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(54) NOVEL COUPLING COMPONENTS

(76) Inventors: **Georg Knuebel**, Duesseldorf (DE); **Horst Hoeffkes**, Duesseldorf (DE); **Ralph Nemitz**, Juechen (DE)

Correspondence Address:
DANN DORFMAN HERRELL AND SKILLMAN
A PROFESSIONAL CORPORATION
1601 MARKET STREET
SUITE 2400
PHILADELPHIA, PA 19103-2307 (US)

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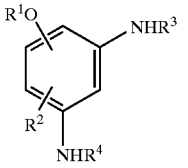
(57) ABSTRACT

Keratinic fibers, especially human hair are dyed by an agent containing a coupling component which is an m-phenylenediamine derivative of the formula



(I)

wherein R^1 is a C_{1-4} alkyl group or a C_{1-4} monohydroxy alkyl group, R^2 is a hydrogen atom, a methyl or an ethyl group and each of R^3 and R^4 is independently a branched or linear C_{2-6} hydroxyalkyl group, with the proviso that the R^1O group is in the ortho or meta position to both amino groups; and a cosmetically acceptable carrier. These agents afford desired color nuances in a sufficient intensity and fastness, exhibit good fiber affinity and are safe from a toxicological and dermatological point of view.

NOVEL COUPLING COMPONENTS

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application is a continuation under 35 U.S.C. § 365(c) and 35 U.S.C. § 120 of international application PCT/EP2003/014368, filed on Dec. 17, 2003. This application also claims priority under 35 U.S.C. § 119 of DE 102 60 834.2, filed Dec. 23, 2002. Each of the aforementioned applications is incorporated herein by reference in its entirety.

BACKGROUND OF THE INVENTION

[0002] The present invention relates to agents for dyeing keratinic fibers, which contain, especially m-phenylenediamine derivatives, a method for dyeing hair with these agents, as well as some of these m-phenylenediamine derivatives themselves and intermediate products, which are formed during the synthesis of these compounds.

[0003] Because of their intensive colors and good fastness properties, the so-called oxidation dyes play an important role in dyeing keratin fibers, especially human hair. Such dyeing agents contain oxidation dye precursors, so-called developer components and coupling components. Under the influence of oxidizing agents or of oxygen from the air, the developer components form the actual dyes with one another or by coupling with one or more coupling components.

[0004] Usually, primary aromatic amines with a further free or substituted hydroxy or amino group in the para or ortho position, diaminopyridine derivatives, heterocyclic hydrazones, 4-aminopyrazolone derivatives as well as 2,4,5,6-tetraminopyrimidine and its derivatives are used as developer components.

[0005] Special representatives are, for example, p-phenylenediamine, p-toluylenediamine, 2,4,5,6-tetraminopyrimidine, p-aminophenol, N,N-bis(2-hydroxyethyl)-p-phenylenediamine, 2-(2,5-diaminophenyl)-ethanol, 2-(2,5-diaminophenoxy)-ethanol, 1-phenyl-3-carboxyamido-4-amino-pyrazolone-5,4-amino-3-methylphenol, 2-aminomethyl-4-aminophenol, 2-hydroxy-4,5,6-triaminopyrimidine, 2,4-dihydroxy-5,6-diaminopyrimidine, 2,5,6-triamino-4-hydroxypyrimidine and 1,3-N,N'-bis(2-hydroxyethyl)-N,N'-bis(4-aminophenyl)-diamino-propane-2-ol.

[0006] Usually, m-phenylenediamine derivatives, napthols, resorcinol and resorcinol derivatives, pyrazolones and m-aminophenols are used as coupling components. In particular, 1-naphthol, 1,5-, 2,7- and 1,7-dihydroxynaphthalene, 5-amino-2-methylphenol, m-aminophenol, resorcinol, resorcinol monomethylether, m-phenylenediamine, 1-phenyl-3-methyl-pyrazolone-5, 2,4-dichloro-3-aminophenol, 1,3-bis-(2,4-diaminophenoxy)-propane, 2-chlororesorcinol, 4-chlororesorcinol, 2-chloro-6-methyl-3-aminophenol, 2-methylresorcinol, 5-methylresorcinol and 2-methyl-4-chloro-5-aminophenol are suitable as coupling substances.

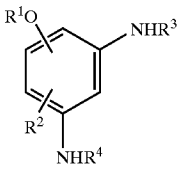
[0007] Good oxidation dye precursors should primarily fulfill the following prerequisites. During oxidative coupling, they must form the desired color nuances in a sufficient intensity and fastness. Furthermore, they must have a good affinity for the fibers. Especially in the case of human hair, there must be no noticeable differences between stressed and freshly washed hair (leveling capability). They should be resistant to the effects of light, heat, perspiration, friction and the effects of chemical reducing agents, such as permanent waving liquids. Finally, if they are to be used as hair-dyeing agents, they should not dye the scalp too much and, above all, they should be safe from a toxicological and dermatological point of view. Finally, it should be easily possible to remove the dyeing achieved from the hair by bleaching in the event that it does not meet the individual requirements of the particular person involved and is to be undone.

[0008] As a rule, it is not possible to achieve a hair shade, which has a natural appearance, with only one developer component or only one special coupling/developer combination. In practice, therefore, combinations of different developers and/or coupling components are usually used. There is therefore a constant need for new, improved dye components, which are problem-free also from a toxicological and dermatological point of view.

[0009] It is therefore an object of the present invention to develop new coupling components, which fulfill the requirements imposed on oxidation dye precursors with respect especially to toxicological and dermatological properties and make dyeings possible over a wide spectrum of colors with good fastness properties.

SUMMARY OF THE INVENTION

[0010] Surprisingly, it has now been found that special m-phenylenediamine derivatives fulfill to a high degree the requirements imposed on coupling components. These derivatives form components of agents for dyeing keratinic fibers, especially human hair, which are comprised of a cosmetically acceptable carrier and a coupling component which is a m-phenylenediamine derivative of Formula (I)



(I)

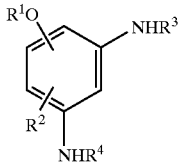
[0011] wherein R^1 is a C_{1-4} alkyl group or a C_{1-4} monohydroxy alkyl group, R^2 is a hydrogen atom, a methyl or an ethyl group and each of R^3 and R^4 is independently a branched or linear C_{2-6} hydroxyalkyl group, with the proviso that the R^1O group is in the ortho or meta position to both amino groups The coupling components according to the invention, especially p-toluylenediamine, 1-(2-hydroxyethyl)-2,5-diaminobenzene, 2,4,5,6-tetraminopyrimidine and bis-(2-hydroxy-5-aminophenyl)methane, make possible dyeings with high color intensities and good to very good fastness properties in the red and violet regions.

[0012] Another aspect of the present invention is the use of the m-phenylenediamine derivatives for dyeing keratinic fibers according to the invention.

[0013] Yet another aspect of the present invention is a method for dyeing keratinic fibers, for which the hair-dyeing

agent according to the invention is applied on the fibers and, after a period of action, rinsed off once again.

[0014] A further aspect of the present invention are m-phenylenediamine derivatives of Formula (I)



(I)

[0015] wherein R^1 is a C_{1-4} alkyl group or a C_{1-4} monohydroxy alkyl group, R^2 is a hydrogen atom, a methyl or an ethyl group and each of R^3 and R^4 is independently a branched or linear C_{2-6} hydroxyalkyl group, with the proviso that the R^1O group is in the ortho or meta position to both amino groups. m-Phenylenediamine derivatives, which are selected from the group formed by 2,6-bis-((2-hydroxyethyl)amino)$_4$-methylanisole and 2,6-bis-((2-hydroxyethyl)amino)-anisole, are preferred pursuant to the invention.

[0016] Still another aspect of the present invention are the first intermediate stages of the synthesis of the m-phenylenediamines according to the invention, selected from the group formed by bis(2-chloroethyl)(2-methoxy-5-methyl-1,3-phenylene) biscarbamate and bis(2-chloroethyl)(2-methoxy-1, 3-phenylene) biscarbamate.

[0017] An even further aspect of the present invention are the second intermediate stages of the synthesis of the m-phenylenediamines according to the invention, selected from the group formed by 3,3'-(2-methoxy-5-methyl-1,3-phenylene)bis(1,3-oxazolidine-2-one) and 3,3'-(2-methoxy-1,3-phenylene)bis(1,3-oxazolidine-2-one).

DETAILED DESCRIPTION OF CERTAIN EMBODIMENTS OF THE INVENTION

[0018] Pursuant to the invention, keratinic fibers are understood to be fur, wool, feathers and, in particular, human hair. Although the oxidation dyes according to the invention are primarily suitable for dyeing keratinic fibers, there is, in principle, no reason why they cannot also be used in other fields, especially in color photography.

[0019] Since the m-phenylenediamine derivatives according to the invention are amino compounds, the known acid addition salts can be prepared in the normal way from these. All statements in this publication and, accordingly, the claimed scope of protection therefore relates to the compounds present in free form as well as to their water-soluble, physiologically acceptable salts. Examples of such salts are hydrochlorides, hydrobromides, sulfates, phosphates, acetates, propionates, citrates and lactates. Moreover, the hydrochlorides and sulfates are particularly preferred.

[0020] Methyl, ethyl, propyl, isopropyl, butyl, pentyl and hexyl are examples of C_1 to C_6 alkyl groups, named as substituents in the compounds according to the invention, ethyl and methyl being preferred. Hydroxymethyl, 2-hydroxyethyl, 3-hydroxypropyl or 4-hydroxybutyl are named as preferred C_1 to C_6 monohydroxyalkyl groups, a 2-hydroxyethyl group being particularly preferred.

[0021] The m-phenylenediamine derivatives of Formula (I) can be synthesized with the help of conventional organic methods. By way of example, reference is made here to the experimental methods described in the Examples.

[0022] Some structurally related m-phenylenediamine derivatives are already known from the art as coupling components. The International Offlengungschrift WO-A2-93/10 744 discloses a method for dyeing hair in an acidic medium (pH<7), for which structurally related m-phenylenediamine derivatives are used. The compound 2,4-di-(β-hydroxyethylamino)-1-methoxybenzene is described concretely there. The compounds, now claimed, differ from this compound owing to the fact that they are structural isomers. References to the compounds, which are now claimed, and to their outstanding dyeing properties, cannot be inferred from this publication.

[0023] Pursuant to the invention, m-phenylenediamine derivatives of Formula (I) are preferred, for which the substituents R^3 and R^4 are identical. Preferably the substituents R^3 and R^4 represent a 2-hydroxyethyl group or a 3-hydroxypropyl group. A 2-hydroxyethyl group is most particularly preferred.

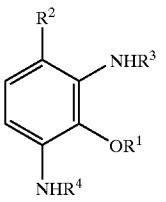
[0024] Moreover, the m-phenylenediamine derivatives of Formula (I), in which the R^1 substituent represents a C_1 to C_4 alkyl group, are preferred pursuant to the invention. Compounds of Formula (I), are preferred, in which R^1 represents a methyl group.

[0025] Furthermore, the m-phenylenediamine derivatives of Formula (I), in which R^2 represents a methyl group, may be preferred pursuant to the invention.

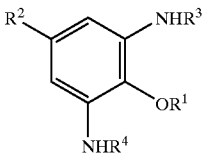
[0026] It is possible to differentiate between two groups of isomers, depending on the position of the R^1O substituent in relation to both amino groups.

[0027] Within the scope of a first embodiment of the present invention, isomers are preferred, in which the R^1O is in the ortho position to both amino groups. Aside from the compounds, in which R^2 represents hydrogen, the following compounds of are included with the scope of this embodiment

(Ia)



(Ib)

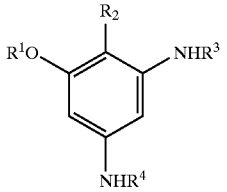


[0028] 2,6-Bis-((2-hydroxyethyl)amino)-anisole and 2,6-bis-((2-hydroxyethyl)amino)-4-methylanisole are particularly preferred compounds of this embodiment.

[0029] Within the scope of a second embodiment of the present invention, those isomers are preferred, in which the

R^1O group is in the meta position with respect to both amino groups. Within the scope of this embodiment, the following compounds are included.

(Ic)



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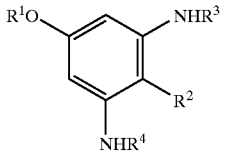
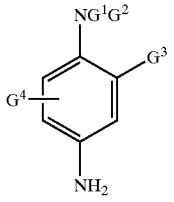


[0030] Aside from m-phenylenediamine derivatives of Formula (1), the dyes according to the invention furthermore may contain at least one developer component.

[0031] As developer component, primary aromatic amines with a further free or substituted hydroxy or amino group in the para or ortho position, diaminopyridine derivatives, heterocyclic hydrazones, 4-amino-pyrazole derivatives, such as 2,4,5,6-tetraminopyrimdine and its derivatives, are usually used.

[0032] Pursuant to the invention, the use of a p-phenylenediamine derivate or one of its physiologically acceptable salts, may be preferred. Particularly preferred are p-phenylenediamine derivates of Formula (E1)

(E1)



in which

[0033] G^1 represents a hydrogen atom, a C_1 to C_4 alkyl group, a C_1 to C_4 monohydroxyalkyl group, a C_2 to C_4 polyhydroxyalkyl group, a (C_1 to C_4) alkoxy (C_1 to C_4) alkyl group, a 4'-aminophenyl group or a C_1 to C_4 alkyl group, which is substituted with an nitrogen-containing group, a phenyl group or a 4'-aminophenyl group,

[0034] G^2 represents a hydrogen atom, a C_1 to C_4 alkyl group, a C_1 to C_4 monohydroxyalkyl group, a C_2 to C_4 polyhydroxyalkyl group, a (C_1 to C_4) alkoxy (C_1 to C_4) alkyl group or a C_1 to C_4 alkyl group, which is substituted with a nitrogen-containing group,

[0035] G^3 represents a hydrogen atom, a halogen atom, such as a chlorine, bromine, iodine or fluorine atom, a C_1 to C_4 alkyl group, a C_1 to C_4 monohydroxyalkyl group, a C_2 to C_4 polyhydroxyalkyl group, a C_1 to C_4 hydroxyalkoxy group, a C_1 to C_4 acetylaminoalkoxy group, a C_1 to C_4 mesylaminoalkoxy group or a C_1 to C_4 carbamoylaminoalkoxy group.

[0036] G^4 represents a hydrogen atom, a halogen atom or a C_1 to C_4 alkyl group or

[0037] when G^3 and G^4 are in an ortho position to one another, they may jointly form a bridging α,ω-alkylenedioxy group, such as an ethylenedioxy group.

[0038] Examples of the C_1 to C_4 alkyl groups, named as substituents in the compounds according to the invention, are the methyl, ethyl, propyl, isopropyl and butyl groups, ethyl and methyl groups being preferred alkyl groups. For example, methoxy or ethoxy groups are C_1 to C_4 alkoxy groups, which are preferred pursuant to the invention. Furthermore, a hydroxymethyl group, a 2-hydroxyethyl group, a 3-hydroxypropyl group or a 4-hydroxybutyl group may be named as a preferred example of a C_1 to C_4 hydroxyalkyl group, a 2-hydroxyethyl group being particularly preferred. The 1,2-dihydroxyethyl group is a particularly preferred C_2 to C_4 polyhydroxyalkyl group. F, Cl or Br atoms are examples of halogen atoms pursuant to the invention, Cl atoms being particularly preferred. The further concepts used can be derived from the definitions given here. Especially the amino group, 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 are examples of nitrogen-containing groups of Formula (E1).

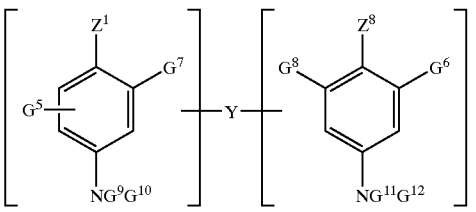
[0039] Especially preferred p-phenylenediamines of Formula (E1) are selected from p-phenylenediamine, p-toluylenediamine, 2-chloro-p-phenylenediamine, 2,3-dimethyl-p-phenylenediamine, 2,6-dimethyl-p-phenylenediamine, 2,6-diethyl-p-phenylenediamine, 2,5-dimethyl-p-phenylenediamine, N,N-dimethyl-p-phenylenediamine, 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-chloroaniline, 2-(β-hydroxyethyl)-p-phenylenediamine, 2-(α,β-dihydroxyethyl)-p-phenylenediamine, 2-fluoro-p-phenylenediamine, 2-isopropyl-p-phenylenediamine, N-(β-hydroxypropyl)-p-phenylenediamine, 2-hydroxymethyl-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-hydroxyethyloxy)-p-phenylenediamine, 2-(β-acetylaminoethyloxy)-p-phenylenediamine, N-(β-methoxyethyl)-p-phenylenediamine and 5,8-diaminobenzo-1,4-dioxane as well as their physiologically acceptable salts.

[0040] Pursuant to the invention, p-phenylenediamine, p-toluylenediamine, 2-(β-hydroxyethyl)-p-phenylenediamine, 2-(α,β-dihydroxyethyl)-p-phenylenediamine and N,N-bis-(β-hydroxyethyl)-p-phenylenediamine are particularly preferred p-phenylenediamine derivatives of Formula (E1).

[0041] Furthermore, pursuant to the invention, the use of compounds, containing at least two aromatic ring, which are

substituted by amino and/or hydroxyl groups, as developer components, may be preferred.

[0042] The two-ring developer components, which may be used in the dye compositions according to the invention, include, in particular, those corresponding to the following Formula (E2) as well as their physiologically tolerated salts



(E2)

in which

[0043] Z^1 and Z^2, independently of one another, represent a hydroxyl or amine group, which optionally is substituted by a C_1 to C_4 alkyl group, a C_1 to C_4 hydroxyalkyl group and/or a Y bridging group or which optionally is part of a bridging ring system,

[0044] the Y bridging group represents an alkylene group with 1 to 14 carbon atoms, such as a linear or branched alkylene chain or an alkylene ring, which may be interrupted or terminated by one or more nitrogen-containing groups and/or one or more hetero atoms, such as oxygen, sulfur or nitrogen atoms, and possibly by one or more hydroxyl or C_1 to C_8 alkoxy group, or a direct bond,

[0045] G^5 and G^6, independently of one another, represent a hydrogen atom or halogen atom, a C_1 to C_4 alkyl group, a C_1 to C_4 monohydroxyalkyl group, a C_1 to C_4 polyhydroxyalkyl group, a C_1 to C_4 amino alkyl group or a direct connection to the Y bridging group,

[0046] G^7, G^8, G^9, G^{10}, G^{11} and G^{12}, independently of one another represent a hydrogen atom, a direct bond to the Y bridging group or a C_1 to C_4 alkyl group, with the proviso that

[0047] the compounds of Formula (E2) contain only one Y bridging group per molecule and

[0048] the compounds of Formula (E2) contain at least one amino group, which carried as least one hydrogen atom.

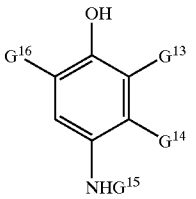
[0049] The substituents, used in Formula (E2) are defined, pursuant to the invention, analogously to the above comments.

[0050] Preferred, two-ring developer compounds of Formula (E2) 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-methyl-aminophenyl)-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 their physiologically acceptable salts.

[0051] Particularly preferred two-ring developer components of Formula (E2) are N,N'-bis-(β-hydroxyethyl)-N,N'-bis-(4'-aminophenyl)-1,3-diamino-propan-2-ol, bis-(2-hydroxy-5-aminophenyl)-methane, 1,3-bis-(2,5-diaminophenoxy)-propan-2-ol, N,N'-bis-(4'-aminophenyl)-1,4-diazacycloheptane and 1,10-bis-(2',5'-diaminophenyl)-1,4,7,10-tetraoxadecane or their physiologically acceptable salts.

[0052] Bis-(2-hydroxy-5-aminophenyl)-methane is a particularly preferred two-ring developer component of Formula (E2).

[0053] Furthermore, the use of a p-aminophenol derivative or one of its physiologically salts may be preferred pursuant to the invention. Particularly preferred are p-aminophenol derivatives of Formula (E3)



(E3)

in which:

[0054] G^{13} represents a hydrogen atom, a halogen atom, a C_1 to C_4 alkyl group, a C_1 to C_4 monohydroxyalkyl group, a C_2 to C_4 polyhydroxyalkyl group, a (C_1 to C_4)-alkoxy-(C_1 to C_4)-alkyl group, a C_1 to C_4 aminoalkyl group, a hydroxy-(C_1 to C_4)-alkylamino group, a C_1 to C_4 hydroxyalkoxy group, a C_1 to C_4 hydroxyalkyl-(C_1 to C_4)-aminoalkyl group or a (di-C_1 to C_4 alkylamino)-(C_1 to C_4)-alkyl group and

[0055] G^{14} represents a hydrogen atom or a halogen atom, a C_1 to C_4 alkyl group, a C_1 to C_4 monohydroxyalkyl group, a C_2 to C_4 polyhydroxyalkyl group, a (C_1 to C_4)-alkoxy-(C_1 to C_4)-alkyl group, a C_1 to C_4 aminoalkyl group or a C_1 to C_4 cyanoalkyl group,

[0056] G^{15} represents hydrogen, a C_1 to C_4 alkyl group a C_1 to C_4 monohydroxyalkyl group, a C_2 to C_4 polyhydroxyalkyl group, a phenyl group or a benzyl group, and

[0057] G^{16} represents a hydrogen atom or a halogen atom.

[0058] Pursuant to the invention, the substituents in Formula (E3) are similar to those defined above.

[0059] Preferred p-aminophenol of Formula (E3) are, in particular, p-aminophenol, N-methyl-p-aminophenol, 4-amino-3-methyl-phenol, 4-amino-3-fluorophenol, 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-methoxymethyl-phenol, 4-amino-2-aminomethylphenol, 4-amino-2-(β-hydroxyethyl-aminomethyl)-phenol, 4-amino-2-(α,β-dihydroxyethyl)-phenol, 4-amino-2-fluorophenol, 4-amino-2-chlorophenol, 4-amino-2,6-dichlorophenol, 4-amino-2-(diethyl-aminomethyl)-phenol as well as their physiologically acceptable salts.

[0060] p-Aminophenol, 4-amino-3-methylphenol, 4-amino-2-aminomethylphenol, 4-amino-2-(α,β-dihydroxyethyl)-phenol and 4-amino-2-(diethyl-aminomethyl)-phenol are especially preferred compounds of Formula (E3).

[0061] Furthermore, the developer component can be selected from o-aminophenol and its derivatives, such as, 2-amino-4-methylphenol, 2-amino-5-methylphenol or 2-amino-4-chlorophenol.

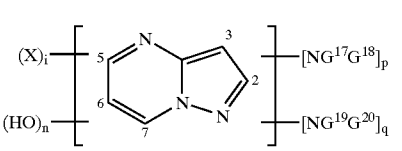
[0062] Furthermore, the developer component may be selected from heterocyclic developer components, such as pyridine, pyrimidine, pyrazole, pyrazole-pyrimidine derivatives and their physiologically acceptable salts.

[0063] Preferred pyridine derivatives are, in particular, the compounds, which are described in the British patents 1,026,978 and 1,153,196, such as 2,5-diamino-pyridine, 2-(4'-methoxyphenyl)-amino-3-amino-pyridine, 2,3-diamino-6-methoxy-pyridine, 2-(β-methoxyethyl)-amino-3-amino-6-methoxy-pyridine and 3,4-diamino-pyridine.

[0064] Preferred pyrimidine derivatives are, in particular, the compounds, which are described in the German patent DE 2 359 399, the Japanese publication JP 02019576 A2 or in the Offenlegungsschrift WO 96/15765, such as 2,4,5,6-tetraminopyrimidine, 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.

[0065] Preferred pyrazole derivatives are, in particular, the compounds, which are described in the German patents 3 843 892 and 4 133 957 and in the 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-hydrazinopyrazole, 1-benzyl-4,5-diamino-3-methylpyrazole, 4,5-diamino-3-t-butyl-1-methylpyrazole, 4,5-diamino-1-t-butyl-3-methylpyrazole, 4,5-diamino-1-(β-hydroxyethyl)-3-methylpyrazole, 4,5-diamino-1-ethyl-3-methylpyrazole, 4,5-diamino-1-ethyl-3-(4'-methoxyphenyl)-pyrazole, 4,5-diamino-1-ethyl-3-hydroxymethylpyrazole, 4,5-diamino-3-hydroxymethyl-1-methylpyrazole, 4,5-diamino-3-hydroxymethyl-1-isopropylpyrazole, 4,5-diamino-3-methyl-1-isopropylpyrazole, 4-amino-5-(β-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.

[0066] Preferred pyrazole pyrimidine derivatives are, in particular, the derivatives of pyrazole-(1,5-a)-pyrimidine of the following Formula (E4) and its tautomeric forms, provided that there is a tautomeric equilibrium:



(E4)

in which:

[0067] G^{17}, G^{18}, G^{19} and G^{20}, independently of one another, represent a hydrogen atom, a C_1 to C_4 alkyl group, an aryl group, a C_1 to C_4 hydroxyalkyl group, a C_2 to C_4 polyhydroxyalkyl group, a (C_1 to C_4)-alkoxy-(C_1 to C_4)-alkyl group, a C_1 to C_4 aminoalkyl group, which optionally is protected by an acetyl ureido or a sulfonyl group, a (C_1 to C_4)-alkylamino-(C_1 to C_4)-alkyl group, a di-((C_1 to C_4)-alkyl)-(C_1 to C_4)-aminoalkyl group, the dialkyl groups optionally forming an allicyclic ring or a heterocyclic ring with 5 or 6 carbon elements, a C_1 to C_4 hydroxyalkyl or a di-(C_1 to C_4)-(hydroxyalkyl)-(C_1 to C_4)-aminoalkyl group,

[0068] the X groups, independently of one another represent a hydrogen atom, a C_1 to C_4 alkyl group, an aryl group, a C_1 to C_4 hydroxyalkyl group a C_2 to C_4 polyhydroxyalkyl group, a C_1 to C_4 aminoalkyl group, a (C_1 to C_4)-alkylamino-(C_1 to C_4)-alkyl group, a di-((C_1 to C_4)alkyl)-(C_1 to C_4)-aminoalkyl group, the dialkyl group optionally forming an alicyclic ring or a heterocyclic ring with 5 or 6 chain elements, a C_1 to C_4 hydroxyalkyl or a di-(C_1 to C_4-hydroxyalkyl)-aminoalkyl group, an amino group, a C_1 to C_4 alkyl or di(C_1 to C_4 hydroxyalkyl)-amino group, a halogen atom, a carboxyl group or a sulfonic acid group,

[0069] i has a value of 0, 1, 2 or 3,

[0070] p has a value of 0 or 1,

[0071] q has a value of 0 or 1 and

[0072] n has a value of 0 or 1,

with the proviso that

[0073] the sum of p+q in not equal to 0,

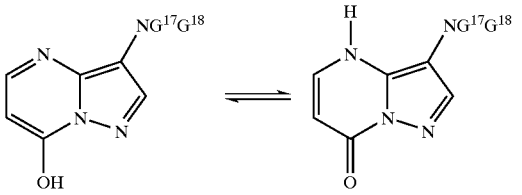
[0074] when p+q=2, n has a value of 0 and the $NG^{17}G^{18}$ and $NG^{19}G^{20}$ groups occupy the positions (2,3); (5,6); (6,7); (3,5) or (3,7),

[0075] when p+q=1, n has a value of 1 and the $NG^{17}G^{18}$ (or $NG^{19}G^{20}$) and the OH group occupy positions (2,3); (5,6); (6,7); (3,5) or (3,7).

[0076] Pursuant to the invention, the substituents used in Formula (E4) are similar to those defined above.

[0077] If the pyrazole-(1,5-a)-pyrimidine of the above Formula (E4) contains a hydroxy group at one of the positions 2, 5 or 7 of the ring system, there is a tautomeric

equilibrium, which can be represented, for example, by the following equation:



[0078] Of the pyrazole-(1,5-a)-pyrimidines of the above Formula (E4), the following may be mentioned in particular:

[0079] pyrazole-(1,5-a)-pyrimidine-3,7-diamine;

[0080] 2,5-dimethyl-pyrazole-(1,5-a)-pyrimidine-3,7-diamine;

[0081] pyrazole-(1,5-a)-pyrimidine-3,5-diamine;

[0082] 2,7-dimethyl-pyrazole-(1,5-a)-pyrimidine-3,5-diamine;

[0083] 3-aminopyrazole-(1,5-a)-pyrimidine-7-ol;

[0084] 3-aminopyrazole-(1,5-a)-pyrimidine-5-ol;

[0085] 2-(3-aminopyrazole-(1,5-a)-pyrimidine-7-ylamino)-ethanol;

[0086] 2-(7-aminopyrazole-(1,5-a)-pyrimidine-3-ylamino)-ethanol;

[0087] 2-((3-aminopyrazole-(1,5-a)-pyrimidine-7-yl)-2-hydroxy-ethyl)-amino)-ethanol;

[0088] 2-((7-aminopyrazole-(1,5-a)-pyrimidine-3-yl)-(2-hydroxy-ethyl)-amino)-ethanol;

[0089] 5,6-dimethylpyrazole-(1,5-a)-pyrimidine-3,7-diamine;

[0090] 2,6-dimethylpyrazole-(1,5-a)-pyrimidine-3,7-diamine;

[0091] 3-amino-7-dimethylamino-2,5-dimethylpyrazole-(1,5-a)-pyrimidine;

as well as their physiologically acceptable salts and their tautomeric forms, if there is a tautomeric equilibrium.

[0092] As described in the literature, the pyrazole-(1,5-a)-pyrimidines of the above formula may be synthesized by cyclizing starting out from an amino pyrazole or from hydrazine.

[0093] In a further preferred embodiment, the dyeing agent according to the invention contain at least one further coupling component.

[0094] As a rule, m-phenylenediamine derivatives, naphthols, resorcinol and resorcinol derivatives, pyrazolones and m-aminophenol derivatives are used as coupling components. In particular, 1-naphthol, 1,5-, 2,7- and 1,7-dihydroxynaphthalene, 5-amino-2-methylphenol, m-aminophenol, resorcinol, resorcinol monomethylether, m-phenylenediamine, 1-phenyl-3-methyl-pyrazolone-5, 2,4-dichloro-3-aminophenol, 1,3-bis-(2',4'-diaminophenoxy)-propane, 2-chlororesorcinol, 4-chlororesorcinol, 2-chloro-6-methyl-3-aminophenol, 2-amino-3-hydroxypyridine, 2-methylresorcinol, 5-methylresorcinol and 2-methyl-4-chloro-5-aminophenol are suitable as coupling substances.

[0095] Coupling components, preferred pursuant to the invention, are

[0096] m-aminophenol and its derivatives, such as, 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-methyphenol and 2,4-dichloro-3-aminophenol,

[0097] o-aminophenol and its derivatives,

[0098] m-diaminobenzene and its derivatives, such as 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-methyl benzene and 1-amino-3-bis-(2'-hydroxyethyl)-aminobenzene,

[0099] o-diaminobenzene and its derivatives, such as 3,4-diaminobenzoic acid and 2,3-diamino-1-methylbenzene,

[0100] di- or trihydroxyl derivatives, such as resorcinol, resorcinol monomethyl ether, 2-methylresorcinol, 5-methylresorcinol, 2,5-dimethylresorcinol, 2-chlororesorcinol, 4-chlororesorcinol, pyrogallol and 1,2,4-trihydroxybenzene,

[0101] pyridine derivatives, such as, 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,

[0102] naphthalene derivatives, such as 1-napthol, 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,

[0103] morpholine derivatives, such as 6-hydroxybenzomorpholine and 6-amino-benzomorpholine,

[0104] quinoxaline derivatives, such as 6-methyl-1,2,3,4-tetrahydroquinoxaline,

[0105] pyrazole derivatives, such as, 1-phenyl-3-methylpyrazole-5-one,

[0106] indole derivatives, such as, 4-hydroxyindole, 6-hydroxyindole and 7-hydroxyindole,

[0107] pyrimidine derivatives, such as, 4,6-diaminopyrimidine, 4-amino-2,6-dihydroxypyrimidine, 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

[0108] methylenedioxybenzene derivatives, such as 1-hydroxy-3,4-methylenedioxybenzene, 1-amino-3,4-methylenedioxybenzene and 1-(2'-hydroxyethyl)-amino-3,4-methylenedioxybenzene.

[0109] 1-Naphthol, 1,5-, 2,7- and 2,7-dihydroxynaphthalene, 3-aminophenol, 5-amino-2-methylphenol, 2-amino-3-hydroxypyridine, resorcinol, 4-chlororesorcinol, 2-chloro-6-methyl-3-aminophenol, 2-methyl-resorcinol, 5-methylresorcinol, 2,5-dimethylresorcinol and 2,6-dihydroxy-3,4-dimethylpyridine are coupling components, which are particularly preferred pursuant to the invention.

[0110] The following coupler/developer combinations have proven to be particularly suitable pursuant to the invention:

[0111] 2,6-bis-((2-hydroxyethyl)amino)-4-methylanisole/p-toluylenediamine,

[0112] 2,6-bis-((2-hydroxyethyl)amino)-4-methylanisole/1-(2-hydroxyethyl-2,5-diaminobenzene,

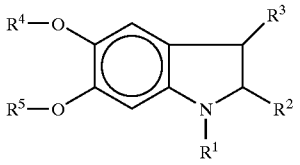
[0113] 2,6-bis-((2-hydroxyethyl)amino)$_4$-methylanisole/bis-(2-hydroxy-5-aminophenyl)methane

[0114] 2,6-bis-((2-hydroxyethyl)amino)$_4$-methylanisole/2,4,5,6-tetraminopyrimidine.

[0115] The hair-dyeing agents according to the invention contain the developer components as well as the coupling components preferably in an amount of 0.005 to 20% by weight and especially 0.1 to 5% by weight, based in each case on the total oxidative dyeing agent. Moreover, developer components and coupling components generally are used in the equal molar amounts. Even though the molar use has proven to be appropriate, a certain excess of individual oxidation dye precursors is not disadvantageous, so that the developer component and coupler component may be contained a molar ratio of 1:0.5 to 1:3 and especially of 1:1 to 1:2.

[0116] In a further embodiment of the present invention, the dyeing agents may contain at least one precursor of a dye similar to a natural product. Preferably, as precursor of dyes, similar to natural products, those indoles and indolines are used, which have at least one hydroxy or amino group, preferably as a substituent in the six-membered ring. These groups may carry further substituents, for example, in the form of an etherification or an esterification of the hydroxy group or an alkylation of the amino group. In a second preferred embodiment, the dyeing agents contain at least one indole derivative and/or indoline derivative.

[0117] Derivatives of 5,6-dihydroxyindolines of Formula (IIa),



(IIa)

are particularly suitable as precursors of hair dyes, similar to natural products,

in which, independently of one another

[0118] R^1 represents hydrogen, a C_1 to C_4 alkyl group or a C_1 to C_4 hydroxyalkyl group,

[0119] R^2 represents hydrogen or a —COOH group, or a —COOH group, which may also be present as a salt with a physiologically acceptable cation

[0120] R^3 represents hydrogen or a C_1 to C_4 alkyl group,

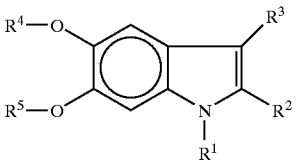
[0121] R^4 represents hydrogen, a C_1 to C_4 alkyl group or a —CO—R^6 group, in which R^6 represents a C_1 to C_4 alkyl group, and

[0122] R^5 represents only one of the groups named under R^4, as well as physiologically acceptable salts of these compounds with an organic or inorganic acid.

[0123] 5,6-Dihydroxyindoline, N-methyl-5,6-dihydroxyindoline, N-ethyl-5,6-dihydroxyindoline, N-propyl-5,6-dihydroxyindoline, N-butyl-5,6-dihydroxyindoline, 5,6-dihydroxyindoline-2-carboxylic acid, as well as 6-hydroxyindoline, 6-aminoindoline and 4-aminoindoline are particularly derivatives of indoline.

[0124] Within this group, N-methyl-5,6-dihydroxyindoline, N-ethyl-5,6-dihydroxyindoline, N-propyl-5,6-dihydroxyindoline, N-butyl-5,6-dihydroxyindoline and especially 5,6-dihydroxyindoline are to be emphasized especially.

[0125] Furthermore, the derivatives of 5,6-dihydroxyindole of Formula (IIB)



(IIb)

are outstandingly suitable as precursors of dyes, similar to natural products, in which, independently of one another,

[0126] R^1 represents hydrogen, a C_1 to C_4 alkyl group or a C_1 to C_4 hydroxyalkyl group,

[0127] R^2 represents hydrogen or a —COOH group, which may also be present as the salt with a physiologically acceptable cation

[0128] R^3 represents hydrogen or a C_1 to C_4 alkyl group,

[0129] R^4 represents hydrogen, a C_1 to C_4 alkyl group or a —CO—R^6 group, in which R^6 represents a C_1 to C_4 alkyl group, and

[0130] R^5 represents groups named under R^4, as well as physiologically acceptable salts of these compounds with an organic or inorganic salt.

[0131] 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-di hydroxyindole-2-carboxylic acid, 6-hydroxyindole, 6-aminoindole and 4-aminoindole are particularly preferred derivatives of indole.

[0132] Within this group, N-methyl-5,6-dihydroxyindole, N-ethyl-5,6-dihydroxyindole, N-propyl-5,6-dihydroxyindole, N-butyl-5,6-dihydroxyindole and especially 5,6-dihydroxyindole are to be emphasized.

[0133] In the dyeing agents according to the invention, the indole derivatives and the indoline derivatives may be used as the free bases as well as in the form of their physiologically acceptable salts with organic or inorganic acid, such as the hydrochlorides, the sulfates and hydrobromides. The indole derivatives or indoline derivatives are usually contained in these in amounts of 0.05 to 10% by weight and preferably of 0.2 to 5% by weight.

[0134] In a further embodiment, it may be preferred pursuant to the invention to use the indoline derivatives or indole derivatives in dyeing agents in combination with at least one amino acid or one oligopeptide. The amino acid advantageously is an α-amino acid and particularly preferred α-amino acids are arginine, ornithine, lysine, serine and histidine, especially arginine.

[0135] In a further, preferred embodiment of the present invention, the dyeing agents according to the invention may contain, in addition to the m-phenylenediamine derivatives of Formula (I) according to the invention, one or more substantive dyes for nuancing. Usually, substantive dyes are nitrophenylenediamines, nitroaminophenoles, azo dyes, anthraquinone or indophenole. Preferred substantive dyes are the compounds known under the international names or trade names as 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 its salts, 2-amino-6-chloro-4-nitrophenol, 4-ethylamino-3-nitrobenzoic acid and 2-chloro-6-ethylamino-1-hydroxy-4-nitrobenzene.

[0136] Furthermore, the agents according to the invention may contain a cationic substantive dye. Particularly preferred in this connection are

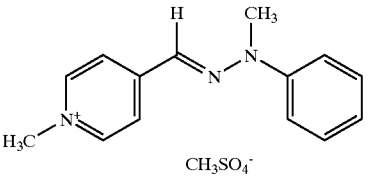
[0137] (a) cationic triphenylmethane dyes, such as Basic Blue 7, Basic Blue 26, Basic Violet 2 and Basic Violet 14,

[0138] (b) aromatic systems, which are substituted by a quaternary nitrogen group, such as Basic Yellow 57, Basic Red 76, Basic Blue 99, Basic Brown 16 and Basic Brown 17, and

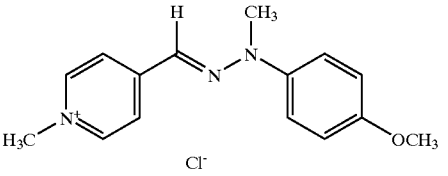
[0139] (c) substantive dyes, which contain a heterocyclic ring, which has at least one quaternary nitrogen atom, as named, for example, in claims **6** to **11** of EP-A2-998 908, to which reference is made explicitly here.

[0140] The following compounds, in particular, are cationic substantive dyes of group (c):

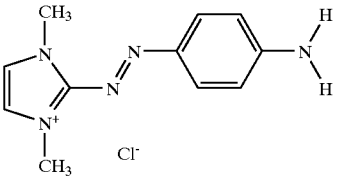
(DZ1)



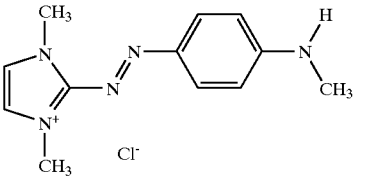
(DZ2)



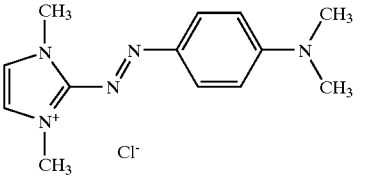
(DZ3)



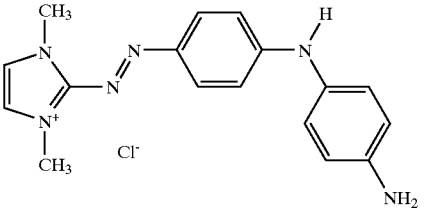
(DZ4)



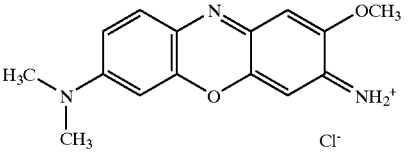
(DZ5)



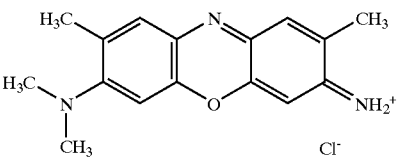
(DZ6)



(DZ7)



(DZ8)



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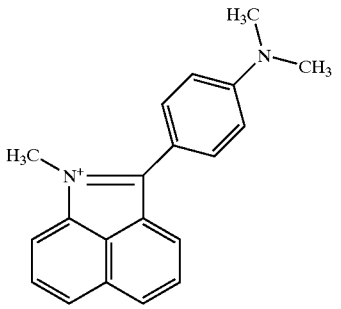
(DZ9)



[0141] The compounds of Formulas (DZ1), (DZ3) and (DZ5), which are also known under the names Basic Yellow 87, Basic Orange 31 and Basic Red 51, are particularly preferred cationic substantive dyes of group (c).

[0142] The cationic substantive dyes, which are sold under the trade name Arianor® are, pursuant to the invention, also particularly preferred cationic substantive dyes.

[0143] The agents of this embodiment according to the invention contain the substantive dyes in amounts of 0.01 to 20% by weight based on the whole of the dyeing agent.

[0144] Furthermore, the preparations according to the invention may also be contained in naturally occurring dyes such as, in particular, henna red, henna natural, henna black, chamomile flowers, sandalwood, black tea, buckthorn bark, sage, dogwood, madder root, catechu, sedre and alkanet.

[0145] Furthermore, it is not necessary that the oxidation dye precursors or the substantive dyes in each represent uniform compounds. Instead, due to the methods of producing the individual dyes, other components may be contained in subordinate amounts in the hair-dyeing agents according to the invention, provided that they do not have a negative effect on the dyeing result or are precluded for other reasons, such as toxicological reasons.

[0146] With respect to the dyes, which can be used in the hair dyeing and tinting agents according to the invention, reference is furthermore made explicitly to the Ch. Zviak monograph, "The Science of Hair Care, Chapter 7, (pages 248-250; Substantive Dyes), as well as to Chapter 8, pages 264-267, Oxidation Dye Precursors), published as Volume 7 of the series "Dermatology" (by: Ch. Culnan and H. Maibach), Marcel Dekker Inc., New York, Basel, 1986, as well as to the "Europäische Inventar der Kosmetik-Rohstoffe (European Inventory of Cosmetic Raw Materials)" published by the European Community, obtainable in diskette form from Bundesverband Deutscher Industrie- und Handelsunternehmen for Arzneimittel, Reformwaren und Korperpflegemittel e.V., Mannheim.

[0147] The dyeing agents according to the invention furthermore may contain all active ingredients, additives and auxiliary materials, which are known for such preparations. In many cases, the dyeing agents contain at least one surfactant, anionic as well as zwitterionic, ampholytic, nonionic and cationic surfactants, in principle, being suitable. However, in many cases, it has proven to be advantageous to select the surfactants from anionic, zwitterionic or nonionic surfactants.

[0148] All anionic, surface-active materials, suitable for use on the human body, are suitable as anionic surfactants in the preparation according to the invention. They are characterized, by a water-solubilizing, anionic group, such as a carboxylate, sulfate, sulfonate or phosphate group and a lipophilic alkyl group with about 10 to 22 carbon atoms. In addition, glycol ether groups or polyglycol ether groups, ester, ether and amide groups, as well as hydroxyl groups may be contained in the molecule. Examples of suitable anionic surfactants, always in the form of the sodium, potassium and ammonium salts, as well as the mono-, di- and trialkylanol ammonium salts with 2 or 3 carbon atoms in the alkanol group, are

[0149] linear fatty acids with 10 to 22 carbon atoms (soaps),

[0150] ether carboxylic acids of the Formula R—O—$(CH_2—CH_2O)_x—CH_2—COOH$, in which R represents a linear alkyl group with 10 to 22 carbon atoms and x=0 or 1 to 16,

[0151] acyl sarcosides with 10 to 18 carbon atoms in the acyl group,

[0152] acyl taurides with 10 to 18 carbon atoms in the acyl group,

[0153] acyl isothionates with 10 to 18 carbon atoms in the acyl group,

[0154] monoalkyl and dialkyl esters of sulfosuccinic acid with 8 to 18 carbon atoms in the alkyl group and monoalkyl polyethylene oxide esters of sulfosuccinic acid with 8 to 18 carbon atoms in the alkyl group and 1 to 6 ethylene oxide groups,

[0155] linear alkanesulfonates with 12 to 18 carbon atoms,

[0156] linear α-olefinsulfonates with 12 to 18 carbon atoms,

[0157] methyl esters of alpha-sulfo fatty acids, the latter containing 12 to 18 carbon atoms,

[0158] alkylsulfates and alkylpolyglycol ether sulfates of Formula R—$O(CH_2—CH_2O)_c—SO_3H$, in which R is a preferably linear alkyl group with 10 to 18 carbon atoms and x=0 or 1 to 12

[0159] mixtures of surface-active hydroxysulfonates of DE-A-37 25 030,

[0160] sulfated hydroxyalkyl polyethylene ethers and/or hydroxyalkyl polypropylene glycol ether of DE-A-37 23 354,

[0161] sulfonates of unsaturated fatty acids with 12 to 24 carbon atoms and 1 to 6 double bonds of DE-A-39 26 344,

[0162] esters of tartaric acid and citric acids with alcohols, which represent addition products of about 2 to 15 molecules of ethylene oxide and/or propylene oxide and fatty alcohols with 8 to 22 carbon atoms.

[0163] Alkyl sulfate, alkylpolyglycol ether sulfates and ether carboxylic acids with 10 to 18 carbon atoms in the alkyl group and up to 12 glycol ether groups on the molecule, as well as, in particular, salts of saturated and espe-

cially unsaturated C_8 to C_{22} carboxylic acids, such as oleic acids, stearic acids, isostearic acids and palmitic acids, are preferred anionic surfactants.

[0164] As hydrophilic groups, nonionic surfactants contain, for example, a polyol group, a polyalkylene glycol ether group or a combination of a polyol ether and a polyglycol ether group. Such compounds are, for example,

[0165] addition products of 2 to 30 moles of ethylene oxide and/or 0 to 5 moles of propylene oxide and linear fatty alcohols with 8 to 22 carbon atoms, fatty acids with 12 to 22 carbon atoms and alkylphenols with 8 to 15 carbon atoms in the alkyl group,

[0166] C_{12}-C_{22} fatty acid monoesters and diesters of addition product of 1 to 30 moles of ethylene oxide and glycerin,

[0167] C_8 to C_{22} alkyl monoglucosides and oligoglucosides and their ethoxylated analogs, as well as

[0168] addition products of 5 to 60 moles of ethylene oxide and castor oil and hydrogenated castor oil.

[0169] Alkyl polyglycosides of the general formula $R_1O-(Z)_x$ are preferred nonionic surfactants. These compounds are characterized by the following parameters.

[0170] The R^1 alkyl group contains 6 to 22 carbon atoms and may be linear as well as branched. Primary linear aliphatic groups and aliphatic groups, which are methyl-branched in the 2 position, are preferred. Such alkyl groups are, for example, 1-octyl, 1-decyl, 1-lauryl, 1-myristyl, 1-cetyl and 1-stearyl, 1-octyl, 1-decyl, 1-lauryl, 1-myristyl being particularly preferred. When so-called "oxo alcohols" are used as starting materials, compounds with an odd number of carbon atoms in the alkyl chain predominate.

[0171] Alkylpolyglycosides, which can be used pursuant to the invention, may, for example, have only one particular R^1 alkyl group. Usually, however, these compounds are synthesized starting from natural fats or oils or mineral oils. In this case, mixtures, corresponding to the starting compounds or to the respective working up of these compounds, are present as R alkyl groups.

[0172] Particularly preferred alkylpolyglycosides are those, in which R^1 consists essentially of

[0173] C_8 and C_{10} alkyl groups,

[0174] C_{12} and C_{1-4} alkyl groups,

[0175] C_8 to C_{16} alkyl groups or

[0176] C_{12} to C_{16} alkyl groups.

[0177] Any monosaccharides or oligosaccharides can be used as the Z sugar component. Usually, sugars with 5 to 6 carbon atoms and the corresponding oligosaccharides are used. Examples of such sugars are glucose, fructose, galactose, arabinose, ribose, xylose, lyxose, allose, altrose, mannose, glucose, idose, talose and sucrose, glucose, fructose, galactose, arabinose and sucrose being preferred and glucose being particularly preferred.

[0178] Alkyl polyglycosides, which can be used pursuant to the invention, contain, on the average 1.1 to 5 sugar units. Alkyl polyglycosides, in which x has values of 1.1 to 1.6, are preferred. Alkylglycosides, in which x has a value from 1.1 to 1.4, are particularly preferred.

[0179] Aside from their surfactant effect, the alkyl glycoside can also improve the fixation of a fragrance component on the hair. In the event that the effect of a perfume oil is to go beyond the duration of the hair treatment, someone of ordinary skill in the art will therefore preferably resort to this class of substances as a further component of the preparation according to the invention.

[0180] The alkoxylated homologs of said alkylpolyglycosides can also be used pursuant to the invention. These homologs may, on the average, contain up to 10 ethylene oxide and/or propylene units per alkyl glycoside units.

[0181] Moreover, zwitterionic surfactants in particular may be used as co-surfactants. Zwitterionic surfactants are those surface-active compounds, which contain, in the molecule at least one quaternary ammonium group and at least one $—COO^{(-)}$- or $—SO_3(-)$ group. Particularly suitable as zwitterionic surfactants are the so-called betaines, such as the N-alkyl-N,N-dimethylammonium glycinates, for example, the coconut alkyl-dimethylammonium glycinate, N-acyl-aminopropyl-N,N-dimethylammonium glycinates, for example, the coconut acylaminopropyl-dimethylammonium glycinate, and 2-alkyl-3-carboxylmethyl-3-hydroxyethyl imidazolines with, in each case 8 to 18 carbon atoms in the alkyl or acyl group, as well as the coconut acylaminoethyl hydroxyethylcarboxymethyl glycinate. The fatty acid amide derivative, known under the INCI name as cocoamidopropyl betaine, is a preferred zwitterionic surfactant.

[0182] Ampholytic surfactants are likewise especially suitable as co-surfactants. Ampholytic surfactants are understood to be surface-active compounds, which contain, aside from a C_8-C_{18} alkyl or acyl group, at least one free amino group and at least one —COOH— or $—SO_3H$ group in the molecule and are capable of forming internal salts. Suitable ampholytic surfactants are, for example, N-alkyl glycines, N-alkylpropionic acids, N-alkylamino butyric acids, N-alkyliminodipropionic acids, N-hydroxyethyl-N-alkylamidopropyl glycines, N-alkyl taurines, N-alkyl sarcosines, 2-alkylaminopropionic acids and alkylaminoacetic acids with, in each case, 8 to 18 carbon atoms in the alkyl group. The N-coconut alkyl amino propionate, the coconut acylamino ethylamino propionate and the C_{12-18} acyl sarcosine are particularly preferred ampholytic surfactant.

[0183] Pursuant to the invention, surfactants, especially of the quaternary ammonium compounds, esterquats and the amidoamines type, are used as cationic surfactant.

[0184] Ammonium halides are preferred quaternary ammonium compounds. They include, in particular, the chlorides and bromides, such as the alkyltrimethylammonium chlorides, dialkyldimethylammonium chlorides and trialkylmethylammonium chlorides, such as, cetyltrimethylammonium chloride, stearyltrimethylammonium chloride, distearyldimethylammonium chloride, lauryldimethylammonium chloride, lauryldimethylbenzylammonium chloride and tricetylmethylammonium chloride, as well as the imidazolium compounds, known under the INCI name as Quaternium 27 and Quaternium 83. Preferably, the long alkyl chains of the surfactants named above have 10 to 18 carbon atoms.

[0185] Esterquats are known materials, which contain at least one ester function and at least one quaternary ammo-

nium group as structural element. 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-dihydroxypropyldialkylamines are preferred esterquats. Such products are sold, for example, under the trade names of Stepanex®, Dehyquart® and Armocare®. Armocare® VGH-70 and N,N-bis(2-palmitoyloxyethyl)dimethylammonium chloride, as well as Dehyquart® F-75 and Dehyquart® AU-35 are examples of such esterquats.

[0186] The aklyamidoamines usually are synthesized by amidation of natural or synthetic fatty acids and fatty acid fractions with dialkylaminoamines. The stearamidopropyl dimethylamine, obtainable commercially under the name Tegoamide® 18, is a compound of this group of substances, which is particularly suitable pursuant to the invention.

[0187] The quaternized protein hydrolysates represent further cationic surfactants, which may be used pursuant to the invention.

[0188] Cationic silicone oils, such as the commercially available Q2-7224 (Manufacturer: Dow Corning: a stabilized trimethylsilylamodimethicone), Dow Corning 929 Emulsion (containing a hydroxylamino-modified silicone, which is also referred to as amodimethicone), SM-2059 (Manufacturer: General Electric), SLM-55067 (Manufacturer: Wacker) as well as Abil®-Quat 3270 and 3272 (Manufacturer: Th. Goldschmidt; diquaternary polydimethylsiloxanes, Quaternium-80), are also suitable pursuant to the invention.

[0189] The commercial product Glucquat®100, which, according to INCI name, is a "Lauryl Methyl Gluceth-10 Hydroxypropyl Dimonium Chloride", represents an example of a quaternary sugar derivative, which can be used as a cationic surfactant.

[0190] The compounds with alkyl groups, used as surfactants, may be uniform substances. As a rule, however, during the production of these materials, it is usually preferred to start out from natural vegetable or animal raw materials, so that substance mixtures with different alkyl chains, the lengths of which depend on the respective raw materials, are obtained.

[0191] For the surfactants, which represent addition products of ethylene oxide and/or propylene oxide and fatty alcohols or derivative of these addition products, products with a "normal" distribution of homologs as well as those with a narrowed distribution of homologs can be used. Homologs of a "normal" distribution are understood to be mixtures of homologs, which are obtained from the reaction of fatty alcohol and alkylene oxide using alkali metals, alkali metal hydroxides or alkali metal alcoholates as catalysts. On the other hand, homologs of a narrowed distribution are obtained when, for example, hydrotalcites, alkaline earth metal salts of ether carboxylic acids or alkaline earth metal oxides, hydroxides or alcoholates are used as catalysts. The use of products with a narrowed distribution of homologs may be preferred.

[0192] Furthermore, the dyeing agent according to the invention may contain further active ingredients, auxiliary materials and additives, such as

[0193] nonionic polymers, such as, vinyl pyrrolidone/vinyl acrylate copolymers, polyvinyl pyrrolidone and vinyl pyrrolidone/vinyl acetate copolymers and polysiloxanes,

[0194] cationic polymers, such as quaternized cellulose derivates, polysiloxanes with quaternary groups, dimethyldiallyl ammonium chloride polymers, acrylamide-dimethyldiallyl ammonium chloride copolymers, dimethylamino-ethyl methacrylate-vinyl pyrrolidone copolymers, quaternized with dimethyl sulfate, vinyl pyrrolidone imidazolinium-methochloride copolymers and quaternized polyvinyl alcohol,

[0195] zwitterionic and amphoteric polymers, such as, acrylamidopropyl-trimethylammonium chloride/acrylate copolymers and octylacrylamide/methyl methacrylate/t-butylaminoethyl methacrylate/2-hydroxypropyl methacrylate copolymers,

[0196] anionic polymers, such as, polyacrylic acids, cross-linked polyacrylic acids, vinyl lactate/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-t-butyl acrylamide terpolymers,

[0197] thickeners, such as agar, guar gum, alginates, xanthan gum, gum Arabic, gum karaya, carob seed flour, linseed gum, dextrans, cellulose derivates, such as, methylcellulose, hydroxyalkylcellulose and carboxymethylcellulose, starch fractions and derivatives, such as, amylose, amylopectin and dextrin, clays, such as bentonite or fully synthetic hydrocolloids, such as polyvinylalcohol,

[0198] structurants, such as maleic acid and lactic acid,

[0199] hair conditioning compounds, such as phospholipids, for example, soybean lecithin, egg lecithin and cephalins,

[0200] protein hydrolysates, especially elastin, collagen, keratin, casein, soy protein and wheat protein hydrolysates, and their condensation products with fatty acids, as well as quaternized protein hydrolysates, perfume oils, dimethylisosorbid and cyclodextrines,

[0201] solvents and solubilizers, such as ethanol, isopropanol, ethylene glycol, propylene glycol, glycerin and diethylene glycol,

[0202] active ingredients to improve fiber structure, such as mono-, di- and oligosaccharides, for example, glucose, galactose, fructose, levulose and lactose,

[0203] quaternized amines, such as methyl-1-alkylamidoethyl-2-alkylimidazolinium methosulfate

[0204] defoamers, such as silicones,

[0205] dyes for dyeing the agent,

[0206] anti-dandruff materials, such as piroctone olamines, zinc omadines and climbazole,

[0207] light protectants, especially derivatized benzophenones, cinnamic acid derivatives and triazine,

[0208] substances for adjusting the pH, such as conventional acids and, in particular, edible acids and bases,

[0209] active ingredients, such as allantoin, pyrollidone carboxylic acids and their salts, as well as bisabolol,

[0210] vitamins, provitamins and vitamin precursors, especially those of groups A, B_3, B_5, B_6, C, E, F and H,

[0211] plant extracts, such as extracts of green tea, oak bark, stinging nettle, hamamelis, hops, chamomile, burr root, horsetail, hawthorn, linden tree flowers, almond, aloe vera, pine needles, horse chestnuts, sandalwood, juniper, coconut, mango, apricot, lemon, wheat, kiwi, melon, orange, grapefruit, sage, rosemary, birch, mallow, meadow cress, creeping thyme, milfoil, thyme, melissa, restharrow, coltsfoot, hibiscus, meristem, ginseng and gingerroot,

[0212] cholesterol

[0213] thickeners, such as sugar esters, polyol esters or polyol alkyl ethers,

[0214] fats and waxes, such as spermaceti, beeswax, lignite wax and paraffins,

[0215] fatty acid alkanolamides,

[0216] complexing agents, such as EDTA, NTA, β-alanine diacetic acid and phosphonic acids,

[0217] swelling agents and penetrants, such as glycerin, propylene glycol monomethyl ethers, carbonates, hydrogen carbonates, guanidines, ureas, as well as primary, secondary and tertiary phosphates,

[0218] opacifiers, such as latex, styrene/PVP copolymers and styrene/acrylamide copolymers,

[0219] pearl glossing agents, such as ethylene glycol monostearate and distearate as well as PEG-3 distearate,

[0220] pigments,

[0221] stabilizers for hydrogen peroxides and other oxidizing agents,

[0222] blowing agents, such as propane-butane mixtures, N_2O, dimethylether, carbon dioxide and air

[0223] antioxidants.

[0224] With respect to further optional components, as well as the amounts of these components used, reference is made explicitly to the relevant handbooks, which are known to those of ordinary skill in the art, such as Kh. Schrader, Grundlagen und Rezepturen der Kosmetika (Fundamentals and Formulations of Cosmetics), 2nd Edition, Hüthig Buch Verlag, Heidelberg, 1989.

[0225] The agents according to the invention contain the dyeing agent precursors preferably in a suitable aqueous, alcoholic or aqueous-alcoholic carrier. For the purpose of dyeing hair, such carriers are, for example, creams, emulsions, gels or also surfactant-containing foaming solutions, such as shampoos, foaming aerosols or other preparations, which are suitable for application on the hair. However, it is also conceivable to integrate the dyeing agent precursors in a powdery formulation or also in a tablet-like formulation.

[0226] Within the scope of the invention, aqueous-alcoholic solutions are aqueous solutions containing 3 to 70% by weight of a C_1-C_4 alcohol, especially ethanol or isopropanol. Additionally, the agents according to the invention may contain further organic solvents, such as methoxybutanol, benzyl alcohol, ethyl diglycol or 1,2-propylene glycol. In this connection, all water-soluble organic solvents are preferred.

[0227] The actual oxidative dyeing of the fibers can basically take place with oxygen from the air. Preferably, however, a chemical oxidizing agent is used, especially when human hair is to be brightened as well as dyed. Persulfates, chlorites and, in particular, hydrogen peroxide or its addition products with urea, melamin and sodium borates come into consideration as oxidizing agents. However, pursuant to the invention, the oxidation dyeing agent can also be applied on the hair together with a catalyst, which activates the oxidation of the dye precursors, for example, with oxygen from the air. Metal ions, iodides, quinones or certain enzymes are such catalysts.

[0228] Zn^{2+}, Cu^{2+}, Fe^{2+}, Fe^{3+}, Mn^{2+}, Mn^{4+}, Li^{+}, Mg^{2+}, Ca^{2+} and Al^{3+}, for example, are suitable metal ions, Zn^{2+}, Cu^{2+}, Mn^{2+} being particularly suitable. In principle, the metal ions may be used in the form of any physiologically acceptable salts or in the form of a complex compound. Acetates, sulfates, halides, lactates and tartrates are preferred salts. The use of these metal salts can accelerate the coloration and selectively influence the color shade.

[0229] Suitable enzymes are, for example, peroxidases, which can clearly intensify the action of small amounts of hydrogen peroxide. Furthermore, those enzymes are suitable pursuant to the invention, which oxidize the oxidation dye precursor directly with the help of oxygen from the air, such as the laccases, or produce hydrogen peroxide in situ in small amounts and, in this way, activate the oxidation of dye precursors biocatalytically. Particularly suitable catalysts for the oxidation of the dye precursors are the so-called 2-electron oxidoreductases in combination with the substrates specific for this purpose, such as

[0230] pyranose oxidase and, for example, D-glucose or galactose,

[0231] glucose oxidase and D-glucose,

[0232] glycerin oxidase and glycerin,

[0233] pyruvate oxidase and pyruvic acid or its salts,

[0234] alcohol oxidase and alcohol (MeOH, EtOH),

[0235] lactate oxidase and lactic acid and its salts,

[0236] tyrosinase oxidase and tyrosine,

[0237] uricase and uric acid or its salts,

[0238] choline oxidase and choline,

[0239] amino oxidase and amino acids.

[0240] The actual hair-dyeing agent is prepared advisably immediately before use by mixing the preparation of the oxidizing agent with the preparation containing the dye precursors. The thereby resulting, ready-for-use hair-dyeing preparation preferably should have a pH ranging from 6 to 12. The use of the hair-dyeing agents in a weakly alkaline medium is particularly preferred. The application temperatures may range from 150 and 40° C. After a period of action of 5 to 45 minutes, the hair-dyeing agent is removed by rinsing from the hair, which is to be dyed. Subsequent

washing with a shampoo may be omitted if a carrier, containing a surfactant in an appropriate amount, such as a dyeing shampoo, was used.

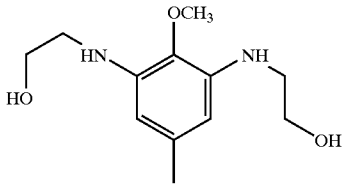
[0241] Particularly in the case of hair, which is difficult to dye, the preparation with the dye precursor may also be applied on the hair without previously being mixed with the oxidizing component. After a period of action of 20 to 30 minutes, optionally after an intermediate rinsing, the oxidizing component is applied. After a further period of action of 10 to 20 minutes, the hair is then rinsed and, if desired, shampooed. For this embodiment and in accordance with a first variation, for which the prior application of the dye precursors is to bring about a better penetration into the hair, the corresponding agent is adjusted to a pH of about 4 to 7. In accordance with a second variation, oxidation by air is aimed for at first, the agent applied preferably having a pH of 7 to 10. During the subsequent accelerated oxidation, the use of acidically adjusted peroxidisulfate solutions as oxidizing agent may be preferred.

EXAMPLES

1 Syntheses

1.1 2,6-Bis-((2-hydroxyethyl)amino)-4-methylanisole

[0242]



1.1.1 2,6-Diamino-4-methylanisole dihydrochloride

[0243] 2,6-Dinitro-4-methylanisole (100 g), 1.35 L of methanol, 150 mL of water and 1 g of Pd/C (5%) were placed in an autoclave and hydrogenated for 12 hours at 50° C. with hydrogen at a pressure of 50 bar. Subsequently, the autoclave was allowed to cool down and the formulation was poured into 1.0 L of half concentrated HCl. The catalyst was filtered off and the filtrate was evaporated to dryness in a rotary evaporator and dried under vacuum overnight.

[0244] Yield: quantitative

1.1.2 Bis(2-chloroethyl)(2-methoxy-5-methyl-1,3-phenylene) biscarbamate

[0245] 2,6-Diamino-4-methylanisole dihydrochloride (56 g) and 134 g of calcium carbonate were added to 1 L of dioxane and heated to 90° C. Within a period of 15 minutes, 80 g of 2-chloroethyl chloroformate were added and the formulation was stirred for a further 4 hours at this temperature and then allowed to cool down, the mineral salts being filtered off. The filtrate was poured into ice water and the resulting light brown crystals were filtered off and dried under vacuum.

[0246] Yield: 50.4 g (63%)

[0247] Melting point: 116°-118° C.

1.1.3 3,3'-(2-Methoxy-5-methyl-1,3-phenylene)bis(1,3-oxazol idin-2-one)

[0248] To 200 mL of 20% sodium hydroxide solution, heated to 45° C., 50 g of bis(2-chloroethyl)(2-methoxy-5-methyl-1,3-phenylene) biscarbamate were added in portions, the formulation was diluted with 200 mL of dioxane and stirred for a further 2 hours at 45° C. After being stirred overnight at room temperature, the formulation was poured onto ice and neutralized with hydrochloric acid. The precipitated products was filtered off with suction and dried overnight under a vacuum.

[0249] Yield: 24 g (59%)

[0250] Melting point: 173° C.

1.1.4 2,6-Bis-((2-hydroxyethyl)amino)-4-methylanisole

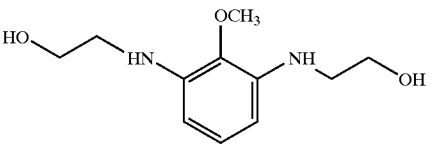
[0251] 3,3'-(2-Methoxy-5-methyl-1,3-phenylene)bis(1,3-oxazolidin-2-one) (33.5 g) in 500 mL of 20% KOH was refluxed for 10 hours, and allowed to cool to room temperature. The precipitated residues were filtered off. The filtrate was diluted with 200 mL of ethanol and adjusted to a pH of 8 with concentrated HCl. The precipitated KCl was filtered off and the filtrate evaporated in a rotary evaporator.

[0252] Yield: quantitative

[0253] Melting point: 82°-84° C.

1.2 2,6-Bis-((2-hydroxyethyl)amino) anisole

[0254]



1.2.1 4-Chloro-2,6-dinitroanisole

[0255] To 100 mL of fuming nitric acid at 50 to 10° C., 50 g of 4-chloroanisole were added slowly, dropwise, at this temperature. This was followed by the dropwise addition of 50 mL of concentrated sulfuric acid and a further 50 mL of fuming nitric acid. Stirring was continued for 15 minutes, after which the formulation was poured onto 500 mL of ice. The precipitate was filtered off with suction, washed until neutral and dried under a vacuum.

[0256] Yield: 71.7 g (88%)

[0257] Melting point: 61°-62° C.

1.2.2 2,6-Diaminoanisole

[0258] 2,6-Dinitro-4-chloroanisole (23.3 g), 450 mL of ethanol, 50 mL of water, 9.8 g of potassium acetate and 0.1

g of Pd/C (5%) were added to an autoclave and hydrogenated for 12 hours at 50° C. with hydrogen under a pressure of 50 bar. Subsequently, the autoclave was allowed to cool down, the catalyst was filtered was off and the filtrate evaporated to dryness in a rotary evaporator. The residue was subsequently distilled in a Kugelrohr.

[0259] Yield: 4.1 g (29%)

1.2.3 Bis(2-chloroethyl)(2-methoxy-1,3-phenylene) biscarbamate

[0260] To 14 g of 2,6-diaminoanisole and 18.9 g of calcium carbonate in 0.5 L of dioxane, heated to 90° C., 35.8 g of chloroethyl chloroformate was added over a period of 15 minutes and stirring was continued at this temperature for 4 hours. After subsequent cooling, the mineral salts were filtered off. The filtrate was poured onto ice water and the light brown crystals formed were filtered off and dried under vacuum.

[0261] Yield: 19.6 g (56%)

[0262] Melting point: 135°-137° C.

1.2.4 3,3'-(2-Methoxy-1,3-phenylene)bis(1,3-oxazolidin-2-one)

[0263] To 100 mL of 20% sodium hydroxide solution, heated to 45° C., 19 g of bis(2-chloroethyl)(2-methoxy-1,3-phenylene) biscarbamate were added in portions. The mixture was diluted with 100 mL of dioxane and stirred for a further 2 hours at 45° C. After being stirred overnight at room temperature, the mixture was poured onto ice, neutralized with hydrochloric acid and extracted several times with ethyl acetate. The combined organic phases were evaporated to dryness under vacuum.

[0264] Yield: 6.2 g (41%)

1.2.5 2,6-Bis-((2-hydroxyethyl)amino) anisole

[0265] 3,3'-(2-Methoxy-1,3-phenylene)bis(1,3-oxazolidin-2-one) (6.2 g) was heated for 10 hours under reflux in 100 mL of 20% KOH and then allowed to cool to room temperature, after which the precipitated KCl was filtered off. The filtrate was diluted with 200 mL of ethanol and its pH was adjusted to a value of 8 with concentrated HCl. The precipitated KCl was filtered off and the filtrate evaporated in a rotary evaporator. The residue was subsequently distilled in a Kugelrohr.

[0266] Yield: 3.7 g (73%)

[0267] Melting point: 82°-84° C.

2 Colorations

2.1 Experimental Procedure

[0268] For preparing the dyeing cream, 50 g of a cream base were weighed into a 250 mL beaker and melted at 80° C. The cream base used had the following formulation:

Hydrenol ® D[1]	17.0% by weight
Lorol ® tech.[2]	4.0% by weight
Texapon ® NSO[3]	40.0% by weight
Dehyton ® K[4]	25.0% by weight
Eumulgin ® B2[5]	1.5% by weight
water	12.5% by weight

[1]C_{16-18} Fatty alcohol (INCI name: Cetearyl alcohol) (Cognis)
[2]C_{12-18} Fatty alcohol (INCI name: Coconut alcohol) (Cognis)
[3]Sodium salt of lauryl ether sulfate (approx. 27.5% active substance; INCI name: Sodium Laureth Sulfate) (Cognis)
[4]N,N-Dimethyl-N-(C_{8-18}-coconut amidopropyl) ammonium acetobetaine (approx. 30% active substance; INCI name: Aqua (water), Cocamidopropyl Betaine) (Cognis)
[5]Cetyl stearyl alcohol with approximately 20 EO units (INCI name: Ceteareth-20) (Cognis)

[0269] In each case, 1/400 moles of the developer component and the coupling component were suspended separately in distilled water and dissolved by heating. Subsequently, ammonium hydroxide (less than 1 mL; 25% ammonium hydroxide solution) was added until the pH was between 9 and 10.

[0270] The dissolved dye precursors were incorporated consecutively into the hot cream. Subsequently, distilled water was added to a total weight of 97 g and the pH was adjusted with ammonium hydroxide to a value of 9.5. After adding distilled water to 100 g, the formulation was stirred until cool (below 30° C.), a homogeneous cream being formed.

[0271] Unless noted otherwise, 25 g of dyeing cream were mixed with 25 g of the following preparation of oxidizing agents for the dyeings.

dipicolinic acid	0.1% by weight
sodium pyrophosphate	0.03% by weight
Turpinal ® SL[6]	1.50% by weight
Texapon ® N28[7]	2.00% by weight
Acrysol ® 22[8]	0.60% by weight
hydrogen peroxide, 50%	12.00% by weight
sodium hydroxide solution, 45%	0.80% by weight
water	up to 100% by weight

[6]1-Hydroxyethane-1,1-diphosphonic acid (approx. 58–61% active substance content; INCI name: Etidronic Acid, Aqua (water) (Solutia)
[7]Sodium salt of lauryl ether sulfate (at least 26.5% active substance content; INCI name: Sodium Laureth Sulfate (Cognis)
[8]Acrylate polymer (approx. 29.5–30.5% solids in water; INCI name: Acrylates/Steareth-20 Methacrylate Copolymer)

[0272] A hair strand (turned 80% grey; 330 mg to 370 mg in weight) was added to each of the mixtures so obtained. Subsequently, the mixtures and the hair strands were added to a clock glass and the hair strands were embedded in the dyeing cream. After a 30 minute (±1 minute) period of action at room temperature, the hair strands were removed and washed with aqueous Texapon® EVR solutions[9], until the excess dye had been removed. The hair strands were dried in air and their color shade was determined under a daylight lamp (color testing device HE240A) and noted (Taschenlexikon der Farben (Pocket Lexicon of Colors), A. Kornerup and J. H. Wanscher, 3rd Unchanged Edition 1981, MUSTER-SCHMIDT Verlag, Zurich, Gottingen).

[9] Sodium salt of lauryl ether sulfate with special additives (approx. 34 to 37% active substance content; INCI name: Sodium Lauryl Sulfate, Sodium Laureth Sulfate, Lauramide MIPA, Cocamide MEA, Glycol Stearate, Laureth-10) (Cognis)

[0273] The results obtained during the dyeing investigations are listed in the following Tables.

2.2 Colorations with 2,6-bis-((2-hydroxyethyl)amino)-4-methylanisole

[0274]

Developer Component	Coloration
p-toluylenediamine sulfate	dark purple
2,4,5,6-tetraaminopyrimidine sulfate	strawberry
p-aminophenol	cerise
4,5-diamino-1-(2-hydroxyethyl)pyrazole sulfate	dark purple
2-(2,5-diaminophenyl)ethanol sulfate	deep violet
4-amino-3-methylphenol	dull red
4-amino-2-((5-amino-2-hydroxyphenyl)methyl)phenol dihydrochloride	gray magenta

2.3 Colorations with 2,6-bis-((2-hydroxyethyl)amino) anisole

[0275]

Developer Component	Coloration
p-toluylenediamine sulfate	deep magenta
2,4,5,6-tetraaminopyrimidine sulfate	brownish red
p-aminophenol	brown
4,5-diamino-1-(2-hydroxyethyl)pyrazole sulfate	deep violet
2-(2,5-diaminophenyl)ethanol sulfate	dark violet
4-amino-3-methylphenol	dark blond
4-amino-2-((5-amino-2-hydroxyphenyl)methyl)phenol dihydrochloride	violet brown

3 Further Colorations

3.1 Formulation 1

[0276]

Raw Material	% by weight
C_{10}–C_{22} mixture of fatty alcohols	6.0
Stenol ® 1618[10]	3.5
Kokoslorol ®[11]	1.5
behenyl alcohol	1.0
Eumulgin ® B 1[12]	0.3
Eumulgin ® B 2	0.3
Texapon ® NSO	10.0
Dehyton ® K	5.0
Polymer JR ® 400[13]	0.3
Gafquat ® 755[14]	0.3
Celquat ® L 200[15]	0.1
ascorbic acid	0.2
sodium metabisulfite	0.3
ammonium sulfate	0.4
hydroxyethane diphosphonic acid	0.2
40% waterglass solution	0.5
perfume oil	0.3
1,10-bis-(2,5-diaminophenyl)-1,4,7,10-tetraoxadecane tetrahydrochloride	0.05
p-toluylenediamine sulfate	0.22
N,N-bis-(2'-hydroxyethyl)-p-phenylenediamine sulfate	0.15
2-(2'-hydroxyethyl)-p-phenylenediamine sulfate	0.24
bis-(5-amino-2-hydroxyphenyl)methane dihydrochloride	0.17
2,4-bis-(2'-hydroxyethyl)amino-6-methylanisole	0.50
2,6-bis-((2'-hydroxyethyl))-amino-4-methylanisole	0.05
25% ammonium hydroxide	to a pH of 10
water	up to 100

[10]$C_{16–18}$ Fatty alcohol (INCI name: Cetearyl Alcohol) (Cognis)
[11]$C_{12–18}$ Fatty alcohol (INCI name: Coconut alcohol) (Cognis)
[12]Cetyl stearyl alcohol with approximately 12 EO units (INCI name: Ceteareth-12) (Cognis)
[13]Quaternized hydroxyethyl cellulose (INCI name: Polyquaternium-10) (Amerchol)
[14]Dimethylaminoethyl methacrylate vinyl pyrrolidone copolymer, quaternized with diethylsulfate (approximately 19% solids in water, INCI name: Polyquaternium-11) (ISP)
[15]Quaternized cellulose derivative (INCI name: Polyquaternium-4) (National Starch)

3.2 Formulation 2

[0277]

Raw Material	% by weight
C_{10}–C_{22} mixture of fatty alcohol	6.0
Eumulgin ® B 1	0.3
Eumulgin ® B 2	0.3
Texapon ® NSO	10.0
Dehyton ® K	5.0
Polymer JR ® 400	0.3
Gafquat ® 755	0.3
Celquat ® L 200	0.1
ascorbic acid	0.2
sodium metabisulfite	0.3
ammonium sulfate	0.4
hydroxyethane diphosphonic acid	0.2
40% waterglass solution	0.5
perfume oil	0.3
1,3-N,N'-bis-(2'-hydroxyethyl)-N,N'-bis-(4-aminophenyl)-diaminopropane-2-ol tetrahydrochloride	0.1
p-phenylenediamine dihydrochloride	0.09
p-toluylenediamine sulfate	0.11
4-aminophenol	0.03
4-amino-3-methylphenol	0.01
4-amino-2-aminomethylphenol dihydrochloride	0.01
4-amino-2-((diethylamino) methyl)phenol dihydrochloride	0.01
bis-(5-amino-2-hydroxyphenyl) methane dihydrochloride	0.40
4,5-diamino-2-(2'-hydroxyethyl)pyrazole sulfate	0.24
2,4-bis-(2'-hydroxyethyl) amino-6-methylanisole	0.11
2,6-bis-((2'-hydroxyethyl)) amino-4-methylanisole	0.65
25% ammonium hydroxide	to a pH of 10
water	up to 100

3.3 Formulation 3

[0278]

Raw Material	% by weight
C_{10}–C_{22} mixture of fatty alcohol	6.0
Eumulgin ® B 1	0.3

-continued

Raw Material	% by weight
Eumulgin ® B 2	0.3
Texapon ® NSO	10.0
Dehyton ® K	5.0
Polymer JR ® 400	0.3
Gafquat ® 755	0.3
Celquat ® L 200	0.1
ascorbic acid	0.2
sodium metabisulfite	0.3
ammonium sulfate	0.4
hydroxyethane diphosphonic acid	0.2
40% waterglass solution	0.5
perfume oil	0.3
2,4,5,6-tetraaminopyrimidine sulfate	0.88
4-hydroxy-2,5,6-triaminopyrimidine sulfate	0.07
2,4-bis-(2'-hydroxyethyl) amino-6-methylanisole	0.34
2,6-bis-((2'-hydroxyethyl))-amino-4-methylanisole	0.36
resorcinol	0.02
2-methylresorcinol	0.08
4-chlororesorcinol	0.01
resorcinol monomethyl ether	0.01
25% ammonium hydroxide	to a pH of 10
water	up to 100

3.4 Formulation 4

[0279]

Raw Material	% by weight
C_{10}–C_{22} mixture of fatty alcohol	10.0
Texapon ® K 14 S 70 C[16]	2.5
Plantaren ® 1200 UP[17]	2.0
Akypo Soft ® 45 NV[18]	12.0
Eutanol ® G[19]	1.0
Eumulgin ® B 1	0.5
Eumulgin ® B 2	0.5
Polymer W ® 37194[20]	2.0
Cosmedia Guar ® C 261[21]	0.2
Mirapol ® A 15[22]	0.5
ascorbic acid	0.2
disodium salt of EDTA	0.1
sodium metabisulfite	0.3
ammonium sulfate	0.5
perfume oil	0.4
Promois ® WK[23]	2.0
Dow Corning ® Q2-1401[24]	0.2
Gluadin ® WQ[25]	1.0
p-toluylenediamine sulfate	0.55
N,N-bis-(2'-hydroxyethyl)-p-phenylenediamine sulfate	0.94
4-amino-3-methylphenol	0.03
2,4,5,6-tetraaminopyrimidine sulfate	1.0
2,4-bis-(2'-hydroxyethyl) amino-6-methylanisole	0.10
2,6-bis-((2'-hydroxyethyl))-amino-4-methylanisole	0.05
resorcinol	0.11
2-methylresorcinol	0.54
3-aminophenol	0.06
1,3-bis-(2',4'-diaminophenoxy) propane tetrahydrochloride	0.001
2-amino-3-hydroxypyridine	0.30
2-methylamino-3-amino-6-methoxypyridine	0.001
2,7-dihydroxynaphthalene	0.03

-continued

Raw Material	% by weight
25% ammonium hydroxide	to a pH of 10
water	up to 100

[16]Sodium salt of lauryl myristyl ether sulfate (approx. 68% to 73% active substance; INCI name: Sodium Myreth Sulfate) (Cognis)
[17]C_{12}–C_{16} Fatty alcohol-1,4-glucoside not preserved, free of boron (approx. 50–53% active substance) (Cognis Corporation (Emery))
[18]Lauryl alcohol-4,5-EO-acetic acid (at least 21% active substance; INCI name: Sodium Laureth-6-Carboxylate) (Chem-Y)
[19]2-Octyldodecyl alcohol (INCI name: Octyldodecanol) (Cognis)
[20]Approx. 20% by weight active substance in water, INCI name: Acrylamidopropyltrimonium Chloride/Acrylates Copolymer) (Stockhausen)
[21]Guarhydroxypropyltrimethylammonium chloride (at least 93% solids; INCI name: Guar Hydroxypropyltrimonium Chloride) (Cognis Corporation Cosmedia)
[22]Poly(N-(3-(dimethylammonium)propyl)-N'-(3-ethyleneoxyethylenedimethylammonium)-propyl)-urea dichloride (approx. 64% solids in water; INCI name: Polyquaternium-2) (Rhodia)
[23]Keratin hydrolysate (INCI name: Aqua (Water), Hydrolyzed Keratin, Methylparabene, Propylparabene) (Seiwa (Interorgana))
[24]Dimethylcyclosiloxane dimethylpolysiloxanol mixture (approx. 13% solids; INCI name: Cyclomethicone, Dimethiconol) (Dow Corning)
[25]Wheat protein hydrolysate (approx. 31–35% solids; INCI name: Aqua (Water), Laurdimonium Hydroxypropyl Hydrolyzed Wheat Protein, Ethylparabene, Methylparabene) (Cognis)

3.5 Formulation 5

[0280]

Raw Material	% by weight
C_{10}–C_{22} mixture of fatty alcohol	10.0
Texapon ® K 14 S 70 C	2.5
Plantaren ® 1200 UP	2.0
Akypo Soft ® 45 NV	12.0
Eutanol ® G	1.0
Eumulgin ® B 1	0.5
Eumulgin ® B 2	0.5
Polymer W ® 37194	2.0
Cosmedia Guar ® C 261	0.2
Mirapol ® A 15	0.5
ascorbic acid	0.2
disodium salt of EDTA	0.1
sodium metabisulfite	0.3
ammonium sulfate	0.5
perfume oil	0.4
Promois ® WK	2.0
Dow Corning ® Q2-1401	0.2
Gluadin ® WQ	1.0
p-phenylenediamine dihydrochloride	0.10
N,N-bis-(2'-hydroxyethyl)-p-phenylenediamine sulfate	0.16
2-(2'-hydroxyethyl)-p-phenylenediamine sulfate	0.34
4,5-diamino-2-(2'-hydroxyethyl) pyrazole sulfate	0.30
2,4-bis-(2'-hydroxyethyl) amino-6-methylanisole	0.05
2,6-bis-(2'-hydroxyethyl)-amino-4-methylanisole	0.10
resorcinol	0.09
5-(2'-hydroxyethyl) amino-2-methylphenol	0.07
3-amino-2-chloro-6-methylphenol	0.20
2,4-diaminophenoxyethanol sulfate	0.01
1,3-bis-(2',4'-diaminophenoxy) propane tetrahydrochloride	0.01
2-amino-3-hydroxypyridine	0.09
3,5-diamino-2,6-dimethoxypyridine	0.005
2,6-bis-(2'-hydroxyethylamino) toluene	0.1
5,6-dihydroxyindoline hydrobromide	0.05
4-amino-2-nitro-diphenylamine-2'-carboxylic acid	0.05

-continued

Raw Material	% by weight
25% ammonium hydroxide	to a pH of 10
water	up to 100

3.6 Formulation 6

[0281]

Raw Material	% by weight
C_{10}–C_{22} mixture of fatty alcohol	10.0
Texapon ® K 14 S 70 C	2.5
Plantaren ® 1200 UP	2.0
Akypo Soft ® 45 NV	12.0
Eutanol ® G	1.0
Eumulgin ® B 1	0.5
Eumulgin ® B 2	0.5
Polymer W ® 37194	2.0
Cosmedia Guar ® C 261	0.2
Mirapol ® A 15	0.5
ascorbic acid	0.2
disodium salt of EDTA	0.1
sodium metabisulfite	0.3
ammonium sulfate	0.5
perfume oil	0.4
Promois ® WK	2.0
Dow Corning ® Q2-1401	0.2
Gluadin ® WQ	1.0
2-(2'-hydroxyethyl)-p-phenylenediamine sulfate	0.83
4-aminophenol	0.2
4-amino-3-methylphenol	0.01
bis-(5-amino-2-hydroxyphenyl) methane dihydrochloride	0.10
2,4,5,6-tetraaminopyrimidine sulfate	1.10
4-hydroxy-2,5,6-triaminopyrimidine sulfate	0.15
2,4-bis-(2'-hydroxyethyl) amino-6-methylanisole	0.25
2,6-bis-(2'-hydroxyethyl)-amino-4-methylanisole	0.05
resorcinol	0.1
2-methylresorcinol	0.60
4-chlororesorcinol	0.03
3-aminophenol	0.004
5-amino-2-methylphenol	0.03
3-amino-2-chloro-6-methylphenol	0.03
2-amino-3-hydroxypyridine	0.24
2,6-dihydroxy-3,4-dimethylpyridine	0.10
2,7-dihydroxynaphthalene	0.02
1-phenyl-3-methylpyrazole-5-one	0.01
25% ammonium hydroxide	to a pH of 10
water	up to 100

3.7 Formulation 7

[0282]

Raw Material	% by weight
Stenol ® 1618	4.5
Kokoslorol ®	2.5
behenyl alcohol	1.0
Texapon ® NSO	2.0
Dehyton ® K	1.0
potassium oleate	2.0
potassium isostearate	2.0
potassium myristate	1.0
Westvaco ® Diacid H240, K-Salz [26]	2.0
Merquat ® 550 [27]	0.2

-continued

Raw Material	% by weight
Luviquat ® FC 370 [28]	0.1
Merquat ® 280 [29]	0.1
Gafquat ® HS-100 [30]	0.1
ascorbic acid	0.4
hydroxyethane diphosphonic acid	0.2
perfume oil	0.4
p-toluylenediamine-sulfate	0.10
N,N-bis-(2'-hydroxyethyl)-p-phenylenediamine sulfate	0.88
2-(2'-hydroxyethyl)-p-phenylenediamine sulfate	0.1
4,5-diamino-2-(2'-hydroxyethyl) pyrazole sulfate	0.72
2,4-bis-(2'-hydroxyethyl) amino-6-methylanisole	0.68
2,6-bis-(2'-hydroxyethyl)-amino-4-methylanisole	0.72
resorcinol	0.02
2-methylresorcinol	0.03
4-chlororesorcinol	0.02
5-amino-2-methylphenol	0.01
5-(2'-hydroxyethyl) amino-2-methylphenol	0.05
5-amino-4-chloro-2-methylphenol	0.24
3-amino-2-chloro-6-methylphenol	0.07
1-naphthol	0.01
1,5-dihydroxynaphthalene	0.05
2,6-bis-(2'-hydroxyethylamino) toluene	0.15
HC Red 1 [31]	0.05
HG Red BN [32]	0.05
HG Red B 54 [33]	0.05
Basic Red 51 [34]	0.05
25% ammonium hydroxide	to a pH of 10
water	up to 100

[26] Potassium salt of 4-hexyl-5(6)-carboxy-2-cyclohexene-1-octanoic acid (approx. 41% active substance in water) (Westvaco Chemicals)
[27] Dimethyldiallyl ammonium chloride acrylamide copolymer (approx. 8.1–9.1% active substance in water; INCI name: Polyquaternium-7) (Ondeo-Nalco)
[28] Vinylimidazolium methochloride vinyl pyrrolidone copolymer (30:70) (38–42% solids in water; INCI name: Polyquaternium-16) (BASF)
[29] Dimethyldiallyl ammonium chloride acrylic acid copolymer (approx. 35 active substance in water); INCI name: Polyquaternium-22) (Ondeo-Nalco)
[30] Vinyl pyrrolidone, methacrylamidopropyltrimethyl ammonium chloride copolymer (19–21% active substance in water; INCI name: Polyquaternium-28) (ISP)
[31] 4-Amino-2-nitrodiphenylamine
[32] 4((3-Hydroxypropyl)amino)-3-nitrophenol
[33] 4-((2-Hydroxyethyl)amino)-3-nitrophenol (INCI name: 3-Nitro-p-Hydroxyethylaminophenol)
[34] Azo dye (CIBA)

3.8 Formulation 8

[0283]

Raw Material	% by weight
Stenol ® 1618	6.0
Kokoslorol ®	6.0
Eumulgin ® B 1	3.0
Eumulgin ® B 2	3.0
Eumulgin ® RH 40 [35]	1.0
Polydiol ® 400 [36]	5.0
Aminoxyd ® WS 35 [37]	1.0
EDTA disodium salt	0.1
Natrosol ® 250 HHR [38]	1.0
ascorbic acid	0.1
hydroxyethane diphosphonic acid	0.2
perfume oil	0.3
2,4,5,6-tetraaminopyrimidine-sulfate	1.19
2,4-bis-(2'-hydroxyethyl) amino-6-methylanisole	0.23
2,6-bis-(2'-hydroxyethyl)-amino-4-methylanisole	0.72
2-methylresorcinol	0.03
4-chlororesorcinol	0.02

-continued

Raw Material	% by weight
2,6-bis-(2'-hydroxyethylamino) toluene	0.21
1,2,3,4-tetrahydro-6-nitroquinoxaline	0.15
HC-Yellow 5 [39]	0.05
4-amino-3-nitrophenol	0.02
Basic Yellow 87 [40]	0.05
Basic Orange 31 [41]	0.10
Basic Red 51	0.05
25% ammonium hydroxide	to a pH of 10
water	up to 100

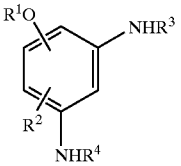
[35] Hydrogenated castor oil with approximately 40-EO units (INCI name: Peg-40 Hydrogenated Castor Oil) (Cognis)
[36] Polyethylene glycol (INCI name: PEG-8) (Cognis)
[37] N,N-Dimethyl-N(C_{8-18} coconut acylamidopropyl)amine-N-oxide (approx. 35% active substance in water; INCI name: Cocamidopropylamine Oxide) (Goldschmidt)
[38] Hydroxyethylcellulose (INCI name: Hydroxyethylcellulose) (Hercules)
[39] N^1-(2-Hydroxyethyl)-4-nitro-1,2-phenylenediamine
[40] Methine dye (CIBA)
[41] Azo dye (CIBA)

[0284] Formulations 1 to 8 were mixed with the above-described oxidizing agent (item 2.1) and the resulting application preparation was applied on strands (Kerling, natural white). After a period of action of 30 minutes at room temperature, the fibers were thoroughly rinsed with water, dried with a blower and the colorations were evaluated. The following results were obtained:

Formulation Number	Color Results
1	intensive wine red
2	intensive violet
3	intensive orange red
4	blackish red
5	dark violet
6	dark ruby
7	dark aubergine
8	luminous orange red

What is claimed is:

1. An agent for dyeing keratinic fibers, especially human hair, comprising a coupling component which is an m-phenylenediamine derivative of the formula (I)



(I)

wherein R^1 is a C_{1-4} alkyl group or a C_{1-4} monohydroxy alkyl group, R^2 is a hydrogen atom, a methyl or an ethyl group and each of R^3 and R^4 is independently a branched or linear C_{2-6} hydroxyalkyl group, with the proviso that the R^1O group is in the ortho or meta position to both amino groups; and a cosmetically acceptable carrier.

2. The agent of claim 1 wherein R^3 and R^4 are the same.

3. The agent of claim 1 wherein each of R^3 and R^4 is a 2-hydroxyethyl group.

4. The agent of claim 1 wherein R^1 is a methyl group.

5. The agent of claim 1 wherein R^2 is a methyl group.

6. The agent of claim 1 wherein R^1O is in the ortho position to both amino groups.

7. The agent of claim 1 wherein the m-phenylenediamine derivative of Formula (I) is 2,6-bis-((2-hydroxyethyl)amino)-anisole or 2,6-bis-((2-hydroxyethyl)amino)-4-methylanisole.

8. The agent of claim 1 wherein R^1O is in the meta position to both amino groups.

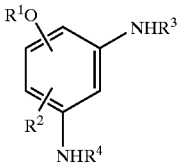
9. The agent of claim 1 further comprising at least one developer component.

10. The agent of claim 1 further comprising at least one substantive dye.

11. The agent of claim 10 wherein the substantive dye is cationic.

12. A method for dyeing keratinic fibers comprising applying to keratinic fibers an agent in accordance with claim 1 and washing off the applied agent after a period of action.

13. An m-phenylenediamine derivative of the Formula (I)



(I)

wherein R^1 is a C_{1-4} alkyl group or a C_{1-4} monohydroxy alkyl group, R^2 is a hydrogen atom, a methyl or an ethyl group and each of R^3 and R^4 is independently a branched or linear C_{2-6} hydroxyalkyl group, with the proviso that the R^1O group is in the ortho or meta position to both amino groups

14. A biscarbamate selected from the group consisting of bis(2-chloroethyl)(2-methoxy-5-methyl-1,3-phenylene) biscarbamate and bis(2-chloroethyl)(2-methoxy-1,3-phenylene) biscarbamate.

15. A bis(1,3-oxazolidin-2-one) selected from the group consisting of 3,3'-(2-methoxy-5-methyl-1,3-phenylene)bis(1,3-oxazolidin-2-one) and 3,3'-(2-methoxy-1,3-phenylene)bis (1,3-oxazolidin-2-one).

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