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(71) Applicant(s)
Henkel Kommanditgesellschaft auf Aktien

(72) Inventor(s)
Doring, Thomas;Babiel, Sabine Geb. Kainz;Hollenberg, Detlef;Brockmann, Claudia

(74) Agent / Attorney
Spruson & Ferguson, L 35 St Martins Tower 31 Market St, SYDNEY, NSW, 2000

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(71) Anmelder *(für alle Bestimmungsstaaten mit Ausnahme von US)*: **HENKEL KOMMANDITGESELLSCHAFT AUF AKTIEN** [DE/DE]; Henkelstrasse 67, 40589 Düsseldorf (DE).

(72) Erfinder; und
(75) Erfinder/Anmelder *(nur für US)*: **DÖRING, Thomas** [DE/DE]; Waldstr. 1, 41542 Dormagen (DE). **BROCKMANN, Claudia** [DE/DE]; Waldenburger Weg 15, 40627 Düsseldorf (DE). **KAINZ, Sabine** [DE/DE]; Walter-Karentz-Str. 3, 47447 Moers (DE). **HOLLENBERG, Detlef** [DE/DE]; Fliederweg 31, 40699 Erkrath (DE).

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Zur Erklärung der Zweibuchstaben-Codes und der anderen Abkürzungen wird auf die Erklärungen ("Guidance Notes on Codes and Abbreviations") am Anfang jeder regulären Ausgabe der PCT-Gazette verwiesen.

(54) Title: OXIDATIVE HAIR TREATMENT WITH REDUCED HAIR DAMAGE

(54) Bezeichnung: OXIDATIVE HAARBEHANDLUNG MIT VERRINGERTER HAARSCHÄDIGUNG

(57) Abstract: During oxidative hair treatment, α-lipoic acids and their derivatives are particularly well suited for reducing hair damage and irritation of the scalp. By means of a method for oxidative hair treatment in which an oxidative cosmetic substance, containing at least one oxidation substance in a cosmetic carrier, is applied to the hair and rinsed off after an exposure time, wherein - a cosmetic substance containing at least one compound from the group formed from α-lipoic acid and its derivatives in a cosmetic carrier is applied just before the application of the oxidative cosmetic substance and is also rinsed off after an exposure time, and/or with the oxidative cosmetic substances containing, in addition, at least one compound from the group formed from α-lipoic acid and its derivatives, - it was possible successfully to reduce hair damage caused by oxidative processes, as well as to reduce irritation of the scalp.

(57) Zusammenfassung: α-Liponsäure bzw. deren Derivate eignen sich hervorragend im Rahmen einer oxidativen Haarbehandlung zur Verringerung der Haarschädigung und zur Reduzierung der Missempfindungen auf der Kopfhaut. Mittels eines Verfahrens zur oxidativen Haarbehandlung, in dem ein oxidatives kosmetisches Mittel, enthaltend in einem kosmetischen Träger mindestens ein Oxidationsmittel auf das Haar aufgetragen wird und nach einer Einwirkungszeit vom Haar gespült wird, wobei - unmittelbar vor dem Auftragen des oxidativen kosmetischen Mittels ein kosmetisches Mittel, enthaltend in einem kosmetischen Träger mindestens eine Verbindung aus der Gruppe, die aus α-Liponsäure und deren Derivate gebildet wird, aufgetragen und gegebenenfalls nach einer Einwirkungszeit wieder abgespült wird und/oder - das oxidative kosmetische Mittel zusätzlich mindestens eine Verbindung aus der Gruppe, die gebildet wird, aus α-Liponsäure und deren Derivate, enthält, konnte erfolgreich die Haarschädigung durch die oxidativen Prozesse verringert, sowie das Kopfhautempfinden verbessert werden.

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OXIDATIVE HAIR TREATMENT WITH REDUCED HAIR DAMAGE

[0002] The present invention relates to the cosmetic use of α-lipoic acid and the derivatives thereof during oxidative hair treatment for reducing hair damage and for improving scalp sensation. The present invention also provides a corresponding method for oxidative hair treatment and the preparations usable therein.

[0003] Human hair is nowadays treated in many different ways with hair cosmetic preparations. Such treatments include for instance cleaning hair with shampoos, caring for and regenerating hair with conditioners and tonics and bleaching, dyeing and shaping hair with dyes, tints, permanent-wave compositions and styling preparations.

[0004] Permanent, oxidative dyeing and hair bleaching and fixing in the context of a permanent wave usually proceed as an oxidative hair treatment in the presence of oxidizing agents, such as hydrogen peroxide. Unfortunately, the oxidizing agent does not only achieve the desired cosmetic effect, but additionally damages the structure of the hair keratin. The cystine in the keratin is here oxidized to form cysteic acid, which has a negative impact on the stability, tactile properties and appearance of the hair fibers. Hair damaged in this manner appears dull and brittle. In extreme cases, hair breakage may even occur.

[0005] Furthermore, the scalp comes into contact with the oxidizing agent during oxidative hair treatment. For this reason, a sensitive individual will often experience an abnormal sensation on the scalp during oxidative hair treatment. This sensation is usually described as prickling or itching.

[0006] According to document US-A-20030180337, α-lipoic acid may be used for combating oxidative damage due to weathering. However, no mention is made therein of using α-lipoic acid in conjunction with an oxidizing agent in the context of an oxidative hair treatment.

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[0007] The object of the present invention is to reduce the above-described side-effects of oxidative hair treatments even during the oxidative hair treatment, without impairing the effectiveness of the oxidative cosmetic preparation, in particular with regard to color intensity, color fastness, lightening effect or permanent-wave action.

[0008] It has now surprisingly been found that the object is excellently achieved by using α-lipoic acid. The effect occurs during the oxidative hair treatment

[0009] Herein disclosed is the cosmetic use of α-lipoic acid and/or the derivative thereof,

- for reducing oxidative hair damage,
- for reducing scalp irritation,
- for alleviating abnormal sensations on the scalp, such as in particular prickling or itching,

in each case in the context of oxidative hair treatment.

[0010] The reduction in oxidative hair damage is manifested, for example, in improved combability of the hair or in strengthening of the internal structure of the hair, i.e. improved preservation of the hair's natural internal structure. This improved preservation of the hair's internal structure is achieved despite simultaneous or directly subsequent oxidative hair treatment.

[0011] An oxidative hair treatment is defined according to the invention as the action of an oxidative cosmetic preparation containing at least one oxidizing agent in a cosmetic carrier on the hair.

[0012] The oxidizing agents for the purposes of the invention differ from atmospheric oxygen and from α-lipoic acid or the derivatives thereof and have an oxidation potential which permits disulfide bridges to be linked within or between the proteins of the hair keratin, and/or the natural coloring pigment melanin to be oxidatively lightened and/or an oxidation dye precursor of the developer type to be oxidized.

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[0013] An oxidizing agent which may preferably be considered is hydrogen peroxide and/or at least one addition product thereof, in particular an inorganic or organic compound, such as for example sodium perborate, sodium percarbonate, magnesium percarbonate, sodium percarbamide, polyvinyl-pyrrolidone·n H_2O_2 (n is a positive integer greater than 0), urea peroxide and melamine peroxide.

[0014] The oxidative cosmetic preparation
may also be applied onto the hair together with a catalyst which activates the oxidation of the substrate, such as for example oxidation dye precursors or melanin. Such catalysts are for example metal ions, iodides, quinones or certain enzymes.

[0015] Suitable metal ions are for example Zn^{2+}, Cu^{2+}, Fe^{2+}, Fe^{3+}, Mn^{2+}, Mn^{4+}, Li^{+}, Mg^{2+}, Ca^{2+} and Al^{3+}. Zn^{2+}, Cu^{2+} and Mn^{2+} are particularly suitable. The metal ions may in principle be used in the form of any desired, physiologically acceptable salt or in the form of a complex compound. Preferred salts are acetates, sulfates, halides, lactates and tartrates. By using these metal salts, it is possible both to accelerate dye formation and to have a targeted influence on color shade.

[0016] Suitable enzymes are for example peroxidases, which are capable of distinctly enhancing the action of small quantities of hydrogen peroxide. Enzymes which are furthermore suitable according to the invention are those which produce small quantities of hydrogen peroxide in situ from atmospheric oxygen and so biocatalytically activate oxidation of the dye precursors. Particularly suitable catalysts for the oxidation of dye precursors are "two-electron oxidoreductases" in combination with their specific substrates, for example

- pyranose oxidase and for example D-glucose or galactose,
- glucose oxidase and D-glucose, glycerol oxidase and glycerol,
- pyruvate oxidase and pyruvic acid or the salts thereof,
- alcohol oxidase and alcohol (MeOH, EtOH),

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- lactate oxidase and lactic acid and the salts thereof,
- tyrosinase oxidase and tyrosine,
- uricase and uric acid or the salts thereof,
- choline oxidase and choline,
- amino acid oxidase and amino acids.

[0017] The oxidizing agent is preferably present in the oxidative cosmetic in a quantity of 1.0 to 10 wt.%, in particular from 3.0 to 10.0 wt.%, in each case relative to the weight of the ready-to-use preparation.

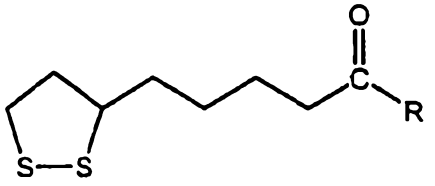
[0018] The α-lipoic acid (derivatives) are preferably used immediately before or during the oxidative hair treatment in the form of an agent containing α-lipoic acid (or the derivative thereof) in a cosmetic carrier.

[0019] "Immediately before the oxidative hair treatment" is taken to mean use directly followed by the oxidative
hair treatment, the preparation containing α-lipoic acid (derivative) previously being rinsed off the hair or preferably left on the hair and the hair preferably still being wet or at least having a perceptible residual moisture content. Examples of suitable pretreatment preparations may be found in sections 2.4 and 2.5 of the Examples.

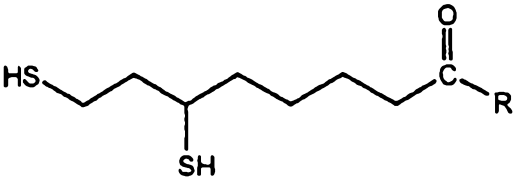
[0020] All explanations extend to α-lipoic acid and/or the derivatives thereof, i.e. to the free α-lipoic acid, to derivatives of α-lipoic acid (which inter alia also include 6,8-dimercaptooctane (dihydrolipoic acid) and the derivatives thereof as a reduced form of α-lipoic acid) and to the salt forms of the corresponding α-lipoic acid compounds.

[0021] The compounds used according to the invention from the group of α-lipoic acid or the derivatives thereof preferably comply with the formula (Ia) or the in each case reduced form of the formula (Ib),

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(Ia)



(Ib)

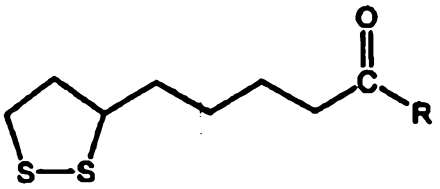
in which in each case R denotes a residue

-NR'R", in which R' and R" mutually independently denote a hydrogen atom, a (C_1 to C_{22}) alkyl group, (C_2 to C_{22}) alkenyl group, a (C_1 to C_{20}) hydroxyalkyl group, a sulfo-(C_1 to C_6)-alkyl group, an optionally substituted (C_1 to C_6) carboxyalkyl group, or

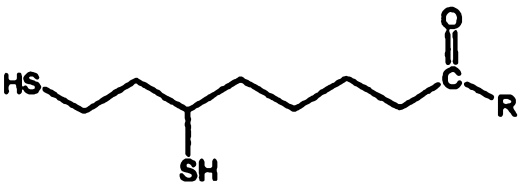
-OM, in which M means a hydrogen atom, a (C_1 to C_{22}) alkyl group, (C_2 to C_{22}) alkenyl group, a (C_1 to C_{20}) hydroxyalkyl group or an equivalent of a mono- or polyvalent cation.

[0021a] Thus, according to one embodiment of the present invention, there is provided a use of α-lipoic acid and/or a derivative thereof

according to formula (Ia) or a reduced form of formula (Ib).



(Ia)



(Ib)

in which in each case R denotes a residue

-NR'R", in which R' and R" mutually independently denote a hydrogen atom, a (C_1 to C_{22}) alkyl group, (C_2 to C_{22}) alkenyl group, a (C_1 to C_{20}) hydroxyalkyl group, a sulfo-(C_1 to C_6)-alkyl group, an optionally substituted (C_1 to C_6) carboxyalkyl group, or

-OM, in which M means a hydrogen atom, a (C_1 to C_{22}) alkyl group, (C_2 to C_{22}) alkenyl group, a (C_1 to C_{20}) hydroxyalkyl group or an equivalent of a mono- or polyvalent cation

for reducing oxidative hair damage during oxidative hair treatment.

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[0022] Optionally substituted (C_1 to C_6) carboxyalkyl groups which may preferably be considered are those (C_1 to C_6)carboxyalkyl fragments which are derived from amino acids or oligopeptides (which are preferably made up of 2 to 10 amino acids). Preferred amino acids are in each case glycine, alanine, valine, leucine, isoleucine, proline, phenylalanine, tyrosine, tryptophan, methionine, serine, threonine, arginine, lysine, histidine, cysteine, aspartic acid, asparagine, glutamic acid, glutamine.

[0023] Preferred (C_1 to C_{22}) alkyl groups are methyl, ethyl, n-propyl, iso-propyl, n-butyl, sec-butyl, iso-butyl, tert.-butyl, n-pentyl, n-hexyl, n-heptyl, 2-ethylhexyl, n-octyl, n-decyl, n-dodecyl, n-tetradecyl, n-hexadecyl, 16-methyl-heptadecyl, n-octadecyl, n-eicosyl.

[0024] The (C_1 to C_{22}) hydroxyalkyl groups according to the invention comprise one or more hydroxyl groups. These also include "polyols" and glycosides.

[0025] Preferred (C_1 to C_{22}) alkenyl groups are alkyl, but-2-en-1-yl, but-3-en-1-yl, octadec-9-en-1-yl (in particular the Z isomer), octadeca-9,12-dien-1-yl (in particular the *all*-Z isomer), octadeca-9,12,15-trien-1-yl (in particular the *all-Z* isomer).

[0026] It is preferred if, according to formula (Ia) or (Ib), the residue R denotes a group -OM, in which M means a hydrogen atom or an equivalent of a mono- or polyvalent cation.

[0027] Suitable α-lipoic acid compounds are particularly preferably those which comply with the formula (Ia).

[0028] If the compounds of the formulae (Ia) or (Ib) assume acid form (R = -OM), the residue M means a hydrogen atom. In this case, the fragment -COOM of the formula (Ia) or (Ib) (with R = -OM) forms a carboxyl group. If the compounds of the formulae (Ia) or (Ib) assume salt form, M of the residue R denotes an equivalent of a mono- or polyvalent cation. The mono- or polyvalent cation M^{z+} with a charge number z of one or higher merely serves for reasons of electroneutrality to compensate for the single negative charge of the carboxylate fragment $-COO^-$ in formula (Ia) or (Ib) present in the case of salt formation. The equivalent of the corresponding cation to be used for this purpose amounts to 1/z. The fragment -COOM (R = -OM) of the formulae (Ia) or (Ib) denotes in the case of salt formation the group: $-COO^- 1/z\ (M^{z+})$.

[0029] Mono- or polyvalent cations M^{z+} which may in principle be considered are any physiologically acceptable cations. In particular, these are metal cations of the physiologically acceptable metals from groups Ia, Ib, IIa, IIb, IIIb, VIa or VIII of the periodic table of elements, ammonium ions, and cationic organic compounds with a quaternized nitrogen atom. The latter are formed, for example, by protonation of primary, secondary or tertiary organic amines with an acid, such as for example with compounds of the formula (I) in their acidic form, or by permanent quaternization of said organic amines. Examples of these cationic organic ammonium compounds are 2-ammonioethanol and 2-trimethylammonioethanol. In the formula (Ia) or (Ib), M preferably denotes a hydrogen atom, an ammonium ion, an alkali metal ion, half an equivalent of an alkaline earth metal ion or half an equivalent of a zinc ion, particularly preferably a hydrogen atom, an ammonium ion, a sodium ion, a potassium ion, ½ calcium ion, ½ magnesium ion or ½ zinc ion.

[0030] Particularly preferred compounds are those selected from α-lipoic acid and/or the reduced form thereof (6,8-dimercaptooctanoic acid), in each case in the form of the free acid and/or in salt form. α-Lipoic acid (formula (Ia): R = -OM) in the form of the free acid or in salt form is very particularly preferably suitable.

[0031] The α-lipoic acid or the derivative thereof used according to the invention bears a chiral centre on the carbon atom in position six of the carbon skeleton. The stereochemistry of the α-lipoic acid or the stereochemistry of the derivative is immaterial for the use according to the invention. Consequently, not only the enantiomerically pure forms but also any desired mixtures of the enantiomers (such as in particular racemates) may be used according to the invention.

[0032] The α-lipoic acid or the derivatives thereof and in each case the reduced forms thereof are preferably used in a cosmetic carrier. Suitable cosmetic carriers according to the invention are in particular creams, emulsions, gels or also surfactant-containing foaming solutions, such as for example shampoos, foam aerosols or other preparations which are in particular suitable for use on the hair. It is, however, also conceivable to incorporate the ingredients into a formulation in powder or also tablet form which is dissolved in water before use. The cosmetic carriers may in particular be aqueous or aqueous-alcoholic.

[0033] An aqueous cosmetic carrier contains at least 50 wt.% water.

[0034] For the purposes of the present invention, aqueous-alcoholic cosmetic carriers should be taken to be aqueous solutions containing 3 to 70 wt.% of a C_1-C_4 alcohol, in particular ethanol or isopropanol. The preparations according to the invention may additionally contain further organic solvents, such as for example methoxybutanol, benzyl alcohol, diethylene glycol monoethyl ether or 1,2-propylene glycol. Any water-soluble organic solvents are here preferred.

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[0035] When the oxidative cosmetic preparation and a cosmetic preparation containing α-lipoic acid or the derivatives thereof are used simultaneously, the two preparations may be mixed with one another, optionally only immediately before use, or applied in succession onto the hair without an intermediate rinsing step. In a preferred embodiment, the oxidative cosmetic preparation used according to the invention therefore additionally contains α-lipoic acid and/or the derivatives thereof.

[0036] Also herein disclosed are cosmetic preparations containing in a cosmetic carrier a combination of

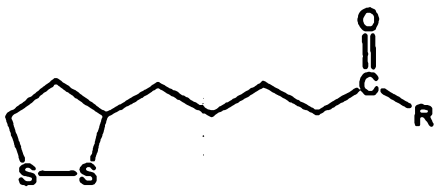
(i) at least one oxidizing agent and

(ii) at least one compound selected from the group formed by α-lipoic acid and the derivatives thereof.

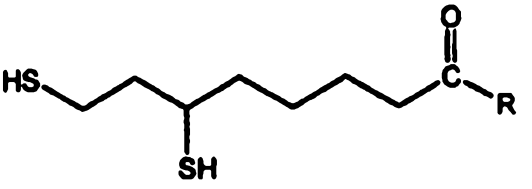
[0036a] Thus, according to another embodiment of the invention, there is provided a preparation containing in a cosmetic carrier a combination of

(i) at least one oxidizing agent and

(ii) at least one compound from the group formed by α-lipoic acid and derivatives thereof according to formula (Ia) or a reduced form of formula (Ib),



(Ia)



(Ib)

in which in each case R denotes a residue

-NR'R", in which R' and R" mutually independently denote a hydrogen atom, a (C_1 to C_{22}) alkyl group, (C_2 to C_{22}) alkenyl group, a (C_1 to C_{20}) hydroxyalkyl group, a sulfo-(C_1 to C_6)-alkyl group, an optionally substituted (C_1 to C_6) carboxyalkyl group, or

-OM, in which M means a hydrogen atom, a (C_1 to C_{22}) alkyl group, (C_2 to C_{22}) alkenyl group, a (C_1 to C_{20}) hydroxyalkyl group or an equivalent of a mono- or polyvalent cation.

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[0037] Corresponding α-lipoic acid (derivatives) and preferred representatives thereof have already been stated in the context of the explanations relating to the first subject matter of the invention.

[0038] Preferred cosmetic carriers are those of the first subject matter of the invention.

[0039] Corresponding oxidizing agents and the preferred representatives thereof have likewise been defined in the context of the first subject matter of the invention.

[0040] The cosmetic preparations according to the invention contain the compounds, selected from compounds of the group formed by α-lipoic acid and the derivatives thereof, preferably in a quantity of 0.001 to 5.0 wt.%, particularly preferably of 0.01 to 2.0 wt.%, very particularly preferably of 0.1 to 1 wt.%, in each case relative to the weight of the ready-to-use preparation.

[0041] It is preferred according to the invention to use the preparation according to the invention in the context of a change to hair color. The cosmetic preparations additionally contain for this purpose at least one color-modifying component.

[0042] The color-modifying component is in turn preferably selected from

(a) at least one oxidation dye precursor of the developer component type and optionally additionally at least one coupler component

and/or

(b) oxo dye precursors

and/or

(c) at least one direct dye

and/or

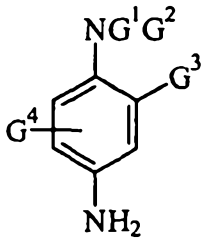
(d) at least one precursor of nature-analogous dyes

and/or

(e) at least one bleach booster.

[0043] The developer components used are conventionally primary aromatic amines with a further free or substituted hydroxyl or amino group located in para or ortho position, diaminopyridine derivatives, heterocyclic hydrazones, 4-aminopyrazole derivatives and 2,4,5,6-tetraaminopyrimidine and the derivatives thereof.

[0044] It may be preferred according to the invention to use a p-phenylenediamine derivative or one of the physiologically acceptable salts thereof as the developer component. Particularly preferred p-phenylenediamine derivatives are those of the formula (Ent1)



(Ent1)

wherein

- G^1 denotes a hydrogen atom, a C_1 to C_4 alkyl residue, a C_1 to C_4 monohydroxyalkyl residue, a C_2 to C_4 polyhydroxyalkyl residue, a (C_1 to C_4)-alkoxy-(C_1 to C_4)-alkyl residue, a 4'-aminophenyl residue or a C_1 to C_4 alkyl residue, which is substituted with a nitrogenous group, a phenyl or a 4'-aminophenyl residue;

- G^2 denotes a hydrogen atom, a C_1 to C_4 alkyl residue, a C_1 to C_4 monohydroxyalkyl residue, a C_2 to C_4 polyhydroxyalkyl residue, a (C_1 to C_4)-alkoxy-(C_1 to C_4)-alkyl residue or a C_1 to C_4 alkyl residue, which is substituted with a nitrogenous group;
- G^3 denotes a hydrogen atom, a halogen atom, such as a chlorine, bromine, iodine or fluorine atom, a C_1 to C_4 alkyl residue, a C_1 to C_4 monohydroxyalkyl residue, a C_2 to C_4 polyhydroxyalkyl residue, a C_1 to C_4 hydroxyalkoxy residue, a C_1 to C_4 acetylaminoalkoxy residue, a C_1 to C_4 mesylaminoalkoxy residue or a C_1 to C_4 carbamoylaminoalkoxy residue;
- G^4 denotes a hydrogen atom, a halogen atom or a C_1 to C_4 alkyl residue or
- if G^3 and G^4 are in ortho position relative to one another, they may together from a bridging α,ω-alkylenedioxo group, such as for example an ethylenedioxy group.

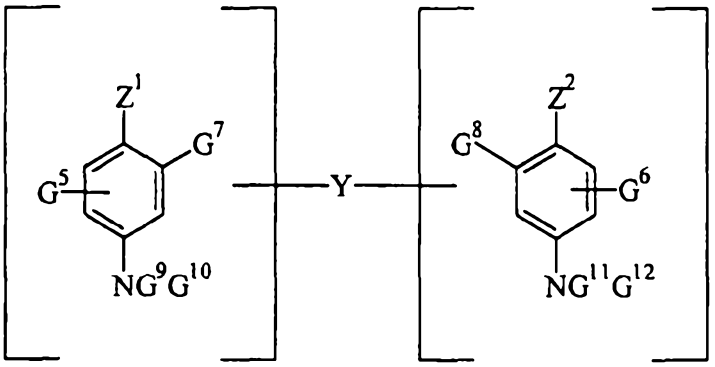
[0045] Examples of the C_1 to C_4 alkyl residues stated as substituents in the compounds according to the invention are the groups methyl, ethyl, propyl, isopropyl and butyl. Ethyl and methyl are preferred alkyl residues. C_1 to C_4 alkoxy residues which are preferred according to the invention are for example a methoxy or an ethoxy group. A hydroxymethyl, 2-hydroxyethyl, 3-hydroxypropyl or 4-hydroxybutyl group may furthermore be mentioned as preferred examples of a C_1 to C_4 hydroxyalkyl group. A 2-hydroxyethyl group is particularly preferred. A particularly preferred C_2 to C_4 polyhydroxyalkyl group is the 1,2-dihydroxyethyl group. Examples of halogen atoms according to the invention are F, Cl or Br atoms, Cl atoms being very particularly preferred. The further terminology used is derived according to the invention from the definitions stated here. Examples of nitrogenous groups of the formula (Ent1) are in particular amino groups, C_1 to C_4 monoalkylamino groups, C_1 to C_4 dialkylamino groups, C_1 to C_4 trialkylammonium groups, C_1 to C_4 monohydroxyalkylamino groups, imidazolinium and ammonium.

[0046] Particularly preferred p-phenylenediamines of the formula (Ent1) are selected from p-phenylenediamine, p-tolylenediamine, 2-chloro-p-phenylenediamine, 2,3-dimethyl-p-phenylenediamine, 2,6-dimethyl-p-phenylenediamine, 2,6-diethyl-p-phenylenediamine, 2,5-dimethyl-p-phenylenediamine, N,N-dimethyl-p-phenylenediamine, N,N-diethyl-p-phenylenediamine, N,N-dipropyl-p-phenylenediamine, 4-amino-3-methyl-(N,N-diethyl)aniline, N,N-bis-(β-hydroxyethyl)-p-phenylenediamine, 4-N,N-bis-(β-hydroxyethyl)amino-2-methylaniline, 4-N,N-bis-(β-hydroxyethyl)-amino-2-chloraniline, 2-(β-hydroxyethyl)-p-phenylenediamine, 2-(α,β-dihydroxy-ethyl)-p-phenylenediamine, 2-fluoro-p-phenylenediamine, 2-isopropyl-p-phenylenediamine, N-(β-hydroxypropyl)-p-phenylenediamine, 2-hydroxy-methyl-p-phenylenediamine, N,N-dimethyl-3-methyl-p-phenylenediamine, N,N-(ethyl,β-hydroxyethyl)-p-phenylenediamine, N-(β,γ-dihydroxypropyl)-p-phenylenediamine, N-(4'-aminophenyl)-p-phenylenediamine, N-phenyl-p-phenylenediamine, 2-(β-hydroxyethyl)-p-phenylenediamine, 2-(β-acetylaminoethyloxy)-p-phenylenediamine, N-(β-methoxyethyl)-p-phenylene-diamine and 5,8-diaminobenzene-1,4-dioxane and the physiologically acceptable salts thereof.

[0047] p-Phenylenediamine derivatives of the formula (Ent1) which are very particularly preferred according to the invention are p-phenylenediamine, p-tolylenediamine, 2-(β-hydroxyethyl)-p-phenylenediamine, 2-(α,β-dihydroxy-ethyl)-p-phenylenediamine and N,N-bis-(β-hydroxyethyl)-p-phenylenediamine.

[0048] It may furthermore be preferred according to the invention to use compounds which contain at least two aromatic nuclei which are substituted with amino and/or hydroxyl groups as the developer component.

[0049] Among binuclear developer components which may be used in the preparations according to the invention, mention may in particular be made of the compounds which correspond to the following formula (Ent2) and the physiologically acceptable salts thereof:



(Ent2)

wherein:

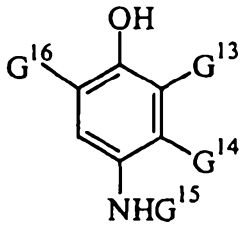
- Z^1 and Z^2 mutually independently denote a hydroxyl or NH_2 residue, which is optionally substituted by a C_1 to C_4 alkyl residue, by a C_1 to C_4 hydroxyalkyl residue and/or by a bridging member Y or which is optionally part of a bridging ring system,
- the bridging member Y denotes an alkylene group with 1 to 14 carbon atoms, such as for example a linear or branched alkylene chain or an alkylene ring which may be interrupted or terminated by one or more nitrogenous groups and/or one or more heteroatoms such as oxygen, sulfur or nitrogen atoms and may optionally be substituted by one or more hydroxyl or C_1 to C_8 alkoxy residues, or a direct bond,
- G^5 and G^6 mutually independently denote a hydrogen or halogen atom, a C_1 to C_4 alkyl residue, a C_1 to C_4 monohydroxyalkyl residue, a C_2 to C_4 polyhydroxyalkyl residue, a C_1 to C_4 aminoalkyl residue or a direct link to the bridging member Y,
- G^7, G^8, G^9, G^{10}, G^{11} and G^{12} mutually independently denote a hydrogen atom, a direct bond to the bridging member Y or a C_1 to C_4 alkyl residue, providing that
- the compounds of the formula (Ent2) contain only one bridging member Y per molecule and
- the compounds of the formula (Ent2) contain at least one amino group which bears at least one hydrogen atom.

[0050] The substituents used in formula (Ent2) are defined according to the invention in a similar manner to the above explanations.

[0051] Preferred binuclear developer components of the formula (Ent2) are in particular: N,N'-bis-(β-hydroxyethyl)-N,N'-bis-(4'-aminophenyl)-1,3-diamino-propan-2-ol, N,N'-bis-(β-hydroxyethyl)-N,N'-bis-(4'-aminophenyl)-ethylenediamine, N,N'-bis-(4-aminophenyl)-tetramethylenediamine, N,N'-bis-(β-hydroxyethyl)-N,N'-bis-(4-aminophenyl)-tetramethylenediamine, N,N'-bis-(4-methylaminophenyl)-tetramethylenediamine, N,N'-diethyl-N,N'-bis-(4'-amino-3'-methylphenyl)-ethylenediamine, bis-(2-hydroxy-5-aminophenyl)methane, 1,3-bis-(2,5-diaminophenoxy)propan-2-ol, N,N'-bis-(4'-aminophenyl)-1,4-diazacycloheptane, N,N'-bis-(2-hydroxy-5-aminobenzyl)piperazine, N-(4'-aminophenyl)-p-phenylenediamine and 1,10-bis-(2',5'-diaminophenyl)-1,4,7,10-tetraoxadecane and the physiologically acceptable salts thereof.

[0052] Very particularly preferred binuclear developer components of the formula (Ent2) are N,N'-bis-(β-hydroxyethyl)-N,N'-bis-(4'-aminophenyl)-1,3-diaminopropan-2-ol, bis-(2-hydroxy-5-aminophenyl)methane, 1,3-bis-(2,5-diaminophenoxy)propan-2-ol, N,N'-bis-(4'-aminophenyl)-1,4-diaza-cycloheptane and 1,10-bis-(2',5'-diaminophenyl)-1,4,7,10-tetraoxadecane or one of the physiologically acceptable salts thereof.

[0053] It may furthermore be preferred according to the invention to use a p-aminophenol derivative or one of the physiologically acceptable salts thereof as the developer component. Particular preference is given to p-amino-phenol derivatives of the formula (Ent3)



(Ent3)

wherein:

- G^{13} denotes a hydrogen atom, a halogen atom, a C_1 to C_4 alkyl residue, a C_1 to C_4 monohydroxyalkyl residue, a C_2 to C_4 polyhydroxyalkyl residue, a (C_1 to C_4)-alkoxy-(C_1 to C_4)-alkyl residue, a C_1 to C_4 amino-alkyl residue, a hydroxy-(C_1 to C_4)-alkylamino residue, a C_1 to C_4

hydroxyalkoxy residue, a C_1 to C_4-hydroxyalkyl(C_1 to C_4)-aminoalkyl residue or a (di-C_1 to C_4-alkylamino)-(C_1 to C_4)-alkyl residue, and

- G^{14} denotes a hydrogen or halogen atom, a C_1 to C_4 alkyl residue, a C_1 to C_4 monohydroxyalkyl residue, a C_2 to C_4 polyhydroxyalkyl residue, a (C_1 to C_4)-alkoxy-(C_1 to C_4)-alkyl residue, a C_1 to C_4 aminoalkyl residue, or a C_1 to C_4cyanoalkyl residue,
- G^{15} denotes hydrogen, a C_1 to C_4 alkyl residue, a C_1 to C_4 monohydroxyalkyl residue, a C_2 to C_4 polyhydroxyalkyl residue, a phenyl residue or a benzyl residue, and
- G^{16} denotes hydrogen or a halogen atom.

[0054] The substituents used in formula (Ent3) are defined according to the invention in a manner similar to the above explanations.

[0055] Preferred p-aminophenols of the formula (Ent3) are in particular p-aminophenol, N-methyl-p-aminophenol, 4-amino-3-methylphenol, 4-amino-3-fluorophenyl, 2-hydroxymethylamino-4-aminophenol, 4-amino-3-hydroxymethylphenol, 4-amino-2-(β-hydroxyethoxy)phenol, 4-amino-2-methylphenol, 4-amino-2-hydroxymethylphenol, 4-amino-2-methoxymethylphenol, 4-amino-2-aminomethylphenol, 4-amino-2-(β-hydroxyethylaminomethyl)phenol, 4-amino-2-(α,β-dihydroxyethyl)phenol, 4-amino-2-fluorophenyl, 4-amino-2-chlorophenol, 4-amino-2,6-dichlorophenyl, 4-amino-2-(diethylaminomethyl)phenol and the physiologically acceptable salts thereof.

[0056] Very particularly preferred compounds of the formula (Ent3) are p-aminophenol, 4-amino-3-methylphenol, 4-amino-2-aminomethylphenol, 4-amino-2-(α,β-dihydroxyethyl)phenol and 4-amino-2-(diethylaminomethyl)-phenol.

[0057] The developer component may furthermore be selected from o-aminophenol and the derivatives thereof, such as for example 2-amino-4-methylphenol, 2-amino-5-methylphenol or 2-amino-4-chlorophenol.

[0058] The developer component may furthermore be selected from heterocyclic developer components, such as for example pyridine, pyrimidine, pyrazole, pyrazole-pyrimidine derivatives and the physiologically acceptable salts thereof.

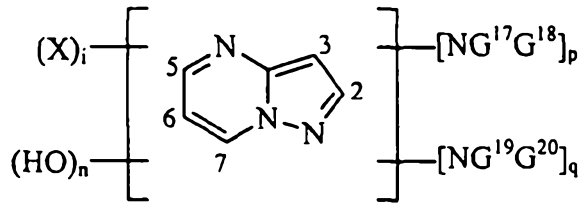
[0059] Preferred pyridine derivatives are in particular the compounds described in patents GB 1 026 978 and GB 1 153 196, such as 2,5-diamino-pyridine, 2-(4'-methoxyphenyl)amino-3-aminopyridine, 2,3-diamino-6-methoxy-pyridine, 2-(β-methoxyethyl)amino-3-amino-6-methoxypyridine and 3,4-diaminopyridine.

[0060] Preferred pyrimidine derivatives are in particular the compounds described in German patent DE 2 359 399, Japanese published patent application JP 02019576 A2 or in published patent application WO 96/15765, such as 2,4,5,6-tetraaminopyrimidine, 4-hydroxy-2,5,6-triaminopyrimidine, 2-hydroxy-4,5,6-triaminopyrimidine, 2-dimethylamino-4,5,6-triaminopyrimidine, 2,4-dihydroxy-5,6-diaminopyrimidine and 2,5,6-triaminopyrimidine.

[0061] Preferred pyrazole derivatives are in particular the compounds described in patents DE 3 843 892, DE 4 133 957 and patent applications WO 94/08969, WO 94/08970, EP-740 931 and DE 195 43 988, such as 4,5-diamino-1-methylpyrazole, 4,5-diamino-1-(β-hydroxyethyl)pyrazole, 3,4-diaminopyrazole, 4,5-diamino-1-(4'-chlorobenzyl)pyrazole, 4,5-diamino-1,3-dimethylpyrazole, 4,5-diamino-3-methyl-1-phenylpyrazole, 4,5-diamino-1-methyl-3-phenylpyrazole, 4-amino-1,3-dimethyl-5-hydrazino-pyrazole, 1-benzyl-4,5-diamino-3-methylpyrazole, 4,5-diamino-3-tert.-butyl-1-methylpyrazole, 4,5-diamino-1-tert.-butyl-3-methylpyrazole, 4,5-diamino-1-(β-hydroxyethyl)-3-methylpyrazole, 4,5-diamino-1-ethyl-3-methyl-pyrazole, 4,5-diamino-1-ethyl-3-(4'-methoxyphenyl)pyrazole, 4,5-diamino-1-ethyl-3-hydroxymethylpyrazole, 4,5-diamino-3-hydroxy-methyl-1-methylpyrazole, 4,5-diamino-3-hydroxymethyl-1-isopropylpyrazole, 4,5-diamino-3-methyl-1-isopropylpyrazole, 4-amino-5-(2-aminoethyl)amino-1,3-dimethylpyrazole, 3,4,5-triaminopyrazole, 1-methyl-3,4,5-triaminopyrazole,

3,5-diamino-1-methyl-4-methylaminopyrazole and 3,5-diamino-4-(β-hydroxyethyl)amino-1-methylpyrazole.

[0062] Preferred pyrazolopyrimidine derivatives are in particular the derivatives of the pyrazolo[1,5-a]pyrimidine of the following formula (Ent4) and the tautomeric forms thereof, where a tautomeric equilibrium prevails:



(Ent4)

wherein

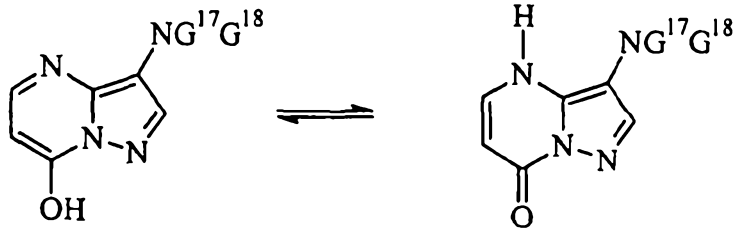
- G^{17}, G^{18}, G^{19} and G^{20} mutually independently denote a hydrogen atom, a C_1 to C_4 alkyl residue, an aryl residue, a C_1 bis C_4 hydroxyalkyl residue, a C_2 to C_4 polyhydroxyalkyl residue, a (C_1 to C_4)-alkoxy-(C_1 to C_4)-alkyl residue, a C_1 to C_4 aminoalkyl residue, which may optionally be protected by an acetyl ureide or a sulfonyl residue, a (C_1 to C_4)-alkylamino-(C_1 to C_4)-alkyl residue, a di-[(C_1 to C_4)-alkyl]-(C_1 to C_4)-aminoalkyl residue, the dialkyl residues optionally forming a carbocycle or a heterocycle with 5 or 6 chain links, a C_1 to C_4-hydroxyalkyl- or a di-(C_1 to C_4)-[hydroxyalkyl]-(C_1 to C_4)-aminoalkyl residue,
- the X residues mutually independently denote a hydrogen atom, a C_1 to C_4 alkyl residue, an aryl residue, a C_1 bis C_4 hydroxyalkyl residue, a C_2 to C_4 polyhydroxyalkyl residue, a C_1 to C_4 aminoalkyl residue, a (C_1 to C_4)-alkylamino-(C_1 to C_4)-alkyl residue, a di-[(C_1 to C_4)alkyl]-(C_1 to C_4)-aminoalkyl residue, the dialkyl residues optionally forming a carbocycle or a heterocycle with 5 or 6 chain links, a C_1 to C_4-hydroxyalkyl- or a di-(C_1 to C_4-hydroxyalkyl)aminoalkyl residue, an amino residue, a C_1 to C_4-alkyl- or di-(C_1 to C_4-hydroxyalkyl)amino residue, a halogen atom, a carboxylic acid group or a sulfonic acid group,
- i has the value 0, 1, 2 or 3,
- p has the value 0 or 1,
- q has the value 0 or 1 and

- n has the value 0 or 1,

  providing that
- the sum of p + q does not equal 0,
- if p + q is equal to 2, n has the value 0, and the groups $NG^{17}G^{18}$ and $NG^{19}G^{20}$ occupy positions (2,3); (5,6); (6,7); (3,5) or (3,7);
- if p + q is equal to 1, n has the value 1, and the groups $NG^{17}G^{18}$ (or $NG^{19}G^{20}$) and the group OH- occupy positions (2,3); (5,6); (6,7); (3,5) or (3,7);

[0063] The substituents used in formula (Ent4) are defined according to the invention in a manner similar to the above explanations.

[0064] If the pyrazolo[1,5a]pyrimidine of the above-stated formula (Ent4) contains a hydroxyl group in one of positions 2, 5 or 7 of the ring system, a tautomeric equilibrium prevails, which is shown for example in the following scheme:



[0065] Pyrazolo[1,5a]pyrimidines of the above-stated formula (Ent4) which may in particular be mentioned are:

- pyrazolo[1,5a]pyrimidine-3,7-diamine;
- 2,5-dimethylpyrazolo[1,5a]pyrimidine-3,7-diamine;
- pyrazolo[1,5a]pyrimidine-3,5-diamine;
- 2,7-dimethylpyrazolo[1,5a]pyrimidine-3,5-diamine;
- 3-aminopyrazolo[1,5-a]pyrimidin-7-ol;
- 3-aminopyrazolo[1,5-a]pyrimidin-5-ol;
- 2-(3-aminopyrazolo[1,5-a]pyrimidin-7-ylamino)-ethanol;
- 2-(7-aminopyrazolo[1,5-a]pyrimidin-3-ylamino)-ethanol;
- 2-[(3-aminopyrazolo[1,5-a]pyrimidin-7-yl)-(2-hydroxyethyl)amino]ethanol;
- 2-[(7-aminopyrazolo[1,5-a]pyrimidin-3-yl)-(2-hydroxyethyl)amino]ethanol;

- 5,6-dimethylpyrazolo[1,5a]pyrimidine-3,7-diamine;
- 2,6-dimethylpyrazolo[1,5a]pyrimidine-3,7-diamine;
- 3-amino-7-dimethylamino-2,5-dimethylpyrazolo[1,5-a]pyrimidine;

and the physiologically acceptable salts thereof and the tautomeric forms thereof, if a tautomeric equilibrium exists.

[0066] The pyrazolo[1,5-a]pyrimidines of the above-stated formula (Ent4) may be produced as described in the literature by cyclization starting from an aminopyrazole or from hydrazine.

[0067] The coupler components used are generally m-phenylenediamine derivatives, naphthols, resorcinol, and resorcinol derivatives, pyrazolones and m-aminophenol derivatives as well as heterocyclic compounds.

[0068] Coupler components which are preferred according to the invention are

- m-aminophenol and the derivatives thereof such as for example 5-amino-2-methylphenol, N-cyclopentyl-3-aminophenol, 3-amino-2-chloro-6-methylphenol, 2-hydroxy-4-aminophenoxyethanol, 2,6-dimethyl-3-aminophenol, 3-trifluoroacetylamino-2-chloro-6-methylphenol, 5-amino-4-chloro-2-methylphenol, 5-amino-4-methoxy-2-methylphenol, 5-(2'-hydroxyethyl)-amino-2-methylphenol, 3-(diethylamino)-phenol, N-cyclopentyl-3-aminophenol, 1,3-dihydroxy-5-(methylamino)-benzene, 3-ethylamino-4-methylphenol and 2,4-dichloro-3-aminophenol,
- o-aminophenol and the derivatives thereof,
- m-diaminobenzene and the derivatives thereof such as for example 2,4-diaminophenoxyethanol, 1,3-bis-(2',4'-diaminophenoxy)propane, 1-methoxy-2-amino-4-(2'-hydroxyethylamino)benzene, 1,3-bis-(2',4'-diaminophenyl)propane, 2,6-bis-(2'-hydroxyethylamino)-1-methylbenzene, 2-({3-[(2-hydroxyethyl)amino]-4-methoxy-5-methylphenyl}amino)ethanol, 2-({3-[(2-hydroxyethyl)amino]-2-methoxy-5-methylphenyl}amino)ethanol, 2-({3-[(2-hydroxyethyl)amino]-4,5-dimethylphenyl}amino)ethanol, 2-[3-morpholin-4-ylphenyl)-

amino]ethanol, 3-amino-4-(2-methoxyethoxy)-5-methylphenylamine and 1-amino-3-bis-(2'-hydroxyethyl)-aminobenzene,

- o-diaminobenzene and the derivatives thereof such as for example 3,4-diaminobenzoic acid, and 2,3-diamino-1-methylbenzene,
- di- or trihydroxybenzene derivatives such as for example resorcinol, resorcinol monomethyl ether, 2-methylresorcinol, 5-methylresorcinol, 2,5-dimethylresorcinol, 2-chlororesorcinol, 4-chlororesorcinol, pyrogallol and 1,2,4-trihydroxybenzene,
- pyridine derivatives such as for example 2,6-dihydroxypyridine, 2-amino-3-hydroxypyridine, 2-amino-5-chloro-3-hydroxypyridine, 3-amino-2-methylamino-6-methoxypyridine, 2,6-dihydroxy-3,4-dimethylpyridine, 2,6-dihydroxy-4-methylpyridine, 2,6-diaminopyridine, 2,3-diamino-6-methoxypyridine and 3,5-diamino-2,6-dimethoxypyridine,
- naphthalene derivatives such as for example 1-naphthol, 2-methyl-1-naphthol, 2-hydroxymethyl-1-naphthol, 2-hydroxyethyl-1-naphthol, 1,5-dihydroxynaphthalene, 1,6-dihydroxynaphthalene, 1,7-dihydroxynaphthalene, 1,8-dihydroxynaphthalene, 2,7-dihydroxynaphthalene and 2,3-dihydroxynaphthalene,
- morpholine derivatives such as for example 6-hydroxybenzomorpholine and 6-aminobenzomorpholine,
- quinoxaline derivatives such as for example 6-methyl-1,2,3,4-tetrahydroquinoxaline,
- pyrazole derivatives such as for example 1-phenyl-3-methylpyrazol-5-one,
- indole derivatives such as for example 4-hydroxyindole, 6-hydroxyindole and 7-hydroxyindole,
- pyrimidine derivatives, such as for example 4,6-diaminopyrimidine, 4-amino-2,6-dihydroxypyrimidin, 2,4-diamino-6-hydroxypyrimidine, 2,4,6-trihydroxypyrimidine, 2-amino-4-methylpyrimidine, 2-amino-4-hydroxy-6-methylpyrimidine and 4,6-dihydroxy-2-methylpyrimidine, or

- methylenedioxybenzene derivatives such as for example 1-hydroxy-3,4-methylenedioxybenzene, 1-amino-3,4-methylenedioxybenzene and 1-(2'-hydroxyethyl)-amino-3,4-methylenedioxybenzene

and the physiologically acceptable salts thereof.

[0069] Coupler components which are particularly preferred according to the invention are 1-naphthol, 1,5-, 2,7- and 1,7-dihydroxynaphthalene, 3-amino-phenol, 5-amino-2-methylphenol, 2-amino-3-hydroxypyridine, resorcinol, 4-chlororesorcinol, 2-chloro-6-methyl-3-aminophenol, 2-methylresorcinol, 5-methylresorcinol, 2,5-dimethylresorcinol and 2,6-dihydroxy-3,4-dimethyl-pyridine and the physiologically acceptable salts of the above-stated compounds.

[0070] The cosmetic preparations according to the invention preferably contain the developer components in a quantity of 0.005 to 10 wt.%, preferably of 0.1 to 5 wt.%, in each case relative to the entire preparation.

[0071] The cosmetic preparations according to the invention preferably contain the coupler components in a quantity of 0.005 to 10 wt.%, preferably of 0.1 to 5 wt.%, in each case relative to the entire preparation.

[0072] The preparation according to the invention may contain as color-modifying component in the form of the oxo dye precursors at least one combination of at least one compound of component

1 compounds which contain a reactive carbonyl group with at least one compound of component

2 compounds selected from (a) CH-acidic compounds, (b) compounds with a primary or secondary amino group or hydroxyl group, selected from primary or secondary aromatic amines, nitrogenous heterocyclic compounds and aromatic hydroxyl compounds.

[0073] Compounds according to the invention with a reactive carbonyl group (hereinafter also referred to as reactive carbonyl compounds or component 1) have at least one carbonyl group as a reactive group which

reacts with the component 2 compounds to form a chemical bond which links the two components together. According to the invention, component 1 also includes those compounds in which the reactive carbonyl group is derivatized or masked in such a manner that the reactivity of the carbon atom of the derivatized or masked carbonyl group towards component 2 is always present. These derivatives are preferably condensation compounds of reactive carbonyl compounds with

a) amines and the derivatives thereof resulting in the formation of imines or oximes as the condensation compound
b) alcohols resulting in the formation of acetals or ketals as the condensation compound
c) water resulting in the formation of hydrates as the condensation compound of aldehydes.

[0074] Component 1 is preferably selected from the group composed of acetophenone, propiophenone, 2-hydroxyacetophenone, 3-hydroxyacetophenone, 4-hydroxyacetophenone, 2-hydroxypropiophenone, 3-hydroxypropiophenone, 4-hydroxypropiophenone, 2-hydroxybutyrophenone, 3-hydroxybutyrophenone, 4-hydroxybutyrophenone, 2,4-dihydroxyacetophenone, 2,5-dihydroxyacetophenone, 2,6-dihydroxyacetophenone, 2,3,4-trihydroxyacetophenone, 3,4,5-trihydroxyacetophenone, 2,4,6-trihydroxyacetophenone, 2,4,6-trimethoxyacetophenone, 3,4,5-trimethoxyacetophenone, 3,4,5-trimethoxyacetophenone diethyl ketal, 4-hydroxy-3-methoxyacetophenone, 3,5-dimethoxy-4-hydroxyacetophenone, 4-aminoacetophenone, 4-dimethylaminoacetophenone, 4-morpholinoacetophenone, 4-piperidinoacetophenone, 4-imidazolinoacetophenone, 2-hydroxy-5-bromoacetophenone, 4-hydroxy-3-nitroacetophenone, acetophenone-2-carboxylic acid, acetophenone-4-carboxylic acid, benzophenone, 4-hydroxybenzophenone, 2-aminobenzophenone, 4,4'-dihydroxybenzophenone, 2,4-dihydroxybenzophenone, 2,4,4'-trihydroxybenzophenone, 2,3,4-trihydroxybenzophenone, 2-hydroxy-1-acetonaphthone, 1-hydroxy-2-acetonaphthone, chromone, chromone-2-carboxylic acid, flavone, 3-hydroxyflavone, 3,5,7-trihydroxyflavone, 4',5,7-trihydroxyflavone, 5,6,7-trihydroxyflavone, quercetin, 1-indanone,

9-fluorenone, 3-hydroxyfluorenone, anthrone, 1,8-dihydroxyanthrone, vanillin, coniferyl aldehyde, 2-methoxybenzaldeyde, 3-methoxybenzaldeyde, 4-methoxybenzaldeyde, 2-ethoxybenzaldeyde, 3-ethoxybenzaldeyde, 4-ethoxybenzaldeyde, 4-hydroxy-2,3-dimethoxybenzaldeyde, 4-hydroxy-2,5-dimethoxybenzaldeyde, 4-hydroxy-2,6-dimethoxybenzaldeyde, 4-hydroxy-2-methylbenzaldeyde, 4-hydroxy-3-methylbenzaldeyde, 4-hydroxy-2,3-dimethylbenzaldeyde, 4-hydroxy-2,5-dimethylbenzaldeyde, 4-hydroxy-2,6-dimethylbenzaldeyde, 4-hydroxy-3,5-dimethoxybenzaldeyde, 4-hydroxy-3,5-dimethylbenzaldeyde, 3,5-diethoxy-4-hydroxybenzaldeyde, 2,6-diethoxy-4-hydroxybenzaldeyde, 3-hydroxy-4-methoxybenzaldeyde, 2-hydroxy-4-methoxybenzaldeyde, 2-ethoxy-4-hydroxybenzaldeyde, 3-ethoxy-4-hydroxybenzaldeyde, 4-ethoxy-2-hydroxybenzaldeyde, 4-ethoxy-3-hydroxybenzaldeyde, 2,3-dimethoxybenzaldeyde, 2,4-dimethoxybenzaldeyde, 2,5-dimethoxybenzaldeyde, 2,6-dimethoxybenzaldeyde, 3,4-dimethoxybenzaldeyde, 3,5-dimethoxybenzaldeyde, 2,3,4-trimethoxybenzaldeyde, 2,3,5-trimethoxybenzaldeyde, 2,3,6-trimethoxybenzaldeyde, 2,4,6-trimethoxybenzaldeyde, 2,4,5-trimethoxybenzaldeyde, 2,5,6-trimethoxybenzaldeyde, 2-hydroxybenzaldeyde, 3-hydroxybenzaldeyde, 4-hydroxybenzaldeyde, 2,3-dihydroxybenzaldeyde, 2,4-dihydroxybenzaldeyde, 2,5-dihydroxybenzaldeyde, 2,6-dihydroxybenzaldeyde, 3,4-dihydroxybenzaldeyde, 3,5-dihydroxybenzaldeyde, 2,3,4-trihydroxybenzaldeyde, 2,3,5-trihydroxybenzaldeyde, 2,3,6-trihydroxybenzaldeyde, 2,4,6-trihydroxybenzaldeyde, 2,4,5-trihydroxybenzaldeyde, 2,5,6-trihydroxybenzaldeyde, 4-hydroxy-2-methoxybenzaldeyde, 4-dimethylaminobenzaldeyde, 4-diethylaminobenzaldeyde, 4-dimethylamino-2-hydroxybenzaldeyde, 4-diethylamino-2-hydroxybenzaldeyde, 4-pyrrolidinobenzaldeyde, 4-morpholinobenzaldeyde, 2-morpholinobenzaldeyde, 4-piperidinobenzaldeyde, 2-methoxy-1-naphthaldeyde, 4-methoxy-1-naphthaldeyde, 2-hydroxy-1-naphthaldeyde, 2,4-dihydroxy-1-napthaldeyde, 4-hydroxy-3-methoxy-1-naphthaldeyde, 2-hydroxy-4-methoxy-1-naphthaldeyde, 3-hydroxy-4-methoxy-1-naphthaldeyde, 2,4-dimethoxy-1-naphthaldeyde, 3,4-dimethoxy-1-naphthaldeyde, 4-hydroxy-1-naphthaldeyde, 4-dimethyl-

amino-1-naphthaldeyd, 2-methoxycinnamaldeyde, 4-methoxycinnamaldeyde, 4-hydroxy-3-methoxycinnamaldeyde, 3,5-dimethoxy-4-hydroxycinnamaldeyde, 4-dimethylaminocinnamaldeyde, 2-dimethylaminobenzaldeyde, 2-chloro-4-dimethylaminobenzaldeyde, 4-dimethylamino-2-methylbenzaldeyde, 4-diethylaminocinnamaldeyde, 4-dibutylaminobenzaldeyde, 4-diphenylamino-benzaldeyde, 4-dimethylamino-2-methoxybenzaldeyde, 4-(1-imidazolyl)-benz-aldeyde, piperonal, 2,3,6,7-tetrahydro-1H,5H-benzo[ij]quinolizine-9-carbox-aldeyde, 2,3,6,7-tetrahydro-8-hydroxy-1H,5H-benzo[ij]quinolizine-9-carbox-aldeyde, N-ethylcarbazole-3-aldehyde, 2-formylmethylene-1,3,3-trimethyl-indoline (Fischer's aldehyde or tribasic aldehyde), 2-indolealdeyde, 3-indole-aldeyde, 1-methylindole-3-aldehyde, 2-methylindole-3-aldehyde, 1-acetylindole-3-aldehyde, 3-acetylindole, 1-methyl-3-acetylindole, 2-(1',3',3'-trimethyl-2-indolinylidene)-acetaldeyde, 1-methylpyrrole-2-aldehyde, 1-methyl-2-acetylpyrrole, 4-pyridinealdeyde, 2-pyridinealdeyde, 3-pyridine-aldeyde, 4-acetylpyridine, 2-acetylpyridine, 3-acetylpyridine, pyridoxal, quinoline-3-aldehyde, quinoline-4-aldehyde, antipyrine-4-aldehyde, furfural, 5-nitrofurfural, 2-thenoyltrifluoroacetone, chromone-3-aldehyde, 3-(5'-nitro-2'-furyl)-acrolein, 3-(2'-furyl)-acrolein and imidazole-2-aldehyde, 1,3-diacetylbenzene, 1,4-diacetylbenzene, 1,3,5-triacetylbenzene, 2-benzo-ylacetophenone, 2-(4'-methoxybenzoyl)-acetophenone, 2-(2'-furoyl)-aceto-phenone, 2-(2'-pyridoyl)-acetophenone and 2-(3'-pyridoyl)-acetophenone, benzylideneacetone, 4-hydroxybenzylideneacetone, 2-hydroxybenzylidene-acetone, 4-methoxybenzylideneacetone, 4-hydroxy-3-methoxybenzylidene-acetone, 4-dimethylaminobenzylideneacetone, 3,4-methylenedioxy-benzylideneacetone, 4-pyrrolidinobenzylideneacetone, 4-piperidino-benzylideneacetone, 4-morpholinobenzylideneacetone, 4-diethylamino-benzylideneacetone, 3-benzylidene-2,4-pentanedione, 3-(4'-hydroxy-benzylidene)-2,4-pentanedione, 3-(4'-dimethylaminobenzylidene)-2,4-pentanedione, 2-benzylidenecyclohexanone, 2-(4'-hydroxybenzylidene)-cyclohexanone, 2-(4'-dimethylaminobenzylidene)-cyclohexanone, 2-benzylidene-1,3-cyclohexanedione, 2-(4'-hydroxybenzylidene)-1,3-cyclo-hexanedione, 3-(4'-dimethylaminobenzylidene)-1,3-cyclohexanedione,

2-benzylidene-5,5-dimethyl-1,3-cyclohexanedione, 2-(4'-hydroxybenzylidene)-5,5-dimethyl-1,3-cyclohexanedione, 2-(4'-hydroxy-3-methoxybenzylidene)-5,5-dimethyl-1,3-cyclohexanedione, 2-(4'-dimethylaminobenzylidene)-5,5-dimethyl-1,3-cyclohexanedione, 2-benzylidencyclopentanone, 2'-(4-hydroxybenzylidene)-cyclopentanone, 2-(4'-dimethylaminobenzylidene)-cyclopentanone, 5-(4-dimethylaminophenyl)penta-2,4-dienal, 5-(4-diethylaminophenyl)penta-2,4-dienal, 5-(4-methoxyphenyl)penta-2,4-dienal, 5-(3,4-dimethoxyphenyl)penta-2,4-dienal, 5-(2,4-dimethoxyphenyl)-penta-2,4-dienal, 5-(4-piperidinophenyl)penta-2,4-dienal, 5-(4-morpholino-phenyl)penta-2,4-dienal, 5-(4-pyrrolidinophenyl)penta-2,4-dienal, 6-(4-dimethyl-aminophenyl)hexa-3,5-dien-2-one, 6-(4-diethylaminophenyl)hexa-3,5-dien-2-one, 6-(4-methoxyphenyl)hexa-3,5-dien-2-one, 6-(3,4-dimethoxy-phenyl)hexa-3,5-dien-2-one, 6-(2,4-dimethoxyphenyl)hexa-3,5-dien-2-one, 6-(4-piperidinophenyl)hexa-3,5-dien-2-one, 6-(4-morpholinophenyl)hexa-3,5-dien-2-one, 6-(4-pyrrolidinophenyl)hexa-3,5-dien-2-one, 5-(4-dimethyl-amino-1-naphthyl)penta-3,5-dienal, 2-nitrobenzaldeyde, 3-nitrobenzaldeyde, 4-nitrobenzaldeyde, 4-methyl-3-nitrobenzaldeyde, 3-hydroxy-4-nitrobenz-aldeyde, 4-hydroxy-3-nitrobenzaldeyde, 5-hydroxy-2-nitrobenzaldeyde, 2-hydroxy-5-nitrobenzaldeyde, 2-hydroxy-3-nitrobenzaldeyde, 2-fluoro-3-nitro-benzaldeyde, 3-methoxy-2-nitrobenzaldeyde, 4-chloro-3-nitrobenzaldeyde, 2-chloro-6-nitrobenzaldeyde, 5-chloro-2-nitrobenzaldeyde, 4-chloro-2-nitro-benzaldeyde, 2,4-dinitrobenzaldeyde, 2,6-dinitrobenzaldeyde, 2-hydroxy-3-methoxy-5-nitrobenzaldeyde, 4,5-dimethoxy-2-nitrobenzaldeyde, 6-nitro-piperonal, 2-nitropiperonal, 5-nitrovanillin, 2,5-dinitrosalicylaldeyde, 5-bromo-3-nitrosalicylaldeyde, 3-nitro-4-formylbenzenesulfonic acid, 4-nitro-1-naphthaldeyde, 2-nitrocinnamaldeyde, 3-nitrocinnamaldeyde, 4-nitro-cinnamaldeyde, 9-methyl-3-carbazolealdeyde, 9-ethyl-3-carbazolealdeyde, 3-acetylcarbazole, 3,6-diacetyl-9-ethylcarbazole, 3-acetyl-9-methylcarbazole, 1,4-dimethyl-3-carbazolealdeyde, 1,4,9-trimethyl-3-carbazolealdeyde, 4-formyl-1-methylpyridinium, 2-formyl-1-methylpyridinium, 4-formyl-1-ethyl-pyridinium, 2-formyl-1-ethylpyridinium, 4-formyl-1-benzylpyridinium, 2-formyl-1-benzylpyridinium, 4-formyl-1,2-dimethylpyridinium, 4-formyl-

1,3-dimethylpyridinium, 4-formyl-1-methylquinolinium, 2-formyl-1-methylquinolinium, 4-acetyl-1-methylpyridinium, 2-acetyl-1-methylpyridinium, 4-acetyl-1-methylquinolinium, 5-formyl-1-methylquinolinium, 6-formyl-1-methylquinolinium, 7-formyl-1-methylquinolinium, 8-formyl-1-methylquinolinium, 5-formyl-1-ethylquinolinium, 6-formyl-1-ethylquinolinium, 7-formyl-1-ethylquinolinium, 8-formyl-1-ethylquinolinium, 5-formyl-1-benzylquinolinium, 6-formyl-1-benzylquinolinium, 7-formyl-1-benzylquinolinium, 8-formyl-1-benzylquinolinium, 5-formyl-1-allylquinolinium, 6-formyl-1-allylquinolinium, 7-formyl-1-allylquinolinium and 8-formyl-1-allylquinolinium, 5-acetyl-1-methylquinolinium, 6-acetyl-1-methylquinolinium, 7-acetyl-1-methylquinolinium, 8-acetyl-1-methylquinolinium, 5-acetyl-1-ethylquinolinium, 6-acetyl-1-ethylquinolinium, 7-acetyl-1-ethylquinolinium, 8-acetyl-1-ethylquinolinium, 5-acetyl-1-benzylquinolinium, 6-acetyl-1-benzylquinolinium, 7-acetyl-1-benzylquinolinium, 8-acetyl-1-benzylquinolinium, 5-acetyl-1-allylquinolinium, 6-acetyl-1-allylquinolinium, 7-acetyl-1-allylquinolinium and 8-acetyl-1-allylquinolinium, 9-formyl-10-methylacridinium, 4-(2'-formylvinyl)-1-methylpyridinium, 1,3-dimethyl-2-(4'-formylphenyl)-benzimidazolium, 1,3-dimethyl-2-(4'-formylphenyl)-imidazolinium, 2-(4'-formylphenyl)-3-methylbenzothiazolium, 2-(4'-acetylphenyl)-3-methylbenzothiazolium, 2-(4'-formylphenyl)-3-methylbenzoxazolium, 2-(5'-formyl-2'-furyl)-3-methylbenzothiazolium, 2-(5'-formyl-2'-furyl)-3-methylbenzothiazolium, 2-(5'-formyl-2'-thienyl)-3-methylbenzothiazolium, 2-(3'-formylphenyl)-3-methylbenzothiazolium, 2-(4'-formyl-1-naphthyl)-3-methylbenzothiazolium, 5-chloro-2-(4'-formylphenyl)-3-methylbenzothiazolium, 2-(4'-formylphenyl)-3,5-dimethylbenzothiazolium salts, preferably with benzenesulfonate, p-toluenesulfonate, methanesulfonate, perchlorate, sulfate, chloride, bromide, iodide, tetrachlorozincate, methylsulfate, trifluoromethanesulfonate or tetrafluoroborate as the counterion, isatin, 1-methylisatin, 1-allylisatin, 1-hydroxymethylisatin, 5-chloroisatin, 5-methoxyisatin, 5-nitroisatin, 6-nitroisatin, 5-sulfoisatin, 5-carboxyisatin, quinisatin, 1-methylquinisatin, and any desired mixtures of the above-stated compounds.

[0075] CH-acidic compounds are in general considered to be those which bear a hydrogen atom attached to an aliphatic carbon atom, the corresponding carbon-hydrogen bond being activated due to electron-attracting substituents. According to the invention, CH-acidic compounds also include enamines which arise by alkaline treatment of quaternized N-heterocycles with a CH-acidic alkyl group in conjugation with the quaternary nitrogen.

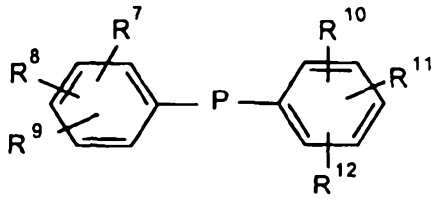
[0076] The CH-acidic component 2 compounds are preferably selected from the group consisting of 1,2,3,3-tetramethyl-3H-indolium iodide, 1,2,3,3-tetramethyl-3H-indolium p-toluenesulfonate, 1,2,3,3-tetramethyl-3H-indolium methanesulfonate, 1,3,3-trimethyl-2-methyleneindoline (Fischer's base), 2,3-dimethylbenzothiazolium iodide, 2,3-dimethylbenzothiazolium p-toluenesulfonate, 2,3-dimethylnaphtho[1,2-d]thiazolium p-toluenesulfonate, 3-ethyl-2-methylnaphtho[1,2-d]thiazolium p-toluenesulfonate, rhodanine, rhodanine-3-acetic acid, 1,4-dimethylquinolinium iodide, 1,2-dimethyl-quinolinium iodide, barbituric acid, thiobarbituric acid, 1,3-dimethylthiobarbituric acid, 1,3-diethylthiobarbituric acid, 1,3-diethylbarbituric acid, oxindole, 3-indoxyl acetate, 2-coumaranone, 5-hydroxy-2-coumaranone, 6-hydroxy-2-coumaranone, 3-methyl-1-phenylpyrazolin-5-one, indane-1,2-dione, indane-1,3-dione, indan-1-one, benzoylacetonitrile, 3-dicyanomethyleneindan-1-one, 2-amino-4-imino-1,3-thiazoline hydrochloride, 5,5-dimethylcyclohexane-1,3-dione, 2H-1,4-benzoxazin-4H-3-one, 3-ethyl-2-methylbenzoxazolium iodide, 3-ethyl-2-methylbenzothiazolium iodide, 1-ethyl-4-methylquinolinium iodide, 1-ethyl-2-methylquinolinium iodide, 1,2,3-trimethylquinoxalinium iodide, 3-ethyl-2-methylbenzoxazolium p-toluenesulfonate, 3-ethyl-2-methylbenzo-thiazolium p-toluenesulfonate, 1-ethyl-4-methylquinolinium p-toluenesulfonate, 1-ethyl-2-methylquinolinium p-toluenesulfonate and 1,2,3-trimethyl-quinoxalinium p-toluenesulfonate.

[0077] Preferred component 2 primary or secondary aromatic amines are selected from N,N-dimethyl-p-phenylenediamine, N,N-diethyl-p-phenylene-diamine, N-(2-hydroxyethyl)-N-ethyl-p-phenylenediamine, N,N-bis-(2'-hydroxy-ethyl)-p-phenylenediamine, N-(2-methoxyethyl)-p-phenylenediamine,

2,3-dichloro-p-phenylenediamine, 2,4-dichloro-p-phenylenediamine, 2,5-dichloro-p-phenylenediamine, 2-chloro-p-phenylenediamine, 2,5-dihydroxy-4-morpholinoaniline, 2-aminophenol, 3-aminophenol, 4-aminophenol, 2-amino-methyl-4-aminophenol, 2-hydroxymethyl-4-aminophenol, o-phenylenediamine, m-phenylenediamine, p-phenylenediamine, 2,5-diaminotoluene, 2,5-diamino-phenol, 2,5-diaminoanisole, 2,5-diaminophenetol, 4-amino-3-methylphenol, 2-(2,5-diaminophenol)ethanol, 2,4-diaminophenoxyethanol, 2-(2,5-diamino-phenoxy)ethanol, 3-amino-4-(2-hydroxyethyloxy)phenol, 3,4-methyl-enedioxyphenol, 3,4-methylenedioxyaniline, 3-amino-2,4-dichlorophenyl, 4-methylaminophenol, 2-methyl-5-aminophenol, 3-methyl-4-aminophenol, 2-methyl-5-(2-hydroxyethylamino)phenol, 3-amino-2-chloro-6-methylphenol, 2-methyl-5-amino-4-chlorophenol, 5-(2-hydroxyethylamino)-4-methoxy-2-methylphenol, 4-amino-2-hydroxymethylphenol, 2-(diethylamino-methyl-4-aminophenol, 4-amino-1-hydroxy-2-(2-hydroxyethylaminomethyl)-benzene, 1-hydroxy-2-amino-5-methylbenzene, 1-hydroxy-2-amino-6-methyl-benzene, 2-amino-5-acetamidophenol, 1,3-dimethyl-2,5-diaminobenzene, 5-(3-hydroxypropylamino-)2-methylphenol, 5-amino-4-methoxy-2-methylphenol, N,N-dimethyl-3-aminophenol, N-cyclopentyl-3-aminophenol, 5-amino-4-fluoro-2-methylphenol, 2,4-diamino-5-fluorotoluene, 2,4-diamino-5-(2-hydroxyethoxy)-toluene, 2,4-diamino-5-methylphenetol, 3,5-diamino-2-methoxy-1-methylbenzene, 2-amino-4-(2'-hydroxyethylamino)-anisole, 2,6-bis-(2-hydroxyethylamino)-1-methylbenzene, 1,3-diamino-2,4-dimethoxybenzene, 3,5-diamino-2-methoxytoluene, 2-aminobenzoic acid, 3-aminobenzoic acid, 4-aminobenzoic acid, 2-aminophenylacetic acid, 3-aminophenylacetic acid, 4-aminophenylacetic acid, 2,3-diaminobenzoic acid, 2,4-diaminobenzoic acid, 2,5-diaminobenzoic acid, 3,4-diaminobenzoic acid, 3,5-diaminobenzoic acid, 4-aminosalicylic acid, 5-aminosalicylic acid, 3-amino-4-hydroxybenzoic acid, 4-amino-3-hydroxybenzoic acid, 2-amino-benzenesulfonic acid, 3-aminobenzenesulfonic acid, 4-aminobenzenesulfonic acid, 3-amino-4-hydroxybenzenesulfonic acid, 4-amino-3-hydroxy-naphthalene-1-sulfonic acid, 6-amino-7-hydroxynaphthalene-2-sulfonic acid, 7-amino-4-hydroxynaphthalene-2-sulfonic acid, 4-amino-5-hydroxy-

naphthalene-2,7-disulfonic acid, 3-amino-2-naphthoic acid, 3-aminophthalic acid, 5-aminoisophthalic acid, 1,3,5-triaminobenzene, 1,2,4-triaminobenzene, 1,2,4,5-tetraaminobenzene, 2,4,5-triaminophenol, pentaaminobenzene, hexaaminobenzene, 2,4,6-triaminoresorcinol, 4,5-diaminopyrocatechol, 4,6-diaminopyrogallol, 1-(2-hydroxy-5-aminobenzyl)-2-imidazolidinone, 4-amino-2-((4-[(5-amino-2-hydroxyphenyl)methyl]piperazinyl)methyl)phenol, 3,5-diamino-4-hydroxypyrocatechol, 1,4-bis-(4-aminophenol)-1,4-diazacycloheptane, aromatic nitriles, such as 2-amino-4-hydroxybenzonitrile, 4-amino-2-hydroxybenzonitrile, 4-aminobenzonitrile, 2,4-diaminobenzonitrile, nitro group-containing amino compounds, such as 3-amino-6-methylamino-2-nitro-pyridine, picramic acid, [8-[(4-amino-2-nitrophenyl)-azo]-7-hydroxy-naphth-2-yl]trimethylammonium chloride, [8-((4-amino-3-nitrophenyl)azo]-7-hydroxy-naphth-2-yl]trimethylammonium chloride (Basic Brown 17), 1-hydroxy-2-amino-4,6-dinitrobenzene, 1-amino-2-nitro-4-[bis-(2-hydroxyethyl)amino]benzene, 1-amino-2-(2-hydroxyethyl)-amino-5-nitrobenzene (HC Yellow No. 5), 1-amino-2-nitro-4[(2-hydroxyethyl)amino]benzene (HC Red No. 7), 2-chloro-5-nitro-N-2-hydroxyethyl-1,4-phenylenediamine, 1-[(2-hydroxyethyl)-amino-2-nitro-4-aminobenzene (HC Red No. 3), 4-amino-3-nitrophenol, 4-amino-2-nitrophenol, 6-nitro-o-toluidine, 1-amino-3-methyl-4-[(2-hydroxyethyl)-amino]-6-nitrobenzene (HC Violet No. 1), 1-amino-2-nitro-4-[(2,3-dihydroxypropyl)amino]-5-chlorobenzene (HC Red No. 10), 2-(4-amino-2-nitroanilino)-benzoic acid, 6-nitro-2,5-diaminopyrimidine, 2-amino-6-chloro-4-nitrophenol, 1-amino-2-(3-nitrophenylazo)-7-phenylazo-8-naphthol-3,6-disulfonic acid disodium salt (Acid Blue No. 29), 1-amino-2-(2-hydroxy-4-nitrophenylazo)-8-naphthol-3,6-disulfonic acid disodium salt (Palatinchrome Green), 1-amino-2-(3-chloro-2-hydroxy-5-nitrophenylazo)-8-naphthol-3,6-disulfonic acid disodium salt (Gallion), 4-amino-4'-nitrostilbene-2,2'-disulfonic acid disodium salt, 2,4-diamino-3',5'-dinitro-2'-hydroxy-5-methylazobenzene (Mordant Brown 4), 4'-amino-4-nitrodiphenylamine-2-sulfonic acid, 4'-amino-3'-nitrobenzophenone-2-carboxylic acid, 1-amino-4-nitro-2-(2-nitrobenzylideneamino)-benzene, 2-[2-(diethylamino)ethylamino]-5-nitroaniline, 3-amino-4-hydroxy-5-nitrobenzenesulfonic

acid, 3-amino-3'-nitrobiphenyl, 3-amino-4-nitro-acenaphthene, 2-amino-1-nitro-naphthalene, 5-amino-6-nitrobenzo-1,3-dioxole, anilines, in particular nitro group-containing anilines, such as 4-nitroaniline, 2-nitroaniline, 1,4-diamino-2-nitrobenzene, 1,2-diamino-4-nitrobenzene, 1-amino-2-methyl-6-nitrobenzene, 4-nitro-1,3-phenylenediamine, 2-nitro-4-amino-1-(2-hydroxy-ethylamino)-benzene, 2-nitro-1-amino-4-[bis-(2-hydroxyethyl)-amino]- benzene, 4-amino-2-nitrodiphenylamine-2'-carboxylic acid, 1-amino-5-chloro-4-(2-hydroxyethylamino)-2-nitrobenzene, aromatic anilines or phenols with a further aromatic residue, as are shown in the formula II



(II)

in which

- R^7 denotes a hydroxyl or an amino group, which may be substituted by C_{1-4} alkyl, C_{1-4} hydroxyalkyl, C_{1-4} alkoxy or C_{1-4}-alkoxy-C_{1-4}-alkyl groups,
- R^8, R^9, R^{10}, R^{11} and R^{12} mutually independently denote a hydrogen atom, a hydroxyl or an amino group which may be substituted by C_1-C_4 alkyl, C_1-C_4 hydroxyalkyl, C_1-C_4 alkoxy, C_1-C_4 aminoalkyl or C_1-C_4-alkoxy-C_1-C_4-alkyl groups, and
- P denotes a direct bond, a saturated or unsaturated carbon chain with 1 to 4 carbon atoms optionally substituted by hydroxyl groups, a carbonyl, sulfoxy, sulfonyl or imino group, an oxygen or sulfur atom, or a group of the formula III

  $-Q'-(CH_2-Q-CH_2-Q'')_o-$ (III)

  in which

  - Q means a direct bond, a CH_2 or CHOH group,
  - Q' and Q'' mutually independently denote an oxygen atom, an NR^{13} group, in which R^{13} means a hydrogen atom, a C_{1-4} alkyl or a hydroxy-C_{1-4}-alkyl group, the two groups possibly forming a 5-, 6- or 7-membered ring together with the residual molecule, the

group O-$(CH_2)_p$-NH or NH-$(CH_2)_p$-O, in which p and p' are 2 or 3 and

- o means a number from 1 to 4,

such as for example 4,4'-diaminostilbene and the hydrochloride thereof, 4,4'-diaminostilbene-2,2'-disulfonic acid mono- or disodium salt, 4-amino-4'-dimethylaminostilbene and the hydrochloride thereof, 4,4'-diaminodiphenylmethane, 4,4'-diaminodiphenyl sulfide, 4,4'-diaminodiphenyl sulfoxide, 4,4'-diaminodiphenylamine, 4,4'-diaminodiphenylamine-2-sulfonic acid, 4,4'-diaminobenzophenone, 4,4'-diaminodiphenyl ether, 3,3',4,4'-tetraaminodiphenyl, 3,3',4,4'-tetraaminobenzophenone, 1,3-bis-(2,4-diaminophenoxy)-propane, 1,8-bis-(2,5-diaminophenoxy)-3,6-dioxaoctane, 1,3-bis-(4-aminophenylamino)propane, 1,3-bis-(4-aminophenylamino)-2-propanol, 1,3-bis-[N-(4-aminophenyl)-2-hydroxyethylamino]-2-propanol, N,N-bis-[2-(4'-aminophenoxy)-ethyl]methylamine, N-phenyl-1,4-phenylenediamine and bis-(5-amino-2-hydroxyphenyl)methane.

[0078] The above-stated compounds may be used both in free form and in the form of the physiologically acceptable salts thereof, in particular as salts of inorganic acids, such as hydrochloric or sulfuric acid.

[0079] Suitable nitrogenous heterocyclic compounds are for example 2-aminopyridine, 3-aminopyridine, 4-aminopyridine, 2-amino-3-hydroxypyridine, 2,6-diaminopyridine, 2,5-diaminopyridine, 2-(aminoethylamino)-5-aminopyridine, 2,3-diaminopyridine, 2-dimethylamino-5-aminopyridine, 2-methylamino-3-amino-6-methoxypyridine, 2,3-diamino-6-methoxypyridine, 2,6-dimethoxy-3,5-diaminopyrimidine, 2,4,5-triaminopyridine, 2,6-dihydroxy-3,4-dimethylpyridine, N-[2-(2,4-diaminophenyl)aminoethyl]-N-(5-amino-2-pyridyl)amine, N-[2-(4-aminophenyl)aminoethyl]-N-(5-amino-2-pyridyl)amine, 2,4-dihydroxy-5,6-diaminopyrimidine, 4,5,6-triaminopyrimidine, 4-hydroxy-2,5,6-triaminopyrimidine, 2-hydroxy-4,5,6-triaminopyrimidine, 2,4,5,6-tetraaminopyrimidine, 2-methylamino-4,5,6-triaminopyrimidine, 2,4-diaminopyrimidine, 4,5-diaminopyrimidine, 2-amino-4-methoxy-6-methylpyrimidine, 3,5-diaminopyrazole, 3,5-diamino-1,2,4-triazole, 3-aminopyrazole,

3-amino-5-hydroxypyrazole, 1-phenyl-4,5-diaminopyrazole, 1-(2-hydroxyethyl)-4,5-diaminopyrazole, 1-phenyl-3-methyl-4,5-diaminopyrazole, 4-amino-2,3-dimethyl-1-phenyl-3-pyrazolin-5-one (4-aminoantipyrin), 1-phenyl-3-methyl-pyrazol-5-one, 2-aminoquinoline, 3-aminoquinoline, 8-aminoquinoline, 4-amino-quinaldine, 2-aminonicotinic acid, 6-aminonicotinic acid, 5-aminoisoquinoline, 5-aminoindazole, 6-aminoindazole, 5-aminobenzimidazole, 7-amino-benzimidazole, 5-aminobenzothiazole, 7-aminobenzothiazole, 2,5-dihydroxy-4-morpholinoaniline together with indole and indoline derivatives, such as 4-aminoindole, 5-aminoindole, 6-aminoindole, 7-aminoindole, 5,6-dihydroxy-indole, 5,6-dihydroxyindoline and 4-hydroxyindoline. The hydroxypyrimidines disclosed in DE-U1-299 08 573 may furthermore be used according to the invention as heterocyclic compounds. The above-stated compounds may be used both in free form and in the form of the physiologically acceptable salts thereof, for example as salts of inorganic acids, such as hydrochloric or sulfuric acid.

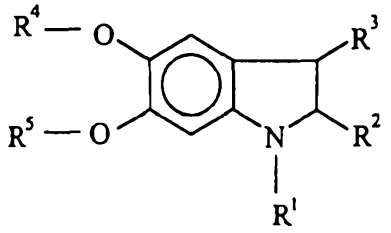
[0080] Suitable aromatic hydroxyl compounds are for example 2-methyl-resorcinol, 4-methylresorcinol, 5-methylresorcinol, 2,5-dimethylresorcinol, resorcinol, 3-methoxyphenol, pyrocatechol, hydroquinone, pyrogallol, phloroglucinol, hydroxyhydroquinone, 2-methoxyphenol, 3-methoxyphenol, 4-methoxyphenol, 3-dimethylaminophenol, 2-(2-hydroxyethyl)phenol, 3,4-methylenedioxyphenol, 2,4-dihydroxybenzoic acid, 3,4-dihydroxybenzoic acid, 2,4-dihydroxyphenylacetic acid, 3,4-dihydroxyphenylacetic acid, gallic acid, 2,4,6-trihydroxybenzoic acid, 2,4,6-trihydroxyacetophenone, 2-chlororesorcinol, 4-chlororesorcinol, 1-naphthol, 1,5-dihydroxynaphthalene, 2,3-dihydroxynaphthalene, 2,7-dihydroxynaphthalene, 6-dimethyl-amino-4-hydroxy-2-naphthalenesulfonic acid and 3,6-dihydroxy-2,7-naphthalenesulfonic acid.

[0081] The component 1 compounds and the component 2 compounds are preferably used in the cosmetic preparations in each case in a quantity of from 0.03 to 65 mmol, in particular from 1 to 40 mmol, relative to 100 g of the entire coloring preparation. The molar ratio of the component 1 compound and

the component 2 compound may be in the range from 0.5 bis 2.0, with equimolar quantities preferably being used. Where components 1 and 2 are stored separately, the ready-to-use preparation is produced by mixing immediately before use.

[0082] Precursors of nature-analogous dyes used as an oxidation dye precursor of the developer type are preferably those indoles and indolines which comprise at least one hydroxyl or amino group, preferably as a substituent on the six-membered ring. These groups may bear further substituents, for example in the form of etherification or esterification of the hydroxyl group or alkylation of amino group. In a second preferred embodiment, the dyes contain at least one derivative of indole and/or indoline.

[0083] Derivatives of 5,6-dihydroxyindoline of the formula (IVa) are particularly suitable as precursors of nature-analogous hair dyes,



(IVa)

in which, mutually independently,

- R^1 denotes hydrogen, a C_1-C_4 alkyl group or a C_1-C_4 hydroxyalkyl group,
- R^2 denotes hydrogen or a -COOH group, the -COOH group possibly also assuming the form of a salt with a physiologically acceptable cation,
- R^3 denotes hydrogen or a C_1-C_4 alkyl group,
- R^4 denotes hydrogen, a C_1-C_4 alkyl group or a -CO-R^6 group, in which R^6 denotes a C_1-C_4 alkyl group, and
- R^5 denotes one of the groups stated for R^4,

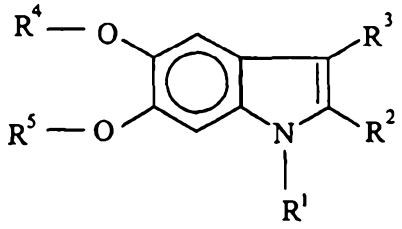
and physiologically acceptable salts of these compounds with an organic or inorganic acid.

[0084] Particularly preferred indoline derivatives are 5,6-dihydroxy-indoline, N-methyl-5,6-dihydroxyindoline, N-ethyl-5,6-dihydroxyindoline, N-propyl-5,6-dihydroxyindoline, N-butyl-5,6-dihydroxyindoline, 5,6-dihydroxy-

indoline-2-carboxylic acid and 6-hydroxyindoline, 6-aminoindoline and 4-amino-indoline.

[0085] Within this group, particular emphasis should be placed on N-methyl-5,6-dihydroxyindoline, N-ethyl-5,6-dihydroxyindoline, N-propyl-5,6-dihydroxyindoline, N-butyl-5,6-dihydroxyindoline and in particular 5,6-dihydroxyindoline.

[0086] Derivatives of 5,6-dihydroxyindole of the formula (IVb) are furthermore outstandingly suitable as precursors of nature-analogous hair dyes,



(IVb)

in which, mutually independently,

- R^1 denotes hydrogen, a C_1-C_4 alkyl group or a C_1-C_4 hydroxyalkyl group,
- R^2 denotes hydrogen or a -COOH group, the -COOH group possibly also assuming the form of a salt with a physiologically acceptable cation,
- R^3 denotes hydrogen or a C_1-C_4 alkyl group,
- R^4 denotes hydrogen, a C_1-C_4 alkyl group or a -CO-R^6 group, in which R^6 denotes a C_1-C_4 alkyl group, and
- R^5 denotes one of the groups stated for R^4,
- and physiologically acceptable salts of these compounds with an organic or inorganic acid.

[0087] Particularly preferred indole derivatives are 5,6-dihydroxyindole, N-methyl-5,6-dihydroxyindole, N-ethyl-5,6-dihydroxyindole, N-propyl-5,6-dihydroxyindole, N-butyl-5,6-dihydroxyindole, 5,6-dihydroxy-indole-2-carboxylic acid, 6-hydroxyindole, 6-aminoindole and 4-aminoindole.

[0088] Within this group, particular emphasis should be placed on N-methyl-5,6-dihydroxyindole, N-ethyl-5,6-dihydroxyindole, N-propyl-

5,6-dihydroxyindole, N-butyl-5,6-dihydroxyindole, and in particular 5,6-dihydroxyindole.

[0089] Preferred direct dyes which are used as a color-modifying component in the cosmetic preparations are nitrophenylenediamines, nitroaminophenols, azo dyes, anthraquinones or indophenols. Preferred direct dyes are the compounds known by the international names or trade names HC Yellow 2, HC Yellow 4, HC Yellow 5, HC Yellow 6, HC Yellow 12, Acid Yellow 1, Acid Yellow 10, Acid Yellow 23, Acid Yellow 36, HC Orange 1, Disperse Orange 3, Acid Orange 7, HC Red 1, HC Red 3, HC Red 10, HC Red 11, HC Red 13, Acid Red 33, Acid Red 52, HC Red BN, Pigment Red 57:1, HC Blue 2, HC Blue 12, Disperse Blue 3, Acid Blue 7, Acid Green 50, HC Violet 1, Disperse Violet 1, Disperse Violet 4, Acid Violet 43, Disperse Black 9, Acid Black 1, and Acid Black 52 as well as 1,4-diamino-2-nitrobenzene, 2-amino-4-nitrophenol, 1,4-bis-(β-hydroxyethyl)amino-2-nitrobenzene, 3-nitro-4-(β-hydroxyethyl)aminophenol, 2-(2'-hydroxyethyl)amino-4,6-dinitrophenol, 1-(2'-hydroxyethyl)amino-4-methyl-2-nitrobenzene, 1-amino-4-(2'-hydroxyethyl)amino-5-chloro-2-nitrobenzene, 4-amino-3-nitrophenol, 1-(2'-ureidoethyl)amino-4-nitrobenzene, 4-amino-2-nitrodiphenylamine-2'-carboxylic acid, 6-nitro-1,2,3,4-tetrahydroquinoxaline, 2-hydroxy-1,4-naphthoquinone, picramic acid and the salts thereof, 2-amino-6-chloro-4-nitrophenol, 4-ethylamino-3-nitrobenzoic acid and 2-chloro-6-ethylamino-1-hydroxy-4-nitrobenzene.

[0090] The cosmetic preparations may furthermore contain a cationic direct dye, the following being particularly preferred

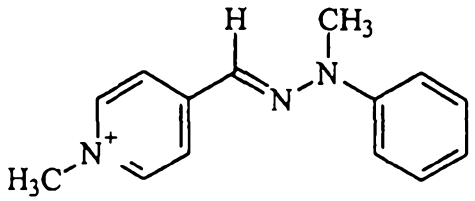
(a) cationic triphenylmethane dyes, such as for example Basic Blue 7, Basic Blue 26, Basic Violet 2 and Basic Violet 14,

(b) aromatic systems substituted with a quaternary nitrogen group, such as for example Basic Yellow 57, Basic Red 76, Basic Blue 99, Basic Brown 16 and Basic Brown 17, and

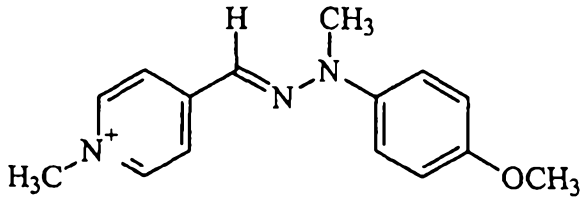
(c) direct dyes containing a heterocycle which comprises at least one quaternary nitrogen atom, as are for example mentioned in claims

6 to 11 in EP-A2-998 908, to which explicit reference is here made.

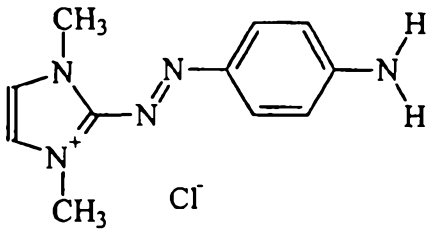
[0091] Preferred cationic direct dyes of group (c) are in particular the following compounds:



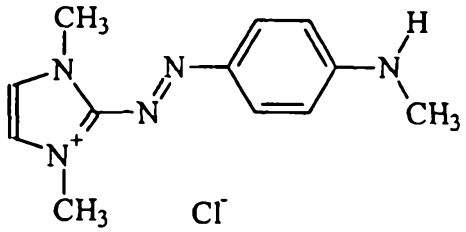
(DZ1)



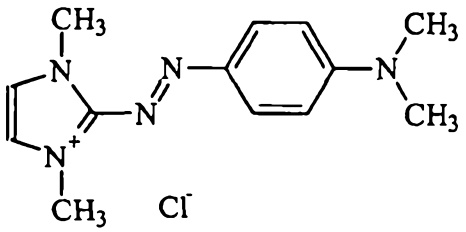
(DZ2)



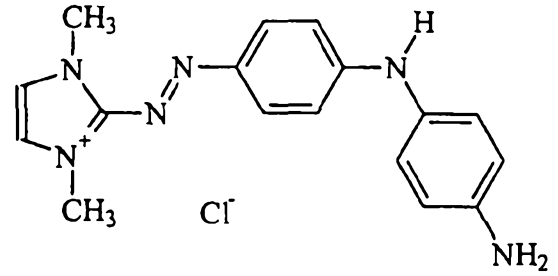
(DZ3)



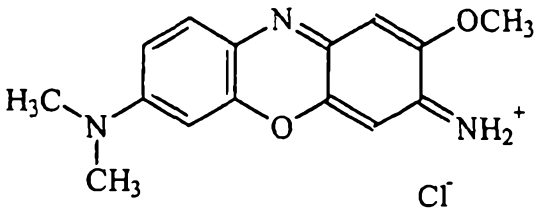
(DZ4)



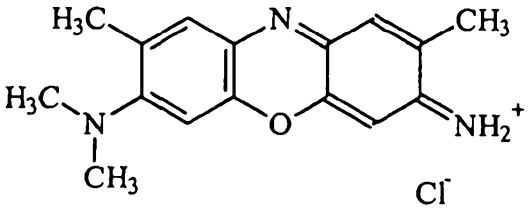
(DZ5)



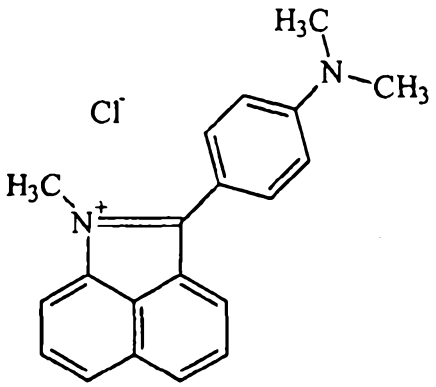
(DZ6)



(DZ7)



(DZ8)



(DZ9)

[0092] The compounds of the formulae (DZ1), (DZ3) and (DZ5), which are also known by the names Basic Yellow 87, Basic Orange 31 and Basic Red 51, are very particularly preferred cationic direct dyes of group (c).

[0093] The cationic direct dyes distributed under the trademark Arianor® are cationic direct dyes which are likewise very particularly preferred according to the invention.

[0094] The cosmetic preparations preferably contain the direct dyes in a quantity of 0.01 to 20 wt.%, relative to the ready-to-use preparation.

[0095] The cosmetic preparations according to the invention may furthermore also contain naturally occurring dyes as are present for example in henna red, henna neutral, henna black, chamomile flowers, sandalwood, black tea, alder buckthorn bark, sage, logwood, madder root, catechu, lotus tree and alkanet root.

[0096] It is not necessary for the oxidation dye precursors or the direct dyes in each case to be uniform compounds. Instead, as a result of the production processes for the individual dyes, the cosmetic preparations may contain subordinate quantities of still further components, provided that these do not have a disadvantageous effect on the dyeing result or must be excluded for other, for example toxicological, reasons.

[0097] With regard to further optional components and the quantities of these components used, reference is explicitly made to the relevant handbooks known to a person skilled in the art, for example Kh. Schrader, Grundlagen und Rezepturen der Kosmetika, 2nd edition, Hüthig Buch Verlag, Heidelberg, 1989.

[0098] When the dye precursors and the oxidizing agent are stored separately, the actual oxidative dye is produced by mixing immediately before use. In a preferred embodiment, the cosmetic preparation is accordingly mixed before use from one composition containing at least one color-modifying component in a cosmetic carrier and a further composition containing at least one oxidizing agent in a cosmetic carrier.

[0099] When oxidizing agents are used, the ready-to-use preparation is conveniently produced immediately before use by mixing a composition containing the oxidizing agent with the composition containing the color-modifying components. The resultant ready-to-use hair preparation should preferably have a pH value in the range from 6 to 12, in particular from pH 7.5 to 10.

[0100] In the case of a color change by means of lightening or bleaching the hair, at least one bleach booster is preferably used in the cosmetic preparations according to the invention in addition to the oxidizing agents.

[0101] Bleach boosters are preferably used in blonding products to increase the blonding action of the oxidizing agent, in particular of the hydrogen peroxide.

[0102] Bleach boosters which may be used are compounds which, under perhydrolysis conditions, yield aliphatic peroxycarboxylic acids having preferably 1 to 10 C atoms, in particular 2 to 4 C atoms, and/or optionally substituted perbenzoic acid. Suitable substances are those which bear O- and/or N-acyl groups having the stated number of C atoms and/or optionally substituted benzoyl groups. Preferred compounds are repeatedly acylated alkylenediamines, in particular tetraacetylethylenediamine (TAED), acylated triazine derivatives, in particular 1,5-diacetyl-2,4-dioxohexahydro-1,3,5-triazine (DADHT), acylated glycolurils, in particular tetraacetylglycoluril (TAGU), N-acylimides, in particular N-nonanoylsuccinimide (NOSI), acylated phenol-sulfonates, in particular n-nonanoyl or isononanoyl oxybenzenesulfonate (n- or iso-NOBS), carboxylic anhydrides, in particular phthalic anhydride, acylated polyhydric alcohols, in particular triacetin, ethylene glycol diacetate and 2,5-diacetoxy-2,5-dihydrofuran.

[0103] Bleach boosters which may preferably be used according to the invention are carbonate or hydrogencarbonate salts. These are preferably selected from the group of ammonium, alkali metal (in particular sodium and potassium) and alkaline earth metal (in particular calcium) carbonate salts or hydrogencarbonate salts. Particularly preferred carbonate or hydrogencarbonate salts are ammonium hydrogencarbonate, ammonium carbonate, sodium hydrogencarbonate, disodium carbonate, potassium hydrogencarbonate, dipotassium carbonate and calcium carbonate. These particularly preferred salts may be used alone or in mixtures of at least two representatives thereof as bleach boosters.

[0104] Bleach boosters of the monoalkyl carbonate type and the derivatives thereof which are preferably used in the method according to the invention are at least one carbonic acid monoester and/or at least one carbonic acid monoamide. Preferably usable carbonic acid monoesters are the carbonic acid monoesters of the formula (V),



(V)

in which R denotes a saturated or unsaturated, straight-chain, branched or cyclic, substituted or unsubstituted hydrocarbon residue, or a substituted or unsubstituted aryl group or a substituted or unsubstituted heterocycle.

[0105] In the formula (V), R preferably denotes a substituted or unsubstituted, straight-chain or branched alkyl, alkenyl or alkynyl residue, with hydroxy, amino, nitro, sulfonic acid groups or halogens preferably being considered as substituents. Further preferred residues R are phenyl and benzyl residues and further substituted representatives. R particularly preferably denotes a C_{1-6} alkyl group. Examples of C_1-C_6 alkyl groups according to the invention are the groups methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, iso-butyl, tert.-butyl, pentyl, iso-pentyl and hexyl.

[0106] Compositions which are particularly preferably used according to the invention are characterized in that the residue R in the formula (V) is selected from methyl, ethyl, n-propyl, isopropyl, n-butyl, iso-butyl, tert.-butyl and hydroxymethyl and hydroxyethyl residues.

[0107] As an alternative to the carbonic acid monoester or in conjunction therewith, carbonic acid monoamides may be used as bleach boosters in the anhydrous compositions. In this case, it is preferred according to the invention to use at least one carbonic acid monoamide of the formula (VI)



(VI)

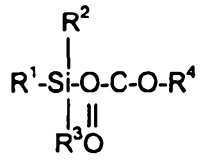
in which R denotes a saturated or unsaturated, straight-chain, branched or cyclic, substituted or unsubstituted hydrocarbon residue, or a substituted or unsubstituted aryl group or a substituted or unsubstituted heterocycle.

[0108] In the formula (VI), R preferably denotes a substituted or unsubstituted, straight-chain or branched alkyl, alkenyl or alkynyl residue, with hydroxy, amino, nitro, sulfonic acid groups or halogens preferably being considered as substituents. Further preferred residues R are phenyl and benzyl residues and further substituted representatives. R particularly preferably denotes a C_{1-6} alkyl group. Examples of C_1-C_6 alkyl groups according to the invention are the groups methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, iso-butyl, tert.-butyl, pentyl, iso-pentyl and hexyl.

[0109] Bleach boosters of the formula (VI) which are particularly preferably used according to the invention are characterized in that the residue R in the formula (VI) is selected from methyl, ethyl, n-propyl, isopropyl, n-butyl, iso-butyl, tert.-butyl and hydroxymethyl and hydroxyethyl residues.

[0110] The acidic H atom of the carbonic acid monoester or monoamide may also assume neutralized form, i.e. salts of carbonic acid monoesters or carbonic acid monoamides may also be used according to the invention. In this case, carbonic acid monoesters or carbonic acid monoamides preferred according to the invention are those which assume entirely or partially neutralized form, preferably the form of alkali metal, ammonium, alkaline earth metal or aluminum salts and in particular the form of the sodium salt thereof.

[0111] Bleach boosters of the silyl carbonate type and the derivatives thereof which are preferably incorporated into the compositions according to the invention are at least one silyl carbonate and/or at least one silyl carbamate. Silyl carbonates according to the formula (VII) are preferably used,



(VII)

in which the residues R^1, R^2 and R^3 mutually independently denote a hydrogen atom, a saturated or unsaturated, straight-chain, branched or cyclic, substituted or unsubstituted hydrocarbon residue or a trialkylsilyl group, preferably a trimethylsilyl group or a substituted or unsubstituted aryl group or a substituted or unsubstituted heterocycle or a halogen, a substituted or unsubstituted hydroxyl, oxo, amino group and the residue R^4 denotes a chemical bond to the Si atom or to one of the residues R^1, R^2 or R^3, a hydrogen atom, a saturated or unsaturated, straight-chain, branched or cyclic, substituted or unsubstituted hydrocarbon residue or a substituted or unsubstituted silyl or aluminyl group or a substituted or unsubstituted aryl group or a substituted or unsubstituted heterocycle.

[0112] Preferred residues R^1, R^2 and R^3 in the above-stated formula (VII) are substituted or unsubstituted, straight-chain or branched alkyl residues. Among these, alkyl residues with 1 to 5 carbon atoms and hydroxyalkyl residues are preferred, such that preferred anhydrous compositions according to the invention are characterized in that the residues R^1, R^2 and R^3 in the formula (VII) are selected from methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, tert.-butyl and hydroxymethyl and hydroxyethyl residues.

[0113] Preferred residues R^4 in the above-stated formula (VII) are hydrogen, substituted or unsubstituted, straight-chain or branched alkyl residues and trialkylsilyl residues. Among these, hydrogen, methyl, ethyl, tert.-butyl and trimethylsilyl residues are preferred.

[0114] The anhydrous composition according to the invention may contain at least one silyl carbamate of the formula (VIII) as bleach booster,



(VIII)

the residues R^1, R^2 and R^3 mutually independently denoting a hydrogen atom, a saturated or unsaturated, straight-chain, branched or cyclic, substituted or unsubstituted hydrocarbon residue or a trialkylsilyl group, preferably a trimethyl-

silyl group or a substituted or unsubstituted aryl group or a substituted or unsubstituted heterocycle or a halogen, a substituted or unsubstituted hydroxy, oxo, amino group and the residues R^4 and R^5 mutually independently denoting a chemical bond to the Si atom or to one of the residues R^1, R^2 or R^3, a hydrogen atom, a saturated or unsaturated, straight-chain, branched or cyclic, substituted or unsubstituted hydrocarbon residue or a substituted or unsubstituted silyl or aluminyl group or a substituted or unsubstituted aryl group or a substituted or unsubstituted heterocycle.

[0115] Preferred residues R^1, R^2 and R^3 in the above-stated formula (VIII) are substituted or unsubstituted, straight-chain or branched alkyl residues. Among these, alkyl residues with 1 to 5 carbon atoms and hydroxyalkyl residues are preferred, such that preferably used compositions are characterized in that the residues R^1, R^2 and R^3 in the formula (VIII) are selected from methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, tert.-butyl and hydroxymethyl and hydroxyethyl residues.

[0116] Preferred residues R^4 and R^5 in the above-stated formula (VIII) are hydrogen, substituted or unsubstituted, straight-chain or branched alkyl residues and trialkylsilyl residues. Among these, hydrogen, methyl, ethyl, tert.-butyl and trimethylsilyl residues are preferred.

[0117] At least one compound selected from acetic acid, lactic acid, tartaric acid, citric acid, salicylic acid and ortho-phthalic acid may be present as further additional bleach boosters in the compositions according to the invention.

[0118] Bleach boosters are preferably peroxo compounds. Bleach-boosting peroxo compounds according to the invention include neither addition products of hydrogen peroxide onto other components nor hydrogen peroxide itself. Selection of the peroxo compounds is not subject to any further limitations. Preferred peroxo compounds are peroxydisulfate salts, persulfate salts, (in particular ammonium peroxydisulfate, potassium peroxydisulfate, sodium peroxydisulfate, ammonium persulfate, potassium persulfate, sodium

persulfate, potassium peroxydiphosphate) and peroxides (such as barium peroxide and magnesium peroxide). Among these peroxo compounds, which may also be used in combination, it is the inorganic compounds which are preferred according to the invention. Peroxydisulfates, in particular ammonium peroxydisulfate, are particularly preferred.

[0119] The cosmetic preparations according to the invention preferably contain the bleach boosters in quantities of 5-30 wt.%, in particular in quantities of 8-20 wt.%.

[0120] If acting as bleaching agents, the cosmetic preparations of the invention contain as a preferred alkalizing agent at least one compound selected from ammonium, alkali metal and alkaline earth metal hydroxides, carbonates, hydrogencarbonates, hydroxycarbonates, metasilicates and carbamides together with alkali metal phosphates.

[0121] The cosmetic preparations used in the method according to the invention may furthermore contain any active ingredients, additives and auxiliary materials known for such preparations.

[0122] Rewashing with a shampoo is not required if a carrier with an elevated surfactant content has been used.

[0123] In many cases, the preparations contain at least one surfactant, with not only anionic but also in principle zwitterionic, ampholytic, nonionic and cationic surfactants being suitable. In many cases, however, it has proven advantageous to select the surfactants from among anionic, zwitterionic or nonionic surfactants.

[0124] Anionic surfactants which are suitable in the cosmetic preparations are any anionic surface-active substances suitable for use on the human body. These are characterized by an anionic water-solubilizing group such as for example a carboxylate, sulfate, sulfonate or phosphate group and a lipophilic alkyl group having approx. 10 to 22 C atoms. The molecule may additionally contain glycol or polyglycol ether groups, ester, ether and amide

groups and hydroxyl groups. Examples of suitable anionic surfactants are, in each case in the form of the sodium, potassium and ammonium and the mono-, di- and trialkanolammonium salts having 2 or 3 C atoms in the alkanol group,

- linear fatty acids having 10 to 22 C atoms (soaps),
- ether carboxylic acids of the formula $R\text{-}O\text{-}(CH_2\text{-}CH_2O)_x\text{-}CH_2\text{-}COOH$, in which R is a linear alkyl group having 10 to 22 C atoms and x = 0 or 1 to 16,
- acyl sarcosides having 10 to 18 C atoms in the acyl group,
- acyl taurides having 10 to 18 C atoms in the acyl group,
- acyl isethionates having 10 to 18 C atoms in the acyl group,
- sulfosuccinic acid mono- and dialkyl esters having 8 to 18 C atoms in the alkyl group and sulfosuccinic acid monoalkyl polyoxyethyl esters having 8 to 18 C atoms in the alkyl group and 1 to 6 oxyethyl groups,
- linear alkane sulfonates having 12 to 18 C atoms,
- linear alpha-olefin sulfonates having 12 to 18 C atoms,
- alpha-sulfofatty acid methyl esters of fatty acids having 12 to 18 C atoms,
- alkyl sulfates and alkyl polyglycol ether sulfates of the formula $R\text{-}O(CH_2\text{-}CH_2O)_x\text{-}SO_3H$, in which R is a preferably linear alkyl group having 10 to 18 C atoms and x = 0 or 1 to 12,
- anionic alkyl oligoglycosides or anionic alkenyl oligoglycoside derivatives, selected from alkyl and/or alkenyl oligoglycoside carboxylates, sulfates, phosphates and/or isethionates derived from alkyl and/or alkenyl oligoglycosides of the general formula (IX),

  $R\text{-}O\text{-}(G)_p$ (IX)

  with the meaning

  R $C_{6\text{-}22}$ alkyl or $C_{6\text{-}22}$ alkenyl,

  G glycoside unit which is derived from a sugar having 5 or 6 carbon atoms,

  p number from 1 to 10,

  in particular the lauryl glucoside carboxylate, as may be obtained as Plantapon® LGC from Cognis Deutschland,

- mixtures of surface-active hydroxysulfonates according to DE-A-37 25 030,
- sulfated hydroxyalkyl polyethylene and/or hydroxyalkylene propylene glycol ethers according to DE-A-37 23 354,
- sulfonates of unsaturated fatty acids having 12 to 24 C atoms and 1 to 6 double bonds according to DE-A-39 26 344,
- esters of tartaric acid and citric acid with alcohols, which are addition products of approx. 2-15 molecules of ethylene oxide and/or propylene oxide onto fatty alcohols having 8 to 22 C atoms.

[0125] Preferred anionic surfactants are alkyl sulfates, alkyl polyglycol ether sulfates and ether carboxylic acids having 10 to 18 C atoms in the alkyl group and up to 12 glycol ether groups per molecule and in particular salts of saturated and in particular unsaturated C_8-C_{22} carboxylic acids, such as oleic acid, stearic acid, isostearic acid and palmitic acid.

[0126] Nonionic surfactants contain as hydrophilic group for example a polyol group, a polyalkylene glycol ether group or a combination of a polyol group and polyglycol ether group. Such compounds are for example

- addition products of 2 to 30 mol of ethylene oxide and/or 0 to 5 mol of propylene oxide onto linear fatty alcohols having 8 to 22 C atoms, onto fatty acids having 12 to 22 C atoms and onto alkylphenols having 8 to 15 C atoms in the alkyl group,
- C_{12}-C_{22} fatty acid mono- and diesters of addition products of 1 to 30 mol of ethylene oxide onto glycerol,
- C_8-C_{22} alkyl mono- and oligoglycosides and the ethoxylated analogues thereof and
- addition products of 5 to 60 mol of ethylene oxide onto castor oil and hardened castor oil.

[0127] Preferred nonionic surfactants are alkylpolyglycosides of the general formula R^1O-$(Z)_x$. These compounds are characterized by the following parameters.

[0128] The alkyl residue R^1 contains 6 to 22 carbon atoms and may be both linear and branched. Primary linear aliphatic residues and those methyl-branched in position 2 are preferred. Such alkyl residues are for example 1-octyl, 1-decyl, 1-lauryl, 1-myristyl, 1-cetyl and 1-stearyl. 1-Octyl, 1-decyl, 1-lauryl, 1-myristyl are particularly preferred. When "oxo alcohols" are used as starting materials, compounds having an uneven number of carbon atoms in the alkyl chain predominate.

[0129] Alkylpolyglycosides usable according to the invention may for example contain only one specific alkyl residue R^1. Conventionally, however, these compounds are produced starting from natural fats and oils or mineral oils. In this case, alkyl residues R which are present are mixtures corresponding to the starting compounds or corresponding to the particular processing of these compounds.

[0130] Particularly preferred such alkylpolyglycosides are those in which R^1

- substantially consists of C_8 and C_{10} alkyl groups,
- substantially consists of C_{12} and C_{14} alkyl groups,
- substantially consists of C_8 to C_{16} alkyl groups or
- substantially consists of C_{12} to C_{16} alkyl groups.

[0131] The sugar building block Z used may be any desired mono- or oligosaccharides. Sugars having 5 or 6 carbon atoms and the corresponding oligosaccharides are conventionally used. Such sugars are for example glucose, fructose, galactose, arabinose, ribose, xylose, lyxose, allose, altrose, mannose, gulose, idose, talose and sucrose. Preferred sugar building blocks are glucose, fructose, galactose, arabinose and sucrose; glucose is particularly preferred.

[0132] Alkylpolyglycosides usable according to the invention contain on average 1.1 to 5 sugar units. Alkylpolyglycosides with x values of 1.1 to 1.6 are preferred. Alkylglycosides in which x is 1.1 to 1.4 are very particularly preferred.

[0133] In addition to their surfactant action, the alkylglycosides may also serve to improve the fixing of fragrance components to the hair. In the event that an action of the perfume oil on the hair extending beyond the duration of the hair treatment is desired, a person skilled in the art will preferably make use of this class of substances as a further constituent of the preparations according to the invention.

[0134] The alkoxylated homologues of the stated alkylpolyglycosides may also be used according to the invention. These homologues may contain on average up to 10 ethylene oxide and/or propylene oxide units per alkylglycoside unit.

[0135] Zwitterionic surfactants may furthermore be used, in particular as co-surfactants. Those surface-active compounds which bear at least one quaternary ammonium group and at least one $-COO^{(-)}$ or $-SO_3^{(-)}$ group on each molecule are designated as zwitterionic surfactants. Particularly suitable zwitterionic surfactants are "betaines" such as N-alkyl N,N-dimethylammonium glycinates, for example cocoalkyldimethylammonium glycinate, N-acylamino-propyl-N,N-dimethylammonium glycinates, for example cocoacylamino-propyldimethylammonium glycinate, and 2-alkyl-3-carboxymethyl-3-hydroxy-ethylimidazolines having in each case 8 to 18 C atoms in the alkyl or acyl group and cocoacylaminoethylhydroxyethylcarboxymethyl glycinate. One preferred zwitterionic surfactant is the fatty acid amide derivative known by the INCI name Cocamidopropyl Betaine.

[0136] Ampholytic surfactants are likewise in particular suitable as co-surfactants. Ampholytic surfactants are taken to mean those surface-active compounds which, in addition to a C_8-C_{18} alkyl or acyl group, contain at least one free amino group and at least one -COOH or $-SO_3H$ group per molecule and are capable of forming internal salts. Examples of suitable ampholytic surfactants are N-alkylglycines, N-alkylpropionic acids, N-alkylaminobutyric acids, N-alkyliminodipropionic acids, N-hydroxyethyl-N-alkylamidopropyl-glycines, N-alkyltaurines, N-alkylsarcosines, 2-alkylaminopropionic acids and

alkylaminoacetic acids having in each case approx. 8 to 18 C atoms in the alkyl group. Particularly preferred ampholytic surfactants are N-cocoalkyl amino-propionate, cocoacylaminoethyl aminopropionate and C_{12-18}-acyl sarcosine.

[0137] Cationic surfactants which are used according to the invention are in particular those of the quaternary ammonium compound, ester quat and amidoamine type.

[0138] Preferred quaternary ammonium compounds are ammonium halides, in particular chlorides and bromides, such as alkyltrimethylammonium chlorides, dialkyldimethylammonium chlorides and trialkylmethylammonium chlorides, for example cetyltrimethylammonium chloride, stearyltrimethyl-ammonium chloride, distearyldimethylammonium chloride, lauryldimethyl-ammonium chloride, lauryldimethylbenzylammonium chloride and tricetylmethylammonium chloride and imidazolinium compounds known by the INCI names Quaternium-27 and Quaternium-83. The long alkyl chains of the above-stated surfactants preferably comprise 10 to 18 carbon atoms.

[0139] Ester quats are known substances which contain both at least one ester function and at least one quaternary ammonium group as a structural element. Preferred ester quats are quaternized ester salts of fatty acids with triethanolamine, quaternized ester salts of fatty acids with diethanolalkylamines and quaternized ester salts of fatty acids with 1,2-dihydroxy-propyldialkylamines. Such products are distributed, for example, under the trademarks Stepantex®, Dehyquart® and Armocare®. The products Armocare® VGH-70, an N,N-bis(2-palmitoyloxyethyl)dimethylammonium chloride, and Dehyquart® F-75 and Dehyquart® AU-35 are examples of such ester quats.

[0140] The alkylamidoamines are conventionally produced by amidating natural or synthetic fatty acids and fatty acid cuts with dialkylaminoamines. One compound from this group of substances which is particularly suitable according to the invention is stearamidopropyldimethylamine, which is commercially available under the name Tegoamid® S 18.

[0141] Quaternized protein hydrolysates are further cationic surfactants which are usable according to the invention.

[0142] Cationic silicone oils are likewise suitable according to the invention, such as for example the commercially obtainable products Q2-7224 (manufacturer: Dow Corning; a stabilized trimethylsilylamodimethicone), Dow Corning 929 Emulsion (containing a hydroxylamine-modified silicone which is also designated an amodimethicone), SM-2059 (manufacturer: General Electric), SLM-55067 (manufacturer: Wacker) and Abil®-Quat 3270 and 3272 (manufacturer: Th. Goldschmidt; diquaternary polydimethylsiloxane, Quaternium-80).

[0143] One example of a quaternary sugar derivative usable as a cationic surfactant is the commercial product Glucquat®100, according to INCI nomenclature a "Lauryl Methyl Gluceth-10 Hydroxypropyl Dimonium Chloride".

[0144] The compounds with alkyl groups used as surfactant may in each case comprise uniform substances. It is, however, generally preferred to start from native plant or animal raw materials when producing these substances, such that mixtures of substances having a differing alkyl chain lengths depending on the particular raw material are obtained.

[0145] The surfactants, which are addition products of ethylene and/or propylene oxide onto fatty alcohols or derivatives of these addition products, may be used both as products with a "normal" homologue distribution and as products with a narrow homologue distribution. A "normal" homologue distribution is here taken to mean mixtures of homologues which are obtained on reacting fatty alcohol and alkylene oxide using alkali metals, alkali metal hydroxides or alkali metal alkoxides as catalysts. Narrow homologue distributions, in contrast, are obtained if hydrotalcite, alkaline earth metal salts of ether carboxylic acids, alkaline earth metal oxides, hydroxides or alkoxides are for example used as catalysts. It may be preferred to use products with a narrow homologue distribution.

[0146] The preparations according to the invention may additionally contain at least one silicone. Silicones, if present in the preparations according to the invention, are preferably contained in quantities of 0.05 to 5 wt.%, preferably of 0.2 to 5 wt.%, in each case relative to the ready-to-use preparation.

[0147] The silicones are particularly preferably selected from among at least one representative of the list made up of:

(i) polyalkylsiloxanes, polyarylsiloxanes, polyalkylarylsiloxanes, which are volatile or non-volatile, straight-chain, branched or cyclic, crosslinked or uncrosslinked;

(ii) polysiloxanes which contain in their general structure one or more organofunctional groups which are selected from:
   a) substituted or unsubstituted aminated groups;
   b) (per)fluorinated groups;
   c) thiol groups;
   d) carboxylate groups;
   e) hydroxylated groups;
   f) alkoxylated groups;
   g) acyloxyalkyl groups;
   h) amphoteric groups;
   i) bisulfite groups;
   j) hydroxyacylamino groups;
   k) carboxy groups;
   l) sulfonic acid groups; and
   m) sulfate or thiosulfate groups;

(iii) linear polysiloxane(A)/polyoxyalkylene(B) block copolymers of the type $(A\text{-}B)_n$ with $n > 3$;

(iv) grafted silicone polymers having an organic parent structure containing no silicone, which polymers consist of an organic main chain which is formed from organic monomers containing no silicone and onto which at least one polysiloxane macromer has been grafted in the chain and optionally onto at least one chain end;

(v) grafted silicone polymers having a polysiloxane parent structure onto which organic monomers containing no silicone have been grafted, which polymers comprise a polysiloxane main chain onto which at least one organic macromer containing no silicone has been grafted in the chain and optionally onto at least one of the ends thereof, such as for example the commercial product Abil B 8832 from Degussa which is distributed under INCI name Bis-PEG/PPG-20/20 Dimethicone;

(vi) or mixtures thereof.

[0148] Particularly preferred cosmetic or dermatological preparations according to the invention are characterized in that they contain at least one silicone of the formula (Si-1)

$$(CH_3)_3Si\text{-}[O\text{-}Si(CH_3)2]_x\text{-}O\text{-}Si(CH_3)_3 \qquad \text{(Si-1)},$$

in which x denotes a number from 0 to 100, preferably from 0 to 50, more preferably from 0 to 20 and in particular from 0 to 10.

[0149] Preferred cosmetic or dermatological preparations according to the invention contain a silicone of the above formula (Si-1). According to INCI nomenclature, these silicones are known as dimethicones. Silicones of the formula (Si-1) which are preferably used for the purposes of the present invention are the compounds:

$(CH_3)_3Si\text{-}O\text{-}Si(CH_3)_3$
$(CH_3)_3Si\text{-}O\text{-}(CH_3)_2Si\text{-}O\text{-}Si(CH_3)_3$
$(CH_3)_3Si\text{-}[O\text{-}(CH_3)_2Si]_2\text{-}O\text{-}Si(CH_3)_3$
$(CH_3)_3Si\text{-}[O\text{-}(CH_3)_2Si]_3\text{-}O\text{-}Si(CH_3)_3$
$(CH_3)_3Si\text{-}[O\text{-}(CH_3)_2Si]_4\text{-}O\text{-}Si(CH_3)_3$
$(CH_3)_3Si\text{-}[O\text{-}(CH_3)_2Si]_5\text{-}O\text{-}Si(CH_3)_3$
$(CH_3)_3Si\text{-}[O\text{-}(CH_3)_2Si]_6\text{-}O\text{-}Si(CH_3)_3$
$(CH_3)_3Si\text{-}[O\text{-}(CH_3)_2Si]_7\text{-}O\text{-}Si(CH_3)_3$
$(CH_3)_3Si\text{-}[O\text{-}(CH_3)_2Si]_8\text{-}O\text{-}Si(CH_3)_3$

$(CH_3)_3Si$-[O-$(CH_3)_2Si]_9$-O-$Si(CH_3)_3$
$(CH_3)_3Si$-[O-$(CH_3)_2Si]_{10}$-O-$Si(CH_3)_3$
$(CH_3)_3Si$-[O-$(CH_3)_2Si]_{11}$-O-$Si(CH_3)_3$
$(CH_3)_3Si$-[O-$(CH_3)_2Si]_{12}$-O-$Si(CH_3)_3$
$(CH_3)_3Si$-[O-$(CH_3)_2Si]_{13}$-O-$Si(CH_3)_3$
$(CH_3)_3Si$-[O-$(CH_3)_2Si]_{14}$-O-$Si(CH_3)_3$
$(CH_3)_3Si$-[O-$(CH_3)_2Si]_{15}$-O-$Si(CH_3)_3$
$(CH_3)_3Si$-[O-$(CH_3)_2Si]_{16}$-O-$Si(CH_3)_3$
$(CH_3)_3Si$-[O-$(CH_3)_2Si]_{17}$-O-$Si(CH_3)_3$
$(CH_3)_3Si$-[O-$(CH_3)_2Si]_{18}$-O-$Si(CH_3)_3$
$(CH_3)_3Si$-[O-$(CH_3)_2Si]_{19}$-O-$Si(CH_3)_3$
$(CH_3)_3Si$-[O-$(CH_3)_2Si]_{20}$-O-$Si(CH_3)_3$
with $(CH_3)_3Si$-O-$Si(CH_3)_3$, $(CH_3)_3Si$-O-$(CH_3)_2Si$-O-$Si(CH_3)_3$ and/or $(CH_3)_3Si$-[O-$(CH_3)_2Si]_2$-O-$Si(CH_3)_3$ being particularly preferred.

[0150] Mixtures of the above-stated silicones may of course be present in preferred preparations according to the invention.

[0151] Silicones which are preferably usable according to the invention exhibit viscosities at 20°C of 0.2 to 2 mm^2s^{-1}, with silicones having viscosities of 0.5 to 1 mm^2s^{-1} being particularly preferred.

[0152] Particularly preferred preparations according to the invention contain one or more amino-functional silicones. Such silicones may, for example, be described by the formula (Si-2)

$$M(R_aQ_bSiO_{(4-a-b)/2})_x(R_cSiO_{(4-c)/2})_yM \qquad \text{(Si-2)}$$

wherein in the above formula

R is a hydrocarbon or a hydrocarbon residue with 1 to approx. 6 carbon atoms,

Q is a polar residue of the general formula $-R^1HZ$,
in which

R^1 is a divalent connecting group which is joined to hydrogen and the residue Z and is composed of carbon and hydrogen atoms, carbon, hydrogen and oxygen atoms or carbon, hydrogen and nitrogen atoms, and

Z is an organic, amino-functional residue which contains at least one amino-functional group;

a assumes values in the range from approx. 0 to approx. 2,

b assumes values in the range from approx. 1 to approx. 3,

a + b is less than or equal to 3, and

c is a number in the range from approx. 1 to approx. 3, and

x is a number in the range from 1 to approx. 2,000, preferably from approx. 3 to approx. 50 and most preferably from approx. 3 to approx. 25, and

y is a number in the range from approx. 20 to approx. 10,000, preferably from approx. 125 to approx. 10,000 and most preferably from approx. 150 to approx. 1,000, and

M is a suitable silicone end group as known from the prior art, preferably trimethylsilyl.

[0153] Non-limiting examples of the residues represented by R in the formula (Si-2) include alkyl residues, such as methyl, ethyl, propyl, isopropyl, isopropyl, butyl, isobutyl, amyl, isoamyl, hexyl, isohexyl and the like; alkenyl residues, such as vinyl, halovinyl, alkylvinyl, allyl, haloallyl, alkylallyl; cycloalkyl residues, such as cyclobutyl, cyclopentyl, cyclohexyl and the like; phenyl residues, benzyl residues, halogenated hydrocarbon residues, such as 3-chloropropyl, 4-bromobutyl, 3,3,3-trifluoropropyl, chlorocyclohexyl, bromophenyl, chlorophenyl and the like and sulfur-containing residues, such as mercaptoethyl, mercaptopropyl, mercaptohexyl, mercaptophenyl and the like; R is preferably an alkyl residue containing 1 to approx. 6 carbon atoms, and R is most preferably methyl. Examples of R^1 include methylene, ethylene, propylene, hexamethylene, decamethylene, $-CH_2CH(CH_3)CH_2-$, phenylene, naphthylene, $-CH_2CH_2SCH_2CH_{2-}$, $-CH_2CH_2OCH_2-$, $-OCH_2CH_2-$, -

$OCH_2CH_2CH_2$-, -$CH_2CH(CH_3)C(O)OCH_2$-, -$(CH_2)_3CC(O)OCH_2CH_2$-, -$C_6H_4C_6H_4$-, -$C_6H_4CH_2C_6H_4$-; and -$(CH_2)_3C(O)SCH_2CH_2$-.

[0154] According to the formula (Si-2), Z is an organic, amino-functional residue containing at least one functional amino group. One possible formula for said Z is $NH(CH_2)_zNH_2$, in which z is an integer greater than or equal to 1. Another possible formula for said Z is -$NH(CH_2)_z(CH_2)_{zz}NH$, in which both z and zz are mutually independently an integer greater than or equal to 1, this structure comprising diamino ring structures, such as piperazinyl. Said Z is most preferably an -$NHCH_2CH_2NH_2$ residue. Another possible formula for said Z is -$N(CH_2)_z(CH_2)_{zz}NX_2$ or -NX_2, in which each X of X_2 is independently selected from the group consisting of hydrogen and alkyl groups having 1 to 12 carbon atoms, and zz is 0.

[0155] Q according to the formula (Si-2) is most preferably a polar amino-functional residue of the formula -$CH_2CH_2CH_2NHCH_2CH_2NH_2$.

[0156] In the formula (Si-2), a assumes values in the range from 0 to 2, b assumes values in the range from 2 to 3, a + b is less than or equal to 3, and c is a number in the range from 1 to 3. The molar ratio of the $R_aQ_bSiO_{(4-a-b)/2}$ units to the $R_cSiO_{(4-c)/2}$ units in the formula (Si-2) is in the range from approx 1:2 to 1:65, preferably from approx. 1:5 to approx. 1:65 and most preferably from approx. 1:15 to approx. 1:20. If one or more silicones of the above formula (Si-2) are used, then the various variable substituents in the above formula may be different in the various silicone components which are present in the silicone mixture.

[0157] Preferred cosmetic or dermatological preparations according to the invention contain an amino-functional silicone of the formula (Si-3)

$$R_aG_{3-a}\text{-}Si(OSiG_2)_n\text{-}(OSiG_bR'_{2-b})_m\text{-}O\text{-}SiG_{3-a}\text{-}R'_a \quad \text{(Si-3)},$$

in which:

G is -H, a phenyl group, -OH, -O-CH_3, -CH_3, -O-CH_2CH_3, -CH_2CH_3, -O-$CH_2CH_2CH_3$, -$CH_2CH_2CH_3$, -O-$CH(CH_3)_2$, -$CH(CH_3)_2$, -O-$CH_2CH_2CH_2CH_3$, -$CH_2CH_2CH_2CH_3$, -O-$CH_2CH(CH_3)_2$, -$CH_2CH(CH_3)_2$, -O-$CH(CH_3)CH_2CH_3$, -$CH(CH_3)CH_2CH_3$, -O-$C(CH_3)_3$, -$C(CH_3)_3$;

a denotes a number between 0 and 3, in particular 0;

b denotes a number between 0 and 1, in particular 1,

m and n are numbers, the sum of which (m + n) amounts to between 1 and 2000, preferably between 50 and 150, with n preferably assuming values from 0 to 1999 and in particular from 49 to 149 and m preferably assuming values from 1 to 2000, in particular from 1 to 10,

R' is a monovalent residue selected from

-Q-N(R")-CH_2-CH_2-N(R")$_2$

-Q-N(R")$_2$

-Q-N^+(R")$_3A^-$

-Q-N^+H(R")$_2A^-$

-Q-N^+H_2(R")A^-

-Q-N(R")-CH_2-CH_2-N^+R"H_2A^-,

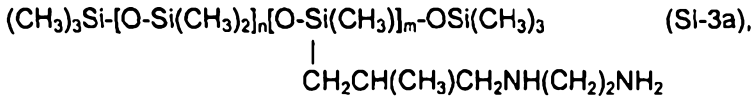
wherein each Q denotes a chemical bond, -CH_2-, -CH_2-CH_2-, -$CH_2CH_2CH_2$-, -$C(CH_3)_2$-, -$CH_2CH_2CH_2CH_2$-, -$CH_2C(CH_3)_2$-, -$CH(CH_3)CH_2CH_2$-,

R" denotes identical or different residues from the group -H, -phenyl, -benzyl, -CH_2-$CH(CH_3)$Ph, C_{1-20} alkyl residues, preferably -CH_3, -CH_2CH_3, -$CH_2CH_2CH_3$, -$CH(CH_3)_2$, -$CH_2CH_2CH_2H_3$, -$CH_2CH(CH_3)_2$, -$CH(CH_3)CH_2CH_3$, -$C(CH_3)_3$, and A represents an anion which is preferably selected from chloride, bromide, iodide or methosulfate.

[0158] Cationic silicone oils which are suitable according to the invention are for example the commercially available Dow Corning 929 Emulsion (containing a hydroxylamine-modified silicone which is designated amodimethicone), DC 2-2078 (manufacturer Dow Corning, INCI name:

Aminopropyl Phenyl Trimethicone), DC 5-7113 (manufacturer Dow Corning, INCI name: Silicone Quaternium 16), SM-2059 (manufacturer: General Electric), SLM-55067 (manufacturer: Wacker) and Abil®-Quat 3270 and 3272 (manufacturer: Th. Goldschmidt; diquaternary polydimethylsiloxanes, Quaternium-80).

[0159] Particularly preferred preparations according to the invention are characterized in that they contain at least one amino-functional silicone of the formula (Si3-a)



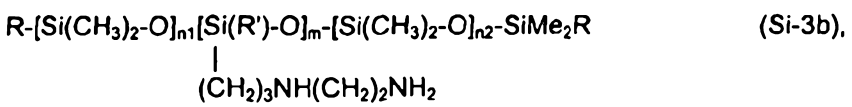
$(CH_3)_3Si\text{-}[O\text{-}Si(CH_3)_2]_n[O\text{-}Si(CH_3)]_m\text{-}OSi(CH_3)_3$ (Si-3a),

$CH_2CH(CH_3)CH_2NH(CH_2)_2NH_2$

in which m and n are numbers, the sum of which (m + n) amounts to between 1 and 2000, preferably between 50 and 150, with n preferably assuming values from 0 to 1999 and in particular from 49 to 149 and m preferably assuming values from 1 to 2000, in particular from 1 to 10.

[0160] According to the INCI declaration, these silicones are designated trimethylsilylamodimethicones and are obtainable for example under the name Q2-7224 (manufacturer: Dow Corning; a stabilized trimethyl-silylamodimethicone).

[0161] Preparations according to the invention which are particularly preferred are those which contain least one amino-functional silicone of the formula (Si-3b)



$R\text{-}[Si(CH_3)_2\text{-}O]_{n1}[Si(R')\text{-}O]_m\text{-}[Si(CH_3)_2\text{-}O]_{n2}\text{-}SiMe_2R$ (Si-3b),

$(CH_2)_3NH(CH_2)_2NH_2$

in which

R denotes -OH, an (optionally ethoxylated and/or propoxylated) (C_1 to C_{20}) alkoxy group or a $-CH_3$ group,

R' denotes -OH, a (C_1 to C_{20}) alkoxy group or a $-CH_3$ group and

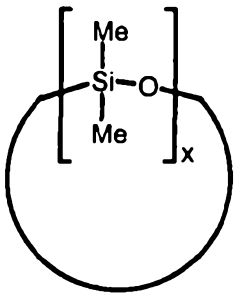
m, n1 and n2 are numbers, the sum of which (m + n1 + n2) amounts to between 1 and 2000, preferably between 50 and 150, with the sum of (n1 + n2) preferably assuming values from 0 to 1999 and in particular from 49 to 149 and m preferably assuming values from 1 to 2000, in particular from 1 to 10.

[0162] According to the INCI declaration, these silicones designated amodimethicones or functionalized amodimethicones, such as for example bis(C13-15 alkoxy) PG amodimethicone (for example obtainable as a commercial product: DC 8500 from Dow Corning), trideceth-9 PG-amodimethicone (for example obtainable as a commercial product Silcare Silicone SEA from Clariant).

[0163] Irrespective of which amino-functional silicones are used, preferred cosmetic or dermatological preparations according to the invention are those which contain an amino-functional silicone, the amine value of which is above 0.25 meq/g, preferably above 0.3 meq/g and in particular above 0.4 meq/g. The amine value here denotes milliequivalents of amine per gram of amino-functional silicone. It can be determined by titration and may also be stated in the unit mg of KOH/g.

[0164] Cosmetic or dermatological preparations which are preferred according to the invention are characterized in that, relative to their weight, they contain 0.01 to 10 wt.%, preferably 0.1 to 8 wt.%, particularly preferably 0.25 to 7.5 wt.% and in particular 0.5 to 5 wt.% of amino-functional silicone(s).

[0165] The cyclic dimethicones designated according to INCI as cyclomethicones may preferably be used according to the invention. Cosmetic or dermatological preparations which are preferred according to the invention are those which contain at least one silicone of the formula (Si-4)



(Si-4)

in which x denotes a number from 0 to 200, preferably from 0 to 10, more preferably from 0 to 7 and in particular 0, 1, 2, 3, 4, 5 or 6.

[0166] The above-described silicones comprise a backbone which is made up of -Si-O-Si units. These Si-O-Si units may, of course, also be interrupted by carbon chains. Corresponding molecules are obtainable by chain extension reactions and are preferably used in the form of silicone-in-water emulsions.

[0167] Silicone-in-water emulsions which are usable according to the invention may be produced using known methods, as are for example disclosed in US 5,998,537 and EP 0 874 017 A1.

[0168] In brief, this production method involves emulsifying mixing of components, one of which contains at least one polysiloxane, the other of which contains at least one organosilicone material which reacts with the polysiloxane in a chain extension reaction, with at least one metal ion-containing catalyst for the chain extension reaction, at least one surfactant and water being present.

[0169] Chain extension reactions with polysiloxanes are known and may for example involve the hydrosilylation reaction, in which an Si-H group reacts with an aliphatically unsaturated group in the presence of a platinum/rhodium catalyst with formation of polysiloxanes with a few Si-$(C)_p$-Si bonds (p = 1-6), the polysiloxanes also being designated polysiloxane-polysilalkylene copolymers.

[0170] The chain extension reaction may also involve the reaction of an Si-OH group (for example a hydroxy-terminated polysiloxane) with an alkoxy group (for example alkoxysilanes, silicates or alkoxysiloxanes) in the presence of a metal-containing catalyst with formation of polysiloxanes.

[0171] The polysiloxanes which are used in the chain extension reaction comprise a substantially linear polymer of the following structure:
$R\text{-}Si(R_2)\text{-}[O\text{-}Si(R_2)\text{-}]_n\text{-}O\text{-}SiR_3$
In this structure, each R mutually independently denotes a hydrocarbon residue having up to 20 carbon atoms, preferably having 1 to 6 C atoms, such as for example an alkyl group (for example methyl, ethyl, propyl or butyl), an aryl group (for example phenyl), or the group required for the chain extension reaction ("reactive group", for example Si-bound H atoms, aliphatically unsaturated groups such as vinyl, allyl or hexenyl, hydroxy, alkoxy such as methoxy, ethoxy or propoxy, alkoxy-alkoxy, acetoxy, amino etc.), with the proviso, that on average one to two reactive groups are present per polymer, n is a positive number >1. A majority of the reactive groups, particularly preferably >90%, and in particular >98% of the reactive groups, are preferably attached to the terminal Si atoms in the siloxane. n preferably denotes numbers which describe polysiloxanes having viscosities of between 1 and 1,000,000 mm^2/s, particularly preferably viscosities of between 1,000 and 100,000 mm^2/s.

[0172] The polysiloxanes may be slightly branched (for example <2 mol% of the siloxane units) or alternatively the polymers are substantially linear, particularly preferably completely linear. The substituents R may themselves in turn be substituted, for example with nitrogenous groups (for example amino groups), epoxy groups, S-containing groups, Si-containing groups, O-containing groups etc.. At least 80% of the residues R are preferably alkyl residues, particularly preferably methyl groups.

[0173] The organosilicone material which reacts with the polysiloxane in the chain extension reaction may either be a second polysiloxane or a molecule which acts as a chain extender. If the organosilicone material is a polysiloxane,

it has the above-mentioned general structure. In these cases, one polysiloxane in the reaction has (at least) one reactive group and a second polysiloxane has (at least) one second reactive group which reacts with the first.

[0174] If the organosilicone material comprises a chain extension agent, the latter may be a material such as for example a silane, a siloxane (for example disiloxane or trisiloxane) or a silazane. A composition which comprises a polysiloxane according to the above-described general structure which comprises at least one Si-OH group may accordingly for example be chain-extended by reacting an alkoxysilane (for example a dialkoxysilane or trialkoxysilane) in the presence of tin- or titanium-containing catalysts.

[0175] The metal-containing catalysts in the chain extension reaction are usually specific for a certain reaction. Such catalysts are known in the prior art and contain for example metals such as platinum, rhodium, tin, titanium, copper, lead, etc.. In a preferred chain extension reaction, a polysiloxane with at least one aliphatically unsaturated group, preferably an end group, is reacted with an organosilicone material in the presence of a hydrosilylation catalyst which is a siloxane or polysiloxane with at least one (preferably terminal) Si-H group. The polysiloxane has at least one aliphatically unsaturated group and complies with the above-stated general formula, in which R and n are as defined above, with on average between 1 and 2 groups R per polymer having an aliphatically unsaturated group. Representative aliphatically unsaturated groups are for example vinyl, allyl, hexenyl and cyclohexenyl or a group $R^2CH=CHR^3$, in which R^2 denotes a divalent aliphatic chain attached to the silicon and R^3 denotes a hydrogen atom or an alkyl group. The organosilicone material with at least one Si-H group preferably has the above-stated structure, in which R and n are as defined above and with on average between 1 and 2 groups R meaning hydrogen and n being 0 or a positive integer.

[0176] This material may be a polymer or a low molecular weight material such as a siloxane (for example a disiloxane or a trisiloxane).

[0177] The polysiloxane with at least one aliphatically unsaturated group and the organosilicone material with at least one Si-H group react in the presence of a hydrosilylation catalyst. Such catalysts are known from the prior art and comprise for example platinum- and rhodium-containing materials. The catalysts may assume any known form, for example platinum or rhodium applied onto supports (such as for example silica gel or activated carbon) or other suitable compounds such as platinum chloride or salts of platinum or chloroplatinic acids. One catalyst which is preferred due to its good dispersibility in organosilicone systems and the slight color change is chloroplatinic acid either as the commercially available hexahydrate or in anhydrous form.

[0178] In a further preferred chain extension reaction, a polysiloxane with at least one Si-OH group, preferably an end group, is reacted with an organosilicone material which has at least one alkoxy group, preferably a siloxane with at least one Si-OR group or an alkoxysilane with at least two alkoxy groups. A metal-containing catalyst is here again used as catalyst.

[0179] Many catalysts are known from the literature for reacting an Si-OH group with an Si-OR group, for example organometallic compounds such as organotin salts, titanates or titanium chelates or complexes. Examples include tin octoate, dibutyltin dilaurate, dibutyltin diacetate, dimethyltin dineodecanoate, dibutyltin dimethoxide, isobutyltin triceroate, dimethyltin dibutyrate, dimethyltin dineodecanoate, triethyltin tartrate, tin oleate, tin naphthenate, tin butyrate, tin acetate, tin benzoate, tin sebacate, tin succinate, tetrabutyl titanate, tetraisopropyl titanate, tetraphenyl titanate, tetraoctadecyl titanate, titanium naphthenate, ethyltriethanolamine titanate, titanium diisopropyl diethyl acetoacetate, titanium diisopropoxydiacetyl acetonate and titanium tetra-alkoxides, in which the alkoxide is butoxy or propoxy.

[0180] Preparations which are likewise preferred according to the invention are those which are characterized in that they contain at least one silicone of the formula (Si-5)

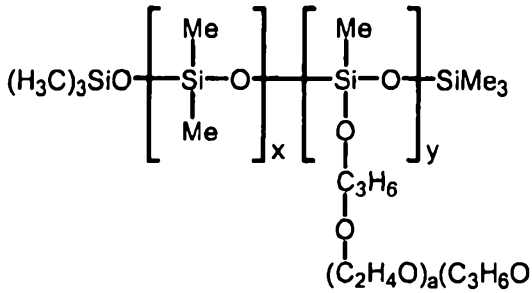
$R_3Si\text{-}[O\text{-}SiR_2]_x\text{-}(CH_2)_n\text{-}[O\text{-}SiR_2]_y\text{-}O\text{-}SiR_3$ (Si-5),

in which R denotes identical or different residues from the group -H, -phenyl, -benzyl, $-CH_2\text{-}CH(CH_3)Ph$, $C_{1\text{-}20}$ alkyl residues, preferably $-CH_3$, $-CH_2CH_3$, $-CH_2CH_2CH_3$, $-CH(CH_3)_2$, $-CH_2CH_2CH_2H_3$, $-CH_2CH(CH_3)_2$, $-CH(CH_3)CH_2CH_3$, $-C(CH_3)_3$, x and y denote a number from 0 to 200, preferably from 0 to 10, more preferably from 0 to 7 and in particular 0, 1, 2, 3, 4, 5 or 6, and n denotes a number from 0 to 10, preferably from 1 to 8 and in particular 2, 3, 4, 5, 6.

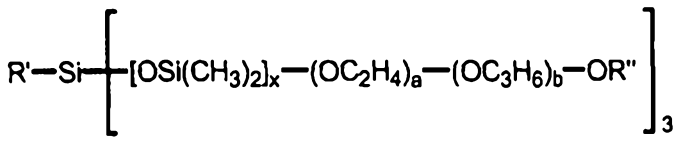
[0181] The silicones are preferably water-soluble. Preparations of the embodiment with a silicone which are preferred according to the invention are characterized in that the silicone is water-soluble.

[0182] Corresponding hydrophilic silicones are selected, for example, from the compounds of the formulae (Si-6) and/or (Si-7). Particularly preferred water-soluble silicone-based surfactants are selected from the group of dimethicone copolyols which are preferably alkoxylated, in particular polyethoxylated or polypropoxylated.

[0183] According to the invention, dimethicone copolyols are preferably taken to mean polyoxyalkylene-modified dimethylpolysiloxanes of the general formulae (Si-6) or (Si-7):



(Si-6)



(Si-7)

in which

- the residue R denotes a hydrogen atom, an alkyl group having 1 to 12 C atoms, an alkoxy group having 1 to 12 C atoms or a hydroxyl group,

- the residues R' and R" mean alkyl groups having 1 to 12 C atoms,
- x denotes an integer from 1 to 100, preferably from 20 to 30,
- y denotes an integer from 1 to 20, preferably from 2 to 10 and
- a and b denote integers from 0 to 50, preferably from 10 to 30.

[0184] Compounds which fall within the above-stated formulae are disclosed in the following patent applications, to which reference is explicitly made: US-A-4,122,029; US-A- 4,265,878; US-A-4,421,769 and GB-A-2,066,659.

[0185] Dimethicone copolyols which are particularly preferred for the purposes of the invention are for example the products commercially distributed under the trade name SILWET (Union Carbide Corporation) and DOW CORNING (Dow).

[0186] Dimethicone copolyols which are particularly preferred according to the invention are Dow Corning 190 and Dow Corning 193 (Dow).

[0187] Preferred preparations according to the invention additionally contain in a cosmetic carrier, apart from the combination of (a) at least one oxidizing agent (preferably hydrogen peroxide) and (b) at least one compound from the group formed by α-lipoic acid and the derivatives thereof, one of the following active ingredient combinations (i) to (xxvii):

(i) at least one color-modifying component and at least one silicone,

(ii) at least one color-modifying component and at least one aminated silicone,

(iii) at least one color-modifying component and at least one silicone of the formula (Si-1),

(iv) at least one color-modifying component and at least one silicone of the formula (Si-2),

(v) at least one color-modifying component and at least one silicone of the formula (Si-3),

(vi) at least one color-modifying component and at least one silicone of the formula (Si-4),

(vii) at least one color-modifying component and at least one silicone of the formula (Si-5),

(viii) at least one color-modifying component and at least one silicone of the formula (Si-6),

(ix) at least one color-modifying component and at least one silicone of the formula (Si-7)

(x) at least one developer component (and optionally a coupler component) and at least one silicone,

(xi) at least one developer component (and optionally a coupler component) and at least one aminated silicone,

(xii) at least one developer component (and optionally a coupler component) and at least one silicone of the formula (Si-1),

(xiii) at least one developer component (and optionally a coupler component) and at least one silicone of the formula (Si-2),

(xiv) at least one developer component (and optionally a coupler component) and at least one silicone of the formula (Si-3),

(xv) at least one developer component (and optionally a coupler component) and at least one silicone of the formula (Si-4),

(xvi) at least one developer component (and optionally a coupler component) and at least one silicone of the formula (Si-5),

(xvii) at least one developer component (and optionally a coupler component) and at least one silicone of the formula (Si-6),

(xviii) at least one developer component (and optionally a coupler component) and at least one silicone of the formula (Si-7),

(xix) at least one bleach booster and at least one silicone,

(xx) at least one bleach booster and at least one aminated silicone,

(xxi) at least one bleach booster and at least one silicone of the formula (Si-1),

(xxii) at least one bleach booster and at least one silicone of the formula (Si-2),

(xxiii) at least one bleach booster and at least one silicone of the formula (Si-3),

(xxiv) at least one bleach booster and at least one silicone of the formula (Si-4),

(xxv) at least one bleach booster and at least one silicone of the formula (Si-5),

(xxvi) at least one bleach booster and at least one silicone of the formula (Si-6),

(xxvii) at least one bleach booster and at least one silicone of the formula (Si-7).

[0188] The preparations according to the invention may additionally contain at least one protein hydrolysate. Protein hydrolysates are product mixtures which are obtained by acidically, basically or enzymatically catalyzed degradation of proteins.

[0189] Protein hydrolysates of both plant and animal origin may be used according to the invention.

[0190] Animal protein hydrolysates are for example elastin, collagen, keratin, silk and milk protein hydrolysates which may also assume salt form. Such products are distributed, for example, under the trademarks Keratin DEC® (Vincience), Dehylan® (Cognis), Promois® (Interorgana), Collapuron® (Cognis), Nutrilan® (Cognis), Gelita-Sol® (Deutsche Gelatine Fabriken Stoess & Co), Lexein® (Inolex) and Kerasol® (Croda).

[0191] It is preferred according to the invention to use protein hydrolysates of plant origin, for example soy, almond, rice, pea, potato and wheat protein hydrolysates. Such products are obtainable, for example, under the trademarks Gluadin® (Cognis), DiaMin® (Diamalt), Lexein® (Inolex) and Crotein® (Croda).

[0192] Although the use of protein hydrolysates is preferred per se, amino acid mixtures or individual amino acids such as for example arginine, lysine, histidine or pyroglutamic acid obtained in a different manner may optionally also be used instead. It is likewise possible to use derivatives of

protein hydrolysates, for example in the form of the fatty acid condensation products thereof. Such products are distributed, for example, under the names Lamepon® (Cognis), Gluadin® (Cognis), Lexein® (Inolex), Crolastin® (Croda) or Crotein® (Croda).

[0193] The protein hydrolysates are preferably present in a quantity of 0.05 to 5 wt.%, particularly preferably from 0.5 to 2.0 wt.%, in each case relative to the weight of the ready-to-use preparation.

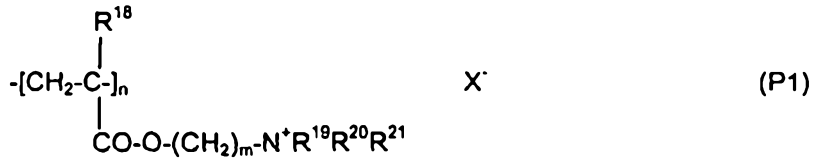
[0194] Preferred preparations according to the invention additionally contain in a cosmetic carrier, apart from the combination of (a) at least one oxidizing agent (preferably hydrogen peroxide) and (b) at least one compound from the group formed by α-lipoic acid and the derivatives thereof, one of the following active ingredient combinations (i) to (xii):

(i) at least one color-modifying component and at least one protein hydrolysate,
(ii) at least one color-modifying component and at least one wheat protein hydrolysate,
(iii) at least one color-modifying component and at least one silk protein hydrolysate,
(iv) at least one color-modifying component and at least one collagen protein hydrolysate,
(v) at least one developer component (and optionally a coupler component) and at least one protein hydrolysate,
(vi) at least one developer component (and optionally a coupler component) and at least one wheat protein hydrolysate,
(vii) at least one developer component (and optionally a coupler component) and at least one silk protein hydrolysate,
(viii) at least a developer component (and optionally a coupler component) and at least one collagen protein hydrolysate,
(ix) at least one bleach booster and at least one protein hydrolysate,
(X) at least one bleach booster and at least one wheat protein hydrolysate,
(xi) at least one bleach booster and at least one silk protein hydrolysate,

(xii) at least one bleach booster and at least one collagen protein hydrolysate.

[0195] In a further embodiment, the preparations according to the invention additionally contain at least one cationic and/or at least one amphoteric polymer.

[0196] Cationic polymers are polymers which comprise groups in the main and/or side chain which may be "temporarily" or "permanently" cationic. Polymers which are designated "permanently cationic" according to the invention are those which, irrespective of the pH value of the preparation, comprise a cationic group. As a rule, these are polymers which contain a quaternary nitrogen atom, for example in the form of an ammonium group. Preferred cationic groups are quaternary ammonium groups. Polymers which have proven particularly suitable are those in which the quaternary ammonium group is bound via a C_{1-4} hydrocarbon group to a main polymer chain synthesized from acrylic acid, methacrylic acid or the derivatives thereof. Homopolymers of the general formula (P1),



(P1)

in which R^{18} is -H or $-CH_3$, R^{19}, R^{20} and R^{21} are mutually independently selected from C_{1-4} alkyl, alkenyl or hydroxyalkyl groups, m = 1, 2, 3 or 4, n is a natural number and X^- a physiologically acceptable organic or inorganic anion, and copolymers substantially consisting of the monomer units listed in formula (P1) and nonionogenic monomer units are particularly preferred cationic polymers. In the context of these polymers, those which are preferred according to the invention are those for which at least one of the following conditions applies:

- R^{18} denotes a methyl group
- R^{19}, R^{20} and R^{21} denote methyl groups
- m has the value 2.

[0197] Physiologically acceptable counterions X^- which may, for example, be considered are halide ions, sulfate ions, phosphate ions, methosulfate ions and organic ions such as lactate, citrate, tartrate and acetate ions. Halide ions, in particular chloride, are preferred.

[0198] A particularly suitable homopolymer is poly(methacryloyloxyethyltrimethylammonium chloride), which may if desired be crosslinked, with the INCI name of polyquaternium-37. Crosslinking may if desired proceed with the assistance of olefinically polyunsaturated compounds, for example divinylbenzene, tetraallyloxyethane, methylenebisacrylamide, diallyl ether polyallyl polyglyceryl ether, or allyl ethers of sugars or sugar derivatives such as erythritol, pentaerythritol, arabitol, mannitol, sorbitol, sucrose or glucose. Methylenebisacrylamide is a preferred crosslinking agent.

[0199] The homopolymer is preferably used in the form of a nonaqueous polymer dispersion which should have a polymer fraction of no less than 30 wt.%. Such polymer dispersions are commercially available under the names Salcare® SC 95 (approx. 50% polymer fraction, further components: mineral oil (INCI name: Mineral Oil) and tridecyl-polyoxypropylene-polyoxyethylene ether (INCI name: PPG-1-Trideceth-6)) and Salcare® SC 96 (approx. 50% polymer fraction, further components: mixture of diesters of propylene glycol with a mixture of caprylic and capric acid (INCI name: Propylene Glycol Dicaprylate/Dicaprate) and tridecyl-polyoxypropylene-polyoxyethylene ether (INCI name: PPG-1-Trideceth-6)).

[0200] Copolymers with monomer units according to the formula (P1) preferably contain acrylamide, methacrylamide, acrylic acid C_{1-4} alkyl esters and methacrylic acid C_{1-4} alkyl esters as nonionogenic monomer units. Acrylamide is particularly preferred among these nonionogenic monomers. These copolymers, as described above for the homopolymers, may also be crosslinked. A copolymer which is preferred according to the invention is crosslinked acrylamide-methacryloyloxyethyltrimethylammonium chloride copolymer. Such copolymers, in which the monomers are present in a weight

ratio of approx 20:80, are commercially available as approx. 50% nonaqueous polymer dispersions under the name Salcare® SC 92.

[0201] Further preferred cationic polymers are for example

- quaternized cellulose derivatives, as are commercially available under the names Celquat® and Polymer JR®. The compounds Celquat® H 100, Celquat® L 200 and polymer JR®400 are preferred quaternized cellulose derivatives,
- cationized honey, for example the commercial product Honeyquat® 50,
- cationic guar derivatives, such as in particular the products distributed under the trade names Cosmedia®Guar and Jaguar®,
- polysiloxanes with quaternary groups, such as for example the commercially available products Q2-7224 (manufacturer: Dow Corning; a stabilized trimethylsilylamodimethicone),
- Dow Corning® 929 Emulsion (containing a hydroxylamino-modified silicone, which is also designated an amodimethicone), SM-2059 (manufacturer: General Electric), SLM-55067 (manufacturer: Wacker) and Abil®-Quat 3270 and 3272 (manufacturer: Th. Goldschmidt; diquaternary polydimethylsiloxanes, Quaternium-80),
- polymeric dimethyldiallylammonium salts and the copolymers thereof with esters and amides of acrylic acid and methacrylic acid. The products commercially available under the names Merquat®100 (poly(dimethyldiallylammonium chloride)) and Merquat®550 (dimethyl-diallylammonium chloride-acrylamide copolymer) are examples of such cationic polymers,
- copolymers of vinylpyrrolidone with quaternized derivatives of dialkylaminoalkyl acrylate and methacrylate, such as for example vinyl-pyrrolidone-dimethylaminoethyl methacrylate copolymers quaternized with diethyl sulfate. Such compounds are commercially available under the names Gafquat®734 and Gafquat®755,
- vinylpyrrolidone-vinylimidazolium methochloride copolymers, as are offered for sale under the names Luviquat® FC 370, FC 550, FC 905 and HM 552,

- quaternized polyvinyl alcohol,

and the polymers known under the names

- Polyquaternium 2 (for example Mirapol® A-15 from Rhodia),
- Polyquaternium 17
- Polyquaternium 18 and
- Polyquaternium 27 with quaternary nitrogen atoms in the polymer main chain.

[0202] The polymers known under the names Polyquaternium-24 (commercial product, for example Quatrisoft® LM 200) may also be used as cationic polymers. Copolymers of vinylpyrrolidone, as are available as commercial products Copolymer 845 (manufacturer: ISP), Gaffix® VC 713 (manufacturer: ISP), Gafquat®ASCP 1011, Gafquat®HS 110, Luviquat®8155 and Luviquat® MS 370 may likewise be used according to the invention.

[0203] Further cationic polymers according to the invention are "temporarily cationic" polymers. These polymers conventionally contain an amino group which at specific pH values assumes the form of a quaternary ammonium group and is thus cationic. Chitosan and the derivatives thereof are for example preferred, as are readily commercially available for example under the trade names Hydagen® CMF, Hydagen® HCMF, Kytamer® PC and Chitolam® NB/101. Chitosans are deacetylated chitins which are commercially available in various degrees of deacetylation and various degrees of degradation (molecular weights). The production thereof is described, for example, in DE 44 40 625 A1 and in DE 1 95 03 465 A1

[0204] Particularly highly suitable chitosans exhibit a degree of deacetylation of at least 80% and a molecular weight of $5 \cdot 10^5$ to $5 \cdot 10^6$ (g/mol).

[0205] In order to produce preparations according to the invention, the chitosan must be converted into the salt form. This may proceed by dissolution in dilute aqueous acids. Suitable acids are both mineral acids such as for example hydrochloric acid, sulfuric acid and phosphoric acid and organic acids,

for example low molecular weight carboxylic acids, polycarboxylic acids and hydroxycarboxylic acids. Relatively high molecular weight alkylsulfonic acids or alkylsulfuric acids or organophosphoric acids may furthermore be used, provided that they have the necessary physiological acceptability. Suitable acids for converting the chitosans into the salt form are for example acetic acid, glycolic acid, tartaric acid, malic acid, citric acid, lactic acid, 2-pyrrolidinone-5-carboxylic acid, benzoic acid or salicylic acid. Low molecular weight hydroxycarboxylic acids such as for example glycolic acid or lactic acid are preferably used.

[0206] Amphoteric polymers are taken to mean those polymers

- which contain both free amino groups and free -COOH- or SO_3H groups in each molecule and are capable of forming internal salts,
- zwitterionic polymers which contain quaternary ammonium groups and $-COO^-$ groups or $-SO_3^-$ groups in each molecule, and
- polymers which contain -COOH groups or SO_3H groups and quaternary ammonium groups.

The polymers with quaternary ammonium groups stated in the list are preferably used according to the invention as amphoteric polymers.

[0207] One example of an amphoteric polymer usable according to the invention is the acrylic resin obtainable under the name Amphomer®, which is a copolymer of tert.-butylaminoethyl methacrylate, N-(1,1,3,3-tetramethylbutyl)-acrylamide and two or more monomers from the group acrylic acid, methacrylic acid and the simple esters thereof.

[0208] Further amphoteric polymers usable according to the invention are the compounds stated in British published patent application 2 104 091, European published patent application 47 714, European published patent application 217 274, European published patent application 283 817 and German published patent application 28 17 369.

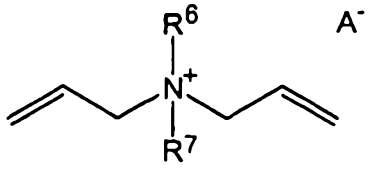
[0209] Amphoteric and/or cationic polymers which are preferred according to the invention are those polymers in which a cationic group is derived from at least one of the following monomers:

- monomers with quaternary ammonium groups of the general formula (M1),

$$R^1\text{-}CH{=}CR^2\text{-}CO\text{-}Z\text{-}(C_nH_{2n})\text{-}N^{(+)}R^3R^4R^5\ A^{(-)} \qquad (M1)$$

in which R^1 and R^2 mutually independently denote hydrogen or a methyl group and R^3, R^4 and R^5 mutually independently denote alkyl groups having 1 to 4 carbon atoms, Z is an NH group or an oxygen atom, n is an integer from 2 to 5 and $A^{(-)}$ is the anion of an organic or inorganic acid,

- monomers with quaternary ammonium groups of the general formula (M2),



(M2)

in which R^6 and R^7 mutually independently denote a (C_1 to C_4) alkyl group, in particular a methyl group and

A^- is the anion of an organic or inorganic acid.

[0210] If a cationic group of the amphoteric or cationic polymer is derived from the monomer of the formula (M1), the residues R^3, R^4 and R^5 in the formula (M1) preferably denote methyl groups, Z is preferably an NH group and $A^{(-)}$ preferably means a halide, methoxysulfate or ethoxysulfate ion. In this case, it is particularly preferred to use acrylamidopropyltrimethylammonium chloride as monomer (M1).

[0211] In the formula (M2), A^- preferably denotes a halide ion, in particular chloride or bromide.

[0212] Preferred amphoteric polymers according to the invention are polymers, the anionic group of which is derived from at least one monomer of the formula (M3)

- monomeric carboxylic acids of the general formula (M3) or the salts thereof with an organic or inorganic acid,

R^8-CH=CR^9-COOH (M3)

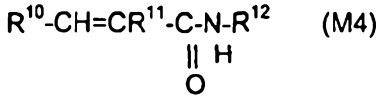
in which R^8 and R^9 are mutually independently hydrogen or methyl groups.

[0213] Acrylic acid is used as the monomer (M3) for preferred amphoteric polymers according to the invention.

[0214] Particularly preferred amphoteric polymers are copolymers prepared from at least one monomer (M1) or (M2) with the monomer (M3), in particular copolymers prepared from monomers (M2) and (M3). Amphoteric polymers which are very particularly preferably used according to the invention are copolymers of diallyldimethylammonium chloride and acrylic acid. These copolymers are distributed under the INCI name Polyquaternium-22, inter alia with the trade name Merquat® 280 (Nalco).

[0215] Apart from a monomer (M1) or (M2) and a monomer (M3), amphoteric polymers according to the invention may furthermore additionally contain a monomer (M4)

- monomeric carboxamides of the general formula (M4),



(M4)

in which R^{10} and R^{11} are mutually independently hydrogen or methyl groups and R^{12} denotes a hydrogen atom or a (C_1- to C_8) alkyl group.

[0216] Amphoteric polymers based on a comonomer (M4) which are very particularly preferably used according to the invention are terpolymers of diallyldimethylammonium chloride, acrylamide and acrylic acid. These copolymers are distributed under the INCI name Polyquaternium-39, inter alia with the trade name Merquat® Plus 3330 (Nalco).

[0217] Particularly preferably used amphoteric polymers are those polymers which are substantially composed of

(i) monomers with quaternary ammonium groups of the general formula (M1),

R^1-CH=CR^2-CO-Z-(C_nH_{2n})-$N^{(+)}R^2R^3R^4$ $A^{(-)}$ (M1)

in which R^1 and R^2 mutually independently denote hydrogen or a methyl group and R^3, R^4 and R^5 mutually independently denote alkyl groups having 1 to 4 carbon atoms, Z is an NH group or an oxygen atom, n is an integer from 2 to 5 and $A^{(-)}$ is the anion of an organic or inorganic acid

and

(ii) monomeric carboxylic acids of the general formula (M3),

R^8-CH=CR^9-COOH (M3)

in which R^8 and R^9 are mutually independently hydrogen or methyl groups.

[0218] With regard to the details of production of these particularly preferred polymers, explicit reference is made to the contents of German published patent application 39 29 973. Very particularly preferred polymers are those in which monomers of type (i) are used, in which R^3, R^4 and R^5 are methyl groups, Z is an NH group and $A^{(-)}$ a halide, methoxysulfate or ethoxysulfate ion; acrylamidopropyltrimethylammonium chloride is a particularly preferred monomer (i). Acrylic acid is preferably used as monomer (ii) for the stated polymers.

[0219] The amphoteric polymers may generally be used according to the invention both directly and in salt form, which is obtained by neutralization of the polymers, for example with an alkali metal hydroxide.

[0220] Preferred preparations according to the invention additionally contain in a cosmetic carrier, apart from the combination of (a) at least one oxidizing agent (preferably hydrogen peroxide) and (b) at least one compound from the group formed by α-lipoic acid and the derivatives thereof, one of the following active ingredient combinations (i) to (xii):

(i) at least one color-modifying component and at least one cationic polymer,

(ii) at least one color-modifying component and at least one amphoteric polymer,

(iii) at least one color-modifying component and at least one cationic polymer derived from at least one monomer of the above-stated formulae (M1) and/or (M2),

(iv) at least one color-modifying component and at least one amphoteric copolymer which is substantially composed of at least one monomer of the formula (M1) and at least one monomer of the formula (M3),

(v) at least one developer component (and optionally a coupler component) and at least one cationic polymer,

(vi) at least one developer component (and optionally a coupler component) and at least one amphoteric polymer,

(vii) at least one developer component (and optionally a coupler component) and at least one cationic polymer derived from at least one monomer of the above-stated formulae (M1) and/or (M2),

(viii) at least one developer component (and optionally a coupler component) and at least one amphoteric copolymer which is substantially composed of at least one monomer of the formula (M1) and at least one monomer of the formula (M3),

(ix) at least one bleach booster and at least one cationic polymer,

(x) at least one bleach booster and at least one amphoteric polymer,

(xi) at least one bleach booster and at least one cationic polymer derived from at least one monomer of the above-stated formulae (M1) and/or (M2),

(xii) at least one bleach booster and at least one amphoteric copolymer which is substantially composed of at least one monomer of the formula (M1) and at least one monomer of the formula (M3).

[0221] In a further preferred embodiment of the invention, action may be further optimized by the addition of at least one fatty substance. Fatty substances should be taken to mean fatty acids, fatty alcohols, natural and synthetic waxes, which may assume both solid form and liquid form in an aqueous dispersion, and natural and synthetic cosmetic oil components.

[0222] Fatty acids which may be used are linear and/or branched, saturated and/or unsaturated fatty acids having 6-30 carbon atoms. Fatty acids having 10-22 carbon atoms are preferred. Such substances which may, for example, be mentioned are isostearic acid, such as the commercial products Emersol® 871 and Emersol® 875, and isopalmitic acids such as the commercial product Edenor® IP 95, and any further fatty acids distributed under the trade name Edenor® (Cognis). Further typical examples of such fatty acids are caproic acid, caprylic acid, 2-ethylhexanoic acid, capric acid, lauric acid, isotridecanoic acid, myristic acid, palmitic acid, palmitoleic acid, stearic acid, isostearic acid, oleic acid, elaidic acid, petroselinic acid, linoleic acid, linolenic acid, elaeostearic acid, arachidic acid, gadoleic acid, behenic acid and erucic acid and the technical mixtures thereof which are obtained, for example, on pressure splitting of natural fats and oils, on oxidation of aldehydes from Roelen's oxo synthesis or on dimerization of unsaturated fatty acids. The fatty acid cuts obtainable from coconut oil or palm oil are conventionally particularly preferred; in general, it is particularly preferred to use stearic acid.

[0223] The quantity used here amounts to 0.1-15 wt.%, relative to the entire preparation. In a preferred embodiment, the quantity amounts to 0.5-10 wt.%, with quantities of 1-5 wt.% being very particularly advantageous.

[0224] Fatty alcohols which may be used are saturated, mono- or polyunsaturated, branched or unbranched fatty alcohols having C_6-C_{30},

preferably C_{10}-C_{22} and very particularly preferably C_{12}-C_{22} carbon atoms. For the purposes of the invention, it is for example possible to use decanol, octanol, octenol, dodecenol, decenol, octadienol, dodecadienol, decadienol, oleyl alcohol, erucic alcohol, ricinol alcohol, stearyl alcohol, isostearyl alcohol, cetyl alcohol, lauryl alcohol, myristyl alcohol, arachidyl alcohol, caprylic alcohol, capric alcohol, linoleyl alcohol, linolenyl alcohol and behenyl alcohol, and the Guerbet alcohols thereof, it being intended for this list to be of an exemplary rather than limiting nature. The fatty alcohols are, however, preferably derived from natural fatty acids, it conventionally being possible to start by isolation from the fatty acid esters by reduction. It is likewise possible according to the invention to use fatty alcohol cuts which are produced by reducing naturally occurring triglycerides such as beef fat, palm oil, peanut oil, rapeseed oil, cottonseed oil, soy oil, sunflower oil and linseed oil or fatty acid esters produced from the transesterification products thereof with corresponding alcohols, and so constitute a mixture of various fatty alcohols. Such substances are commercially available for example under the names Stenol®, for example Stenol® 1618 or Lanette®, for example Lanette® O or Lorol®, for example Lorol® C8, Lorol® C14, Lorol® C18, Lorol® C8-18, HD-Ocenol®, Crodacol®, for example Crodacol® CS, Novol®, Eutanol® G, Guerbitol® 16, Guerbitol® 18, Guerbitol® 20, Isofol® 12, Isofol® 16, Isofol® 24, Isofol® 36, Isocarb® 12, Isocarb® 16 or Isocarb® 24. Wool wax alcohols, as are for example commercially obtainable under the names Corona®, White Swan®, Coronet® or Fluilan®, may, of course also be used according to the invention. The fatty alcohols are used in quantities of 0.1-20 wt.%, relative to the entire preparation, preferably in quantities of 0.1-10 wt.%.

[0225] Natural or synthetic waxes which may be used according to the invention are solid paraffins or isoparaffins, carnauba waxes, beeswaxes, candelilla waxes, ozokerites, ceresin, spermaceti, sunflower wax, fruit waxes such as for example apple wax or citrus wax, PE or PP microwaxes. Such waxes are obtainable for example through Kahl & Co., Trittau.

[0226] Examples of natural and synthetic cosmetic oil bodies capable of enhancing the action of the active ingredient according to the invention which may be mentioned are:

- vegetable oils. Examples of such oils are sunflower oil, olive oil, soy oil, rapeseed oil, almond oil, jojoba oil, orange oil, wheat germ oil, peach stone oil and the liquid fractions of coconut oil. However, other triglyceride oils such as the liquid fractions of beef fat together with synthetic triglyceride oils are also suitable.
- liquid paraffin oils, isoparaffin oils and synthetic hydrocarbons and di-n-alkyl ethers having a total of between 12 to 36 C atoms, in particular 12 to 24 C atoms, such as for example di-n-octyl ether, di-n-decyl ether, di-n-nonyl ether, di-n-undecyl ether, di-n-dodecyl ether, n-hexyl-n-octyl ether, n-octyl-n-decyl ether, n-decyl-n-undecyl ether, n-undecyl-n-dodecyl ether and n-hexyl-n-undecyl ether and di-tert.-butyl ether, di-iso-pentyl ether, di-3-ethyldecyl ether, tert.-butyl-n-octyl ether, iso-pentyl-n-octyl ether and 2-methylpentyl-n-octyl ether. The compounds 1,3-di-(2-ethylhexyl)cyclohexane (Cetiol® S) and di-n-octyl ether (Cetiol®OE) available as commercial products may be preferred.
- ester oils. Ester oils should be taken to mean the esters of C_6-C_{30} fatty acids with C_2-C_{30} fatty alcohols. The monoesters of fatty acids with alcohols having 2 to 24 C atoms are preferred. Examples of fatty acid moieties used in the esters are caproic acid, caprylic acid, 2-ethylhexanoic acid, capric acid, lauric acid, isotridecanoic acid, myristic acid, palmitic acid, palmitoleic acid, stearic acid, isostearic acid, oleic acid, elaidic acid, petroselinic acid, linoleic acid, linolenic acid, elaeostearic acid, arachidic acid, gadoleic acid, behenic acid and erucic acid and the technical mixtures thereof which are obtained, for example, on pressure splitting of natural fats and oils, on oxidation of aldehydes from Roelen's oxo synthesis or on dimerization of unsaturated fatty acids. Examples of fatty alcohol moieties in the ester oils are isopropyl alcohol, caproic alcohol, caprylic alcohol, 2-ethylhexyl alcohol, capric alcohol, lauryl alcohol, isotridecyl alcohol, myristyl alcohol, cetyl alcohol,

palmoleyl alcohol, stearyl alcohol, isostearyl alcohol, oleyl alcohol, elaidyl alcohol, petroselinyl alcohol, linolyl alcohol, linolenyl alcohol, elaeostearyl alcohol, arachyl alcohol, gadoleyl alcohol, behenyl alcohol, erucyl alcohol and brassidyl alcohol and the technical mixtures thereof, which are obtained, for example, on high pressure hydrogenation of technical methyl esters based on fats and oils or aldehydes from Roelen's oxo synthesis and as the monomer fraction on dimerization of unsaturated fatty alcohols. Particularly preferred substances according to the invention are isopropyl myristate (Rilanit® IPM), isononanoic acid C16-18-alkyl ester (Cetiol® SN), 2-ethylhexyl palmitate (Cegesoft® 24), stearic acid 2-ethylhexyl ester (Cetiol® 868), cetyl oleate, glycerol tricaprylate, coconut fatty alcohol caprate/caprylate (Cetiol® LC), n-butyl stearate, oleyl erucate (Cetiol® J 600), isopropyl palmitate (Rilanit® IPP), oleyl oleate (Cetiol®), lauric acid hexyl ester (Cetiol® A), di-n-butyl adipate (Cetiol® B), myristyl myristate (Cetiol® mm), cetearyl isononanoate (Cetiol® SN), oleic acid decyl ester (Cetiol® V).

- dicarboxylic acid esters such as di-n-butyl adipate, di-(2-ethylhexyl)-adipate, di-(2-ethylhexyl)-succinate and diisotridecyl acelate and diol esters such as ethylene glycol dioleate, ethylene glycol diisotridecanoate, propylene glycol (2-ethyl hexanoate), propylene glycol diisostearate, propylene glycol dipelargonate, butanediol diisostearate, neopentyl glycol dicaprylate, symmetrical, asymmetrical or cyclic esters of carbonic acid with fatty alcohols, for example described in DE-OS 197 56 454, glycerol carbonate or dicaprylyl carbonate (Cetiol® CC),
- mono-, di- and trifatty acid esters of saturated and/or unsaturated linear and/or branched fatty acids with glycerol, such as for example Monomuls® 90-018, Monomuls® 90-L12 or Cutina® MD.

[0227] The quantity used amounts to 0.1-50 wt.% relative to the entire preparation, preferably 0.1-20 wt.% and particularly preferably 0.1-15 wt.% relative to the entire preparation.

[0228] The total quantity of oil and fat components in the preparations according to the invention conventionally amounts to 6-45 wt.%, relative to the entire preparation. Quantities of 10-35 wt.-% are preferred according to the invention.

[0229] It has furthermore been found that action may be increased if the preparations according to the invention additionally contain at least one hydroxycarboxylic acid ester. Preferred hydroxycarboxylic acid esters are full esters of glycolic acid, lactic acid, malic acid, tartaric acid or citric acid. Further hydroxycarboxylic acid ester which are suitable in principle are esters of β-hydroxypropionic acid, tartronic acid, D-gluconic acid, saccharic acid, mucic acid or glucuronic acid. Suitable alcohol components of these esters are primary, linear or branched aliphatic alcohols having 8-22 C atoms, thus for example fatty alcohols or synthetic fatty alcohols. The esters of C_{12}-C_{15} fatty alcohols are here particularly preferred. Esters of this type are commercially available, for example under the trademark Cosmacol® from EniChem, Augusta Industriale. The quantity of hydroxycarboxylic acid ester used here amounts to 0.1-15 wt.% relative to the preparation, preferably 0.1-10 wt.% and very particularly preferably 0.1-5 wt.%.

[0230] Preferred preparations according to the invention additionally contain in a cosmetic carrier, apart from the combination of (a) at least one oxidizing agent (preferably hydrogen peroxide) and (b) at least one compound from the group formed by α-lipoic acid and the derivatives thereof, one of the following active ingredient combinations (i) to (xv):

(i) at least one color-modifying component and at least one fatty substance,

(ii) at least one color-modifying component and at least one C_{10} to C_{22} fatty alcohol,

(iii) at least one color-modifying component and at least one C_{10} to C_{22} fatty acid,

(iv) at least one color-modifying component and at least one natural or synthetic wax,

(v) at least one color-modifying component and at least one natural or synthetic oil body,

(vi) at least one developer component (and optionally a coupler component) and at least one fatty substance,

(vii) at least one developer component (and optionally a coupler component) and at least one C_{10} to C_{22} fatty alcohol,

(viii) at least one developer component (and optionally a coupler component) and at least one C_{10} to C_{22} fatty acid,

(ix) at least one developer component (and optionally a coupler component) and at least one natural or synthetic wax,

(x) at least one developer component (and optionally a coupler component) and at least one natural or synthetic oil body,

(xi) at least one bleach booster and at least one fatty substance,

(xii) at least one bleach booster and at least one C_{10} to C_{22} fatty alcohol,

(xiii) at least one bleach booster and at least one C_{10} to C_{22} fatty acid,

(xiv) at least one bleach booster and at least one natural or synthetic wax,

(xv) at least one bleach booster and at least one natural or synthetic oil body.

[0231] It is preferred according to the invention for the preparations additionally to contain at least one alkalizing agent. Alkalizing agents which are usable according to the invention are preferably selected from the group formed by ammonia, basic amino acids, alkali metal hydroxides, alkanolamines, alkali metal metasilicates, urea, morpholine, N-methyl-glucamine, imidazole, alkali metal phosphates and alkali metal hydrogenphosphates. Preferably used alkali metal ions are lithium, sodium, potassium, in particular sodium or potassium.

[0232] The basic amino acids usable for the purposes of the invention as an alkalizing agent according to the invention are preferably selected from the group formed by L-arginine, D-arginine, D,L-arginine, L-histidine, D-histidine, D,L-histidine, L-lysine, D-lysine, D,L-lysine, particularly preferably L-arginine, D-arginine, D,L-arginine.

[0233] The alkali metal hydroxides usable as an alkalizing agent according to the invention are preferably selected from the group formed by sodium hydroxide and potassium hydroxide.

[0234] The alkanolamines usable as an alkalizing agent according to the invention are preferably selected from primary amines with a C_2-C_6 alkyl parent substance which bears at least one hydroxyl group. Particularly preferred alkanolamines are selected from the group formed by 2-aminoethan-1-ol (monoethanolamine), 3-aminopropan-1-ol, 4-aminobutan-1-ol, 5-amino-pentan-1-ol, 1-aminopropan-2-ol, 1-aminobutan-2-ol, 1-aminopentan-2-ol, 1-aminopentan-3-ol, 1-aminopentan-4-ol, 3-amino-2-methylpropan-1-ol, 1-amino-2-methylpropan-2-ol, 3-aminopropane-1,2-diol, 2-amino-2-methyl-propane-1,3-diol. Alkanolamines which are very particularly preferred according to the invention are selected from the group 2-aminoethan-1-ol, 2-amino-2-methylpropan-1-ol and 2-amino-2-methylpropane-1,3-diol.

[0235] The alkalizing agent is particularly preferably selected from at least one compound of the group formed by 2-aminoethanol, 2-amino-2-methyl-propan-1-ol, 2-amino-2-methylpropane-1,3-diol, potassium hydroxide, L-arginine, D-arginine, DL-arginine, N-methylglucamine, morpholine, imidazole and urea.

[0236] Preferred preparations according to the invention additionally contain in a cosmetic carrier, apart from the combination of (a) at least one oxidizing agent (preferably hydrogen peroxide) and (b) at least one compound from the group formed by α-lipoic acid and the derivatives thereof, one of the following active ingredient combinations (i) to (xii):

(i) at least one color-modifying component and ammonia,
(ii) at least one color-modifying component and at least one alkanolamine,
(iii) at least one color-modifying component and 2-aminoethan-1-ol,
(iv) at least one color-modifying component and ammonia and 2-amino-ethan-1-ol,

(v) at least one color-modifying component and 2-aminoethan-1-ol and L-arginine,

(vi) at least one developer component (and optionally a coupler component) and ammonia,

(vii) at least one developer component (and optionally a coupler component) and at least one alkanolamine,

(viii) at least one developer component (and optionally a coupler component) and 2-aminoethan-1-ol,

(ix) at least one developer component (and optionally a coupler component) and ammonia and 2-aminoethan-1-ol,

(x) at least one developer component (and optionally a coupler component) and 2-aminoethan-1-ol and L-arginine,

(xi) at least one bleach booster and ammonia,

(xii) at least one bleach booster and at least one alkanolamine,

(xiii) at least one bleach booster and 2-aminoethan-1-ol,

(xiv) at least one bleach booster and ammonia and 2-aminoethan-1-ol,

(xv) at least one bleach booster and 2-aminoethan-1-ol and L-arginine.

[0237] In a further embodiment, the preparations according to the invention should additionally contain at least one UV light protection filter. UV light protection filters should be taken to be organic substances which are of capable absorbing ultra-violet radiation and reemitting the absorbed energy in the form of longer-wave radiation, for example heat. UVB filters may be oil-soluble or water-soluble. Oil-soluble substances which may be mentioned are, for example:

- 3-benzylidenecamphor and the derivatives thereof, for example 3-(4-methylbenzylidene)camphor;
- 4-aminobenzoic acid derivatives, preferably 4-(dimethylamino)benzoic acid 2-ethylhexyl ester, 4-(dimethylamino)benzoic acid 2-octyl ester and 4-(dimethylamino)benzoic acid amyl ester;
- esters of cinnamic acid, preferably 4-methoxycinnamic acid 2-ethylhexyl ester, 4-methoxycinnamic acid propyl ester, 4-methoxycinnamic acid

isoamyl ester, 2-cyano-3-phenylcinnamic acid 2-ethylhexyl ester (octocrylene);

- esters of salicylic acid, preferably salicylic acid 2-ethylhexyl ester, salicylic acid 4-isopropylbenzyl ester, salicylic acid homomenthyl ester;
- derivatives of benzophenone, preferably 2-hydroxy-4-methoxybenzophenone, 2-hydroxy-4-methoxy-4'-methylbenzophenone, 2,2'-dihydroxy-4-methoxybenzophenone;
- esters of benzalmalonic acid, preferably 4-methoxybenzalmalonic acid di-2-ethylhexyl ester;
- triazine derivatives, such as for example 2,4,6-trianilino-(p-carbo-2'-ethyl-1'-hexyloxy)-1,3,5-triazine and octyl triazone.
- propane-1,3-diones, such as for example 1-(4-tert.-butylphenyl)-3-(4'-methoxyphenyl)propane-1,3-dione;

[0238] Water-soluble substances which may be considered are:

- 2-phenylbenzimidazole 5-sulfonic acid and the alkali and alkaline earth metal, ammonium, alkylammonium, alkanolammonium and glucammonium salts thereof;
- sulfonic acid derivatives of benzophenones, preferably 2-hydroxy-4-methoxybenzophenone 5-sulfonic acid and the salts thereof;
- sulfonic acid derivatives of 3-benzylidenecamphor, such as for example 4-(2-oxo-3-bornylidenemethyl)benzenesulfonic acid and 2-methyl-5-(2-oxo-3-bornylidene)sulfonic acid and the salts thereof.

[0239] Typical UVA filters which may be considered are in particular derivatives of benzoylmethane, such as for example 1-(4'-tert.-butylphenyl)-3-(4'-methoxyphenyl)propane-1,3-dione or 1-phenyl-3-(4'-isopropylphenyl)propane-1,3-dione. The UVA and UVB filters may, of course, also be used in mixtures. Apart from the stated soluble substances, insoluble pigments, namely finely dispersed metal oxides or salts, may also be considered for this purpose, such as for example titanium dioxide, zinc oxide, iron oxide, aluminum oxide, cerium oxide, zirconium oxide, silicates (talcum), barium sulfate and zinc stearate. The particles should here haven an average

diameter of less than 100 nm, preferably between 5 and 50 nm and in particular between 15 and 30 nm. They may have a spherical shape, but such particles having a shape which is ellipsoidal or differs in another way from spherical may also be used. Apart from the two above-stated groups of primary light protection substances, secondary light protection materials of the antioxidant type, which interrupt the series of photochemical reactions which are initiated when UV radiation penetrates into the skin, may also be used Typical examples of these are superoxide dismutase, tocopherols (vitamin E) and ascorbic acid (vitamin C).

[0240] It is furthermore preferred additionally to incorporate at least one plant extract into the preparations according to the invention.

[0241] Suitable plant extracts are obtained by extraction with organic solvents (such as for example ethanol, isopropanol, diethyl ether, gasoline, benzene, chloroform) or by steam distillation. Preferred plant extracts are for example extracts of flowers (lime blossom, chamomile, lily, lavender, rose, jasmine, neroli, ylang-ylang), stems and leaves (blackcurrant, horse chestnut, rooibos, birch, melissa, clover, vine leaves, geranium, patchouli, petitgrain), fruits (aniseed, blackcurrant, coriander, caraway, juniper), fruit peels (bergamot, lemon, orange), roots (mace, angelica, celery, cardamom, costus, iris, calamus), woods (stone pine, sandalwood, guaiac, cedar, rosewood), herbs and grasses (tarragon, lemongrass, sage, thyme, rosemary), needles and branches (spruce, fir, pine, mountain pine, sandalwood), resins and balsams (galbanum, elemi, benzoin, myrrh, olibanum, opoponax).

[0242] The plant extracts are particularly preferably selected from at least one extract of the group witch hazel (Hamamelis virginiana L.), vine leaves (Vitis vinifera L.), rose (Rosa gallica L.), sandalwood (Pterocarpus santalinus), rooibos (Aspalathus linearis), horse chestnut (Aesculus hippocastanum L.), clover (in particular red clover, Trifolium pratense), cinnamon (Cinnamomum zeylanicum Nees) and blackcurrant (in particular from blackcurrant leaves, Ribes nigrum L.).

[0243] Such preferably used extracts are distributed under the names Herbasol® by Cosmetochem or Extrapon® by Symrise.

[0244] The plant extracts are preferably present in the preparations according to the invention in a quantity of 0.05 to 5 wt.%, in particular of 0.1 to 2 wt.%, in each case relative to the weight of the entire preparation.

[0245] The cosmetic preparations may moreover contain active ingredients, auxiliary substances and additives, such as for example

- nonionic polymers such as for example vinylpyrrolidone/vinyl acrylate copolymers, polyvinylpyrrolidone and vinylpyrrolidone/vinyl acetate copolymers and polysiloxanes,
- anionic polymers such as for example polyacrylic acids, crosslinked polyacrylic acids, vinyl acetate/crotonic acid copolymers, vinyl-pyrrolidone/vinyl acrylate copolymers, vinyl acetate/butyl maleate/isobornyl acrylate copolymers, methyl vinyl ether/maleic anhydride copolymers and acrylic acid/ethyl acrylate/N-tert.-butylacrylamide terpolymers,
- texturing agents such as maleic acid and lactic acid,
- hair-conditioning compounds such as phospholipids, for example soy lecithin, egg lecithin and cephalins,
- perfume oils, dimethyl isosorbide and cyclodextrins,
- solvents and solubilizing agents such as ethanol, isopropanol, ethylene glycol, propylene glycol, glycerol and diethylene glycol,
- active ingredients which improve fiber structure, in particular mono-, di- and oligosaccharides such as for example glucose, galactose, fructose, fruit sugars and lactose,
- quaternized amines such as methyl-1-alkylamidoethyl-2-alkylimidazolinium methosulfate
- defoamers such as silicones,
- dyes for coloring the preparation,
- antidandruff active ingredients such as piroctone olamine, zinc omadine and climbazole,

- active ingredients such as allantoin, pyrrolidonecarboxylic acids and the salts thereof and bisabolol,
- vitamins, provitamins and vitamin precursors, in particular those of groups A, B_3, B_5, B_6, C, E, F and H,
- plant extracts such as extracts from green tea, oak bark, stinging nettle, witch hazel, hops, chamomile, burdock root, horsetail, hawthorn, lime blossom, almond, Aloe vera, pine-needle, horse chestnut, sandalwood, juniper, coconut, mango, apricot, lime, wheat, kiwi fruit, melon, orange, grapefruit, sage, rosemary, birch, mallow, lady's smock, wild thyme, yarrow, thyme, melissa, restharrow, coltsfoot, marsh mallow, meristem, ginseng and ginger root,
- cholesterol,
- consistency providers, such as sugar esters, polyol esters or polyol alkyl ethers,
- fatty acid alkanolamides,
- complexing agents such as EDTA, NTA, β-alaninediacetic acid and phosphonic acids,
- swelling and penetrating substances such as glycerol, propylene glycol monoethyl ether, carbonates, hydrogencarbonates, guanidines, ureas and primary, secondary and tertiary phosphates,
- opacifiers such as latex, styrene/PVP and styrene/acrylamide copolymers
- pearlescent agents such as ethylene glycol mono- and distearate and PEG-3 distearate,
- pigments,
- stabilizers for hydrogen peroxide and other oxidizing agents,
- propellants such as propane/butane mixtures, N_2O, dimethyl ether, CO_2 and air,
- antioxidants.

[0246] With regard to further optional components and the quantities of these components used, reference is explicitly made to the relevant handbooks

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known to a person skilled in the art, for example Kh. Schrader, Grundlagen und Rezepturen der Kosmetika, 2nd edition, Hüthig Buch Verlag, Heidelberg, 1989.

[0247] The statements made regarding the first subject matter of the invention apply,mutatis mutandis to the second.

[0248] Also herein disclosed is a method for oxidative hair treatment, in which an oxidative cosmetic preparation containing at least one oxidizing agent in a cosmetic carrier is applied onto the hair and, after a period of exposure, rinsed out of the hair, wherein,

- immediately before application of the oxidative cosmetic preparation, a cosmetic preparation containing in a cosmetic carrier at least one compound from the group formed by α-lipoic acid and the derivatives thereof is applied and is optionally rinsed off again after a period of exposure

and/or

- the oxidative cosmetic preparation additionally contains at least one compound from the group formed by α-lipoic acid and the derivatives thereof.

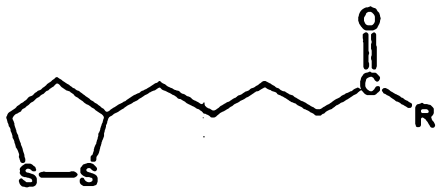
[0248a] Thus, according to another embodiment of the invention, there is provided a method for oxidative hair treatment, in which an oxidative cosmetic preparation containing at least one oxidizing agent in a cosmetic carrier is applied onto the hair and, after a period of exposure, is rinsed out of the hair, wherein

- immediately before application of the oxidative cosmetic preparation, a cosmetic preparation containing in a cosmetic carrier at least one compound from the group formed by a-lipoic acid and the derivatives thereof is applied and is optionally rinsed off again after a period of exposure

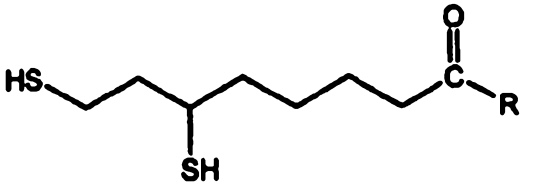
and/or

- the oxidative cosmetic preparation additionally contains at least one compound from the group formed by a-lipoic acid and the derivatives thereof, according to formula (Ia) or the in each case reduced form of the formula (Ib),

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(Ia)



(Ib)

in which in each case R denotes a residue

-NR'R", in which R' and R" mutually independently denote a hydrogen atom, a (C_1 to C_{22}) alkyl group, (C_2 to C_{22}) alkenyl group, a (C_1 to C_{20}) hydroxyalkyl group, a sulfo-(C_1 to C_6)-alkyl group, an optionally substituted (C_1 to C_6) carboxyalkyl group, or

-OM, in which M means a hydrogen atom, a (C_1 to C_{22}) alkyl group, (C_2 to C_{22}) alkenyl group, a (C_1 to C_{20}) hydroxyalkyl group or an equivalent of a mono- or polyvalent cation.

[0249] The period of exposure of the α-lipoic acid or the derivatives thereof is preferably 1 to 100 minutes, particularly preferably 5 to 50 minutes.

[0250] It is in turn preferred according to the invention to apply the method according to the invention in the context of oxidative hair dyeing, oxidative hair bleaching or fixing in the context of a permanent wave. It is here preferred to use the α-lipoic acid or the derivatives thereof together with the oxidizing agent on the hair.

[0251] In a preferred embodiment of the method according to the invention as an oxidative hair dyeing method, the α-lipoic acid or the derivatives thereof is/are used in one step as a constituent of a cosmetic preparation additionally containing in a cosmetic carrier at least one oxidizing agent and at least one oxidation dye precursor.

[0252] In addition, optionally in a further step of the method in the context of post-treatment, a preparation containing in a cosmetic carrier at least one hair-conditioning compound in combination with at least one compound from the group formed by α-lipoic acid and the derivatives thereof, is used on the hair. Examples of these post-treatment preparations may be found in section 2.5 of the Examples.

[0253] The oxidative hair dyes of this embodiment are preferably two-component preparations. The first component contains in a cosmetic carrier at least one compound from the group formed by α-lipoic acid and the derivatives thereof, and at least one oxidation dye precursor. The second component contains at least one oxidizing agent in a cosmetic carrier. These components are preferably formulated separately from one another, in each case in one compartment and provided together in one packaging unit (kit). Shortly before use, the two components are mixed with one another.

[0254] In the embodiment of the method according to the invention as an oxidative hair bleaching method, the α-lipoic acid or the derivatives thereof is/are used in one step as a constituent of a cosmetic preparation additionally containing in a cosmetic carrier at least one oxidizing agent and at least one bleach booster.

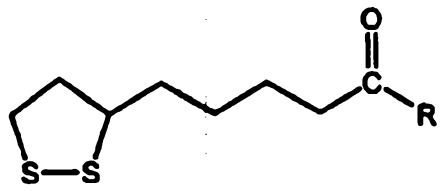
[0255] The oxidative hair bleaching preparations of this embodiment are preferably two- or three-component preparations. The first component contains in a cosmetic carrier at least one compound from the group formed by α-lipoic acid and the derivatives thereof, and optionally at least one bleach booster. The bleach booster may also be formulated separately from the α-lipoic acid or the derivatives thereof, for example in powder form, as an anhydrous paste or anhydrous oil. In this manner, a three-component preparation is obtained. The final component contains at least one oxidizing agent in a cosmetic carrier. All the components are preferably formulated separately from one another, in each case in one compartment and provided together in one packaging unit (kit). Shortly before use, all the components are mixed with one another.

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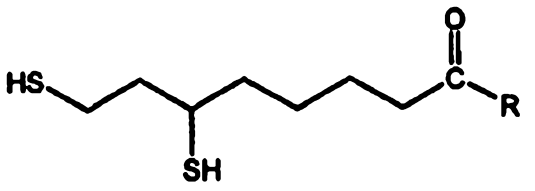
[0256] The above-described multicomponent preparations for carrying out the method according to the invention may be provided in one packaging unit. The packaging unit may either comprise at least one container which contains the preparation of the second subject matter of the invention, or may comprise at least two containers, with one, first container containing an oxidative cosmetic preparation which contains at least one oxidizing agent in a cosmetic carrier, a second container containing a cosmetic preparation which contains in a cosmetic carrier [sic], and optionally a third container which contains at least one bleach booster incorporated in a cosmetic carrier. All the containers may also be chambers of a multichamber container.

[0257] The statements made regarding the first and second subject matters of the invention apply mutatis mutandis to the third.

[0257a] According to a further embodiment of the invention, there is provided a packaging unit, when used for oxidative hair treatment, comprising in a first container an oxidative cosmetic preparation which contains at least one oxidizing agent in a cosmetic carrier and in a second container a cosmetic preparation which contains in a cosmetic carrier at least one compound from the group formed by α-lipoic acid and the derivatives thereof, according to formula (Ia) or the in each case reduced form of the formula (Ib),



(Ia)



(Ib)

in which in each case R denotes a residue

-NR'R", in which R' and R" mutually independently denote a hydrogen atom, a (C_1 to C_{22}) alkyl group, (C_2 to C_{22}) alkenyl group, a (C_1 to C_{20}) hydroxyalkyl group, a sulfo-(C_1 to C_6)-alkyl group, an optionally substituted (C_1 to C_6) carboxyalkyl group, or

-OM, in which M means a hydrogen atom, a (C_1 to C_{22}) alkyl group, (C_2 to C_{22}) alkenyl group, a (C_1 to C_{20}) hydroxyalkyl group or an equivalent of a mono- or polyvalent cation.

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[0258] The following Examples are intended to explain the subject matter of the present invention but without limiting it.

Examples

[0259] The following formulations were prepared using known production methods. The following commercial products were here used as the raw materials:

Hydrenol® D	C_{16}-C_{18} fatty alcohol (INCI name: Cetearyl Alcohol) (Cognis Deutschland)
Lorol® technical	C_{12}-C_{18} fatty alcohol (INCI name: Coconut Alcohol) (Cognis Deutschland)
Stenol® 16/18	C_{16-18} fatty alcohol (INCI name: Cetearyl Alcohol) (Cognis)
Lorol® 16	INCI name: Cetyl Alcohol (Cognis)
Eumulgin® B1	Cetylstearyl alcohol with 12 EO units (INCI name: Ceteareth-12) (Cognis Deutschland)
Eumulgin® B2	Cetylstearyl alcohol with approx. 20 EO units (INCI name: Ceteareth-20) (Cognis Deutschland)
Edenor® C14	Myristic acid (INCI name: Myristic Acid) (Cognis)
Turpinal® SL	1-Hydroxyethane-1,1-diphosphonic acid (INCI name: Etidronic Acid, Aqua (Water)) (Solutia)
Plantapon® LGC	Alkyl polyglucoside carboxylate sodium salt; 30% active substance (Cognis Deutschland)
Texapon® NSO UP	Sodium lauryl ether sulfate (27% active substance; INCI: Sodium Laureth Sulfate) (manufacturer: COGNIS)
Texapon® K14S70C	Lauryl myristyl ether sulfate sodium salt (approx. 68% to 73% active substance content; INCI name: Sodium Myreth Sulfate) (Cognis)
Disponil® FES 77 IS	Fatty alcohol ether sulfate (approx. 31-33% active substance content in water; INCI name: Sodium Coceth-30 Sulfate) (Cognis)
Akypo® Soft 45 NV	2-(C_{12-14} fatty alcohol ethoxylate (4.5 EO))acetic acid sodium salt; 21% active substance; INCI name: Sodium Laureth-5 Carboxylate (KAO)

Gluadin® W 40	wheat protein hydrolysate (at least 40% solids content; INCI name: Aqua (Water), Hydrolyzed Wheat Protein, Sodium Benzoate, Phenoxyethanol, Methylparaben, Propylparaben) (Cognis)
Plantacare® 1200 UP	C_{12-16} fatty alcohol 1,4-glucoside (approx. 50-53% active substance content; INCI name: Lauryl Glucoside, Aqua (Water)) (Cognis)
Lamesoft® PO 65	Alkyl polyglucoside oleic acid monoglyceride mixture (approx. 65-70% solids content; INCI name: Coco-Glucoside, Glyceryl Oleate, Aqua (Water)) (Cognis)
Aculyn® 33	30 wt.-% active substance in water (INCI name: Acrylates Copolymer) (Rohm & Haas)
DOW Corning® DB 110 A	Nonionogenic silicone emulsion (10 wt.% active substance) (INCI name: Dimethicone) (Dow Corning)
Aristoflex® AVC	Copolymer of vinylpyrrolidone and ammonium acryloyldimethyltaurate; (INCI name: Ammonium Acryloyldimethyltaurate/VP copolymer, t-Butyl Alcohol) (Clariant)
Polymer® W 37194	approx. 20 wt.% active substance content in water; INCI name: Acrylamidopropyltrimonium Chloride/Acrylates Copolymer (Stockhausen)
Cremophor® A 25	C_{16-18} fatty alcohol ethoxylated with 25 units of ethylene oxide (INCI name: Ceteareth-25) (BASF)

1. Effectiveness

1.1 Preparation of test formulations

[0260] The following formulations were prepared:

Table 1: Cream formulations

	T-0 (comparison)	T-1 (according to the invention)
Hydrenor D	9.00	9.00
Lorol® technical	3.00	3.00
Eumulgin® B1	0.50	0.50
Eumulgin® B2	0.50	0.50
Isostearic acid	2.00	2.00
Edenor® C14	0.50	0.50
Plantapor® LGC	5.00	5.00
Texapon® NSO UP	7.00	7.00
Potassium hydroxide, 50%	1.20	1.20
Ammonia, 25%	5.50	5.50
Ascorbic acid	0.40	0.40
Turpinal® SL	0.20	0.20
Sodium sulfite	0.50	0.50
Sodium silicate 40/42	0.50	0.50
α-Lipoic acid	-	1.00
Water	ad 100	ad 100

Table 2: Oxidative cosmetic preparation

	T-2
Dipicolinic acid	0.10
Disodium pyrophosphate	0.03
Turpinal® SL	1.50
Texapon® NSO UP	2.00

Aculyn® 33A	12.00
Hydrogen peroxide, 50%	12.00
DOW Corning® DB 110 A	0.07
Ammonia, 25%	0.62
Water	ad 100

1.2 Hair treatment

[0261] Cream formulations T-0 (without alpha-lipoic acid) and T-1 (with 1.0% alpha-lipoic acid) were in each case mixed in a 1:1 ratio by weight with the oxidative cosmetic preparation T-2. This mixture was applied in a ratio by weight to the weight of the test hair of 4 to 1 for 30 min at 32°C onto strands of hair (Kerling natural European hair 6/0). The strands of hair were then rinsed with water and dried. The procedure was repeated 3×.

1.3 Determination of degree of hair damage

[0262] The damage caused to the test strands of hair by the hair treatment from point 1.2 was quantified by two independent methods:

1.3.1 Amino acid analysis

[0263] After complete acidic hydrolysis of the test hair (treated and untreated), amino acid composition was determined by ion exchange chromatography. It is known that oxidative damage to hair proteins is in particular manifested in the formation of cysteic acid from cystine. Relative to the complete amino acid content, a cysteic acid content of 0.39 mol% was measured in the untreated hair. This value rose to 1.20 mol% after treatment with T-0/T-2, but only to 0.85 mol. after treatment with T-1/T-2. A 43% reduction in hair protein damage due to the use of 0.5% of α-lipoic acid (relative to the mixture applied) was thus identified.

1.3.2 Wilhelmy contact angle

[0264] This method was carried out as described in the literature (Molina R et al: Chemical modifications on human hair studies by means of contact angle determination. *J. Coll. Int. Sci.*, 2001, 237, 40-46).

[0265] The contact angle of the untreated hair was 102.4° +/- 1.4° and fell to 75.8° +/- 1.5° after the 3× treatment with T-0/T-2 described in 1.2. As anticipated, this reveals a reduction in hydrophobicity. After the 3× treatment with T-1/T-2 described in 1.2, a value of 80.5° +/- 1.9° was measured. This shows that, by using 0.5% of α-lipoic acid (relative to the mixture applied), the surface of the hair is significantly better protected from the consequences of oxidative hair treatment.

1.3.3. Measurement of combing work

[0266] Strands of hair (Kerling 6/0) were washed with 4% sodium laureth sulfate and precombed manually 3×. Before application of the test formulations, the strands were automatically combed 10× and the work which had to be applied determined with a type U1 A force transfer instrument (Hottinger Baldwin, Germany). The measurements were repeated after application of mixtures T0/T-2 and T-1/T-2. In each case, 20 strands of hair were treated and measured. The value for combing work was in each case the arithmetic mean.

Table 3: Wet combing work values

	Combing work, before [mJ]	Combing work, after [mJ]
T-0/T-1: 0% α-Lipoic acid	60	122
T-1/T-2: 0.5% α-Lipoic acid	69	102

[0267] The data in table 3 show that alpha-lipoic acid reduces the increase in combing work by 56%.

1.3.4. Thermoanalytical investigation

[0268] Differential calorimetry was carried out with a DSC 7 instrument (Perkin Elmer, USA). Approx. 5-10 mg of the particular hair samples were enclosed in steel capsules with 50 µl of water and heated to 170°C at a heating rate of 10°C per minute. Thermal energy was recorded in parallel to a reference sample. The denaturation temperature was determined from the peak maximum of the calorimetric curve. Mixtures T-0/T-2 and T-1/T-2 were applied three times. The values from table 4 are the arithmetic mean of 5 measurements.

Table 4: Denaturation temperatures

	Denaturation temperature, [°C]
T-0/T-1: 0% α-lipoic acid	151.8+/-0.3
T-1/T-2: 0.5% α-lipoic acid	153.4+/-0.3

[0269] Denaturation temperature is dependent on the density of cystine crosslinks in the matrix proteins (Wortmann J. F. et al., J. Cosmet. Sci. 53 (2002) 219-228). The higher values in the presence of α-lipoic acid (table 4) are therefore in line with reduced oxidative cleavage of the cystine crosslinks (see 1.3.1.)

1.4 Dye cream storage test

[0270] A sample of cream T-1 was stored at a pH value of pH 10 at room temperature and a further sample was stored at a pH value of pH 10 at 40°C. In each case, 98% of the introduced α-lipoic acid was retained after storage. Even in the presence of 0.5 wt.% of sodium sulfite, no reduction of α-lipoic acid to dihydrolipoic acid was detected in either sample.

2. Example formulations

[0271] Unless otherwise indicated, the quantities stated are weight percentages relative to the total weight of the particular formulation.

2.1 Blonding product

[0272] Blonding products B1, B2 and B3 in each case consist of a blonding cream and an associated developer, together with a bleach booster. The ready-to-use blonding product was prepared by adding 50 g of the bleach booster to 50 g of the corresponding blonding cream. 20 g of the corresponding developer were stirred in. After application onto head hair and a period of exposure of 30 minutes, excellent lightening was observed after rinsing and drying.

2.1.1 Blonding cream

	B1	B2	B3
Stenol 1618	10.00	10.00	10.00
Lorol technical	3.00	3.00	3.00
Eumulgin B2	3.00	3.00	3.00
Ammonium sulfate	1.00	1.00	1.00
Turpinal SL	0.20	0.20	0.20
Gluadin W 40	4.00	4.00	4.00
Ammonia, 25%	0.62	0.62	0.62
α-Lipoic acid	0.10	0.50	1.00
Water	ad 100	ad 100	ad 100

2.1.2 Developer

	B1	B2	B3
Lorol technical	3.60	3.60	3.60
Eumulgin B2	0.90	0.90	0.90
Disponil FES 77 IS	2.25	2.25	2.25
Hydrogen peroxide, 50%	24.0	24.0	24.0
Turpinal SL	1.50	1.50	1.50

Aculyn 33A	15.0	15.0	15.0
Water	ad 100	ad 100	ad 100

2.1.3 Bleach booster

$(NH_4)_2S_2O_8$ 96

Aerosil 200 4

2.2 Oxidative dyes

[0273] Dyes F1 to F16 consist in each case of a dye cream and an associated developer. The ready-to-use dye was prepared by stirring together 50 g of the dye cream with 50 g of the corresponding developer. After application onto head hair and a period of exposure of 30 minutes, an excellent dyeing result was observed after rinsing and drying.

2.2.1 Dye creams

	F1	F2	F3	F4	F5	F6	F7	F8
Hydrenol D	5.50	5.50	5.50	5.50	5.50	5.50	5.50	5.50
Lorol 16	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00
Eumulgin B1	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50
Eumulgin B2	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50
Lamesoft PO 65	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00
Akypo Soft 45 NV	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00
Texapon K 14 S, 70%	2.80	2.80	2.80	2.80	2.80	2.80	2.80	2.80
Ammonia, 25%	6.50	6.50	6.50	6.50	6.50	6.50	6.50	6.50
Turpinal SL	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20
p-Tolylenediamine sulfate	2.50	0.40	0.30	0.05	0.30	2.50	0.40	0.30
Resorcinol	0.40	0.10	1.00	0.02	0.03	0.40	0.10	1.00
2,4-Diaminophenoxyethanol, 2 HCl	2.00	-	-	-	-	2.00	-	-
2-Methylresorcinol	-	1.00	0.03	-	0.50	-	1.00	0.03
2,4,5,6-Tetraaminopyrimidine sulfate	-	1.50	-	-	-	-	1.50	-
Bis-(5-amino-2-hydroxy-phenyl)methane, 2 HCl	-	0.06	-	-	-	-	0.06	-
m-Aminophenol	-	-	0.01	0.03	0.02	-	-	0.01
4-Chlororesorcinol	-	-	0.60	0.01	0.10	-	-	0.60

	F1	F2	F3	F4	F5	F6	F7	F8
Ascorbic acid	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10
Sodium sulfite, 96%	0.40	0.40	0.40	0.40	0.40	0.40	0.40	0.40
α-Lipoic acid	0.10	0.10	0.10	0.20	0.20	1.00	1.00	0.50
Aqua	<----------ad 100---------->							

2.2.2 Developer

	F9	F10	F11	F12	F13	F14	F15	F16
Cetearyl alcohol	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00
Lorol	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00
Eumulgin B2	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00
Ascorbic acid	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50
Sodium sulfite, 96%	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50
Turpinal SL	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20
Gluadin W 40	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00
Ammonia, 25%	6.00	6.00	6.00	6.00	6.00	6.00	6.00	6.00
Resorcinol	0.10	8.00	8.00	8.00	8.00	8.00	8.00	8.00
p-Tolylenediamine sulfate	0.15	0.70	1.80	0.15	0.70	1.80	0.70	1.80
4-Chlororesorcinol	0.03	0.02	0.50	0.03	0.02	0.50	0.02	0.50
2-Amino-2-methyl-amino-6-methoxypyridine	0.01	-	-	0.01	-	-	-	-
2,6-Dihydroxy-3,4-dimethyl-pyridine	-	0.02	-	-	0.02	-	0.02	-
2,7-Dihydroxynaphthalene	-	0.01	-	-	0.01	-	0.01	-
2-Methylresorcinol	-	0.05	-	-	0.05	-	0.05	-
m-Aminophenol	-	0.10	-	-	0.10	-	0.10	-
2,4-Diaminophenoxyethanol, 2 HCl	-	0.01	-	-	0.01	-	0.01	-
3-Amino-2-methyl-amino-6-methoxypyridine	-	0.01	0.10	-	0.01	0.10	0.01	0.10
1,3-Bis-(2,4-diamino-phenoxy)propane, 4 HCl	-	-	0.30	-	-	0.30	-	0.30
α-Lipoic acid	0.10	0.20	0.50	1.00	0.50	0.01	1.00	0.20
Water	<----------ad 100---------->							

2.2.2 Developer

	F1	F2	F3	F4	F5	F6	F7	F8

	F1	F2	F3	F4	F5	F6	F7	F8
Dipicolinic acid	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10
Disodium pyrophosphate	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03
Turpinal SL	1.50	1.50	1.50	1.50	1.50	1.50	1.50	1.50
Texapon NSO UP	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00
Aculyn 33A	12.00	12.00	12.00	12.00	12.00	12.00	12.00	12.00
Hydrogen peroxide, 50%	12.00	6.00	12.00	6.00	12.00	6.00	12.00	6.00
Ammonia	0.62	0.62	0.62	0.62	0.62	0.62	0.62	0.62
Water	<----------ad 100---------->							

	F9	F10	F11	F12	F13	F14	F15	F16
Lorol C16	3.50	3.50	3.50	3.50	3.50	3.50	3.50	3.50
Eumulgin B2	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Disponil FES 77 IS	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50
Hydrogen peroxide, 50%	24.00	20.00	12.00	24.00	20.00	12.00	24.00	20.00
Turpinal SL	1.50	1.50	1.50	1.50	1.50	1.50	1.50	1.50
Aculyn 33A	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0
Water	<----------ad 100---------->							

2.3 Ammonia-free oxidative dye

[0274] Dyes F17 to F25 consist in each case of a dye cream and the developer stated below. The ready-to-use dye was prepared by stirring together 50 g of the dye cream with 50 g of the developer. After application onto head hair and a period of exposure of 30 minutes, an excellent dyeing result was observed after rinsing and drying.

2.3.1 Dye creams

	F17	F18	F19	F20	F21	F22	F23	F24	F25
Hydrenol D	7.15	7.15	7.15	7.15	7.15	7.15	7.15	7.15	7.15
Lorol	2.60	2.60	2.60	2.60	2.60	2.60	2.60	2.60	2.60
Eumulgin B1	0.65	0.65	0.65	0.65	0.65	0.65	0.65	0.65	0.65
Eumulgin B2	0.65	0.65	0.65	0.65	0.65	0.65	0.65	0.65	0.65
Akypo Soft 45 NV	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0
Texapon K 14 S, 70%	2.80	2.80	2.80	2.80	2.80	2.80	2.80	2.80	2.80
Plantacare 1200	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00

	F17	F18	F19	F20	F21	F22	F23	F24	F25
Product W 37194	3.75	3.75	3.75	3.75	3.75	3.75	3.75	3.75	3.75
2-Aminoethan-1-ol	3.10	2.80	2.00	3.10	2.80	2.00	3.10	2.80	2.00
L-Arginine	-	1.00	-	-	1.00	-	-	1.00	-
2-Amino-2-methyl-propanol	-	-	1.50	-	-	1.50	-	-	1.50
Sodium chloride	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50
Sodium sulfite	0.40	0.40	0.40	0.40	0.40	0.40	0.40	0.40	0.40
Ascorbic acid	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10
Turpinal SL	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20
Soda water glass 40/42	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50
Potassium hydroxide, 50%	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Glycine	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
α-Lipoic acid	1.00	1.00	1.00	0.50	0.50	0.50	0.10	0.10	0.10
p-Tolylenediamine sulfate	0.40	0.40	0.40	0.40	0.40	0.40	0.40	0.40	0.40
2,7-Dihydroxy-naphthalene	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03
Resorcinol	0.12	0.12	0.12	0.12	0.12	0.12	0.12	0.12	0.12
4-Chlororesorcinol	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06
2-Methylresorcinol	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02
m-Aminophenol	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02
Water	<----------ad 100---------->								

2.3.2 Developer

Dipicolinic acid	0.10
Disodium pyrophosphate	0.03
Turpinal SL	1.50
Texapon NSO UP	2.00
Aculyn 33A	12.00
Hydrogen peroxide, 50%	12.00
Water	ad 100

2.4 Methods with pretreatment

[0275] The following tinctures were prepared for pretreatment:

	Ti1	Ti2	Ti3	Ti4	Ti5	Ti6	Ti7
D-Panthenol, 75%	0.20	0.20	0.10	0.20	0.20	0.10	0.20
Allantoin	0.10	0.10	0.10	0.10	0.10	0.10	0.10
Cremophor A25	0.20	-	-	0.20	-	-	-
Ethanol	40.00	15.00	24.00	40.00	15.00	24.00	15.00
Aristoflex AVC	-	0.40	-	-	0.40	-	0.40
Menthol, natural	-	0.01	-	-	0.01	-	0.01
PEG-40 hydrogenated castor oil	-	0.50	0.30	-	0.50	0.30	0.50
Urea, technical, 46% N	-	-	5.00	-	-	5.00	-
Vitamin E acetate	-	-	0.30	-	-	0.30	-
D,L-α-bisabolol	-	-	0.10	-	-	0.10	-
α-Lipoic acid	1.00	1.00	1.00	0.50	0.50	0.50	2.00
Water	ad 100	ad 100	ad 100	ad 100	ad 100	ad 100	ad 100

	Ti8	Ti9	Ti10	Ti11
Cutina GMS-V	0.3	0.3	0.2	0.2
Dehyquart F 75	0.8	0.8	1.0	1.0
Lanette O	4.0	4.0	3.0	3.0
Eumulgin B2	0.2	0.2	0.3	0.3
Paraffinum liquidum	0.8	0.8	-	-
Varisoft W 575 PG	-	-	4.0	4.0
Isopropyl myristate	-	-	1.0	1.0
Tego Amid S 18	-	-	0.3	0.3
Salcare SC 96	-	-	0.6	0.6
Citric acid	-	-	0.4	0.4
D-Panthenol	-	-	0.2	0.2
Ajidew NL 50	-	-	1.0	1.0
Dehyquart A CA	3.0	3.0	-	-
Lactic acid	0.5	0.5	-	-
Phenoxyethanol	0.4	0.4	0.3	0.3
Wacker-Belsil ADM 8020 VP	0.9	0.9	-	-
α-Lipoic acid	0.1	0.3	0.1	0.2

	Ti8	Ti9	Ti10	Ti11
Water	ad 100	ad 100	ad 100	ad 100

[0276] A tress of hair (Kerling natural European hair 6/0) was immersed in the above-stated tinctures, left there for 3 minutes and removed from the tincture. The tress was not rinsed, but instead only gently blotted with a cloth. 20 g of dye F1 (see point 2.2) were then applied onto the tress and, once a period of exposure of 30 minutes had elapsed, rinsed off again. The tress was dried.

2.5 Examples of pre- and post-treatment preparations

2.5.1 Hair protection shampoo for pre- or post-treatment

	1	2	3	4
Texapon N 70	15.0	15.0	15.0	15.0
Arlypon F			1.0	1.0
Antil 141 L			1.0	1.0
Gluadin WQ			0.3	0.3
Dow Corning 193 fluid			0.5	0.5
Sodium benzoate	0.5	0.5	0.5	0.5
Dehyton PS	6.0	6.0	6.0	6.0
Salicylic acid	0.2	0.2	0.2	0.2
Euperlan PK 3000 AM	2.0	2.0		
D-Panthenol	0.1	0.1		
Nicotinamide	0.1	0.1		
Cetiol HE	0.3	0.3	1.5	1.5
Cremophor CO 40			2.0	2.0
Polyquaternium 10	0.2	0.2	0.5	0.5
Sodium chloride	1.5	1.5	0.3	0.3
α-Lipoic acid	0.1	0.5	0.05	0.2
Water	ad 100	ad 100	ad 100	ad 100

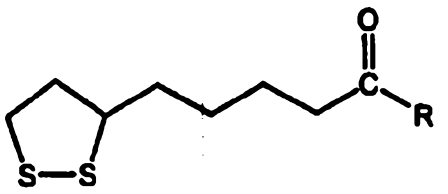
2.5.2 Hair protection shine tonic for post-treatment

	1	2	3	4
Dehyquart A CA	1.0	1.0	-	-
Polyquart H 81	2.0	2.0	-	-
Cremophor CO 40	2.0	2.0	-	-
Phenoxyethanol	0.4	0.4	-	-
Citric acid	0.5	0.5	-	-
Isopropanol	-	-	6.0	6.4
Dow Corning 200 fluid	-	-	2.0	2.0
n-Butane	-	-	91.5	91.5
α-Lipoic acid	0.1	0.5	0.5	0.1
Water	ad 100	ad 100	-	-

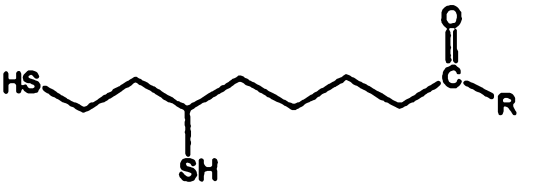
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CLAIMS

1. A use of α-lipoic acid and/or a derivative thereof according to formula (Ia) or a reduced form of formula (Ib).



(Ia)



(Ib)

in which in each case R denotes a residue

-NR'R", in which R' and R" mutually independently denote a hydrogen atom, a (C_1 to C_{22}) alkyl group, (C_2 to C_{22}) alkenyl group, a (C_1 to C_{20}) hydroxyalkyl group, a sulfo-(C_1 to C_6)-alkyl group, an optionally substituted (C_1 to C_6) carboxyalkyl group, or

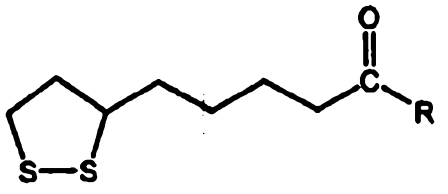
-OM, in which M means a hydrogen atom, a (C_1 to C_{22}) alkyl group, (C_2 to C_{22}) alkenyl group, a (C_1 to C_{20}) hydroxyalkyl group or an equivalent of a mono- or polyvalent cation

for reducing oxidative hair damage during oxidative hair treatment.

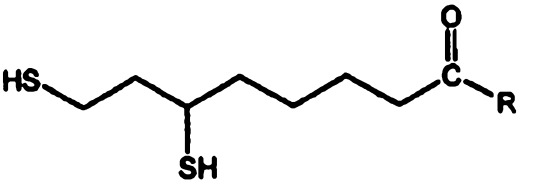
2. A preparation containing in a cosmetic carrier a combination of

(i) at least one oxidizing agent and

(ii) at least one compound from the group formed by α-lipoic acid and derivatives thereof according to formula (Ia) or a reduced form of formula (Ib),



(Ia)



(Ib)

in which in each case R denotes a residue

-NR'R", in which R' and R" mutually independently denote a hydrogen atom, a (C_1 to C_{22}) alkyl group, (C_2 to C_{22}) alkenyl group, a (C_1 to C_{20}) hydroxyalkyl group, a sulfo-(C_1 to C_6)-alkyl group, an optionally substituted (C_1 to C_6) carboxyalkyl group, or

-OM, in which M means a hydrogen atom, a (C_1 to C_{22}) alkyl group, (C_2 to C_{22}) alkenyl group, a (C_1 to C_{20}) hydroxyalkyl group or an equivalent of a mono- or polyvalent cation.

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3. The preparation as claimed in claim 2, wherein the compounds selected from the compounds of the group formed by α-lipoic acid and the derivatives thereof are present in a quantity of 0.001 to 5.0 wt. %, relative to the weight of the ready-to-use preparation.

4. The preparation as claimed in either of claim 2 or claim 3, wherein it additionally contains at least one color-modifying component.

5. The preparation as claimed in claim 4, wherein the color-modifying component is selected from

(a) at least one oxidation dye precursor of the developer component type and optionally additionally at least one coupler component

and/or

(b) oxo dye precursors

and/or

(c) at least one direct dye

and/or

(d) at least one precursor of nature-analogous dyes

and/or

(e) at least one bleach booster.

6. The preparation as claimed in any one of claims 2 to 5, wherein it additionally contains at least one surfactant.

7. The preparation as claimed in any one of claims 2 to 6, wherein the oxidizing agent is hydrogen peroxide and/or at least one addition product of hydrogen peroxide onto inorganic or organic compounds.

8. The preparation as claimed in any one of claims 2 to 7, wherein the oxidizing agent is present in a quantity of 1.0 to 10.0 wt. % relative to the weight of the ready-to-use preparation.

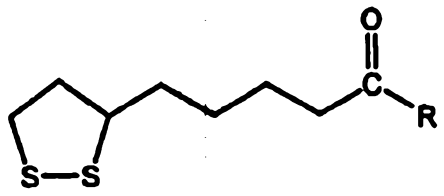
9. A method for oxidative hair treatment, in which an oxidative cosmetic preparation containing at least one oxidizing agent in a cosmetic carrier is applied onto the hair and, after a period of exposure, is rinsed out of the hair, wherein

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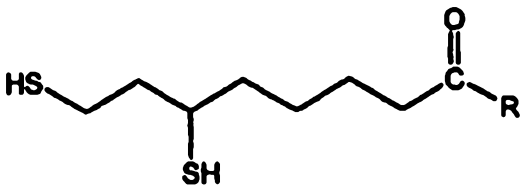
- immediately before application of the oxidative cosmetic preparation, a cosmetic preparation containing in a cosmetic carrier at least one compound from the group formed by α-lipoic acid and the derivatives thereof is applied and is optionally rinsed off again after a period of exposure

and/or

- the oxidative cosmetic preparation additionally contains at least one compound from the group formed by α-lipoic acid and the derivatives thereof, according to formula (Ia) or the in each case reduced form of the formula (Ib),



(Ia)



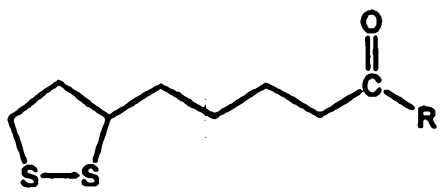
(Ib)

in which in each case R denotes a residue

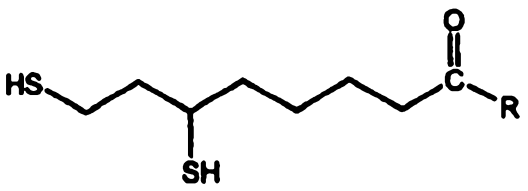
-NR'R", in which R' and R" mutually independently denote a hydrogen atom, a (C_1 to C_{22}) alkyl group, (C_2 to C_{22}) alkenyl group, a (C_1 to C_{20}) hydroxyalkyl group, a sulfo-(C_1 to C_6)-alkyl group, an optionally substituted (C_1 to C_6) carboxyalkyl group, or

-OM, in which M means a hydrogen atom, a (C_1 to C_{22}) alkyl group, (C_2 to C_{22}) alkenyl group, a (C_1 to C_{20}) hydroxyalkyl group or an equivalent of a mono- or polyvalent cation.

10. A packaging unit, when used for oxidative hair treatment, comprising in a first container an oxidative cosmetic preparation which contains at least one oxidizing agent in a cosmetic carrier and in a second container a cosmetic preparation which contains in a cosmetic carrier at least one compound from the group formed by α-lipoic acid and the derivatives thereof, according to formula (Ia) or the in each case reduced form of the formula (Ib),



(Ia)



(Ib)

in which in each case R denotes a residue

-NR'R", in which R' and R" mutually independently denote a hydrogen atom, a (C_1 to C_{22}) alkyl group, (C_2 to C_{22}) alkenyl group, a (C_1 to C_{20}) hydroxyalkyl group, a sulfo-(C_1 to C_6)-alkyl group, an optionally substituted (C_1 to C_6) carboxyalkyl group, or

-OM, in which M means a hydrogen atom, a (C_1 to C_{22}) alkyl group, (C_2 to C_{22})

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alkenyl group, a (C_1 to C_{20}) hydroxyalkyl group or an equivalent of a mono- or polyvalent cation.

11. A use as defined in claim 1, substantially as hereinbefore described with reference to any one of the examples.

12. A preparation as defined in claim 2, substantially as hereinbefore described with reference to any one of the examples.

13. A method for oxidative hair treatment as defined in claim 9, substantially as hereinbefore described with reference to any one of the examples.

Dated 17 May 2012
Henkel Kommanditgesellschaft auf Aktien
Patent Attorneys for the Applicant/Nominated Person
SPRUSON & FERGUSON