3] = 10^{-5}$  Mol/l.  $\Delta R_{460} = 17.3$ .

#### EXAMPLE III

In this Example the bleach performances of  $H_2O_2$  catalyzed with "Co-Co", "Co-Cu" and  $Co-(bipy)_3$  on tea-stained test cloths were compared.

Conditions : Heat up wash  $20^\circ C \rightarrow 40^\circ C$  in 13 minutes;  
 37 minutes at  $40^\circ C$ . 6 g/l conventional STP built detergent composition using  $27^\circ FH$  water.

#### Results

Catalyst	$\Delta R_{460}^*$
None	4.9
$Co(bipy)_3$	7.1
Co-Co	21.7
Co-Cu	20.6

#### EXAMPLE IV

In this Example the  $H_2O_2$  catalysis of the Co-Co-complex of the invention was compared with that of  $[Co(NH_3)_5Cl]Cl_2$  of the art in an isothermal wash with a conventional base powder composition containing EDTA at  $40^\circ C$  on the removal of tea stain. The results were as follows :

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EP 0 408 131 B1

Catalyst	$\Delta R_{460}$
Co-Co	26.3
$[\text{Co}(\text{NH}_3)_5 \cdot \text{Cl}]\text{Cl}_2$	20.6
None	13.0

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EXAMPLES V-VI

10

These Examples show that "Co-Co" is also very effective on catalyzing the bleach performance of peracetic acid (both preformed and prepared in situ from a TAED/sodium perborate system). On tea-stained test cloths the experiments were carried out in an isothermal washing process at 40 °C, using a zeolite built Dutch "All" base powder.

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Catalyst	$\Delta R_{460}$	
	Peracetic acid	TAED/perborate
None	11.1	16.2
Co-Co	28.1	37.4

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EXAMPLE VII

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This Example shows that Co-Co is also effective in catalyzing the bleach performance of potassium monopersulphate. The experiments were carried out in an isothermal washing process at 40 °C, using a conventional detergent powder composition in the presence of a polyphosphonate sequestrant (Dequest ® 2041 ex Monsanto).

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The results are :

without catalyst	$\Delta R = 12.5$
with "Co-Co"	$\Delta R = 16.0$

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EXAMPLE IX

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Peroxide bleaching results on tea-stained test cloths were monitored in isothermal washing tests at 40 °C, pH 10, for one hour with H<sub>2</sub>O<sub>2</sub> at a concentration of 9 m.Mol/l, and using different bi-nuclear M.M.-complexes as catalyst :

45

Catalyst	$\Delta R_{460}$
Cu-Zn	6.2
Cu-Cu	2.8
Ni-Ni	3.8
Fe-Fe	8.9
Co-Cu	21.5
Co-Co	26.0

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These results clearly demonstrate that only the Co-complexes of the invention are really effective.

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EXAMPLE X

Bleaching experiments were conducted with Co-SALEN's and Co-SALPD's as bleach catalyst having different Q-substituents. The conditions for the bleach experiments were :

- 5 Demineralized water;  
 Temperature 40 ° C, isothermal; 60 minutes' washing time; pH 10.5;  
 H<sub>2</sub>O<sub>2</sub> concentration : 8.6 mMol/l;  
 Catalyst concentration :  $2.5 \times 10^{-6}$  to  $2.5 \times 10^{-5}$  Mol/l.  
 Bleach monitor : tea-stained test cloths;  
 10 The  $\Delta R$  results after a second wash without bleach are tabulated below :

1) SALEN-derivatives

Q-substituent	$\Delta R$	[cat]
5-Br	21.1	$2.5 \times 10^{-5}$
H	19.2	$1.25 \times 10^{-5}$
5-NO <sub>2</sub>	18.6	$2.5 \times 10^{-5}$
3-OEth	17.5	$2.5 \times 10^{-5}$
3,5 di-Cl	15.4	$2.5 \times 10^{-5}$

2) SALPD-derivatives

Q-substituents		
3.-OEth	18.2	$2.5 \times 10^{-5}$
H	17.5	$2.5 \times 10^{-6}$
5-Br	16.7	$5 \times 10^{-6}$

30 These results demonstrate that the catalytical effect is maintained with different substituents.

EXAMPLE XI

35 A series of bleaching experiments was carried out in a 20° to 40° C heat-up washing machine cycle, using a conventional detergent base powder + 15% sodium perborate monohydrate, with and without a Co-Co-complex catalyst, wherein the effect on various stains was examined.

Washing conditions :

- 40 6 g/l dosage of perborated powder;  
 0.25 mg/l cobalt;  
 27° F tap water;  
 20° initial temperature,  
 pH 10.5 --> 40° C (pH 9.9) in 13 minutes and kept at 40° C for 37 minutes.

The results are tabulated below.

Test cloth	Initial $\Delta_{460}$ *	Final $\Delta_{R_{460}}$ *	
		- catalyst	+ catalyst
Grass	56.7	78.0	80.1
Coffee + milk	52.5	63.4	67.3
Spaghetti sauce	45.6	58.5	70.5
Tea	32.2	38.8	51.1
Red wine	30.7	48.6	58.3
Dirty motor oil	24.9	26.4	26.2
Black shoe polish	4.0	7.5	8.6

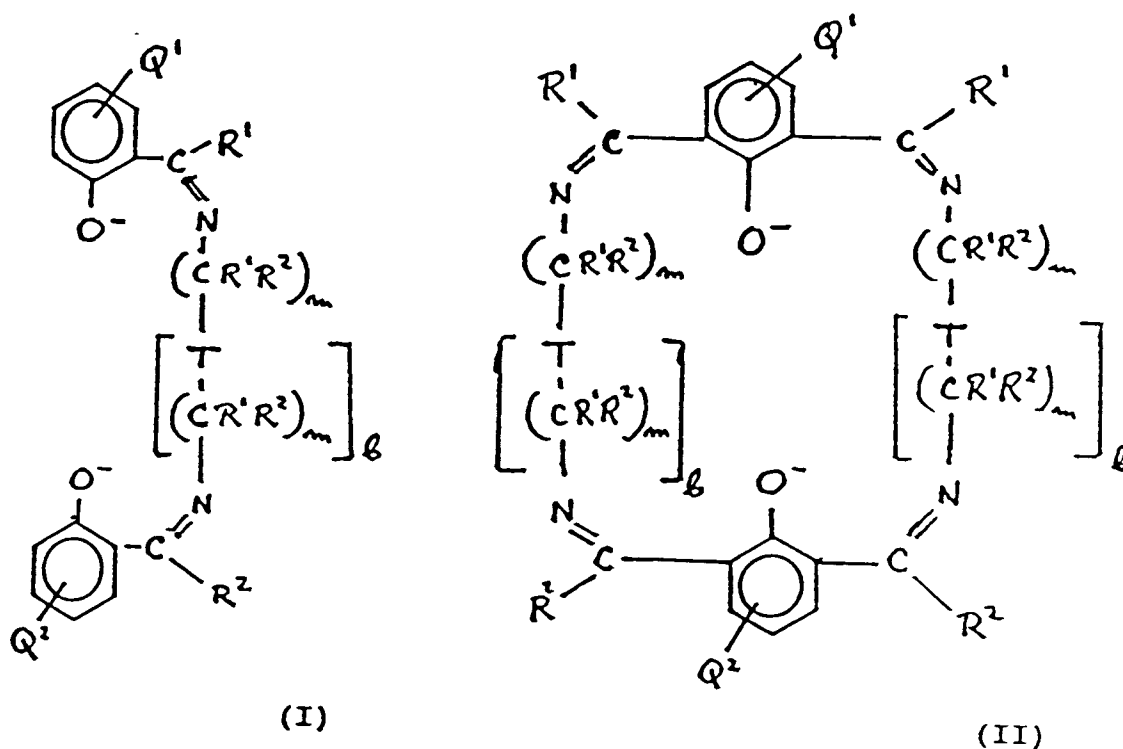
55 These results show the overall effectiveness of the Co-Co-catalyst on a variety of stain types.

## Claims

1. Bleaching or cleaning process employing a peroxy compound bleaching agent selected from the group of hydrogen peroxide, hydrogen peroxide-liberating compounds, peroxyacids and their salts, and peroxyacid bleach precursors, and mixtures thereof, characterized in that said bleaching agent is activated by a catalytic amount of a cobalt complex of general formula A:



wherein M is a metal ion selected from Co and Cu; a is 0 or 1; X is a common anion such as  $Cl^-$ ,  $Br^-$ ,  $I^-$ ,  $NO_3^-$ ,  $ClO_4^-$ ,  $NCS^-$  and  $OH^-$ , or a small co-ordinating ligand such as  $H_2O$ ,  $NH_3$  and pyridine, or a species selected from  $O_2^{2-}$ ,  $O_2^-$ ,  $HO_2^-$  and  $H_2O_2$ ; P is an integer from 0 to 4; Y is a counter-ion, the type of which is dependent upon the charge z of the complex; z denotes the charge of the complex and is an integer which can be positive or negative, whereby, if z is positive, Y is a common anion as denoted for X and, if z is negative, Y is a common cation selected from alkali metal, alkaline earth metal or an alkyl ammonium cation;  $n = z/[charge\ Y]$ ; and L is a ligand being an organic molecule of the general formula I if a = 0, and of the general formula II if a = 1



wherein m is 2-6, preferably 2-3;  $R^1$ ,  $R^2$  are each a substituent selected from H, alkyl, aryl, optionally substituted;  $Q^1$  and  $Q^2$  are each a substituent selected from H, optionally substituted alkyl or aryl,  $NO_2$ ,  $NR_2$ ,  $NR_3^+$ , O-alkyl, O-aryl, halogen,  $SO_3^-$ , alkyl  $SO_3^-$  and aryl  $SO_3^-$ , T is either NR, O, PR or S, herein R =  $R^1$  or  $R^2$  and b is 0-1.

2. Process according to claim 1, characterized in that  $T = NR$ ;  $m = 3$  and R,  $R^1$  and  $R^2$  are H.
3. Process according to claim 1 or 2, characterized in that  $b = 0$ .
4. Process according to claim 2 or 3, characterized in that L is a ligand of general formula II.
5. Process according to claim 4, characterized in that  $Q^1$  and  $Q^2$  are  $-CH_3$ .
6. Bleaching composition comprising a peroxycompound bleach selected from the group of hydrogen peroxide, hydrogen peroxide liberating compounds, peroxyacids and their salts, and peroxyacid bleach



precursors, and mixtures thereof, and a catalyst for the bleaching action of said peroxy compound bleach, characterized in that said catalyst comprises a cobalt complex of general formula A according to any of the preceding claims 1-5.

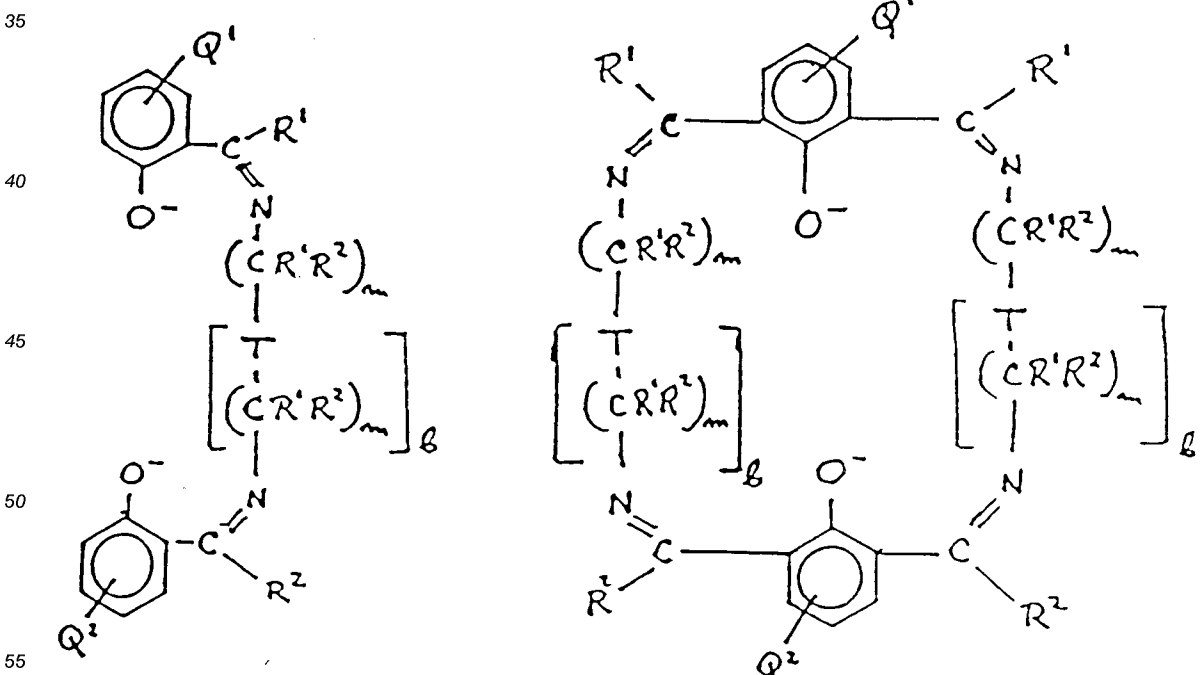
- 5 7. Composition according to claim 6, characterized in that the composition is a detergent bleach composition.
8. Composition according to claim 7, characterized in that the cobalt complex catalyst is present in an amount corresponding to 0.0002 % to 10.0% by weight of transition metal in the composition.
- 10 9. Composition according to claim 8, characterized in that said cobalt complex catalyst is present in an amount corresponding to 0.002% to 1.0% by weight of transition metal in the composition.

**Patentansprüche**

- 15 1. Bleich- oder Reinigungsverfahren unter Anwendung eines Peroxybleichmittels ausgewählt aus der Gruppe Wasserstoffperoxid, Wasserstoffperoxid freisetzende Verbindungen, Peroxysäuren und deren Salze und Peroxysäurebleichvorläufer und Mischungen davon,  
**dadurch gekennzeichnet**, daß das Bleichmittel durch eine katalytische Menge eines Kobaltkomplexes der folgenden allgemeinen Formel (A):



25 worin M ein Metallion ausgewählt aus Co und Cu ist; a 0 oder 1 ist; X ein übliches Anion wie  $Cl^-$ ,  $Br^-$ ,  $I^-$ ,  $NO_3^-$ ,  $ClO_4^-$ ,  $NCS^-$  und  $OH^-$  oder ein kleiner koordinierender Ligand wie  $H_2O$ ,  $NH_3$  und Pyridin oder eine Molekülarart ausgewählt aus  $O_2^{2-}$ ,  $O_2^-$ ,  $HO_2^-$  und  $H_2O_2$  ist; p eine ganze Zahl von 0 bis 4 ist; Y ein Gegenion ist, dessen Art abhängig ist von der Ladung z des Komplexes; z die Ladung des Komplexes bedeutet und eine ganze Zahl ist, die positiv oder negativ sein kann, wobei dann, wenn z positiv ist, Y ein übliches Anion ist, wie für X angegeben und, wenn z negativ ist, Y ein übliches Kation ist ausgewählt aus Alkali-, Erdalkali- oder Alkylammoniumkationen; n = z/[Ladung Y] und L ein Ligand ist, der ein organisches Molekül der allgemeinen Formel I ist, wenn a = 0 ist und der allgemeinen Formel II ist, wenn a = 1 ist,



worin m 2 bis 6, vorzugsweise 2 bis 3 ist; die Reste  $R^1$ ,  $R^2$  jeweils Substituenten sind ausgewählt aus

H, Alkylresten, gegebenenfalls substituierten Arylresten; die Reste Q<sup>1</sup> und Q<sup>2</sup> jeweils Substituenten sind ausgewählt aus H, gegebenenfalls substituierten Alkyl- oder Arylresten, NO<sub>2</sub>, NR<sub>2</sub>, NR<sub>3</sub><sup>+</sup>, O-Alkyl-, O-Arylresten, Halogen, SO<sub>3</sub><sup>-</sup>, Alkyl-SO<sub>3</sub><sup>-</sup> und Aryl-SO<sub>3</sub><sup>-</sup>, T entweder NR, O, PR oder S ist, worin R = R<sup>1</sup> oder R<sup>2</sup> und b 0 bis 1 ist, aktiviert wird.

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2. Verfahren nach Anspruch 1, **dadurch gekennzeichnet**, daß T = NR; m = 3 und R, R<sup>1</sup> und R<sup>2</sup> H sind.

3. Verfahren nach Anspruch 1 oder 2, **dadurch gekennzeichnet**, daß b = 0.

10 4. Verfahren nach Anspruch 2 oder 3, **dadurch gekennzeichnet**, daß L ein Ligand der allgemeinen Formel II ist.

5. Verfahren nach Anspruch 4, , **dadurch gekennzeichnet**, daß Q<sup>1</sup> und Q<sup>2</sup> -CH<sub>3</sub> sind.

15 6. Bleichzusammensetzung umfassend ein Peroxybleichmittel ausgewählt aus der Gruppe Wasserstoffperoxid, Wasserstoffperoxid freisetzende Verbindungen, Peroxysäuren und deren Salze und Peroxysäurebleichvorläufer, und Mischungen davon, und einen Katalysator für die Bleichwirkung des Peroxybleichmittels, **dadurch gekennzeichnet**, daß der Katalysator einen Kobaltkomplex der allgemeinen Formel A nach einem der vorhergehenden Ansprüche 1 bis 5 umfaßt.

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7. Zusammensetzung nach Anspruch 6, **dadurch gekennzeichnet**, daß die Zusammensetzung eine Waschmittelbleichzusammensetzung ist.

25 8. Zusammensetzung nach Anspruch 7, **dadurch gekennzeichnet**, daß der Kobaltkomplexbkatalysator in einer Menge vorhanden ist, die 0,0002 bis 10,0 Gew.-% Übergangsmetall, bezogen auf die Zusammensetzung, entspricht.

30 9. Zusammensetzung nach Anspruch 8, **dadurch gekennzeichnet**, daß der Kobaltkomplexbkatalysator in einer Menge vorhanden ist, die 0,002 bis 1,0 Gew.-% Übergangsmetall, bezogen auf die Zusammensetzung, entspricht.

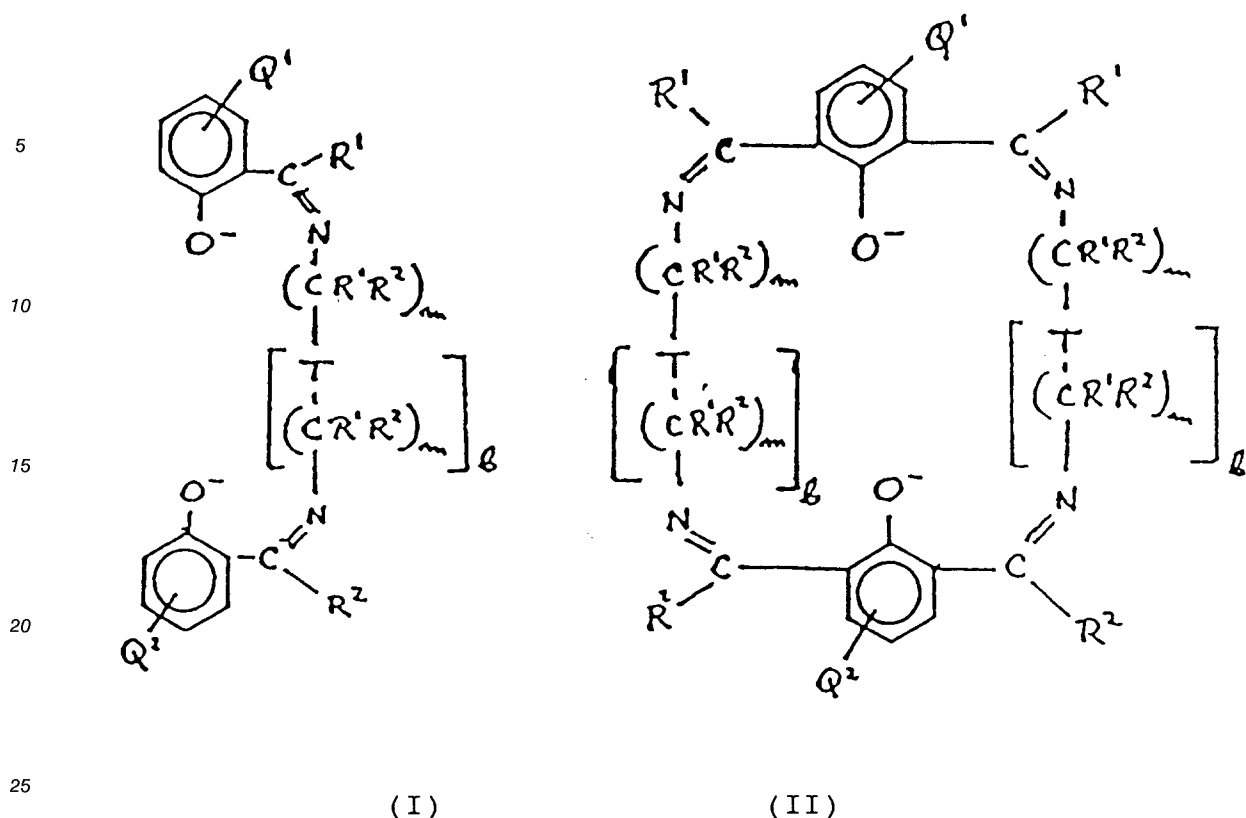
### Revendications

35 1. Procédé de blanchiment ou de nettoyage employant un agent de blanchiment de composé peroxy sélectionné parmi le groupe du peroxyde d'hydrogène, des composés libérant du peroxyde d'hydrogène, des peroxyacides et leurs sels, et des précurseurs de blanchiment au peroxyacide, et des mélanges de ceux-ci, caractérisé en ce que ledit agent de blanchiment est activé par une quantité catalytique d'un complexe au cobalt de formule générale A :

40 (A) [Co.M<sub>a</sub>LX<sub>p</sub>]<sup>z</sup> Y<sub>n</sub>

45 dans laquelle M est un ion de métal sélectionné parmi Co et Cu ; a est 0 ou 1 ; X est un anion commun tel que Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, ClO<sub>4</sub><sup>-</sup>, NCS<sup>-</sup> et OH<sup>-</sup>, ou un petit ligand coordinant tel que H<sub>2</sub>O, NH<sub>3</sub> et la pyridine, ou une espèce sélectionnée parmi O<sub>2</sub><sup>2-</sup>, O<sub>2</sub><sup>-</sup>, HO<sub>2</sub><sup>-</sup> et H<sub>2</sub>O<sub>2</sub> ; P est un nombre entier de 0 à 4 ; Y est un contre-ion, dont le type dépend de la charge z du complexe ; z indique la charge du complexe et est un nombre entier qui peut être positif ou négatif, ainsi, si z est positif, Y est un anion commun comme indiqué pour X et, si z est négatif, Y est un cation commun sélectionné parmi le métal alcalin, le métal de terre alcalin ou un cation alkyle d'ammonium; n = z/[charge Y] ; et L est un ligand qui est une molécule organique de la formule générale I si a = 0, et de la formule générale II si a = 1.

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30 dans lesquelles m est 2 à 6, de préférence 2 à 3 ; R<sup>1</sup>, R<sup>2</sup> sont chacun un groupe substituant sélectionné parmi H, le groupe alkyle, le groupe aryle, facultativement substitués ; Q<sup>1</sup> et Q<sup>2</sup> sont chacun un groupe substituant sélectionné parmi H, facultativement des groupes alkyle et aryle substitués, NO<sub>2</sub>, NR<sub>2</sub>, NR<sub>3</sub><sup>+</sup>, O-alkyle, O-aryle, de l'halogène, SO<sub>3</sub><sup>-</sup>, SO<sub>3</sub><sup>-</sup> alkyle et SO<sub>3</sub><sup>-</sup> aryle, T est soit NR, O, PR soit S, dans lequel R = R<sup>1</sup> ou R<sup>2</sup> et b est 0-1.

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2. Procédé selon la revendication 1, caractérisé en ce que T = NR ; m = 3 et R, R<sup>1</sup> et R<sup>2</sup> sont H.
  3. Procédé selon la revendication 1 ou 2, caractérisé en ce que b = 0.
  4. Procédé selon la revendication 2 ou 3, caractérisé en ce que L est un ligand de formule générale II.
  5. Procédé selon la revendication 4, caractérisé en ce que Q<sup>1</sup> et Q<sup>2</sup> sont -CH<sub>3</sub>.
  6. Composition de blanchiment comprenant un agent de blanchiment de composé de peroxyde sélectionné parmi le groupe du peroxyde d'hydrogène, des composés libérant du peroxyde d'hydrogène, des peroxyacides et de leurs sels, et des précurseurs de blanchiment peroxyacides, et des mélanges de ceux-ci, et un catalyseur pour l'action du blanchiment dudit agent de blanchiment du composé peroxy, caractérisée en ce que ledit catalyseur comprend un complexe au cobalt de formule générale A selon l'une quelconque des revendications précédentes 1 à 5.
  7. Composition selon la revendication 6, caractérisée en ce que la composition est une composition de blanchiment détergente.
  8. Composition selon la revendication 7, caractérisée en ce que le complexe catalyseur au cobalt est présent dans une quantité correspondant à 0,0002 % jusqu'à 10,0 % en poids du métal de transition dans la composition.
  9. Composition selon la revendication 8, caractérisée en ce que ledit complexe catalyseur au cobalt est présent dans une quantité correspondant à 0,002 % jusqu'à 1,0 % en poids du métal de transition dans la composition.