(54) Title: HAIR BLEACHING COMPOSITIONS

(57) Abstract

A hair bleaching composition comprising: (a) a water-soluble peroxypolymer bleach; and (b) a bleaching aid selected from organic peroxyacid bleach precursors and/or preformed organic peroxyacids. The products can provide excellent hair bleaching and in-use efficacy benefits including reduced hair damage at lower pH.
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Hair Bleaching Compositions

Technical Field

This invention relates to hair bleaching compositions, and more especially to hair bleaching compositions comprising a source hydrogen peroxide and a bleaching aid selected from organic per oxyacid bleach precursors and/or preformed organic per oxyacids.

Background of the Invention

The primary colored component of human or animal hair is melanin pigment. Melanin occurs naturally within the hair cortex in 'granular' form. The objective of hair bleaching compositions is to selectively decolorize both the naturally occurring melanin pigment and in addition any synthetic pigments previously applied to the hair with minimal damage to the hair structure. When hair is bleached, the color changes to lighter and lighter shades depending upon the amount of melanin oxidised and removed from the hair in the decoloring process.

Bleaching compositions used on hair differ from those used with textiles, fabrics, hard surface cleansing and the like, such as sodium hypochlorite, in that hair bleaching compositions, in addition to oxidising and destroying the colored melanin of the hair, must be suitable for use in contact with the human skin and must not damage the hair excessively. Furthermore, since hair bleaches are a member of the class of materials known as cosmetics, it is desirable that they be aesthetically acceptable to the user. Finally, it is desirable that a hair bleaching composition remove the melanin coloration from the hair as quickly as possible for the sake of convenience and to help prevent untoward damage to the hair and irritation to the skin and scalp.
Hydrogen peroxide is the most commonly used hair bleaching / melanin oxidising agent. However, hydrogen peroxide treatment of the hair not only solubilises the melanin but can also lead to undesirable hair qualities, such as increased brittleness, and to hair damage, which are in part due to the preferred conditions of conventional peroxide treatment which requires high pH (> pH 9), extended exposure (from 20 to 90 minutes) and relatively high concentration of bleaching solutions (up to 30% volume of oxygen) in order to deliver effective results.

Hair bleaches commonly contain a source of peroxide, bleach activating agents and a variety of additional cosmetic and bleach stabilising agents. Peroxide bleaches must be 'activated' to effect hair bleaching, this typically being accomplished by the use of an 'activating agent' to adjust the pH of the bleaching solution accordingly. The activating material for adjusting the pH of peroxide hair bleaching compositions is an aqueous (alkaline) solution containing ammonia (ammonium hydroxide). A variety of alternative pH adjusting agents to ammonia have also been proposed.

In addition, certain 'activator' materials may also act as hair swelling agents (HSA's). Such HSA's further enhance the bleaching process by swelling the hair fibres to aid the diffusion of the peroxide into the hair and enabling faster, more thorough bleaching (solubilisation/decolorisation of the hair melanin). Ammonia is a particularly effective HSA. However ammonia can cause skin irritation when used at levels of about 1% by weight of composition or higher.

Persulphate type bleaches have been proposed in the hair care area as alternative bleaching systems. However persulphate is a less effective bleach versus conventional peroxide bleaches, requiring higher concentration and longer exposure to effect an equivalent degree of bleaching to conventional bleach.

Neither ammonia-activated, nor alternatively activated bleaching systems comprising conventional bleaching agents or alternative bleaches such as persulphate to date have been able to fully satisfy the desire for effective bleaching in a speedy time with minimal hair damage and at lower pH. Thus a need exists for hair bleaching compositions which can deliver
effective hair bleaching at lower pH values, reduced hair damage and have minimal impact on the skin.

Applicant has now found that hair coloring compositions comprising the combination of conventional peroxide oxidising agents with certain bleaching aids can deliver excellent hair bleaching, reduced hair damage, are effective at a lower pH, and can work in a faster time. Furthermore, applicant has found that the combination of certain bleaching aids with a source of peroxide at particular levels and ratios can deliver excellent hair bleaching results with minimal hair damage at lower pH and in a faster time.

Thus it is an object of the present invention to provide hair bleaching compositions which are fast acting.

It is a further object of the present invention to provide hair bleaching compositions which are effective at low pH.

It is a still further object of the present invention to provide hair bleaching compositions which deliver improved hair bleaching.

It is an additional object of the present invention to provide hair bleaching compositions which impart minimal damage to the hair fibres.

All percentages are by weight of the compositions unless specified otherwise.

Summary of the Invention

The subject of the present invention is a hair bleaching composition, suitable for the treatment of human or animal hair, comprising:

(a) a water-soluble peroxygen bleach; and

(b) a bleaching aid selected from organic peroxyacid bleach
precursors and/or preformed organic peroxyacids

**Detailed Description of the Invention**

As used herein the term 'hair' to be treated may be 'living' i.e. on a living body or may be 'non-living' i.e. in a wig, hairpiece or other aggregation of non-living fibres. Mammalian, preferably human hair is preferred. However wool, fur and other melanin containing fibres are suitable substrates for the compositions according to the present invention.

As used herein the term 'hair bleaching composition' is used in the broad sense in that it is intended to encompass the combinations herein of peroxygen and organic peroxyacid bleach precursor and/or preformed organic peroxyacid bleach as well as other ingredients. Moreover, it is also intended to include complex compositions which contain other components which may or may not be active ingredients. Thus, the term 'hair bleaching composition' is intended to apply to compositions which contain, in addition to a mixture of active oxidising or bleaching agents such things as, by way of example, hair dyes, sequestrants, thickeners, buffers, carriers, surfactants, surface active agents, solvents, alkalising agents, antioxidants, polymers and conditioners.

As discussed above, the hair bleaching compositions according to the present invention comprise a water-soluble peroxygen bleach in combination with a bleaching aid selected from organic peroxyacid bleach precursors and/or preformed organic peroxyacids. Bleaching aid, as used herein is to be regarded as interchangeable with the commonly used term 'bleach accelerator'. Bleach precursor as used herein is intended to cover any organic peroxy based material which can act in combination with a source of peroxyde to deliver enhanced hair bleaching.

The amount of peroxyacid precursor and/or peroxyacid and peroxygen bleach component in the preferred compositions of the present invention may be expressed both in terms of weight or molar ratios' and/or available oxygen' (AO).
In general, the weight ratio of peroxygen bleach to bleaching aid, such as organic peroxyacid precursor, is in the range of from about 20:1 to about 1:20, more preferably from about 10:1 to about 1:10 and especially from about 5:1 to about 1:5. These weight ratios correspond, in general, to molar ratios in the range of from about 400:1 to about 1:5, preferably from about 200:1 to about 1:2 and especially from about 3:1 to about 10:1.

The term 'available oxygen', as further defined in the Example section herein, is the theoretical amount of oxygen that can be delivered to the system from the organic peroxyacid precursor and/or the peroxide material. In preferred compositions the total level of available oxygen from the organic peroxyacid precursor and the peroxide components is from about 0.5 to about 60, preferably from about 2 to about 55 and especially from about 3 to about 50. In highly preferred compositions containing hydrogen peroxide and nonanoyl oxybenzenesulphonate (NOBS) the ratio of AO from the peroxide to NOBS component is in the ratio of from about 8 : 1 to about 12 : 1.

The Hair Bleaching Process
It is understood by those familiar in the art that hair bleaching via use of oxidising agents is a two-step process. Firstly the colored melanin pigment in the hair is solubilised and secondly the solubilised melanin pigment is decolored. It is further understood that in hydrogen peroxide based bleaching systems the reaction between melano-protein and hydrogen peroxide is confined to the mainly protein-combined cystein residues which are subsequently converted to combined cysteic acid. The solubilisation of the melanin pigment is connected with the splitting of the disulphide bridges in the melano protein and it is likely that the disulfide bridge may be the stabilising factor in melanin, as it is in keratins.

The mechanism by which peroxyacid precursor bleaching aids react with peroxygen bleaching agents to generate bleaching components in general, and by which hair is subsequently bleached, in particular, is not completely understood. However, it is generally believed that the peroxyacid bleaching precursor undergoes nucleophilic attack by a perhydroxyl anion (I), which is generated from deprotonation of the hydrogen peroxide, to form a peroxypropionic acid (II). This reaction is commonly referred to as
perhydrolysis. A general representation of the perhydrolysis process is illustrated below:

$$\text{OH}^- + \text{H}_2\text{O}_2 \rightleftharpoons \text{HOO}^- + \text{H}^+ \quad (I)$$

$$\text{R-\text{C-OR'}} + \text{HOO}^- \rightleftharpoons \text{R-\text{C-OR'}} \rightarrow \text{R-\text{C-OOH}} \quad (II)$$

In the above examples R can be an alkyl or aryl group and R' is any suitable leaving group. Suitable examples of R and R' are discussed under the heading Peroxyacid bleach precursor herein. As generation of the perhydroxyl anion (I) from hydrogen peroxide is the initiating step in the perhydrolysis process, the maintenance of optimum reaction conditions to promote this conversion is key. Hydrogen peroxide has a pKa in the range of from about 11.2 to about 11.6, and, as such is generally most effective as a bleaching agent at pHs in the range of from about 9 to about 12. In contrast the pKas of the peroxyacid bleach precursors of the present invention are in the range of from about 7 to about 9.5.

Applicant has found that when the organic peroxyacid bleach precursors and/or preformed peroxyacids of the present invention are used in combination with a source of peroxide to facilitate the perhydrolysis reaction excellent melanin solubilisation and decoloration can be achieved with hair bleaching solutions over a wide range of solution pH of from about 6 to about 12, preferably between about 7 to about 10.5. Such pH values can be maintained by use of substances commonly known as buffering agents, which are optional components of the hair bleaching compositions herein.

The perhydrolysis of the nonoyl oxybenzene sulphonate (NOBS) peroxyacid bleach activator is illustrated by (III) below. Concurrent competitive side reactions which can impact bleach efficacy are hydrolysis and formation of diacylperoxide (DAP) as illustrated by (IV) and (V) below:
Peroxygen Bleaches
The compositions of the invention comprise as an essential feature at least one water-soluble peroxygen bleach compound. Water soluble as defined herein means a bleach compound which can be substantially solubilised in water. Such peroxygen bleaching materials are valuable for the initial solubilisation and decolorisation of the melanin in the hair substrate.

The peroxygen bleaching compounds useful herein are generally inorganic peroxygen bleaches capable of yielding hydrogen peroxide in an aqueous solution. Water-soluble peroxygen bleaching compounds are well known in the art and include hydrogen peroxide, inorganic alkali metal peroxides such as sodium periodate and sodium peroxide and organic peroxides such as urea peroxide, melamine peroxide, and inorganic perhydrate salt bleaching compounds, such as the alkali metal salts of perborates, percarbonates, perphosphates, persilicates, persulphates and the like. These inorganic perhydrate salts may be incorporated as monohydrates, tetrahydrates etc. Mixtures of two or more such bleaching compounds can
be used if desired. Preferred for use in the compositions according to the present invention is hydrogen peroxide.

The peroxxygen bleaching compound is present in the compositions of the present invention at a level of from about 0.5% to about 40%, preferably from about 1% to about 20%, more preferably from about 1.5% to about 7% by weight.

**Bleaching Aid**
As a further essential feature the compositions of the present invention comprise a bleaching aid selected from peroxyacid bleach precursors and/or preformed organic peroxyacid bleach precursors. These peroxy messages are valuable for the enhanced bleaching of the hair in a faster time and at lower pH. While not wishing to be bound by any particular theory it is believed that the peroxyacid bleach precursors of the present invention enhance the bleaching process by acting as bleach accelerators to facilitate more efficient bleaching.

Bleaching aids are preferably incorporated at a level of from 0.5% to 40% by weight, more preferably from 1% to 20% by weight, most preferably from 1.5% to 7% by weight of the hair bleaching compositions.

**Peroxyacid Bleach Precursor**
Peroxyacid bleach precursors are compounds which react with hydrogen peroxide in a perhydrolysis reaction to produce a peroxyacid. Generally peroxyacid bleed precursors may be represented as:

\[
\text{O} \\
\text{X-C-L}
\]

where L is a leaving group and X is essentially any functionality which can facilitate the perhydrolysis reaction and is a poorer leaving group than L, such that upon perhydrolysis the structure of the peroxyacid produced is:

\[
\text{O} \\
\text{X-C-OOH}
\]
Suitable peroxycacid bleach precursor compounds typically contain one or more N- or O-acyl groups in the L position, which precursors can be selected from a wide range of classes. Suitable classes include anhydrides, esters, imides, lactams, enol ethers, sulphonyl ester amides and acylated derivatives of imidazoles and oximes. Examples of useful materials within these classes are disclosed in GB-A-1586789. Suitable esters are disclosed in GB-A-836988, 864798, 1147871, 2143231 and EP-A-0170386.

**Leaving groups**

The leaving group, hereinafter L group, must be sufficiently reactive for the perhydrolysis reaction to occur within the desired time frame (e.g., from 0 to 20 minutes, preferably from 0 to 10 minutes, more preferably from 1 to 5 minutes time exposure).

Preferred L groups are selected from the group consisting of:

- \(-O-\) 
- \(-O-\) 
- \(-N-C-R^1\) 
- \(-N-C-R^1\) 
- \(-O-CH=CH=CH=CH_2\) 
- \(-O-CH=CH=CH=CH_2\) 
- \(-O-C-R^1\) 
- \(-N-C-NR^4\) 
- \(-N-C-NR^4\)
and mixtures thereof, wherein R^1 is an alkyl, aryl, or alkaryl group containing from 1 to 14 carbon atoms, R^3 is an alkyl chain containing from 1 to 8 carbon atoms, R^4 is H or R^3, and Y is H or a solubilizing group wherein the solubilizing group is any suitable hydrophilic group capable of enhancing the water solubility of the L group. Any of R^1, R^3 and R^4 may be substituted by essentially any functional group including, for example alkyl, hydroxy, alkoxy, halogen, amine, nitrosyl, amide and ammonium or alkyl ammonium groups.

The preferred solubilizing groups are -SO_3^2-M^+, -CO_3^2-M^+, -SO_4^2-M^+, -N^+(R^3)_4X^- and O--N(R^3)_3 and most preferably -SO_3^2-M^+ and -CO_3^2-M^+ wherein R^3 is an alkyl chain containing from 1 to 4 carbon atoms, M is a cation which provides solubility to the bleach precursor and X is an anion which provides solubility to the bleach precursor. Preferably, M is an alkali metal, ammonium or substituted ammonium cation, with sodium and potassium being most preferred, and X is a halide, hydroxide, methylsulfate or acetate anion.

A wide variety of bleach precursors are suitable for use in the compositions according to the present invention. These include alkyl percarboxylic acid precursors, amide substituted alkyl peroxyacid precursors, perbenzoic acid precursors, cationic peroxyacid precursors and benzoxazin organic peroxyacid precursors.

**Alkyl percarboxylic acid bleach precursors**

Alkyl percarboxylic acid bleach precursors form percarboxylic acids on perhydrolysis. Preferred precursors of this type provide peracetic acid on perhydrolysis. Suitable alkyl groups for the alkyl percarboxylic bleach precursors hereinafter described may be substituted or unsubstituted and preferably have an average carbon chain length of from about 1 to about 20 carbon atoms.
Preferred alkyl percarboxylic precursor compounds of the imide type include the \(N_N,N^1N^1\) tetra acetylated alkylene amines wherein the alkylen group contains from 1 to 6 carbon atoms, particularly those compounds in which the alkylen group contains 1, 2 and 6 carbon atoms. Tetraacetyl ethylene diamine (TAED) is particularly preferred.

Other preferred alkyl percarboxylic acid precursors include sodium 3,5,5-tri-methyl hexanenoyloxybenzene sulfonate (iso-NOBS), sodium nonanoyloxybenzene sulfonate (NOBS), sodium acetoybenzene sulfonate (ABS) and pentaacetyl glucose. Sodium nonanoyloxybenzene sulfonate is illustrated below:

\[
\text{SO}_3^- \\
\begin{array}{c}
\text{C} \\
\text{R}
\end{array}
\]

In the above example \(R = C_8H_{17}\) wherein \(X = C_8H_{17}\) and \(L = O-C_6H_4\).  

**Amide substituted alkyl peroxyacid bleach precursors**

Amide substituted alkyl peroxyacid precursor compounds are suitable herein, including those of the following general formulae:

\[
\begin{array}{c}
\text{C} \\
\text{R}^1 \\
\text{N} \\
\text{R}^2 \\
\text{C} \\
\text{L} \\
\text{O} \\
\text{R}^5
\end{array}
\]  

or

\[
\begin{array}{c}
\text{C} \\
\text{R}^1 \\
\text{N} \\
\text{C} \\
\text{R}^2 \\
\text{C} \\
\text{L} \\
\text{O} \\
\text{R}^5 \\
\text{O} \\
\text{O}
\end{array}
\]

wherein \(R^1\) is an alkyl group with from 1 to 14 carbon atoms, \(R^2\) is an alkylen group containing from 1 to 14 carbon atoms, and \(R^5\) is H or an alkyl group containing 1 to 10 carbon atoms and L can be essentially any leaving group. Amide substituted bleach activator compounds of this type are described in EP-A-0170386.

**Perbenzoic acid bleach precursor**
Perbenzoic acid precursor compounds provide perbenzoic acid on perhydrolysis. Suitable O-acylated perbenzoic acid precursor compounds include the substituted and unsubstituted benzoyl oxybenzene sulfonates, and the benzoylation products of sorbitol, glucose, and other saccharides with benzoylating agents, and those of the imide type including N-benzoyl succinimide, tetrabenzoyl ethylene diamine and the N-benzoyl substituted ureas. Suitable imidazole type perbenzoic acid precursors include N-benzoyl imidazole, N-benzoyl caprolactam and N-benzoyl benzimidazole. Other useful N-acyl group-containing perbenzoic acid precursors include N-benzoyl pyrrolidone, dibenzoyl taurine and benzoyl pyroglutamic acid. The example below illustrates N-benzoyl caprolactam:

\[
\begin{align*}
\text{Cationic peroxyacid bleach precursors} \\
\text{Cationic peroxyacid precursor compounds produce cationic peroxyacids on perhydrolysis.}
\end{align*}
\]

Typically, cationic peroxyacid precursors are formed by substituting the peroxyacid part of a suitable peroxyacid precursor compound with a positively charged functional group, such as an ammonium or alkyl ammonium group, preferably an ethyl or methyl ammonium group. Cationic peroxyacid precursors are typically present in the compositions herein as a salt with a suitable anion, such as a halide ion.

The peroxyacid precursor compound to be so cationically substituted may be a perbenzoic acid, or substituted derivative thereof, precursor compound as described herein before. Alternatively, the peroxyacid precursor compound may be an alkyl percarboxylic acid precursor compound or an amide substituted alkyl peroxyacid precursor as described hereinafter.

Examples of preferred cationic peroxycacid precursors are described in GB-A-9407944.9 and US-A-08/298903; 08/298650; 08/298904 and 08/298906.

Suitable cationic peroxycacid precursors include any of the ammonium or alkyl ammonium substituted alkyl or benzoyl oxybenzene sulfonates, N-acylated caprolactams, and monobenzoyltetraacetyl glucose benzoyl peroxides. Preferred cationic peroxycacid precursors of the N-acylated caprolactam class include the trialkyl ammonium methylene benzoyl caprolactams and the trialkyl ammonium methylene alkyl caprolactams. Illustrated below are examples of an alkyl ammonium substituted benzoyl oxybenzene sulfonate and a trialkyl ammonium methylene benzoyl caprolactam:

$$
\text{CH}_3 \\
R-N-\text{CH}_2-\text{Ph-}^\text{C-L}
$$

$$
L = \text{Ph-}^\text{SO}_3^- \quad \text{OR} \quad \text{N-}\text{cyclohexyl}
$$

**Benzoxazin organic peroxycacid bleach precursors**

Also suitable are precursor compounds of the benzoxazin-type, as disclosed for example in EP-A-332,294 and EP-A-482,807, particularly those having the formula:
wherein $R_1$ is H, alkyl, alkaryl, aryl, or arylalkyl.

**Preformed organic peroxycacid**

The organic peroxycacid bleaching system may contain, in addition to, or as an alternative to, an organic peroxycacid bleach precursor compound, a preformed organic peroxycacid, typically at a level of from about 0.1% to about 15% by weight, more preferably from about 0.5% to about 10% and especially from about 0.5% to about 5% by weight of the composition.

A preferred class of organic peroxycacid compounds are the amide substituted compounds of the following general formulae:

$$R^1\text{C} = N\text{C} = \text{C} - \text{OOH} \quad R^1\text{N} = \text{C} - \text{R}^2\text{C} - \text{OOH}$$

or

$$R^1\text{N} = \text{C} - \text{R}^2\text{C} - \text{OOH}$$

wherein $R^1$ is an alkyl, aryl or alkaryl group with from 1 to 14 carbon atoms, $R^2$ is an alkylene, arylene, and alkarylene group containing from 1 to 14 carbon atoms, and $R^5$ is H or an alkyl, aryl, or alkaryl group containing 1 to 10 carbon atoms. Amide substituted organic peroxycacid compounds of this type are described in EP-A-0,170,386.

Other organic peroxycacids include peracetic, pernanoic, nonylamidoperoxyacproic acid (NAPCA), diacyl and tetraaclyperoxides, especially diperoxododecanedioc acid, diperoxotetradecanedioc acid and diperoxyhexadecanedioc acid. Mono- and diperazelaic acid, mono- and diperbrassyllic acid and N-phthaloylaminoperoxicaproic acid are also suitable herein.
The preferred peroxycacid materials for use herein are selected from acetyl triethylcitrate (ATC), tetraacetyl ethylene diamine (TAED), nonanoyl oxybenzenesulphonate (NOBS), (6-octaamidocaproyl) oxybenzene sulphonate and (6-decaamindocaproyl) oxybenzene sulphate and peracetic and pernanoic acids and mixtures thereof. In highly preferred compositions the peroxyc acid material is selected from acetyl triethylcitrate (ATC), tetraacetyl ethylene diamine (TAED), nonanoyl oxybenzenesulphonate (NOBS), (6-octaamidocaproyl) oxybenzene sulphonate and (6-decaamindocaproyl) oxybenzene sulphate and mixtures thereof.

**Buffering Agents**

The compositions of the invention have a preferred pH in the range of from about 6 to about 12, more preferably from about 7 to about 10.5.

As herein before described the preferred compositions of the present invention may contain one or more buffering agents to adjust the pH to the desired level. Several different pH modifiers can be used to adjust the pH of the final composition or any constituent part thereof.

This pH adjustment can be effected by using well known acidifying agents in the field of treating keratinous fibres, and in particular human hair, such as inorganic and organic acids such as hydrochloric acid, tartaric acid, citric acid, phosphoric acid and carboxylic or sulphonic acids such as ascorbic acid, acetic acid, lactic acid, sulphuric acid, formic acid, ammonium sulphate and sodium dihydrogenphosphate /phosphoric acid, disodium hydrogenphosphate /phosphoric acid, potassium chloride /hydrochloric acid, potassium dihydrogen phthalate/ hydrochloric acid, sodium citrate / hydrochloric acid, potassium dihydrogen citrate /hydrochloric acid, potassium dihydrogen citrate/ citric acid, sodium citrate / citric acid, sodium tartarate/ tartaric acid, sodium lactate/ lactic acid, sodium acetate/ acetic acid, disodium hydrogenphosphate/ citric acid and sodium chloride/ glycine / hydrochloric acid and mixtures thereof.

Further examples of suitable buffering agents are ammonium hydroxide, ethylamine, dipropylamine, triethylamine and alkanediamines such as 1,3-
diaminopropene, anhydrous alkaline alkanolamines such as, mono or di-
ethanolamine, preferably those which are completely substituted on the
amine group such as dimethylaminoethanol, polyalkylene polyamines such
as diethylenetriamine or a heterocyclic amine such as morpholine as well
as the hydroxides of alkali metals, such as sodium and potassium
hydroxide, hydroxides of alkali earth metals, such as magnesium and
calcium hydroxide, basic amino acids such as L-alginine, lysine,
oxyllysine and histidine and alkanolamines such as dimethylaminoethanol
and aminoalkylpropanediol and mixtures thereof. Also suitable for use
herein are compounds that form HCO₃⁻ by dissociation in water
(hereinafter referred to as 'ion forming compounds'). Examples of
suitable ion forming compounds are Na₂CO₃, NaHCO₃, K₂CO₃,
(NH₄)₂CO₃, NH₄HCO₃, CaCO₃ and Ca(HCO₃) and mixtures thereof.

As herein before described certain alkaline buffering agents such as
ammonium hydroxide and monoethylamine (MEA) can also act as hair
swelling agents (HSA's).

Preferred for use as a buffering agent for the compositions according to
the present invention is ammonium hydroxide.

The compositions according to the present invention may, as will be
described later herein, be comprised of a final solution containing both
peroxide and bleaching aid which have been admixed prior to application
to the hair. As such the compositions according to the present invention
may comprise kits of a number of separate components.

In kits comprising a portion of peroxide bleaching agent, which may be
present in either solid or liquid form, such as hydrogen peroxide, a
buffering agent solution is required to stabilise hydrogen peroxide. Since
hydrogen peroxide is stable in the pH range from 2 to 4, it is necessary to
use a buffering agent having a pH within this range. Dilute acids are
suitable hydrogen peroxide buffering agents. Phosphoric acid is a
preferred agent for buffering hydrogen peroxide solutions.

In kits comprising aperoxy acid precursor bleaching agent, which may be
in solid or liquid form, a buffering agent capable of maintaining a solution
pH in the range of from about 6 to about 12, preferably in the range of from about 8 to about 10, is preferred. Suitable buffering agents include compounds that form HCO₃⁻ by dissociation in water and alkalis generating substantially no irritating odor as well as conventional alkaline buffering agents. Any alkali generating substantially no irritating odour can be used.

**Bleach catalyst**

The compositions optionally contain a transition metal containing bleach catalyst. One suitable type of bleach catalyst is a catalyst system comprising a heavy metal cation of defined bleach catalytic activity, such as copper, iron or manganese cations, an auxiliary metal cation having little or no bleach catalytic activity, such as zinc or aluminium cations, and a sequestrant having defined stability constants for the catalytic and auxiliary metal cations, particularly ethylenediaminetetraacetic acid, ethylenediaminetetra(methyleneephosphonic acid) and water-soluble salts thereof. Such catalysts are disclosed in U.S. Pat. 4,430,243.

Other types of bleach catalysts include the manganese-based complexes disclosed in U.S. Pat. 5,246,621 and U.S. Pat. 5,244,594. Preferred examples of these catalysts include Mn⁴⁺₂(u-O)₃(1,4,7-trimethyl-1,4,7-triazacyclononane)₂−(PF₆)₂, Mn⁶⁺₂(u-O)₁(u-OAc)₂(1,4,7-trimethyl-1,4,7-triazacyclononane)₂−(ClO₄)₂, Mn⁴⁺₄(u-O)₆(1,4,7-triazacyclononane)₄−(ClO₄)₂, Mn⁶⁺Mn⁴⁺₄(u-O)₁(u-OAc)₂(1,4,7-trimethyl-1,4,7-triazacyclononane)₂−(ClO₄)₃, and mixtures thereof. Others are described in EP-A-0,549,272. Other ligands suitable for use herein include 1,5,9-trimethyl-1,5,9-triazacyclododecane, 2-methyl-1,4,7-triazacyclononane, 2-methyl-1,4,7-triazacyclononane, 2-methyl-1,4,7-triazacyclononane, 1,2,4,7-tetramethyl-1,4,7-triazacyclononane, and mixtures thereof.

For examples of suitable bleach catalysts see U.S. Pat. 4,246,612 and U.S. Pat. 5,227,084. See also U.S. Pat. 5,194,416 which teaches mononuclear manganese (IV) complexes such as Mn(1,4,7-trimethyl-1,4,7-triazacyclononane)(OCH₃)₃−(PF₆). Still another type of bleach catalyst, as disclosed in U.S. Pat. 5,114,606, is a water-soluble complex of manganese (III), and/or (IV) with a ligand which is a non-carboxylate
polyhydroxy compound having at least three consecutive C-OH groups. Other examples include binuclear Mn complexed with tetra-N-dentate and bi-N-dentate ligands, including \( \text{Mn}^{III}(u-O)_{2}\text{Mn}^{IV}N_{4} \) and \( [\text{Bipy}_{2}\text{Mn}^{III}(u-O)_{2}\text{Mn}^{IV}\text{bipy}_{2}-(\text{ClO}_{4})_{3} \). Further suitable bleach catalysts are described, for example, in EP-A-0,408,131 (cobalt complex catalysts), EP-A-0,384,503, and EP-A-0,306,089 (metalloporphyrin catalysts), U.S. 4,728,455 (manganese/multidentate ligand catalyst), U.S. 4,711,748 and EP-A-0,224,952, (absorbed manganese on aluminosilicate catalyst), U.S. 4,601,845 (aluminosilicate support with manganese and zinc or magnesium salt), U.S. 4,626,373 (manganese/ligand catalyst), U.S. 4,119,557 (ferric complex catalyst), DE-A-2,054,019 (cobalt chelant catalyst) CA-A-866,191 (transition metal-containing salts), U.S. 4,430,243 (chelants with manganese cations and non-catalytic metal cations), and U.S. 4,728,455 (manganese gluconate catalysts).

**Heavy metal ion sequestrant**

The bleaching compositions of the invention preferably contain as an optional component a heavy metal ion sequestrant. By heavy metal ion sequestrant it is meant herein components which act to sequester (chelate or scavenge) heavy metal ions. These components may also have calcium and magnesium chelation capacity, but preferentially they show selectivity to binding heavy metal ions such as iron, manganese and copper. Such sequestering agents are valuable in hair bleaching compositions as herein described for the delivery of controlled bleaching action (as outlined in WO-A-94/03553) as well as for the provision of good storage stability of the bleaching products.

Heavy metal ion sequestrants are generally present at a level of from about 0.005% to about 20%, preferably from about 0.01% to about 10%, more preferably from about 0.05% to about 2% by weight of the compositions.

Various sequestering agents, including the amino phosphonates, available as Dequest (RTM) from Monsanto, the nitriloacetates, the hydroxyethyl-
ethylene triamines and the like are known for such use. Suitable heavy metal ion sequestrants for use herein include organic phosphonates, such as the amino alkylene poly (alkylene phosphonates), alkali metal ethane 1-hydroxy disphosphonates and nitrilo trimethylene phosphonates.

Preferred among the above species are diethylene triamine penta (methylene phosphonate), ethylene diamine tri (methylene phosphonate) hexamethylene diamine tetra (methylene phosphonate) and hydroxy-ethylene 1,1 diprophosphate.

Preferred biodegradable non-phosphorous heavy metal ion sequestrants suitable for use herein include nitrilotriacetic acid and polyaminocarboxylic acids such as ethylenediaminotetraacetic acid, ethylenetriamine pentaacetic acid, ethylenediamine disuccinic acid, ethylenediamine diglutaric acid, 2-hydroxypropylenediamine disuccinic acid or any salts thereof. Especially preferred is ethylenediamine-N,N'-disuccinic acid (EDDS). see US-A-4,704,233, or the alkali metal, alkaline earth metal, ammonium, or substituted ammonium salts thereof, or mixtures thereof.

Other suitable heavy metal ion sequestrants for use herein are iminodiacetic acid derivatives such as 2-hydroxyethyl diacetic acid or glyceryl imino diacetic acid, described in EP-A-317,542 and EP-A-399,133. The iminodiacetic acid-N-2-hydroxypropyl sulfonic acid and aspartic acid N-carboxymethyl N-2-hydroxypropyl-3-sulfonic acid sequestrants described in EP-A-516,102 are also suitable herein. The \(\beta\)-alanine-N,N'-diacetic acid, aspartic acid-N,N'-diacetic acid, aspartic acid-N-monoacetic acid and iminodisuccinic acid sequestrants described in EP-A-509,382 are also suitable.

EP-A-476,257 describes suitable amino based sequestrants. EP-A-510,331 describes suitable sequestrants derived from collagen, keratin or casein. EP-A-528,859 describes a suitable alkyl iminodiacetic acid sequestrant. Dicarboxilic acid and 2-phosphonoobutane-1,2,4-tricarboxylic acid are also suitable. Glycinamide-N,N'-disuccinic acid (GADS), ethylenediamine-N,N'-diglutaric acid (EDDG) and 2-hydroxypropylenediamine-N,N'-disuccinic acid (HPDDS) are also suitable.
The heavy metal ion sequestering agents of the present invention may be used in their alkali or alkaline earth metal salts.

**Hair Coloring Agents**

The compositions of the present invention may additionally include one or more hair coloring agents. Hair coloring agents suitable for use in the compositions of the present invention include both oxidative and non-oxidative dyes. Such hair coloring agents may be used with the bleaching systems of the present invention to formulate permanent, demi-permanent, semi-permanent or temporary hair dye compositions.

(i) Oxidative dyes

The dye forming intermediates used in oxidative dyes are essentially aromatic diamines, aminophenols and their derivatives. These dye forming intermediates can be classified as; primary and secondary intermediates and nitro dyes. Primary intermediates are chemical compounds which by themselves will form a dye upon oxidation. The secondary intermediates, also known as color modifiers or couplers and are used with other intermediates for specific color effects or to stabilise the color. Nitro dyes are unique in that they are direct dyes which do not require oxidation to dye the hair.

The oxidation dye intermediates which are used in the compositions and processes herein include aromatic diamines, polyhydric phenols, amino phenols and derivatives of these aromatic compounds (e.g., N-substituted derivatives of the amines, and ethers of the phenols). Primary oxidation dye intermediates are generally colorless molecules prior to oxidation. The oxidation dye color is generated when the primary intermediate is 'activated' and subsequently enjoined with a secondary intermediate (coupling agent), which is also generally colorless, to form a colored, conjugated molecule. The primary dye intermediate is generally understood to be 'activated' (oxidised) by active species liberated during the decomposition of the peroxide bleaching agent. The 'activated' dye
intermediate can then react with a coupler to form a larger 'colored' dye. Oxidative dye intermediates diffuse into the hair shaft, which has been pre-swollen by action of the HSA, if present, and then are activated and coupled to form larger dye complexes within the hair shaft which are less readily washed out.

In general terms, oxidation hair dye precursors or intermediates include those monomeric materials which, on oxidation, form oligomers or polymers having extended conjugated systems of electrons in their molecular structure. Because of the new electronic structure, the resultant oligomers and polymers exhibit a shift in their electronic spectra to the visible range and appear colored. For example, oxidation dye precursors capable of forming colored polymers include materials such as aniline, which has a single functional group and which, on oxidation, forms a series of conjugated imines and quinoid dimers, trimers, etc. ranging in color from green to black. Compounds such as p-phenylenediamine, which has two functional groups, are capable of oxidative polymerization to yield higher molecular weight colored materials having extended conjugated electron systems. Color modifiers (couplers), such as those detailed hereinafter, are preferably used in conjunction with the oxidation dye precursors herein and are thought to interpose themselves in the colored polymers during their formation and to cause shifts in the electronic spectra thereof, thereby resulting in slight color changes. A representative list of oxidation dye precursors suitable for use herein is found in Sagarin, "Cosmetic Science and Technology", Interscience, Special Edn. Vol 2 pages 308 to 310. It is to be understood that the bleaching aids of the present invention are suitable for use (in combination with a source of peroxide as detailed herein) with all manner of oxidation dye precursors and color modifiers and that the precursors detailed below are only by way of example and are not intended to limit the compositions and processes herein.

The typical aromatic diamines, polyhydric phenols, amino phenols, and derivatives thereof, described above as primary dye precursors can also have additional substituents on the aromatic ring, e.g. halogen, aldehyde, carboxylic acid, nitro, sulfonic acid and substituted and unsubstituted hydrocarbon groups, as well as additional substituents on the amino
nitrogen and on the phenolic oxygen, e.g. substituted and unsubstituted alkyl and aryl groups.

Examples of suitable aromatic diamines, amino phenols, polyhydric phenols and derivatives thereof, respectively, are compounds having the general formulas (VI), (VII) and (VIII) below:

\[
\begin{align*}
R_1 & \quad \begin{array}{c}
\text{N-} \\
\text{N} \\
\text{Y} \\
\text{N}\text{-R}_3\text{R}_4 \\
\text{R}_5
\end{array} \\
\text{(VI)}
\end{align*}
\]

OR

\[
\begin{align*}
\begin{array}{c}
\text{R}_1 \\
\text{N-} \\
\text{N} \\
\text{Y} \\
\text{N}\text{-R}_3\text{R}_4 \\
\text{R}_5
\end{array} \\
\text{HX}
\end{align*}
\]

wherein \( Y \) is hydrogen, halogen, (e.g. fluorine, chlorine, bromine or iodine), nitro, amino, hydroxyl,

\[
\begin{align*}
\text{O} \\
\text{CH}
\end{align*}
\]

-COOM or -SO_3M (where M is hydrogen or an alkali or alkaline earth metal, ammonium, or substituted ammonium wherein one or more hydrogens on the ammonium ion is replaced with a 1 to 3 carbon atom alkyl or hydroxyalkyl radical), wherein \( R_1, R_2, R_3 \) and \( R_4 \) are the same or different from each other and are selected from the group consisting of
hydrogen, C₁ to C₄ alkyl or alkenyl and C₆ to C₉ aryl, alkaryl or aralkyl, and R₅ is hydrogen, C₁ to C₄ unsubstituted or substituted alkyl or alkenyl wherein the substituents are selected from those designated as Y, above, or C₆ to C₉ unsubstituted or substituted aryl, alkaryl or aralkyl wherein the substituents are selected from those defined as Y, above. Since the precursors of formula (VI) are amines, they can be used herein in the form of peroxide-compatible salts, as noted, wherein X represents peroxide-compatible anions of the type herein before detailed. The general formula of the salt indicated is to be understood to encompass those salts having mono-, di-, and tri-negative anions.

Specific examples of formula (VI) compounds are: o-phenylenediamine, m-phenylenediamine, p-phenylenediamine, 2-chloro-p-phenylenediamine, 2-iodo-p-phenylenediamine, 4-nitro-o-phenylenediamine, 2-nitro-p-phenylenediamine, 1,3,5-triaminobenzene, 2-hydroxy-p-phenylenediamine, 2,4-diamineobenzoic acid, sodium 2,4-diaminobenzoate, calcium di-2,4-, iaminobenzoate, ammonium 2,4-diaminobenzoate, trimethylammonium 2,4-, diaminobenzoate, tri-(2-hydroxyethyl)ammonium 2,4-diaminobenzoate, 2,4-diaminobenzaldehyde carbonate, 2,4-diaminobenzensulfonic acid, potassium 2,4-diaminobenzenesulfonate, N,N-diisopropyl-p-, phenylenediamine bicarbonate, N,N-dimethyl-p-phenylenediamine, N-ethyl-N'-(2-propenyl)-p-phenylenediamine, N-phenyl-p-phenylenediamine, N-phenyl-N-benzyl-p-phenylenediamine, N-ethyl-N'-(3-ethylphenyl)-p-phenylenediamine, 2,4-toluenediamine, 2-ethyl-p-phenylenediamine, 2-(2-bromoethyl)-p-phenylenediamine, 2-phenyl-p-phenylenediamine laurate, 4-(2,5-diaminophenyl)benzaldehyde, 2-benzyl-p-phenylenediamine acetate, 2-(4-nitrobenzyl)-p-phenylenediamine, 2-(4-methylphenyl)-p-phenylenediamine, 2-(2,5-diaminophenyl)-5-methylbenzoic acid, methoxy paraphenylenediamine, dimethyl-p-phenylenediamine, 2,5-dimethylpara-phenylenediamine, 2-methyl-5-methoxy-para-phenylenediamine, 2,6-methyl-5-methoxy-para-phenylenediamine, 3-methyl-4-amino-N,N-diethylaniline, N,N-bis(β-hydroxyethyl)-para-phenylenediamine, 3-methyl-4-amino-N,N-bis(β-hydroxyethyl)aniline, 3-chloro-4-amino-N,N-bis(β-hydroxyethyl)aniline, 4-amino-N-ethyl-N-(carbamethyl)aniline, 3-methyl-4-amino-N-ethyl-N-(carbamethyl)aniline, 4-amino-N-ethyl-(β-piperidonoethyl)aniline, 3-methyl-4-amino-N-ethyl-β
-piperidonoethyl)aniline, 4-amino-N-ethyl-N-(-β-morpholinoethyl)aniline, 3-methyl-4-amino-N-ethyl-N-(-β-morpholinoethyl)aniline, 4-amino-N-ethyl-N-(-β-acetylaminoethyl)aniline, 4-amino-N-(β-methoxyethyl) aniline, 3-methyl-4-amino-N-ethyl-N-(-β-acetylaminoethyl) aniline, 4-amino-N-ethyl-N-(-β-mesylaminoethyl) aniline, 3-methyl-4-amino-N-ethyl-N-(-β-mesylaminoethyl) aniline, 4-amino-N-ethyl-N-(β-sulphoethyl) aniline, 3-methyl-4-amino-N-ethyl-N-(β-sulphoethyl) aniline, N-(4-aminophenyl)morpholine, N-(4-aminophenyl)piperidine, 2,3-dimethyl-p-phenylenediamine, isopropyl-p-phenylenediamine, N,N-bis-(2-hydroxyethyl)-p-phenylenediamine sulphate.

where X and Y are the same as in formula (VI), R₁ and R₂ can be the same or different from each other and are the same as in formula (VI), R₅ is the same as in formula (VI) and R₆ is hydrogen or C₁ to C₄ substituted or unsubstituted alkyl or alkenyl wherein the substituents are selected from those defined as Y in formula (VI).

Specific examples of formula (VII) compounds are: o-aminophenol, m-aminophenol, p-aminophenol, 2-iodo-p-aminophenol, 2-nitro-p-aminophenol, 3,4-dihydroxyaniline, 3,4-diaminophenol, chloroacetate, 2-hydroxy-4-aminobenzoic acid, 2-hydroxy-4-aminobenzaldehyde, 3-amino-4-hydroxybenzenesulfonic acid, N,N-
diisopropyl-p-aminophenol, N-methyl-N-(1-propenyl)-p-aminophenol, N-phenyl-N-benzyl-p-aminophenol sulphate, N-methyl-N-(3-ethylphenyl)-p-aminophenol, 2-nitro-5-ethyl-p-aminophenol, 2-nitro-5-(2-bromoethyl)-p-aminophenol, (2-hydroxy-5-aminophenyl)acetaldehyde, 2-methyl-p-aminophenol, (2-hydroxy-5-aminophenyl)acetic acid, 3-(2-hydroxy-5-aminophenyl)-1-propene, 3-(2-hydroxy-5-aminophenyl)-2-chloro-1-propene, 2-phenyl-p-aminophenol palmitate, 2-(4-nitrophenyl)-p-aminophenol, 2-benzyl-p-aminophenol, 2-(4-chlorobenzyl-p-aminophenol perchlorate, 2-(4-methylphenyl)-p-aminophenol, 2-(2-amino-4-methylphenyl)-p-aminophenol, p-methoxyaniline, 2-bromoethyl-4-aminophenyl ether phosphate, 2-nitroethyl-4-aminophenyl ether bromide, 2-aminoethyl-4-aminophenyl ether, 2-hydroxyethyl-4-aminophenyl ether, (4-aminophenoxo)acetaldehyde, (4-aminophenoxo)acetic acid, (4-aminophenoxo)methanesulfonic acid, 1-propenyl-4-aminophenyl ether isobutyrate, (2-chloro)-1-propenyl-4-aminophenyl ether, (2-nitro)-1-propenyl-4-aminophenyl ether, (2-amino)-propenyl-4-aminophenyl ether, (2-hydroxy)-1-propenyl-4-aminophenyl ether, N-methyl-p-aminophenol, 3-methyl-4-aminophenol, 2-chloro-4-aminophenol, 3-chloro-4-aminophenol, 2,6-dimethyl-4-aminophenol, 3,5-dimethyl-4-aminophenol, 2,3-dimethyl-4-aminophenol, 2,5-dimethyl-4-aminophenol, 2-hydroxymethyl-4-aminophenol, 3-hydroxymethyl-4-aminophenol.

\[
\text{(VIII)}
\]

where Y, R5 and R6 are as defined above in formula (VII).

Specific examples of formula (VIII) compounds are: o-hydroxyphenol (catechol), m-hydroxyphenol (resorcinol), p-hydroxyphenol (hydroquinone), 4-methoxyphenol, 2-methoxyphenol, 4-(2-chloroethoxy) phenol, 4-(2-propenoxy) phenol, 4-(3-chloro-2-propenoxy) phenol, 2-chloro-4-hydroxyphenol (2-chlorohydroquinone), 2-nitro-4-hydroxyphenol(2-nitrohydroquinone), 2-amino-4-hydroxyphenol, 1,2,3-trihydroxybenzene (pyrogallol), 2,4-dihydroxybenzaldehyde, 3,4-dihydroxybenzoic acid, 2,4-dihydroxybenzenesulfonic acid, 3-ethyl-4-
hydroxyphenol, 3-(2-nitroethyl)-4-hydroxyphenol, 3-(2-propenyl)-4-
hydroxyphenol, 3-(3-chloro-2-propenyl)-4-hydroxyphenol, 2-phenyl-4-
hydroxyphenol, 2-(4-chlorophenyl)-4-hydroxyphenol, 2-benzyl-4-
hydroxyphenol, 2-(2-nitrophenyl)-4-hydroxyphenol, 2-(2-methylphenyl)-
4-hydroxyphenol, 2-(2-methyl-4-chlorophenyl)-4-hydroxyphenol, 3-
methoxy-4-hydroxy-benzaldehyde, 2-methoxy-4-(1-propenyl)phenol, 4-
hydroxy-3-methoxycinnamic acid, 2,5-dimethoxyaniline, 2-
methylresorcinol, alpha napthol and salts thereof.

Color modifiers which are suitable for inclusion in the compositions and
processes herein before described include certain aromatic amines and
phenols and derivatives thereof which do not produce color singly, but
which modify the color, shade or intensity of the colors developed by the
primary oxidized dye precursors. Certain aromatic amines and phenolic
compounds, and derivatives thereof, including some aromatic diamines
and polyhydric phenols of the types described by formulas (VI), (VII) and
(VIII) above, but which are well known in the art not to be suitable
oxidation dye precursors, are suitable as color modifiers herein.
Polyhydric alcohols are also suitable for use as color modifiers.

The aromatic amines and phenols and derivatives described above as color
modifiers can also have additional substituents on the aromatic ring, e.g.,
halogen, aldehyde, carboxylic acid, nitro, sulfonyl and substituted and
unsubstituted by hydrocarbon groups, as well as additional substituents on
the amino nitrogen, or phenolic oxygen, e.g. substituted and unsubstituted
alkyl and aryl groups. Again, peroxide-compatible salts thereof are
suitable for use herein.

Examples of aromatic amines, phenols and derivatives thereof are
compounds of the general formulas (IX) and (X) below:
wherein Z is hydrogen, C\textsubscript{1} and C\textsubscript{3} alkyl, halogen (e.g. fluorine, chlorine, bromine or iodine) nitro,

\begin{center}
\begin{tikzpicture}
  \node at (0,0) {\text{OR}};
  \node at (-1,1) {R\textsubscript{1} - N - R\textsubscript{2}};
  \node at (-2,0) {R\textsubscript{7} - Z};
  \node at (1,1) {R\textsubscript{1} - N - R\textsubscript{2}};
  \node at (2,0) {R\textsubscript{7} - Z};
  \node at (0.5,0.5) {HX};
\end{tikzpicture}
\end{center}

-COOM or SO\textsubscript{3}M, (where M is hydrogen or an alkali or alkaline earth metal, ammonium or substituted ammonium wherein one or more hydrogens on the ammonium ion is replaced with a 1 to 3 carbon atom alkyl or hydroxyalkyl radical), wherein R\textsubscript{1} and R\textsubscript{2} are the same or different and are selected from the group consisting of hydrogen, C\textsubscript{1} to C\textsubscript{4} alkyl or alkenyl and C\textsubscript{6} to C\textsubscript{9} aryl, alkaryl or aralkyl and R\textsubscript{7} is hydrogen, C\textsubscript{1} to C\textsubscript{4} unsubstituted or substituted alkyl or alkenyl wherein the substituents are selected from those designated as Z above or C\textsubscript{6} to C\textsubscript{9} unsubstituted or substituted aryl, alkaryl or aralkyl wherein the substituents are selected from those defined as Z above and wherein X is as defined in formula (VI).

Specific examples of formula (IX) compounds are:
aniline, p-chloroaniline, p-fluoroaniline, p-nitroaniline, p-aminobenzaldehyde, p-aminobenzoic acid, sodium-p-aminobenzoate, lithium-p-aminobenzoate, calcium di-p-aminobenzoate, ammonium-p-aminobenzoate, trimethylammonium-p-aminobenzoate, tri(2-hydroxyethyl)-p-aminobenzoate, p-aminobenzenesulfonic acid, potassium p-aminobenzenesulfonate, N-methylaniline, N-propyl-N-phenylaniline, N-
methyl-N-2-propenylaniline, N-benzylaniline, N-(2-ethylphenyl)aniline, 4-methylaniline, 4-(2-bromoethyl)aniline, 2-(2-nitroethyl)aniline, (4-aminophenyl)acetaldehyde, (4-aminophenyl)acetic acid, 4-(2-propenyl)aniline acetate, 4-(3-bromo-2-propenyl)aniline, 4-phenylaniline chloroacetate, 4-(3-chlorophenyl)aniline, 4-benzylaniline, 4-(4-iodobenzyl)aniline, 4-(3-ethylphenyl)aniline, 4-(2-chloro-4-ethylphenyl)aniline.

wherein Z and R7 are defined as in formula (IX) and R8 is hydrogen or C1 to C4 substituted or unsubstituted alkyl or alkenyl wherein the substituents are selected from those defined as Z in formula (IX).

Specific examples of formula (X) compounds are:
phenol, p-chlorophenol, p-nitrophenol, p-hydroxybenzaldehyde, p-hydroxybenzoic acid, p-hydroxybenzenesulfonic acid, ethylphenyl ether, 2-chloroethylphenyl ether, 2-nitroethylphenyl ether, phenoxyacetaldehyde, phenoxyacetic acid, 3-phenoxy-1-propene, 3-phenoxy-2-nitro-1-propene, 3-phenoxy-2-bromo-1-propene, 4-propylphenol, 4-(3-bromopropyl)phenol, 2-(2-nitroethyl)phenol, (4-hydroxyphenyl)acetaldehyde, (4-hydroxyphenyl)acetic acid, 4-(2-propenyl)phenol, 4-phenylphenol, 4-benzylphenol, 4-(3-fluoro-2-propenyl)phenol, 4-(4-chlorobenzyl)phenol, 4-(3-ethylphenyl)phenol, 4-(2-chloro-3-ethylphenyl)phenol, 2,5-xylenol, 2,5-diaminopyridine, 2-hydroxy-5-aminopyridine, 2-amino-3-hydroxy pyridine, tetraaminopyrimidine, 1,2,4-trihydroxybenzene, 1,2,4-trihydroxy-5-(C1-C6-alkyl)benzene, 1,2,3-trihydroxybenzene, 4-aminoresorcinol, 1,2-dihydroxybenzene, 2-amino-1,4-dihydroxybenzene, 2-amino-4-methoxy-phenol, 2,4-diaminophenol, 3-methoxy-1,2-dihydroxy-benzene, 1,4-dihydroxy-2-(N,N-diethylamino)benzene, 2,5-diamino-4-methoxy-1-hydroxybenzene, 4,6-dimethoxy-3-amino-1-hydroxybenzene, 2,6-dimethyl-4-[N-(p-hydroxyphenyl)amino]-1-hydroxybenzene, 1,5-diamino-2-methyl-4-[N-(p-hydroxyphenyl)amino]benzene and salts thereof.
Additional oxidation dye precursors suitable for use herein include catechol species and in particular catechol "dopa" species which includes dopa itself as well as homologs, analogs and derivatives of DOPA. Examples of suitable cachetol species include cysteinyldopa, alpha alkyl dopa having 1 to 4, preferably 1 to 2 carbon atoms in the alkyl group, epinephrine and dopa alkyl esters having 1 to 6, preferably 1 to 2 carbon atoms in the alkyl group.

In general suitable catechols are represented by formula (XI) below:

```
R1
R2
R3
OH
OH
```

wherein R₁, R₂ and R₃, which may be the same or different, are electron donor or acceptor substituents selected from H, lower (C₁-C₆) alkyl, OH, OR, COOR, NHCOR, CN, COOH, Halogen, NO₂, CF₃, SO₃H or NR₄R₅, with the proviso that only one of the R₁, R₂ or R₃ can be CN, COOH, halogen, NO₂, CF₃ or SO₃H: R₄ and R₅, which may be the same or different, are H, lower (C₁-C₆) alkyl or substituted lower (C₁-C₆) alkyl in which the substituent may be OH, OR, NHCOR₆, NHCONH₂, NHCO₂R₆, NHCSNH₂, CN, COOH, SO₃H, SO₂NR₆, SO₂R₆ or CO₂R₆; R₆ is lower (C₁-C₆) alkyl, lower (C₁-C₆) hydroxyalkyl phenyl linked to the nitrogen by an alkylene chain, phenyl or substituted phenyl with the substituent defined as R₁, and R is C₁-C₆ alkyl or C₁-C₆ hydroxyalkyl.

The oxidation dye precursors can be used herein alone or in combination with other oxidation dye precursors, and one or more dye precursors can be used in combination with one or more color modifiers. The choice of a single dye precursors and modifiers will be determined by the color, shade and intensity of coloration which is desired. There are nineteen preferred oxidation dye precursors which can be used herein, singly or in combination, to provide oxidation hair dyes having a variety of shades ranging from ash blonde to black; these are: pyrogallol, resorcinol, p-toluenediamine, p-phenylenediamine, o-phenylenediamine, m-
phenylenediamine, o-aminophenol, p-aminophenol, 4-amino-2-nitrophenol, nitro-p-phenylenediamine, N-phenyl-p-phenylenediamine, m-aminophenol, 2-amino-3-hydroxypyridine, 1-naphthol, N,N bis (2-hydroxyethyl)p-phenylenediamine, 4-amino-2-hydroxytoluene, 1,5-dihydroxynaphthalene and 2,4-diaminoanisole. These can be used in the molecular form or in the form of peroxide-compatible salts, as detailed above.

The concentration of dye precursor (and color modifier, if used) in the coloring solution can be from about 0.001% to about 6% by weight and is preferably from about 0.01% to about 2.0% by weight.

(ii) Non-oxidative dyes

Non-oxidative dyes include both semi-permanent, temporary and other dyes. Non-oxidative dyes as defined herein include the so-called 'direct action dyes', metallic dyes, metal chelate dyes, fibre reactive dyes and other synthetic and natural dyes. Various types of non-oxidative dyes are detailed in: 'Chemical and Physical Behaviour of Human Hair' 3rd Edn. by Clarence Robbins (pp250-259); 'The Chemistry and Manufacture of Cosmetics'. Volume IV. 2nd Edn. Maison G. De Navarre at chapter 45 by G.S. Kass (pp841-920); 'cosmetics: Science and Technology' 2nd Edn., Vol II Balsam Sagarin, Chapter 23 by F.E. Wall (pp 279-343); 'The Science of Hair Care' edited by C. Zviak, Chapter 7 (pp 235-261) and .Hair Dyes', J.C. Johnson, Noyes Data Corp., Park Ridge, U.S.A. (1973), (pp 3-91 and 113-139).

Direct action dyes which do not require an oxidative effect in order to develop the color, are also designated hair tints and have long been known in the art. They are usually applied to the hair in a base matrix which includes surfactant material. Direct action dyes include nitro dyes such as the derivatives of nitroamino benzene or nitroaminophenol; disperse dyes such as nitroaryl amines, aminoanthraquinones or azo dyes; anthraquinone dyes, naphthoquinone dyes; basic dyes such as Acridine Orange C.I. 46005.
Further examples of direct action dyes include the Arianor dyes basic brown 17, C.I.(color index) - no. 12,251; basic red 76, C.I. - 12,245; basic brown 16, C.I. - 12,250; basic yellow 57, C.I. - 12,719 and basic blue 99, C.I. - 56,059 and further direct action dyes such as acid yellow 1, C.I. - 10,316 (D&C yellow no.7); acid yellow 9, C.I. - 13,015; basic violet C.I. - 45,170; disperse yellow 3, C.I. - 11,855; basic yellow 57, C.I. - 12,719; disperse yellow 1, C.I. - 10,345; basic violet 1, C.I. - 42,535, basic violet 3, C.I. - 42,555; greenish blue, C.I. - 42090 (FD&C Blue no.1); yellowish red, C.I.-14700 (FD&C red no.4); yellow, C.I.19140 (FD&C yellow no5); yellowish orange, C.I.15985 (FD&C yellow no.6); bluish green, C.I.42053 (FD&C green no.3); yellowish red, C.I.16035 (FD&C red no.40); bluish green, C.I.61570 (D&C green no.3); orange, C.I.45370 (D&C orange no.5); red, C.I.15850 (D&C red no.6); bluish red, C.I.15850(D&C red no.7); slight bluish red, C.I.45380(D&C red no.22); bluish red, C.I.45410(D&C red no.28); bluish red, C.I.73360(D&C red no.30); reddish purple, C.I.17200(D&C red no.33); dirty blue red, C.I.15880(D&C red no.34); bright yellow red, C.I.12085(D&C red no.36); bright orange, C.I.15510(D&C orange no.4); greenish yellow, C.I.47005(D&C yellow no.10); bluish green, C.I.59040(D&C green no.8); bluish violet, C.I.60730(Ext. D&C violet no.2); greenish yellow, C.I.10316(Ext. D&C yellow no.7);

Fibre reactive dyes include the Procion (RTM), Drimarene (RTM), Cibacron (RTM), Levafix (RTM) and Remazol (RTM) dyes available from ICI, Sandoz, Ciba-Geigy, Bayer and Hoechst respectively.

Natural dyes and vegetable dyes as defined herein include henna (Lawsonia alba), camomile (Matricaria chamomila or Anthemis nobilis), indigo, logwood and walnut hull extract.

Temporary hair dyes, or hair coloring rinses, are generally comprised of dye molecules which are too large to diffuse into the hair shaft and which act on the exterior of the hair. They are usually applied via a leave-in procedure in which the dye solution is allowed to dry on the hair surface. As such these dyes are typically less resistant to the effects of washing and cleaning the hair with surface active agents and are washed off of the hair with relative ease. Any temporary hair dye may suitably be used in
the compositions of the invention and examples of preferred temporary hair dyes are illustrated below.

Violet

Red

Yellow

Blue-Violet

Semi-permanent hair dyes are dyes which are generally smaller in size and effect to temporary hair rinses but are generally larger than permanent (oxidative) dyes. Typically, semi-permanent dyes act in a similar manner to oxidative dyes in that they have the potential to diffuse into the hair shaft. However, semi-permanent dyes are generally smaller in size than the aforementioned conjugated oxidative dye molecules and as such are pre-disposed to gradual diffusion out of the hair again. Simple hair washing and cleaning action will encourage this process and in general semi-permanent dyes are largely washed out of the hair after about 5 to 8 washes. Any semi-permanent dye system may be suitably used in the compositions of the present invention. Suitable semi-permanent dyes for use in the compositions of the present invention are HC Blue 2, HC Yellow 4, HC Red 3, Disperse Violet 4, Disperse Black
9, HC Blue 7, HC Yellow 2, Disperse Blue 3, Disperse violet 1 and mixtures thereof. Examples of semi-permanent dyes are illustrated below:

Blue

Yellow

Red

Typical semi-permanent dye systems incorporate mixtures of both large and small color molecules. As the size of the hair is not uniform from root to tip the small molecules will diffuse both at the root and tip, but will not be retained within the tip, while the larger molecules will be generally only be able to diffuse into the ends of the hair. This
combination of dye molecule size is used to help give consistent color results from the root to the tip of the hair both during the initial dyeing process and during subsequent washing.

**Thickeners**

The compositions of the present invention may additionally include a thickener at a level of from about 0.05% to about 20%, preferably from about 0.1% to about 10%, more preferably from about 0.5% to about 5% by weight. Thickening agents suitable for use in the compositions herein are selected from oleic acid, cetyl alcohol, oleyl alcohol, sodium chloride, cetearyl alcohol, stearyl alcohol, synthetic thickeners such as Carbopol, Aculyn and Acrosyl and mixtures thereof. Preferred thickeners for use herein are Aculyn 22 (RTM), steareth-20 methacrylate copolymer; Aculyn 44 (RTM), polyurethane resin and Acusol 830 (RTM), acrylates copolymer which are available from Rohm and Haas, Philadelphia, PA, USA. Additional thickening agents suitable for use herein include sodium alginate or gum arabic, or cellulose derivatives, such as methyl cellulose or the sodium salt of carboxymethylcellulose or acrylic polymers.

**Solvents**

Water is the preferred principal diluent for the compositions according to the present invention. As such, the compositions according to the present invention may include one or more solvents as additional diluent materials. Generally, the solvent is selected to be miscible with water and innocuous to the skin. Solvents suitable for use herein include C1-C20 mono- or polyhydric alcohols and their ethers, glycerine, with monohydradic and dihydric alcohols and their ethers preferred. In these compounds, alcoholic residues containing 2 to 10 carbon atoms are preferred. Thus, a particularly preferred group includes ethanol, isopropanol, n-propanol, butanol, propylene glycol, ethylene glycol monoothyl ether, and mixtures thereof.

**Enzyme**
A further additional material useful in the hair bleaching compositions according to the present invention is one or more enzymes.

Suitable enzymatic materials include the commercially available lipases, cutinases, amylases, neutral and alkaline proteases, esterases, cellulases, pectinases, lactases and peroxidases conventionally incorporated into detergent compositions. Suitable enzymes are discussed in US Patents 3,519,570 and 3,533,139 incorporated herein by reference.

Peroxidases are haemoproteins specific for peroxide, but using a wide range of substances as donors. Catalase which decomposes peroxide, is included here in view of the fact that it is generally similar in structure and properties and is able to bring about certain oxidations by H₂O₂. The decomposition of H₂O₂ can be regarded as the oxidation of one molecule by the other. It is widespread in aerobic cells and may have some more important function. The coenzyme peroxidases are not haemoproteins and one at least is a flavoprotein. Other flavoproteins such as xanthine oxidase will also use H₂O₂ among other acceptors, and the coenzyme peroxidases resemble these rather than the classical peroxidases in not being specific for H₂O₂. Suitable peroxidases for the compositions of the present invention include horseradish peroxidase, Japanese radish peroxidase, cow’s milk peroxidase, rat liver peroxidase, linginase and haloperoxidase such as chloro- and bromo-peroxidase.

Enzymes are optionally incorporated at levels sufficient to provide up to about 50 mg by weight, more typically about 0.01 mg to about 10 mg of active enzyme per gram of the hair treatment composition of the invention. Stated otherwise the peroxidase enzyme may be incorporated into the compositions in accordance with the invention at a level of from about 0.0001% to about 5%, preferably from about 0.001% to about 1%, more preferably from about 0.01% to about 1% active enzyme by weight of the composition.

Commercially available protease enzymes include those sold under the trade names Alcalase, Savinase, Primase, Durazym, and Esperase by Novo Industries A/S (Denmark), those sold under the tradename Maxatase, Maxacal and Maxapem by Gist-Brocades, those sold by
Genencor International, and those sold under the tradename Opticlean and Optimase by Solvay Enzymes. Protease enzyme may be incorporated into the compositions in accordance with the invention at a level of from 0.0001% to 4% active enzyme by weight of the composition.

Amylases include, for example, α-amylases obtained from a special strain of B. licheniformis, described in more detail in GB-1,269,839 (Novo). Preferred commercially available amylases include for example, those sold under the tradename Rapidase by Gist-Brocades, and those sold under the tradename Termamyl and BAN by Novo Industries A/S. Amylase enzyme may be incorporated into the composition in accordance with the invention at a level of from 0.0001% to 2% active enzyme by weight of the composition.

Lipolytic enzyme may be present at levels of active lipolytic enzyme of from 0.0001% to 2% by weight, preferably 0.001% to 1% by weight, most preferably from 0.001% to 0.5% by weight of the compositions.

The lipase may be fungal or bacterial in origin being obtained, for example, from a lipase producing strain of Humicola sp., Thermomyces sp. or Pseudomonas sp. including Pseudomonas pseudoalcaligenes or Pseudomas fluorescens. Lipase from chemically or genetically modified mutants of these strains are also useful herein. A preferred lipase is derived from Pseudomonas pseudoalcaligenes, which is described in Granted European Patent, EP-B-0218272.

Another preferred lipase herein is obtained by cloning the gene from Humicola lanuginosa and expressing the gene in Aspergillus oryza, as host, as described in European Patent Application, EP-A-0258 068, which is commercially available from Novo Industri A/S, Bagsvaerd, Denmark, under the trade name Lipolase. This lipase is also described in U.S. Patent 4,810,414, Huge-Jensen et al, issued March 7, 1989.

Surfactant Materials
The compositions of the present invention can additionally contain a surfactant system. Suitable surfactants for inclusion in the compositions of the invention generally have a lipophilic chain length of from about 8 to
about 22 carbon atoms and can be selected from anionic, cationic, nonionic, amphoteric, zwitterionic surfactants and mixtures thereof.

(i) Anionic Surfactants

Anionic surfactants suitable for inclusion in the compositions of the invention include alkyl sulphates, ethoxylated alkyl sulphates, alkyl glycercyl ether sulfonates, methyl acyl taurates, fatty acyl glycines, N-acyl glutamates, acyl isethionates, alkyl sulfosuccinates, alkyl ethoxysulphosuccinates, alpha-sulfonated fatty acids, their salts and/or their esters, alkyl ethoxy carboxylates, alkyl phosphate esters, ethoxylated alkyl phosphate esters, alkyl sulphates, acyl sarcosinates and fatty acid/protein condensates, and mixtures thereof. Alkyl and/or acyl chain lengths for these surfactants are C_{12}-C_{22}, preferably C_{12}-C_{18} more preferably C_{12}-C_{14}.

(ii) Nonionic Surfactants

The compositions of the invention can also comprise a water-soluble nonionic surfactants. Surfactants of this class include C_{12}-C_{14} fatty acid mono-and diethanolamides, sucrose polyester surfactants and polyhydroxy fatty acid amide surfactants having the general formula below.

\[
\begin{align*}
R_8 & - C - N - Z_2 \\
& H \\
O & R_9
\end{align*}
\]

The preferred N-alkyl, N-alkoxy or N-aryloxy, polyhydroxy fatty acid amide surfactants according to the above formula are those in which R_8 is C_{5}-C_{31} hydrocarbyl, preferably C_{6}-C_{19} hydrocarbyl, including straight-chain and branched chain alkyl and alkenyl, or mixtures thereof and R_9 is typically C_{1}-C_{8} alkyl or hydroxyalkyl, preferably methyl, or a group of formula -R^1-O-R^2 wherein R^1 is C_2-C_8 hydrocarbyl including straight-chain, branched-chain and cyclic (including aryl), and is preferably C_2-C_4 alkylene, R^2 is C_1-C_8 straight-chain, branched-chain and cyclic hydrocarbyl including aryl and oxyhydrocarbyl, and is preferably C_1-C_4 alkyl, especially methyl, or phenyl. Z_2 is a polyhydroxyhydrocarbyl moiety having a linear hydrocarbyl chain with at least 2 (in the case of...
glyceraldehyde) or at least 3 hydroxyls (in the case of other reducing sugars) directly connected to the chain, or an alkoxylated derivative (preferably ethoxylated or propoxylated) thereof. \( Z_2 \) preferably will be derived from a reducing sugar in a reductive amination reaction, most preferably \( Z_2 \) is a glycytn moiety. Suitable reducing sugars include glucose, fructose, maltose, lactose, galactose, mannose, and xylose, as well as glyceraldehyde. As raw materials, high dextrose corn syrup, high fructose corn syrup, and high maltose corn syrup can be utilised as well as the individual sugars listed above. These corn syrups may yield a mix of sugar components for \( Z_2 \). It should be understood that it is by no means intended to exclude other suitable raw materials. \( Z_2 \) preferably will be selected from the group consisting of \(-\text{CH}_2-(\text{CHOH})_n-\text{CH}_2\text{OH}, \ -\text{CH(\text{CH}_2\text{OH})-(CHOH})_n-1-\text{CH}_2\text{H}, \ -\text{CH}_2(\text{CHOH})_2(\text{CHOR'})\text{CHOH)-CH}_2\text{OH}, \) where \( n \) is an integer from 1 to 5, inclusive, and \( R' \) is \( H \) or a cyclic mono- or polysaccharide, and alkoxylated derivatives thereof. As noted, most preferred are glycicyls wherein \( n \) is 4, particularly \(-\text{CH}_2-(\text{CHOH})_4-\text{CH}_2\text{OH}.\)

The most preferred polyhydroxy fatty acid amide has the formula \( \text{Rg(CO)N(CH}_3)\text{CH}_2(\text{CHOH})_4\text{CH}_2\text{OH} \) wherein \( \text{Rg} \) is a C6-C19 straight chain alkyl or alkenyl group. In compounds of the above formula, \( \text{Rg-CO-N<} \) can be, for example, cocoamide, stearamide, oleamide, lauramide, myristamide, capricamide, palmamidam, tallowamide, etc.

Suitable oil derived nonionic surfactants for use herein include water soluble vegetable and animal-derived emollients such as triglycerides with a polyethyleneglycol chain inserted; ethoxylated mono and di-glycerides, polyethoxylated lanolins and ethoxylated butter derivatives. One preferred class of oil-derived nonionic surfactants for use herein have the general formula below:

\[
\text{RCOCH}_2\text{CH(OH)CH}_2(\text{OCH}_2\text{CH}_2)_n\text{OH}
\]

wherein \( n \) is from about 5 to about 200, preferably from about 20 to about 100, more preferably from about 30 to about 85, and wherein \( \text{R} \) comprises
an aliphatic radical having on average from about 5 to 20 carbon atoms, preferably from about 7 to 18 carbon atoms.

Suitable ethoxylated oils and fats of this class include polyethleneglycol derivatives of glyceryl cокоate, glycercyl caproate, glycercyl caprylate, glyceryl tallowate, glycercyl palmate, glycercyl stearate, glycercyl laurate, glycercyl oleate, glycercyl ricinoleate, and glycercyl fatty esters derived from triglycerides, such as palm oil, almond oil, and corn oil, preferably glycercyl tallowate and glycercyl cocoate.

Preferred for use herein are polyethleneglycol based polyethoxylated C9-C15 fatty alcohol nonionic surfactants containing an average of from about 5 to about 50 ethyleneoxy moieties per mole of surfactant.

Suitable polyethylene glycol based polyethoxylated C9-C15 fatty alcohols suitable for use herein include C9-C11 Pareth-3, C9-C11 Pareth-4, C9-C11 Pareth-5, C9-C11 Pareth-6, C9-C11 Pareth-7, C9-C11 Pareth-8, C11-C15 Pareth-3, C11-C15 Pareth-4, C11-C15 Pareth-5, C11-C15 Pareth-6, C11-C15 Pareth-7, C11-C15 Pareth-8, C11-C15 Pareth-9, C11-C15 Pareth-10, C11-C15 Pareth-11, C11-C15 Pareth-12, C11-C15 Pareth-13 and C11-C15 Pareth-14. PEG 40 hydrogenated castor oil is commercially available under the tradename Cremophor (RTM) from BASF. PEG 7 glyceryl cocoate and PEG 20 glyceryl laurate are commercially available from Henkel under the tradenames Cetiol (RTM) HE and Lamacit (RTM) GML 20 respectively. C9-C11 Pareth-8 is commercially available from Shell Ltd. under the tradename Dobanol (RTM) 91-8. Particulary preferred for use herein are polyethylene glycol ethers of ceteryl alcohol such as Ceteareth 25 which is available from BASF under the trade name Cremaphor A25.

Also suitable for use herein are nonionic surfactants derived from composite vegetable fats extracted from the fruit of the Shea Tree (Butyrospermum Karkii Kotschy) and derivatives thereof. Similarly, ethoxylated derivatives of Mango, Cocoa and Illipe butter may be used in compositions according to the invention. Although these are classified as ethoxylated nonionic surfactants it is understood that a certain proportion may remain as non-ethoxylated vegetable oil or fat.
Other suitable oil-derived nonionic surfactants include ethoxylated derivatives of almond oil, peanut oil, rice bran oil, wheat germ oil, linseed oil, jojoba oil, oil of apricot pits, walnuts, palm nuts, pistachio nuts, sesame seeds, rapeseed, cade oil, corn oil, peach pit oil, poppyseed oil, pine oil, castor oil, soybean oil, avocado oil, safflower oil, coconut oil, hazelnut oil, olive oil, grapeseed oil, and sunflower seed oil.

(iii) Amphoteric Surfactants

Amphoteric surfactants suitable for use in the compositions of the invention include:

(a) imidazolinium surfactants of formula (XII)

\[
\begin{align*}
\text{C}_2\text{H}_4\text{OR}_2 \\
\text{R}_1 & \text{N} & \text{CH}_2 \text{Z} \\
\text{N} & & \text{N} \\
\end{align*}
\]

wherein \(R_1\) is C7-C22 alkyl or alkenyl, \(R_2\) is hydrogen or CH\(_2\)Z, each \(Z\) is independently CO\(_2\)M or CH\(_2\)CO\(_2\)M, and M is H, alkali metal, alkaline earth metal, ammonium or alkanolammonium; and/or ammonium derivatives of formula (XIII)

\[
\begin{align*}
\text{C}_2\text{H}_4\text{OH} \\
\text{R}_1 \text{CONH(CH}_2)\text{Z} \\
\text{N} & \text{CH}_2 \text{Z} \\
\text{R}_2 & & \text{N} \\
\end{align*}
\]

wherein \(R_1, R_2\) and \(Z\) are as defined above;

(b) aminoalkanoates of formula (XIV)

\[
\begin{align*}
\text{R}_1\text{NH(CH}_2)\text{nCO}_2\text{M}
\end{align*}
\]
iminodialkanoates of formula (XV)

\[ R_1N[(CH_2)_mCO_2M]_2 \]

and iminopolyalkanoates of formula (XVI)

\[ R_1-N[(CH_2)_p]qN[CH_2CO_2M]_2 \]

\[ CH_2CO_2M \]

wherein \( n, m, p, \) and \( q \) are numbers from 1 to 4, and \( R_1 \) and \( M \) are independently selected from the groups specified above; and

(c) mixtures thereof.

Suitable amphoteric surfactants of type (a) are marketed under the trade name Miranol and Empigen and are understood to comprise a complex mixture of species. Traditionally, the Miranols have been described as having the general formula (XII), although the CTFA Cosmetic Ingredient Dictionary, 3rd Edition indicates the non-cyclic structure (XIII) while the 4th Edition indicates yet another structural isomer in which \( R_2 \) is O-linked rather than N-linked. In practice, a complex mixture of cyclic and non-cyclic species is likely to exist and both definitions are given here for sake of completeness. Preferred for use herein, however, are the non-cyclic species.

Examples of suitable amphoteric surfactants of type (a) include compounds of formula XII and/or XIII in which \( R_1 \) is \( C_8H_{17} \) (especially iso-capryl), \( C_9H_{19} \) and \( C_{11}H_{23} \) alkyl. Especially preferred are the compounds in which \( R_1 \) is \( C_9H_{19} \), \( Z \) is \( CO_2M \) and \( R_2 \) is \( H \); the compounds in which \( R_1 \) is \( C_{11}H_{23} \), \( Z \) is \( CO_2M \) and \( R_2 \) is \( CH_2CO_2M \); and the compounds in which \( R_1 \) is \( C_{11}H_{23} \), \( Z \) is \( CO_2M \) and \( R_2 \) is \( H \).

In CTFA nomenclature, materials suitable for use in the present invention include cocoamphocarboxypropionate, cocoamphocarboxy propionic acid, and especially cocoamphoacetate and cocoamphodiacetate (otherwise
referred to as cocoamphocarboxyglycinate). Specific commercial products include those sold under the trade names of Ampholak 7TX (sodium carboxy methyl tallow polypropyl amine), Empigen CDL60 and CDR 60 (Albright & Wilson), Miranol H2M Conc. Miranol C2M Conc. N.P., Miranol C2M Conc. O.P., Miranol C2M SF, Miranol CM Special (Rhône-Poulenc); Alkateric 2CIB (Alkaril Chemicals); Amphoterge W-2 (Lonza, Inc.); Monateric CDX-38, Monateric CSH-32 (Mona Industries); Rewoteric AM-2C (Rewo Chemical Group); and Schercotic MS-2 (Scher Chemicals). Further examples of amphoteric surfactants suitable for use herein include Octoxynol-1 (RTM), polyoxethylene (1) octylphenyl ether; Nonoxyol-4 (RTM), polyoxyethylene (4) nonylphenyl ether and Nonoxyol-9, polyoxyethylene (9) nonylphenyl ether.

It will be understood that a number of commercially-available amphoteric surfactants of this type are manufactured and sold in the form of electroneutral complexes with, for example, hydroxide counterions or with anionic sulfate or sulfonate surfactants, especially those of the sulfated C₈-C₁₈ alcohol, C₈-C₁₈ ethoxylated alcohol or C₈-C₁₈ acyl glyceride types. Note also that the concentrations and weight ratios of the amphoteric surfactants are based herein on the uncomplexed forms of the surfactants, any anionic surfactant counterions being considered as part of the overall anionic surfactant component content.

Examples of preferred amphoteric surfactants of type (b) include N-alkyl polytrimethylene poly-, carboxymethylamines sold under the trade names Ampholak X07 and Ampholak 7CX by Berol Nobel and also salts, especially the triethanolammonium salts and salts of N-lauryl-beta-amino propionic acid and N-lauryl-imino-dipropionic acid. Such materials are sold under the trade name Deriphath by Henkel and Mirataine by Rhône-Poulenc.

(iv) Zwitterionic Surfactants
Water-soluble auxiliary zwitterionic surfactants suitable for inclusion in the compositions of the present invention include alkyl betaines of the formula R₅R₆R₇N⁺ (CH₂)ₙCO₂M and amido betaines of the formula (XV) below:
wherein R₅ is C₁₁-C₂₂ alkyl or alkenyl, R₆ and R₇ are independently C₁-C₃ alkyl, M is H, alkali metal, alkaline earth metal, ammonium or alkanolammonium, and n, m are each numbers from 1 to 4. Preferred betaines include cocoamidopropyldimethylcarboxymethyl betaine, laurylamidopropyldimethylcarboxymethyl betaine and Tego betaine (RTM).

Water-soluble auxiliary sultaine surfactants suitable for inclusion in the compositions of the present invention include alkyl sulfaines of the formula (XVI) below:

wherein R₁ is C₇ to C₂₂ alkyl or alkenyl, R₂ and R₃ are independently C₁ to C₃ alkyl, M is H, alkali metal, alkaline earth metal, ammonium or alkanolammonium and m and n are numbers from 1 to 4. Preferred for use herein is coco amido propylhydroxy sultaine.

Water-soluble auxiliary amine oxide surfactants suitable for inclusion in the compositions of the present invention include alkyl amine oxide R₅R₆R₇NO and amido amine oxides of the formula (XVII) below:
wherein R₅ is C₁₁ to C₂₂ alkyl or alkenyl, R₆ and R₇ are independently C₁ to C₃ alkyl, M is H, alkali metal, alkaline earth metal, ammonium or alkanolammonium and m is a number from 1 to 4. Preferred amine oxides include cocoamidopropylamine oxide, lauryl dimethyl amine oxide and myristyl dimethyl amine oxide.

Optional Materials
A number of additional optional materials can be added to the bleaching compositions herein described each at a level of from about 0.001% to about 5%, preferably from about 0.01% to about 3%, more preferably from about 0.05% to about 2% by weight of composition. Such materials include proteins and polypeptides and derivatives thereof; water-soluble or solubilizable preservatives such as DMDM Hydantoin, Germall 115, methyl, ethyl, propyl and butyl esters of hydroxybenzoic acid, EDTA, Euxyl (RTM) K400, natural preservatives such as benzyl alcohol, potassium sorbate and bisabolol; sodium benzoate and 2-phenoxyethanol; antioxidants such as sodium sulphite, hydroquinone, sodium bisulphite, sodium metabisulphite and thymoglycolic acid, sodium dithionite, erythorobic acid and other mercapatans; dye removers such as oxalic acid, sulphated castor oil, salicylic acid and sodium thiosulphate; H₂O₂ stabilisers such as tin compounds such as sodium stannate, stannic hydroxide and stannous octoate, acetalanide, phenacetin colloidal silica such as magnesium silicate, oxyquinoline sulphate, sodium phosphate, and tetrasodium pyrophosphate; and ρ-hydroxybenzoates other moisturising agents such as hyaluronic acid, chitin, and starch-grafted sodium polyacrylates such as Sanwet (RTM) IM-1000, IM-1500 and IM-2500 available from Celanese Superabsorbent Materials, Portsmouth, VA, USA and described in US-A-4,076,663; solvents; anti-bacterial agents such as Oxeco (phenoxy isopropanol); low temperature phase modifiers such as ammonium ion sources (e.g. NH₄Cl); viscosity control agents such as magnesium sulfate and other electrolytes; quaternary amine compounds such as distearyl-, dilauryl-, di-hydrogenated beef tallow-, dimethyl ammonium chloride, dicetyl diethyl ammonium methyl sulphate, ditallowdimethyl ammonium methyl sulphate, disoyya dimethyl ammonium chloride and dicoco dimethyl ammonium chloride; enzyme stabilisers such as water soluble sources of calcium or
borate species; colouring agents; TiO₂ and TiO₂-coated mica; perfumes and perfume solubilizers; and zeolites such as Valfour BV400 and derivatives thereof and Ca²⁺/Mg²⁺ sequestrants such as polycarboxylates, amino polycarboxylates, polyphosphonates, amino polyphosphonates etc. and water softening agents such as sodium citrate. Water is also present at a level preferably of from about 2% to about 99%, preferably from about 5% to about 95%, more preferably at least from about 7% to about 92%, and especially from about 20% to about 90% by weight of the compositions herein.

The present invention is represented by the following non-limiting examples. In the examples, all concentrations are on a 100% active basis and all percentages are by weight unless otherwise stated and the abbreviations have the following designations:

- Peroxyacid precursor 1 (NOBS) sodium nonanoylbenzenesulfonate
- Peroxyacid precursor 2 acetyl triethylcitrate (ATC)
- Peroxyacid precursor 3 6-nonamido caproyl oxybenzene sulphonate
- Chelating agent Ethylenediamine tetraacetic acid
- Enzyme Horseradish peroxidase
- Surfactant 1 Nonoxynol-9
- Surfactant 2 Cocoamidopropyl betaine
- Surfactant 3 Sodium lauryl sulphate
- Thickener Aculyn-44
- Peroxygen bleach hydrogen peroxide
Examples I - VI

The following are hair treatment compositions in the form of hair bleaching compositions which are representative of the present invention.

In the examples, water is used as a common solvent, however water can be replaced, in part, by up to about 50% by liquids such as lower alcohols, e.g., ethylene glycol, ethylene glycol monoethyl ether, diethylene glycol, diethylene glycol monoethyl ether, propylene glycol, 1,3-propane diol, ethanol, isopropyl alcohol, glycerine, butoxyethanol, ethoxydiglycol, hexylene glycol, polyglyceryl-2-oleyl ether and mixtures thereof.

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>I</th>
<th>II</th>
<th>III</th>
<th>IV</th>
<th>V</th>
<th>VI</th>
<th>VII</th>
<th>A</th>
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<tbody>
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<td>5</td>
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<td>2</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
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<td>Peroxyacid precursor 1</td>
<td>5</td>
<td>5</td>
<td>1</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
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<tr>
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<td></td>
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<td>5</td>
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<tr>
<td>Enzyme</td>
<td></td>
<td></td>
<td>0.5</td>
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<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Surfactant 1</td>
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<td>1</td>
<td>3</td>
<td></td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Surfactant 2</td>
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<td>2</td>
<td>1</td>
<td>2</td>
<td>0.5</td>
<td></td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Surfactant 3</td>
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<td>1</td>
<td></td>
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<td>0.1</td>
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<tr>
<td>Thickener</td>
<td>0.5</td>
<td>0.5</td>
<td></td>
<td>0.5</td>
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<td></td>
<td></td>
<td>0.5</td>
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<tr>
<td>Water</td>
<td></td>
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</tr>
</tbody>
</table>

................................. to balance .................................
Available Oxygen Method
As herein before described the bleaching efficacy of the bleaching compositions of the present invention can be described in terms of their level of 'available oxygen', also referred to as 'active oxygen (AO).

Peroxygent compounds contain the peroxyde linkage (-O-O-) in which one of the oxygen atoms is active. This activity can be measured by the oxidation of iodide to iodine under acidic conditions or by a ceric sulphate titration. AO content, usually expressed as a percent, is the atomic weight of active oxygen divided by the molecular weight of the compound. The calculation for determining the theoretical available oxygen from any particular compound is as follows:

\[
AO, \% = 100 \times \text{(no. of active oxygens)} \times \left(\frac{16}{\text{mol wt of compound}}\right)
\]

The theoretical levels of available oxygen for peroxyacid precursors according to the present invention and conventional bleaching agents (assuming 100% perhydrolysis efficacy) are illustrated in Table I below.

<table>
<thead>
<tr>
<th>Material</th>
<th>% AO (theoretical)</th>
</tr>
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<tbody>
<tr>
<td>NOBS</td>
<td>4.7</td>
</tr>
<tr>
<td>TAED</td>
<td>14</td>
</tr>
<tr>
<td>ATC</td>
<td>5</td>
</tr>
<tr>
<td>Peracetic acid</td>
<td>21</td>
</tr>
<tr>
<td>Hydrogen peroxide</td>
<td>47</td>
</tr>
<tr>
<td>Ammonium persulphate</td>
<td>6.8</td>
</tr>
</tbody>
</table>

Bleaching Efficacy Test
The equipment used to measure the bleaching efficiency of the compositions of the present invention is a Hunter Colorquest spectrophotometer.

To illustrate the improved hair bleaching capacity of the compositions according to the present invention example formula I (above) was screened (using brown hair) according to this method versus a standard hydrogen peroxide based formula (Comparative Example A) over a range of pHs. The relative molar ratios of bleaching agents in the example formulae are as follows:

Example I about 1.470 moles in total (about 1.323 moles of H₂O₂ and about 0.147 moles of NOBS)
Example A about 1.470 moles of H₂O₂

Table II illustrates the relative bleaching efficacy of formula I versus hydrogen peroxide formula A (indexed as 100).

<table>
<thead>
<tr>
<th></th>
<th>I</th>
<th>A</th>
</tr>
</thead>
<tbody>
<tr>
<td>Delta E (pH 8)</td>
<td>317</td>
<td>100</td>
</tr>
<tr>
<td>Delta E (pH 9)</td>
<td>311</td>
<td>100</td>
</tr>
<tr>
<td>Delta E (pH 10)</td>
<td>132</td>
<td>100</td>
</tr>
</tbody>
</table>

wherein Delta E is a measure of bleaching efficiency as expressed by a non-directional color change as represented by a factual sum of L, a, and b values such that:

$$\Delta E = (\Delta L^2 + \Delta a^2 + \Delta b^2)^{1/2}$$

and L is a measure of lightness and darkness (color intensity) wherein L = 100 is equivalent to white and L = 0 is equivalent to black. Further, 'a' is a measure of the red and green quotients (color hues) such that positive equates to red and negative equates to green and 'b' is a measure of the yellow and blue quotients (color hues) such that positive equates to yellow and negative equates to blue.
The Hunter Colorquest measurements can be carried out on the Hunter Labscan Colorimeter which is full scanning spectrophotometer with a wavelength of from 400-700 nanometers which records the color of test hair switches (tresses) in terms of 'L', 'a' and 'b' values. The machine is set to: mode - 0/45; port size - 1 inch; view size - 1 inch; light - D65; field of view - 10°; UV lamp/filter - none. The hair is placed in a sample holder designed to hold the hair in a uniform orientation during measurement. Several designs are in existence and all work well as long as the hair does not move during measurement. The hair must be spread to cover the 1 inch port during color measurement. Dots are placed on the switch holder to guide the positioning of the holder at the port. The dots are lined up with a mark on the port and readings are taken at each spot.

Eight measurements are run per switch, 4 on each side, and three switches are run per treatment.

**Method of Manufacture**

Many of the organic peroxyacids and peroxyacid precursors useful in the compositions of the present invention are unstable, particularly in aqueous solution. It is therefore important to employ these solutions within a short period of time after their preparation in order to achieve the desired oxidation effect to the hair. Furthermore, it is important that the organic peroxyacid be in a form which is easy and convenient to prepare and use by the consumer, since the oxidising agent must remain in contact with the hair for a certain period of time and not run or drip off of the hair, possibly causing eye or skin irritation.

To address the above the compositions of the present invention can be provided in kit form as separately packaged components to maintain stability, and mixed by the user immediately prior to application to the hair. One component of the kit comprises an individually packaged oxidising component. A further kit component would comprise an individually packaged bleaching precursor. In one embodiment of the present invention the oxidising component comprises a stabilised aqueous solution of a water-soluble peroxygen bleach compound, most generally hydrogen peroxide in an amount such that the final concentration of the compound for use on the hair is from about 0.5% to about 7.5% by weight.
and the bleaching precursor comprises an organic peroxy acid bleach precursor in an amount such that the final concentration of the compound for use on the hair is from about 0.5% to about 7.5% by weight and optionally a colorant and/or additional agents as herein before described. The compositions can either be mixed by the user immediately prior to application to the hair or can be applied separately. Examples of such a kit are as follows:

I. A hair bleaching kit is assembled comprising a single package including therein: (1) a 50 ml bottle of hydrogen peroxide (10% by weight of H₂O₂); and (2) a foil packet containing an organic peroxyacid bleaching precursor, such as NOBS as herein before described and optionally (3) a 50 ml bottle containing additional agents such as surfactants, antioxidants, thickeners, coloring compounds etc. The bleaching precursor is admixed with the hydrogen peroxide and the contents of the 50 ml bottle are added thereto, where present. The resulting solution is applied to the hair and bleaches or bleaches and colors it.

II. A hair bleaching kit as described above wherein the hydrogen peroxide component is applied to the hair prior to application of the admixed contents of the bleaching precursor component and the additional agents to the hair.

III. A hair bleaching kit as described above wherein the bleaching precursor and additional agents are admixed and applied to the hair prior to application to the hair of the hydrogen peroxide component.

Method of Use

The compositions herein described may be used to bleach hair or may, in combination with certain coloring agents, be used to bleach and color hair. The bleaching compositions herein are applied to the hair for periods of from 1 minute to 90 minutes depending upon the degree of bleaching required. A preferred time is between 5 minutes and 30 minutes.
The products provide excellent hair bleaching and in-use efficacy benefits including reduced hair damage at lower pH.
Claims

1. A hair bleaching composition comprising:

(a) a water-soluble peroxygen bleach; and

(b) a bleaching aid selected from organic peroxyacid bleach precursors and/or preformed organic peroxyacids

2. A composition according to Claim 1 wherein the organic peroxy acid bleach precursor is selected from acetyl triethylcitrate (ATC), tetraacetyl ethylene diamine (TAED), nonanoyl oxybenzenesulphonate (NOBS), (6-octaamidocaproyl) oxybenzene sulphonate and (6-decaamidocaproyl) oxybenzene sulphate and peracetic and pernanoic acids and mixtures thereof

3. A composition according to Claim 1 or 2 wherein the weight ratio of water-soluble peroxygen bleach to bleaching aid is in the range of from about 20:1 to about 1:20, preferably from about 10:1 to about 1:10, more preferably from about 5:1 to about 1:5.

4. A composition according to any of Claims 1 to 3 wherein the molar ratio of peroxygen bleach to bleaching aid is in the range of from about 400:1 to about 1:5, preferably from about 200:1 to about 1:2, more preferably from about 3:1 to about 10:1.

5. A composition according to any of Claims 1 to 4 wherein the peroxygen bleach is present at a level of from about 0.5% to about 40%, preferably from about 1% to about 20%, more preferably from about 1.5% to about 7% by weight of the total composition.

6. A composition according to any of Claims 1 to 5 wherein the bleaching aid is present at a level of from about 0.5% to about 40%, preferably from about 1% to about 20%, more preferably from about 1.5% to about 7% by weight of the total composition.

7. A composition according to any of Claims 1 to 6 additionally comprising one or more buffering and/or hair swelling agents.
8. A composition according to Claim 7 wherein the buffering agent is selected from ammonium hydroxide, ethylamine, dipropylamine, triethylamine and alkanediamines such as 1,3-diaminopropane, anhydrous alkaline alkanolamines such as, mono or diethanolamine, preferably those which are completely substituted on the amine group such as dimethylaminoethanol, polyalkylene polyamines such as diethylenetriamine or a heterocyclic amine such as morpholine as well as the hydroxides of alkali metals, such as sodium and potassium hydroxide, hydroxides of alkali earth metals, such as magnesium and calcium hydroxide, basic amino acids such as L-alginine, lysine, oxyllysine and histidine, alkanolamines such as dimethylaminoethanol and aminoalkylpropanediol, Na2CO3, NaHCO3, K2CO3, (NH4)2CO3, NH4HCO3, CaCO3 and Ca(HCO3) and mixtures thereof.

9. A composition according to any of Claims 1 to 8 additionally comprising one or more peroxygen bleach buffering agents.

10. A composition according to Claim 9 wherein the peroxygen bleach buffering agent is a dilute acids, preferably phosphoric acid.

11. A composition according to any of Claims 1 to 10 additionally comprising one or more surfactants.

12. A composition according to Claim 11 wherein the surfactant is selected from anionic, nonionic, cationic, zwitterionic, amphoteric surfactants and mixtures thereof.

13. A composition according to any of Claims 1 to 12 additionally comprising an enzyme.

14. Use of a composition according to any of Claims 1 to 13 for decoloring or bleaching human or animal hair.

15. A process for bleaching, decolorising human or animal hair comprising applying to the hair an organic peroxy acid precursor and/or organic peroxy acid containing hair bleaching composition which is suitable for use in contact with human skin.
16. A process according to Claim 15 for bleaching, decolorising human or animal hair wherein the hair bleaching composition comprises:

(a) from about 0.5% to about 40% by weight of a water-soluble peroxxygen bleaching compound;

(b) from about 0.5% to about 40% by weight of an organic bleaching aid selected from organic peroxy acid bleach precursor and/or preformed organic peroxy acids; and

(c) from about 20% to about 99% by weight of an inert diluent.

wherein the bleaching composition has a pH of from about 6 to about 12.

17. A hair bleaching or decolorising kit comprising an individually packaged oxidising component and an individually packaged bleaching aid component, wherein the oxidising component and the bleaching aid form, when mixed, the composition of any of Claims 1 to 13, and wherein the oxidising component comprises an aqueous solution of a water-soluble peroxygen bleaching agent at a level of from about 0.5% to about 40% by weight and the bleaching aid comprises an organic peroxy acid bleach precursor and/or organic peroxyacid at a level of from about 0.5% to about 40% by weight of the composition.

18. Use of the hair bleaching or decolorising kit according to Claim 17 for the bleaching or decolorising of hair wherein the bleaching aid and additional agents are admixed and applied to the hair prior to the application of the hydrogen peroxide component to the hair.
# INTERNATIONAL SEARCH REPORT

**International application No.**

**PCT/US96/20169**

## A. CLASSIFICATION OF SUBJECT MATTER

**IPCG(6):** A61K 7/135  
**US CL.:** 8/431, 111; 252/ 186.21, 186.3  
According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

- **U.S.:** 8/431, 111; 252/ 186.21, 186.3; 510/302, 305

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

- **HACHIK'S CHEMICAL DICTIONARY**

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

- Please See Extra Sheet.

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
<thead>
<tr>
<th>Category*</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
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<tr>
<td>X</td>
<td>US 5,227,084 A (MARTENS et al) 13 July 1993, Example IIA.</td>
<td>1-9, 12-13</td>
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<tr>
<td>X</td>
<td>US 4,915,863 A (AOYAGI et al) 10 April 1990, Table 2, Control 2.</td>
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<td>US 5,454,982 A (MURCH et al) 03 October 1995, Examples 7-9.</td>
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<td>X</td>
<td>US 5,478,357 A (MADISON et al) 26 December 1995, Table 2, Example 3 and col. 10, lines 43-50.</td>
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</table>

* Further documents are listed in the continuation of Box C.

- **A** Document defining the general state of the art which is not considered to be of particular relevance.
- **E** Earlier document published on or after the international filing date.
- **L** Document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified).
- **O** Document referring to an oral disclosure, use, exhibition or other means.
- **P** Document published prior to the international filing date but later than the priority date claimed.
- **T** Inter document published after the international filing date or priority date and not in conflict with the application but could not be understood the principle or theory underlying the invention.
- **X** Document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone.
- **Y** Document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- **Z** Document member of the same patent family.

Date of the actual completion of the international search: **07 FEBRUARY 1997**

Date of mailing of the international search report: **24 APRIL 1997**

Name and mailing address of the ISA/US Commissioner of Patents and Trademarks

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  **Washington, D.C. 20231**

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Telephone No. **(703) 308-1111**

Form PCT/ISA/210 (second sheet) (July 1992)*
B. FIELDS SEARCHED
Electronic data bases consulted (Name of data base and where practicable terms used):

APS, DIALOG
search terms: peroxides, peroxygen, persulfate, peracid, peroxyacid, peracetic acid, peroxyacetic acid, hair, keratin, bleach