

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
17 August 2006 (17.08.2006)

PCT

(10) International Publication Number
WO 2006/086374 A2

(51) International Patent Classification:

C07C 215/76 (2006.01) **A61Q 5/10** (2006.01)
C07D 307/52 (2006.01) **A61K 8/49** (2006.01)
C07D 231/38 (2006.01) **C07D 295/12** (2006.01)

Gisela, Dr. [CH/CH]; Route Du Confin 54, CH-1723 Marly (CH). **ROSATO, Franco, Jose** [IT/DE]; Konizstrasse 194a, 3097 Liebefeld (DE). **BRAUN, Hnas-jurgen, Dr.** [DE/CH]; Kapellacker 19, CH-3182 Ueberstorf (CH).

(21) International Application Number:

PCT/US2006/004268

(74) Common Representative: **THE PROCTER & GAMBLE COMPANY**;

Eileen L. Hughett, Winton Hill Business Center, 6110 Center Hill Road, Cincinnati, Ohio 45224 (US).

(22) International Filing Date: 7 February 2006 (07.02.2006)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

102005005875.2 9 February 2005 (09.02.2005) DE

(71) Applicant (for AE, AG, AM, AU, AZ, BB, BF, BJ, BR, BW, BY, BZ, CA, CF, CG, CI, CM, CN, CO, CR, CU, DM, DZ, EC, EG, GA, GD, GE, GH, GM, GN, GQ, GW, ID, IL, IN, JP, KE, KG, KM, KN, KP, KR, KZ, LC, LK, LR, LS, LY, MA, MD, MG, ML, MN, MR, MW, MX, MZ, NA, NE, NG, NI, NO, NZ, OM, PG, PH, RU, SC, SD, SG, SL, SM, SN, SY, SZ, TD, TG, TJ, TM, TN, TT, TZ, UA, UG, UZ, VC, VN, ZA, ZM, ZW only): **THE PROCTER & GAMBLE COMPANY** [US/US]; One Procter & Gamble Plaza, Cincinnati, Ohio 45202 (US).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, LY, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SM, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

(71) Applicant (for AL, AT, BA, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, NL, PL, PT, RO, SE, SI, SK, TR, YU only): **WELLA AKTIEN GESELLSCHAFT** [DE/DE]; Berlin-erstr. 65, D-64274 Darmstadt (DE).

Published:

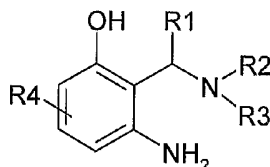
— without international search report and to be republished upon receipt of that report

(72) Inventors; and

(75) Inventors/Applicants (for US only): **UMBRICHT,**

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: 3-AMINO-2-AMINOMETHYLPHENOL DERIVATIVES AND COLORANTS COMPRISING THESE COMPOUNDS



(I)

(57) Abstract: 3-Amino-2-aminomethylphenol derivatives of the general formula (I) or physiologically compatible, water-soluble salts thereof, and agent comprising these compounds for the oxidative coloring of keratin fibers.

3-AMINO-2-AMINOMETHYLPHENOL DERIVATIVES AND COLORANTS COMPRISING THESE COMPOUNDS

The invention relates to agents for the coloring of keratin fibers based on a developer
5 substance-coupler substance combination which comprise 3-amino-2-aminomethylphenol
derivatives as coupler substance, and to novel 3-amino-2-aminomethylphenol derivatives.

In the field of coloring keratin fibers, in particular hair coloring, oxidation dyes have
achieved significant importance. The coloration arises here as a result of the reaction of
10 certain developer substances with certain coupler substances in the presence of a suitable
oxidizing agent. The developer substances used here are, in particular,
2,5-diaminotoluene, 2,5-diaminophenylethyl alcohol, p-aminophenol and
1,4-diaminobenzene, while examples of coupler substances are resorcinol,
4-chlororesorcinol, 1-naphthol, 3-aminophenol and derivatives of m-phenylenediamine.

15 Besides coloring to the desired intensity, numerous additional requirements are placed on
oxidation dyes which are used for coloring human hair. For example, the dyes must be
acceptable from a toxicological and dermatological point of view and the hair colorations
achieved must have good light fastness, permanent wave fastness, acid fastness and
20 rubbing fastness. However, in any case, such colorations must remain stable over a period
of at least 4 to 6 weeks without being affected by light, rubbing and chemical agents.
Furthermore, it is required that, by combining suitable developer substances and coupler
substances, a broad palette of different color nuances can be produced.

25 Using the currently used colorants, as are described, for example, in the monograph by
K.H. Schrader "Grundlagen und Rezepturen der Kosmetika" [Fundamentals and
formulations of cosmetics], 2nd edition (1989), pages 784-799, it is, however, not
possible to satisfy the abovementioned requirements in all aspects. There therefore
continues to be a need for novel developer substances which satisfy the abovementioned
30 requirements to a particular degree.

In this regard, it has now surprisingly been found that certain 3-amino-2-

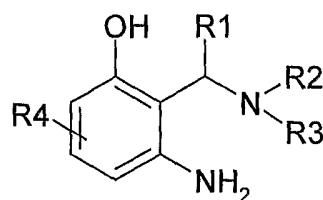
aminomethylphenol derivatives according to the general formula (I) satisfy the requirements placed on coupler substances to a particularly high degree. Thus, when these coupler substances are used with most known developer substances, color-rich color nuances are obtained which are extraordinarily light fast and wash fast.

5

The present invention therefore provides an agent for the oxidative coloring of keratin fibers, such as, for example, hair, furs, feathers or wool, in particular human hair, based on a developer substance-coupler substance combination which comprises, as coupler substance, at least one 3-amino-2-aminomethylphenol derivative of the formula (I) or its

10

physiologically compatible, water-soluble salt,



(I)

in which

15

R1 is hydrogen or a C₁-C₆-alkyl group;

R2 and **R3**, independently of one another, are hydrogen, a saturated

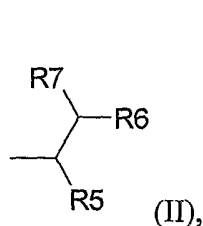
C₁-C₆-alkyl group, an unsaturated C₂-C₆-alkyl group, a C₂-C₄-hydroxyalkyl group, a

C₃-C₄-dihydroxyalkyl group, a C₂-C₄-aminoalkyl group, a C₁-C₄-dimethylaminoalkyl

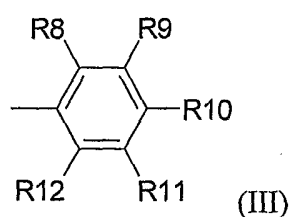
group, a C₂-C₄-acetylaminoalkyl group, a C₁-C₄-methoxyalkyl group, a C₁-C₄-

20

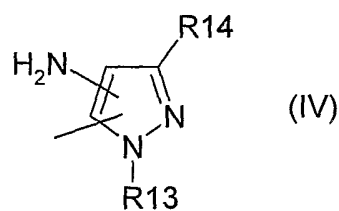
ethoxyalkyl group, a C₁-C₄-cyanoalkyl group, a C₁-C₄-carboxyalkyl group, a C₁-C₄-aminocarbonylalkyl group, a pyridylmethyl group, a furfuryl group, a hydrogenated furfuryl group, a substituted pyridyl group or a radical of the formula (II), (III) or (IV),



(II),

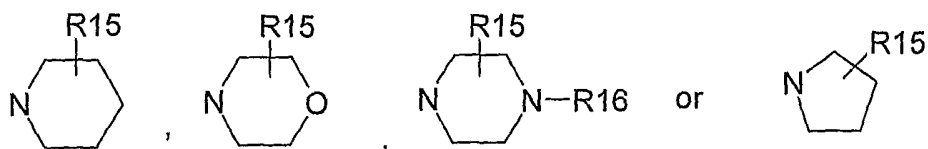


(III)



(IV)

or R2 and R3, together with the nitrogen atom, form a heterocyclic ring of the formula;



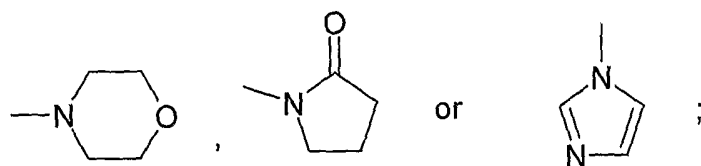
5

R4 is hydrogen, a halogen atom, a C₁-C₄-alkyl group, a C₁-C₄-hydroxyalkyl group or a C₁-C₄-alkoxy group;

R5 is hydrogen, a carboxyl group, or an aminocarbonyl group;

R6 and **R7**, independently of one another, are hydrogen, a hydroxyl group, an aminocarbonyl group, a methylthiomethyl group, a phenyl radical substituted by a phenyl group or hydroxyl group or a radical of the formula

10



R8, R9, R10, R11 and **R12**, independently of one another, are hydrogen, a halogen atom, a cyano group, a hydroxyl group, a C₁-C₄-alkoxy group, a C₁-C₄-hydroxyalkoxy group, a C₁-C₆-alkyl group, a C₁-C₄-alkyl thioether group, a mercapto group, a nitro group, an amino group, an alkylamino group, a hydroxyalkylamino group, a dialkylamino group, a di(hydroxyalkyl)amino group, a (dihydroxyalkyl)amino group, a

(hydroxyalkyl)alkylamino group, a trifluoromethane group, a -C(O)H- group, a -C(O)CH₃- group, a -C(O)CF₃- group, a -Si(CH₃)₃- group, a C₁-C₄-hydroxyalkyl group or a C₃-C₄-dihydroxyalkyl group or two adjacent radicals **R8** to **R12** form an -O-CH₂-O- bridge;

R13 is a C₁-C₄-alkyl group or a C₁-C₄-hydroxyalkyl group;

R14 is hydrogen or a C₁-C₆-alkyl group;

R15 is one or more hydrogen atoms, hydroxyl groups, carboxyl groups, aminocarbonyl groups or hydroxymethyl groups;

25

R16 is hydrogen or a C₁-C₆-alkyl group; where at least one of the radicals **R2** and **R3** is different from hydrogen.

Compounds of the formula (I) which may be mentioned are, for example, the following compounds:

3-amino-2-[(2,3-dihydroxypropyl)aminomethyl]phenol; 3-amino-2-(ethylaminomethyl)phenol; 3-amino-2-(isopropylaminomethyl)phenol; 3-amino-2-(propylaminomethyl)phenol; 3-amino-2-(pyrrolidin-1-ylmethyl)phenol; 3-amino-2-[[2-(furylmethyl)amino]methyl]phenol; 3-amino-2-[(2-methoxyethylamino)methyl]phenol; 3-amino-2-(4-morpholinylmethyl)phenol; 3-amino-2-(2-hydroxy-6-aminobenzylamino)butan-1-ol; 3-amino-2-[(furan-2-ylmethyl)amino]methyl]phenol; 3-amino-2-(4-methylpiperazin-1-ylmethyl)phenol; 1-(2-hydroxy-6-aminobenzyl)piperidin-4-ol; N-[2-(2-hydroxy-6-aminobenzylamino)ethyl]acetamide; 3-amino-2-[(2-morpholin-4-ylethylamino)methyl]phenol; 3-amino-2-(allylaminomethyl)phenol; 2-(2-hydroxy-6-aminobenzylamino)propan-1-ol; 3-amino-2-[(3-imidazol-1-ylpropylamino)methyl]phenol; 3-amino-2-(1-piperidinylmethyl)phenol; 3-amino-2-[[2-(tetrahydrofuran-2-ylmethyl)amino]methyl]phenol; 3-amino-2-[(4-aminophenyl)aminomethyl]phenol; 3-(2-hydroxy-6-aminobenzylamino)phenol; 5-(2-hydroxy-6-aminobenzylamino)-2-methylphenol; 3-amino-2-[(2-dimethylaminoethylamino)methyl]phenol; 4-(2-hydroxy-6-aminobenzylamino)butan-1-ol; 3-amino-2-[(3-ethoxypropylamino)methyl]phenol; 3-amino-2-[(3-methoxyphenylamino)methyl]phenol; 3-amino-2-[(4-chlorophenylamino)methyl]phenol; 3-amino-2-[(cyclopropylmethylamino)methyl]phenol; 2-(2-hydroxy-6-aminobenzylamino)-4-nitrophenol; 3-amino-2-[(4-chloro-benzylamino)methyl]phenol; 2-[(2-hydroxy-6-aminobenzyl)methylamino]ethanol; 2-[(2-hydroxy-6-aminobenzyl)ethylamino]ethanol; 3-amino-2-[[2-(pyridin-4-ylmethyl)amino]methyl]phenol; 1-[3-(2-hydroxy-6-aminobenzylamino)propyl]pyrrolidin-2-one; 3-amino-2-(4-amino-2-methylphenyl)aminomethylphenol; 3-amino-2-(4-amino-3-methylphenyl)aminomethylphenol; 2-[5-amino-2-(2-hydroxy-6-aminobenzylamino)phenyl]ethanol; 3-amino-2-(3-aminophenyl)aminomethylphenol; 4-

[2-(2-hydroxy-6-aminobenzylamino)ethyl]benzenesulfonamide; 2-[4-amino-2-(2-hydroxy-6-aminobenzylamino)phenoxy]ethanol; 2-[(2-hydroxy-6-aminobenzyl)(2-hydroxyethyl)amino]ethanol; [1-(6-amino-2-hydroxybenzyl)pyrrolidin-2-yl]methanol; 1-(6-amino-2-hydroxybenzyl)pyrrolidin-3-ol; 1-(6-amino-2-hydroxybenzyl)pyrrolidine-2-carboxamide; 1-(6-amino-2-hydroxybenzyl)piperidin-3-ol; 2-(6-amino-2-hydroxybenzylamino)propane-1,3-diol; 2-(6-amino-2-hydroxybenzylamino)-3-hydroxypropionamide;

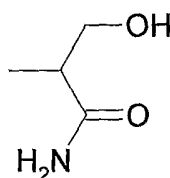
2-(6-amino-2-hydroxybenzylamino)succinic acid; 3-amino-2-cyclopropylaminomethylphenol; 2-(6-amino-2-hydroxybenzylamino)ethanol; (6-amino-2-hydroxybenzylamino)acetic acid; 4-(6-amino-2-hydroxybenzylamino)phenol; 3-amino-2-(benzo[1,3]dioxol-5-ylaminomethyl)phenol; [(6-amino-2-hydroxybenzyl)methylamino]acetonitrile; 3-amino-2-pentylaminomethylphenol; 3-amino-2-[(3-dimethylaminopropylamino)methyl]phenol; 3-amino-2-{[2-(5-nitropyridin-2-ylamino)ethylamino]methyl}phenol; 3-amino-2-[(2-aminoethylamino)methyl]phenol;

3-[2-(6-amino-2-hydroxybenzylamino)-1-hydroxyethyl]phenol; 3-amino-2-[(4-methylpyridin-2-ylamino)methyl]phenol; 2-(6-amino-2-hydroxybenzyl)-1-methyl-1,2,3,4-tetrahydroisoquinoline-6,7-diol; 2-(2-hydroxy-6-aminobenzylamino)-4-methylsulfanylbutyric acid; 1-(2-hydroxy-6-aminobenzyl)pyrrolidine-2-carboxylic acid; 3-amino-2-(1-pyrrolidinylmethyl)phenol; 3-amino-2-phenylaminomethylphenol; 3-amino-2-(4-dimethylaminophenyl)aminomethylphenol; 1-[3-(6-amino-2-hydroxybenzylamino)phenyl]ethanol; 1-[4-(6-amino-2-hydroxybenzylamino)phenyl]ethanol; 1-[2-(6-amino-2-hydroxybenzylamino)phenyl]ethanol; 3-amino-2-[(3,4-dimethoxyphenylamino)methyl]phenol; 3-amino-2-[(3-fluoro-2-methoxyphenylamino)methyl]phenol; 4-chloro-2-(6-amino-2-hydroxybenzylamino)phenol; 3-amino-2-[(4-trifluoromethylphenylamino)methyl]phenol; 3-amino-2-(p-tolylaminomethyl)phenol; 3-amino-2-[(2-aminophenylamino)methyl]phenol; 3-amino-2-[(2-hydroxyphenylamino)methyl]phenol; 3-amino-2-[(2-dimethylaminophenylamino)methyl]phenol; 3-amino-2-[(2-methylphenylamino)methyl]phenol; 3-amino-2-[(2-trifluoromethylphenylamino)methyl]phenol; 3-amino-2-[(3-dimethylaminophenylamino)methyl]phenol; 3-amino-2-[(3-

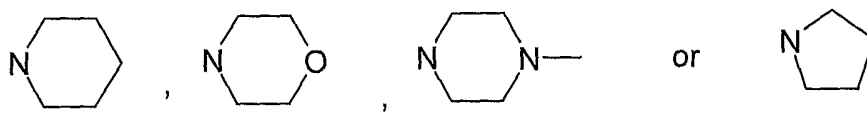
methylphenylamino)methyl]phenol; 3-amino-2-[(3-trifluoromethylphenylamino)methyl]phenol; 3-amino-2-[(2-bromophenylamino)methyl]phenol; 3-amino-2-[(2-cyanophenylamino)methyl]phenol; 3-amino-2-[(2-fluorophenylamino)methyl]phenol; 3-amino-2-[(2-methoxyphenylamino)methyl]phenol; 3-amino-2-[(2-nitrophenylamino)methyl]phenol; 3-amino-2-[(3-bromophenylamino)methyl]phenol; 3-amino-2-[(3-cyanophenylamino)methyl]phenol; 3-amino-2-[(3-fluorophenylamino)methyl]phenol; 3-amino-2-[(3-methoxyphenylamino)methyl]phenol; 3-amino-2-[(3-nitrophenylamino)methyl]phenol; 3-amino-2-[(4-bromophenylamino)methyl]phenol; 3-amino-2-[(4-cyanophenylamino)methyl]phenol; 3-amino-2-[(4-fluorophenylamino)methyl]phenol; 3-amino-2-[(4-methoxyphenylamino)methyl]phenol; 3-amino-2-[(4-nitrophenylamino)methyl]phenol; 3-amino-2-{[2-(1,3-dihydroxypropyl)aminophenylamino)methyl]phenol; 3-amino-2-{[2-di(2-hydroxyethyl)aminophenylamino)methyl]phenol; 3-amino-2-{[2-(2-hydroxyethylamino)phenylamino)methyl]phenol; 3-amino-2-[(2-pyrrolidinephenylamino)methyl]phenol; 3-amino-2-{[3-(1,3-dihydroxypropyl)aminophenylamino)methyl]phenol; 3-amino-2-{[3-di(2-hydroxyethyl)aminophenylamino)methyl]phenol; 3-amino-2-{[3-(2-hydroxyethylamino)phenylamino)methyl]phenol; 3-amino-2-[(3-pyrrolidinephenylamino)methyl]phenol; 3-amino-2-[(4-(1,3-dihydroxypropyl)aminophenylamino)methyl]phenol; 3-amino-2-{[4-di(2-hydroxyethylamino)phenylamino)methyl]phenol; 3-amino-2-{[4-(2-hydroxyethylamino)phenylamino)methyl]phenol; 3-amino-2-[(4-pyrrolidinephenylamino)methyl]phenol; 3-amino-2-{[4-amino-2-(2-hydroxyethoxy)phenylamino)methyl]phenol; 3-amino-2-[(4-amino-2-chlorophenylamino)methyl]phenol; 3-amino-2-[(4-amino-2-hydroxyphenylamino)methyl]phenol; 3-amino-2-[(4-amino-2-methoxyphenylamino)methyl]phenol; 3-amino-2-{[4-amino-3-(2-hydroxyethoxy)phenylamino)methyl]phenol; 3-amino-2-[(4-amino-3-chlorophenylamino)methyl]phenol; 3-amino-2-[(4-amino-3-hydroxyphenylamino)methyl]phenol; 3-amino-2-[(4-amino-3-methoxyphenylamino)methyl]phenol; 3-amino-2-[(3,4-diaminophenylamino)methyl]phenol; 3-amino-2-[(2,4-

diaminophenylamino)methyl]phenol and 2-[5-amino-4-(2-hydroxy-6-aminobenzylamino)pyrazol-1-yl]ethanol.

Preference is given to compounds of the formula (I) in which (i) **R1** and/or **R4** is hydrogen, and/or (ii) **R2** is a methyl group or a C₁-C₄-hydroxyalkyl group and **R3** is a C₁-C₄-hydroxyalkyl group and/or (iii) **R2** is hydrogen and **R3** is a C₁-C₄-hydroxyalkyl group, a substituted pyridyl radical, a furfuryl radical, a hydrogenated furfuryl radical, a substituted phenyl radical, a substituted pyrazoyl radical or a radical of the following formula



and/or (iv) **R2** and **R3** form an aliphatic ring of the formula



Particular preference is given to the following compounds of the formula (I):

3-amino-2-[(2,3-dihydroxypropyl)aminomethyl]phenol; 3-amino-2-[(2-aminoethylamino)methyl]phenol; 3-amino-2-[(2-hydroxyethylamino)methyl]phenol; 3-amino-2-(4-morpholinylmethyl)phenol; 2-[(2-hydroxy-6-aminobenzyl)-methylamino]ethanol; 3-amino-2-(1-pyrrolidinylmethyl)phenol, 3-amino-2-[(2-furylmethyl)amino]methyl}phenol, 2-(2-hydroxy-6-aminobenzylamino)propan-1-ol; 2-[(2-hydroxy-6-aminobenzyl)(2-hydroxyethyl)amino]ethanol; [1-(2-hydroxy-6-aminobenzyl)pyrrolidin-2-yl]methanol; 1-(2-hydroxy-6-aminobenzyl)pyrrolidine-2-carboxamide;

3-amino-2-[(4-methylpyridin-2-ylamino)methyl]phenol; 3-amino-2-(1-piperidinylmethyl)phenol, 3-amino-2-[(4-methyl-1-piperazinyl)methyl]phenol, 3-amino-

2-((2-aminophenylamino)methyl)phenol; 3-amino-2-((2-chloro-phenylamino)-
methyl)phenol; 3-amino-2-[(2-dimethylaminophenylamino)methyl]phenol; 3-amino-2-
[(2-fluorophenylamino)methyl]phenol; 3-amino-2-{[2-(2-
hydroxyethylamino)phenylamino]methyl}phenol; 3-amino-2-{[2-N,N-bis(2-
5 hydroxyethyl)aminophenylamino]methyl}phenol; 3-amino-2-[(2-
pyrrolidinephenylamino)methyl]phenol; 3-amino-2-((3-
aminophenylamino)methyl)phenol; 3-amino-2-[(3-chlorophenylamino)methyl]phenol; 3-
amino-2-[(3-dimethylaminophenylamino)methyl]phenol; 3-amino-2-[(3-fluorophenyl-
amino)methyl]phenol; 3-amino-2-{[3-(2-hydroxyethyl-
10 amino)phenylamino]methyl}phenol; 3-amino-2-{[3-N,N-bis(2-
hydroxyethyl)aminophenylamino]methyl}phenol; 3-amino-2-[(3-
pyrrolidinephenylamino)methyl]phenol; 3-amino-2-[(4-aminophenylamino)methyl]-
phenol; 3-amino-2-((4-chlorophenylamino)methyl)phenol; 3-amino-2-[(4-
dimethylaminophenylamino)methyl]phenol; 3-amino-2-[(4-
15 fluorophenylamino)methyl]phenol; 3-amino-2-{[4-(2-
hydroxyethylamino)phenylamino]methyl}phenol; 3-amino-2-{[4-N,N-bis(2-
hydroxyethyl)aminophenylamino]methyl}phenol; 3-amino-2-[(4-
pyrrolidinephenylamino)methyl]phenol; 3-amino-2-{[2-(2-hydroxyethoxy)-4-
aminophenylamino]methyl}phenol; 3-amino-2-[(2,4-diaminophenyl-
20 amino)methyl]phenol; 3-amino-2-[(2-chloro-4-aminophenylamino)methyl]phenol; 3-
amino-2-[(4-amino-2-hydroxyphenylamino)methyl]phenol; 3-amino-2-[(2-
hydroxyethylamino-4-aminophenylamino)methyl]phenol; 3-amino-2-[(2-methyl-4-
aminophenylamino)methyl]phenol; 3-amino-2-{[3-(2-hydroxyethoxy)-4-
aminophenylamino]methyl}phenol; 3-amino-2-[(3-amino-4-aminophenylamino)-
25 methyl]phenol; 3-amino-2-[(3-chloro-4-aminophenylamino)methyl]phenol; 3-amino-2-
[(3-hydroxy-4-aminophenylamino)methyl]phenol; 3-amino-2-{[3-(2-
hydroxyethylamino)-4-aminophenylamino]methyl}phenol; 3-amino-2-[(3-methyl-4-
aminophenylamino)methyl]phenol; 3-amino-2-{[2-(2-
hydroxyethoxy)phenylamino]methyl}phenol; 3-amino-2-[(2-
30 hydroxyphenylamino)methyl]phenol; 3-amino-2-{[3-(2-
hydroxyethoxy)phenylamino]methyl}phenol; 3-amino-2-[(3-
hydroxyphenylamino)methyl]phenol; 3-amino-2-{[4-(2-

hydroxyethoxy)phenylamino)methyl}phenol; 3-amino-2-[(4-hydroxyphenylamino)methyl}phenol; 3-amino-2-(phenylaminomethyl)phenol and 2-[5-amino-4-(2-hydroxy-6-aminobenzylamino)pyrazol-1-yl]ethanol.

- 5 The compounds of the formula (I) can be used either in the form of free bases or else in the form of their physiologically compatible salts with inorganic or organic acids, such as, for example, hydrochloric acid, sulfuric acid, phosphoric acid, acetic acid, propionic acid, lactic acid or citric acid.
- 10 The 3-amino-2-aminomethylphenol derivatives of the formula (I) are present in the colorant according to the invention in a total amount of from about 0.005 to 20 percent by weight, preference being given to an amount of from about 0.01 to 8 percent by weight and in particular 0.1 to 5 percent by weight.
- 15 Suitable developer substances are preferably 1,4-diaminobenzene (p-phenylenediamine), 1,4-diamino-2-methylbenzene (p-tolylenediamine), 1,4-diamino-2,6-dimethylbenzene, 1,4-diamino-3,5-diethylbenzene, 1,4-diamino-2,5-dimethylbenzene, 1,4-diamino-2,3-dimethylbenzene, 2-chloro-1,4-diaminobenzene, 1,4-diamino-2-(thiophen-2-yl)benzene,
- 20 1,4-diamino-2-(thiophen-3-yl)benzene, 4-(2,5-diaminophenyl)-2-((diethylamino)methyl)thiophene, 2-chloro-3-(2,5-diaminophenyl)thiophene, 1,4-diamino-2-(pyridin-3-yl)benzene, 2,5-diaminobiphenyl, 2,5-diamino-4'-(1-methylethyl)-1,1'-biphenyl, 2,3',5-triamino-1,1'-biphenyl, 1,4-diamino-2-methoxymethylbenzene,
- 25 1,4-diamino-2-aminomethylbenzene, 1,4-diamino-2-((phenylamino)methyl)benzene, 1,4-diamino-2-((ethyl-(2-hydroxyethyl)amino)methyl)benzene, 1,4-diamino-2-hydroxymethylbenzene, 1,4-diamino-2-(2-hydroxyethoxy)benzene, 2-(2-(acetylamino)ethoxy)-1,4-diaminobenzene, 4-phenylaminoaniline, 4-dimethylamino-aniline, 4-diethylaminoaniline, 4-dipropylaminoaniline, 4-[ethyl(2-
- 30 hydroxyethyl)amino]aniline, 4-[di(2-hydroxyethyl)amino]aniline, 4-[di(2-hydroxyethyl)amino]-2-methylaniline, 4-[(2-methoxyethyl)amino]aniline, 4-[(3-hydroxypropyl)amino]aniline,

4-[(2,3-dihydroxypropyl)amino]aniline, 4-(((4-aminophenyl)methyl)amino)aniline, 4-[(4-aminophenylamino)methyl]phenol, 1,4-diamino-N-(4-pyrrolidin-1-yl-benzyl)benzene, 1,3-dihydroxy-2-((2-furylmethyl)aminomethyl)benzene, 1,4-diamino-N-thiophen-2-ylmethylbenzene, 1,4-diamino-N-furan-2-ylmethylbenzene, 1,4-diamino-N-thiophen-3-ylmethylbenzene, 1,4-diamino-N-benzylbenzene, 1,4-diamino-2-(1-hydroxyethyl)benzene, 1,4-diamino-2-(2-hydroxyethyl)benzene, 1,4-diamino-2-(1-methylethyl)benzene, 1,3-bis[(4-aminophenyl)(2-hydroxyethyl)amino]-2-propanol, 1,4-bis[(4-aminophenyl)amino]butane, 1,8-bis(2,5-diaminophenoxy)-3,6-dioxaoctane, 2,5-diamino-4'-hydroxy-1,1'-biphenyl, 2,5-diamino-2'-trifluoromethyl-1,1'-biphenyl, 2,4',5-triamino-1,1'-biphenyl, 4-aminophenol, 4-amino-3-methylphenol, 4-amino-3-(hydroxymethyl)phenol, 4-amino-3-fluorophenol, 4-methylaminophenol, 4-amino-2-(aminomethyl)phenol, 4-amino-2-(hydroxymethyl)phenol, 4-amino-2-fluorophenol, 4-amino-2-[(2-hydroxyethyl)amino]methylphenol, 4-amino-2-methylphenol, 4-amino-2-(methoxymethyl)phenol, 4-amino-2-(2-hydroxyethyl)phenol, 5-aminosalicylic acid, 2,5-diaminopyridine, 2,4,5,6-tetraaminopyrimidine, 2,5,6-triamino-4-(1H)-pyrimidone, 4,5-diamino-1-(2-hydroxyethyl)-1H-pyrazole, 4,5-diamino-1-(1-methylethyl)-1H-pyrazole, 4,5-diamino-1-[(4-methylphenyl)methyl]-1H-pyrazole, 1-[(4-chlorophenyl)methyl]-4,5-diamino-1H-pyrazole, 4,5-diamino-1-methyl-1H-pyrazole, 4,5-diamino-1-pentyl-1H-pyrazole, 4,5-diamino-1-(phenylmethyl)-1H-pyrazole, 4,5-diamino-1-((4-methoxyphenyl)methyl)-1H-pyrazole, 2-aminophenol, 2-amino-6-methylphenol, 2-amino-5-methylphenol, 1,2,4-trihydroxybenzene, 2,4-diaminophenol, 1,4-dihydroxybenzene, 2-(((4-aminophenyl)amino)methyl)-1,4-diaminobenzene.

Furthermore, in addition to the compounds of the formula (I), the colorant according to the invention can also comprise further known coupler substances, for example N-(3-dimethylaminophenyl)urea, 2,6-diaminopyridine, 2-amino-4-[(2-hydroxyethyl)amino]anisole, 2,4-diamino-1-fluoro-5-methylbenzene, 2,4-diamino-1-methoxy-5-methylbenzene, 2,4-diamino-1-ethoxy-5-methylbenzene, 2,4-diamino-1-(2-hydroxyethoxy)-5-methylbenzene, 2,4-di[(2-hydroxyethyl)amino]-1,5-dimethoxybenzene, 2,3-diamino-6-methoxypyridine, 3-amino-6-methoxy-2-(methylamino)pyridine, 2,6-diamino-3,5-dimethoxypyridine, 3,5-diamino-2,6-dimethoxypyridine, 1,3-

- diaminobenzene, 2,4-diamino-1-(2-hydroxyethoxy)benzene, 1,3-diamino-4-(2,3-dihydroxypropoxy)benzene, 1,3-diamino-4-(3-hydroxypropoxy)benzene, 1,3-diamino-4-(2-methoxyethoxy)benzene, 2,4-diamino-1,5-di(2-hydroxyethoxy)benzene, 1-(2-aminoethoxy)-2,4-diaminobenzene, 2-amino-1-(2-hydroxyethoxy)-4-methyl-
- 5 aminobenzene, 2,4-diaminophenoxyacetic acid, 3-[di(2-hydroxyethyl)amino]aniline, 4-amino-2-di[(2-hydroxyethyl)amino]-1-ethoxybenzene, 5-methyl-2-(1-methylethyl)phenol, 3-[(2-hydroxyethyl)amino]aniline, 3-[(2-aminoethyl)amino]aniline, 1,3-di(2,4-diaminophenoxy)propane, di(2,4-diaminophenoxy)methane,
- 10 1,3-diamino-2,4-dimethoxybenzene, 2,6-bis(2-hydroxyethyl)aminotoluene, 4-hydroxyindole, 3-dimethylaminophenol, 3-diethylaminophenol, 5-amino-2-methylphenol, 5-amino-4-fluoro-2-methylphenol, 5-amino-4-methoxy-2-methylphenol, 5-amino-4-ethoxy-2-methylphenol, 3-amino-2,4-dichlorophenol, 5-amino-2,4-dichlorophenol, 3-amino-2-methylphenol,
- 15 3-amino-2-chloro-6-methylphenol, 3-aminophenol, 2-[(3-hydroxyphenyl)amino]acetamide, 5-[(2-hydroxyethyl)amino]-4-methoxy-2-methylphenol, 5-[(2-hydroxyethyl)amino]-2-methylphenol, 3-[(2-hydroxyethyl)amino]phenol, 3-[(2-methoxyethyl)amino]phenol, 5-amino-2-ethylphenol, 5-amino-2-methoxyphenol, 2-(4-amino-2-
- 20 hydroxyphenoxy)ethanol, 5-[(3-hydroxypropyl)amino]-2-methylphenol, 3-[(2,3-dihydroxypropyl)amino]-2-methylphenol, 3-[(2-hydroxyethyl)amino]-2-methylphenol, 2-amino-3-hydroxypyridine, 2,6-dihydroxy-3,4-dimethylpyridine, 5-amino-4-chloro-2-methylphenol, 1-naphthol, 2-methyl-1-naphthol, 1,5-dihydroxynaphthalene, 1,7-dihydroxynaphthalene,
- 25 2,3-dihydroxynaphthalene, 2,7-dihydroxynaphthalene, 2-methyl-1-naphthol acetate, 1,3-dihydroxybenzene, 1-chloro-2,4-dihydroxybenzene, 2-chloro-1,3-dihydroxybenzene, 1,2-dichloro-3,5-dihydroxy-4-methylbenzene, 1,5-dichloro-2,4-dihydroxybenzene, 1,3-dihydroxy-2-methylbenzene, 3,4-methylenedioxyphenol, 3,4-methylenedioxyaniline,
- 30 5-[(2-hydroxyethyl)amino]-1,3-benzodioxol, 6-bromo-1-hydroxy-3,4-methylenedioxybenzene, 3,4-diaminobenzoic acid, 3,4-dihydro-6-hydroxy-1,4(2H)-benzoxazine, 6-amino-3,4-dihydro-1,4(2H)-benzoxazine,

3-methyl-1-phenyl-5-pyrazolone, 5,6-dihydroxyindole, 5,6-dihydroxyindoline, 5-hydroxyindole, 6-hydroxyindole, 7-hydroxyindole and 2,3-indolinedione.

- 5 The additional coupler substances and developer substances may be present in the colorant according to the invention in each case individually or in the mixture with one another, where the total amount of coupler substances and developer substances in the colorant according to the invention (based on the total amount of the colorant) is in each case about 0.005 to 20 percent by weight, preferably about 0.01 to 5 percent by weight
10 and in particular 0.1 to 2.5 percent by weight.

The total amount of the developer substance-coupler substance combination present in the colorant described here is preferably about 0.01 to 20 percent by weight, particular preference being given to an amount of from about 0.02 to 10 percent by weight and in
15 particular 0.2 to 6 percent by weight. The developer substances and coupler substances are generally used in approximately equimolar amounts; however, it is not disadvantageous if the developer substances are present in this regard in a certain excess or deficit.

- 20 In addition, the colorant according to the invention can additionally comprise other color components, for example 6-amino-2-methylphenol and 2-amino-5-methylphenol, and also customary natural, nature-identical or synthetic direct dyes, for example triphenylmethane dyes, such as
4-[(4'-aminophenyl)(4'-imino-2'',5''-cyclohexadien-1''-ylidene)methyl]-2-
25 methylaminobenzene monohydrochloride (C.I. 42 510) and 4-[(4'-amino-3'-methylphenyl)(4''-imino-3''-methyl-2'',5''-cyclohexadien-1''-ylidene)methyl]-2-
methylaminobenzene monohydrochloride (C.I. 42 520), aromatic nitro dyes, such as
4-(2'-hydroxyethyl)aminonitrotoluene,
2-amino-4,6-dinitrophenol, 2-amino-5-(2'-hydroxyethyl)aminonitrobenzene, 2-chloro-6-
30 (ethylamino)-4-nitrophenol, 4-chloro-N-(2-hydroxyethyl-2-nitroaniline, 5-chloro-2-hydroxy-4-nitroaniline, 2-amino-4-chloro-6-nitrophenol or 1-[(2'-ureidoethyl)amino-4-nitrobenzene, azo dyes, such as 6-[(4'-aminophenyl)azo]-5-hydroxynaphthalene-1-

sulfonic acid sodium salt (C.I. 14 805) or dispersion dyes, such as, for example, 1,4-diaminoanthraquinone and 1,4,5,8-tetraaminoanthraquinone, and basic or acidic direct dyes. The colorant can comprise these color components in an amount of from about 0.1 to 4.0 percent by weight.

5

The coupler substances and developer substances and also the other color components, if they are bases, can of course also be used in the form of the physiologically compatible salts with organic or inorganic acids, such as, for example, hydrochloric acid or sulfuric acid, or - if they have aromatic OH groups - in the form of these salts with bases, for example as alkali metal phenoxides.

10

Moreover, if the colorants are to be used for coloring hair, they may also comprise further customary cosmetic additives, for example antioxidants, such as ascorbic acid, thioglycolic acid and sodium sulfite, and perfume oils, complexing agents, wetting agents, emulsifiers, thickeners and care substances. The preparation form of the colorant according to the invention can, for example, be a solution, in particular an aqueous or aqueous-alcoholic solution. The particularly preferred preparation forms are, however, a cream, a gel or an emulsion. Their composition is a mixture of the dye components with the additives customary for such preparations.

15

20

Customary additives in solutions, creams, emulsions or gels are, for example, solvents, such as water, lower aliphatic alcohols, for example ethanol, propanol or isopropanol, glycerol or glycols, such as 1,2-propylene glycol, and also wetting agents or emulsifiers from the classes of anionic, cationic, amphoteric or nonionogenic surface-active substances, such as, for example, fatty alcohol sulfates, oxyethylated fatty alcohol sulfates, alkylsulfonates, alkylbenzenesulfonates, alkyltrimethylammonium salts, alkylbetaines, oxyethylated fatty alcohols, oxyethylated nonylphenols, fatty acid alkanolamides and oxyethylated fatty acid esters, also thickeners, such as higher fatty alcohols, starch, cellulose derivatives, petrolatum, paraffin oil and fatty acids, and also care substances, such as cationic resins, lanolin derivatives, cholesterol, pantothenic acid and betaine. The constituents mentioned are used in the amounts customary for such purposes, for example the wetting agents and emulsifiers in concentrations of from about

25

30

0.5 to 30 percent by weight, the thickeners in an amount of from about 0.1 to 25 percent by weight and the care substances in a concentration of from about 0.1 to 5 percent by weight.

- 5 Depending on the composition, the colorant according to the invention can have a slightly acidic, neutral or alkaline reaction. In particular, it has a pH of from 6.8 to 11.5, the basic adjustment preferably being carried out with ammonia. It is, however, also possible to use organic amines, for example monoethanolamine and triethanolamine, and also inorganic bases, such as sodium hydroxide and potassium hydroxide. For a pH adjustment in the
- 10 acidic range, inorganic or organic acids, for example phosphoric acid, acetic acid, citric acid or tartaric acid, are suitable.

For the use for the oxidative coloring of hair, the colorant described above is mixed directly prior to use with an oxidizing agent, and an amount of this mixture sufficient for

15 the hair-coloring treatment, generally about 60 to 200 grams depending on the fullness of the hair, is applied to the hair.

Suitable oxidizing agents for developing the hair coloration are primarily hydrogen peroxide or its addition compounds onto urea, melamine, sodium borate or sodium

20 carbonate in the form of a 3- to 12 percent strength, preferably 6 percent strength, aqueous solution, but also atmospheric oxygen. If a 6 percent strength hydrogen peroxide solution is used as oxidizing agent, then the weight ratio between hair colorant and oxidizing agent is 5:1 to 1:2, but preferably 1:1. Larger amounts of oxidizing agent are primarily used at higher dye concentrations in the hair colorant, or if stronger bleaching

25 of the hair is intended at the same time.

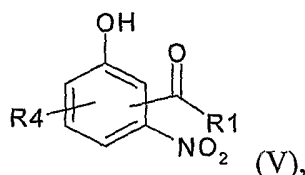
The mixture is left to act on the hair at 15 to 50 degrees Celsius for about 10 to 45 minutes, preferably 30 minutes, then the hair is rinsed with water and dried. If

30 required, this rinsing is followed by washing with a shampoo and possibly after-rinsing with a weak organic acid, such as, for example, citric acid or tartaric acid. The hair is then dried.

The hair colorants according to the invention with a content of 3-amino-2-aminomethylphenol derivatives of the formula (I) as coupler substances permit hair colorations with excellent color fastness, in particular with regard to light fastness, washing fastness and rubbing fastness. With regard to the coloring properties, the hair colorants according to the invention offer, depending on the nature and composition of the color components, a broad palette of different color nuances which ranges from blonde via brown, purple, violet to blue and black shades. The shades are characterized here by their particular color intensity. The very good coloring properties of the hair colorants according to the present application are further evident from the fact that these agents permit a coloring of gray, chemically non-predamaged hair without problems and with good coverage.

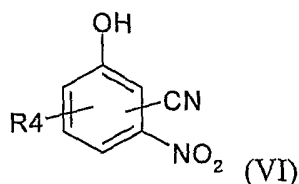
The present application further provides the 3-amino-2-aminomethylphenol derivatives of the formula (I) described above with the proviso that **R1** and **R4** are not hydrogen at the same time if (i) **R2** and **R3** are a methyl group or (ii) **R2** and **R3**, together with the nitrogen atom, form a pyrrolidine ring or piperidine ring.

The aminophenol derivatives of the formula (I) according to the invention can be prepared using known synthesis methods. The synthesis of the compounds according to the invention can, for example, be carried out as follows:
either a) by a reductive amination of a substituted benzene of the formula (V) with subsequent reduction of the nitro group;



or b) by reduction of the nitrile group of the formula (VI),

16



subsequent alkylation of the amino group with a compound of the formula **XR2** and/or **XR3**, and final reduction of the nitro group, where **R1**, **R2**, **R3** and **R4** have the meanings
 5 given above and **X** is a halogen atom.

The 3-amino-2-aminomethylphenol derivatives of the formula (I) according to the invention are readily soluble in water and permit colorations with high color intensity and excellent color fastness, especially with regard to light fastness, washing fastness and
 10 rubbing fastness. The 3-amino-2-aminomethylphenol derivatives of the formula (I) also have excellent storage stability, especially as constituent of the colorants described above.

The examples below are intended to illustrate the subject-matter of the invention in more detail without limiting it thereto.

15

E x a m p l e s

Examples 1 to 5: Synthesis of 3-amino-2-aminomethylphenol derivatives of the formula
 20 (I)

Synthesis of 3-amino-2-aminomethylphenol derivatives (general synthesis procedure)
 0.2 g (1.2 mmol) of 2-hydroxy-6-nitrobenzaldehyde and 1.8 mmol of the corresponding amine are dissolved in 6 ml of methanol. 0.25 ml of acetic acid and 0.15 g of NaBH₃CN
 25 (2.4 mmol) are then added and the reaction mixture is stirred for 1.5 to 5 hours at room temperature under argon in a sealed tube. When the reaction is complete, the reaction mixture is poured into 10 ml of ethyl acetate, and the organic phase is extracted with an aqueous solution of sodium hydrogen carbonate, then dried with magnesium sulfate and filtered. The solvent is distilled off on a rotary evaporator and the residue is purified over

silica gel with petroleum ether/ethyl acetate (9:1). The product obtained in this way is hydrogenated with hydrogen in 4 ml of ethyl acetate in the presence of platinum oxide (20 mg). After 40 minutes, the mixture is filtered through Cellite and the filtrate is concentrated under reduced pressure. The product is produced in a yield of from 35 to 85%, in most cases in the form of an oil.

1. 3-Amino-2-(4-morpholinylmethyl)phenol

Amine used: morpholine

Yield: 0.212 g (85% of theory)

10 Mass spectrum: MH^+ 209 (100)

2. 3-Amino-2-(1-pyrrolidinylmethyl)phenol

Amine used: pyrrolidine

Yield: 0.081 g (35% of theory)

Mass spectrum: MH^+ 193 (100)

15 **3. 3-Amino-2-[(2-furylmethyl)amino]methyl}phenol**

Amine used: 2-furylmethylamine

Yield: 0.165 g (63% of theory)

Mass spectrum: MH^+ 219 (100)

4. 3-Amino-2-(1-piperidinylmethyl)phenol

20 Amine used: piperidine

Yield: 0.158 g (64% of theory)

Mass spectrum: MH^+ 207 (100)

5. 3-Amino-2-[(4-methyl-1-piperazinyl)methyl]phenol

Amine used: 4-methylpiperazine

25 Yield: 0.122 g (46% of theory)

Mass spectrum: MH^+ 222 (100)

Examples 6 to 15: Hair colorants

30

Hair-coloring solutions of the following composition are prepared:

1.25 mmol substance of the formula (I) as in table 1

	1.25 mmol	developer substance as in table 1
	10.0 g	lauryl ether sulfate (28 percent strength aqueous solution)
	9.0 g	ammonia (22 percent strength aqueous solution)
	7.8 g	ethanol
5	0.3 g	ascorbic acid
	0.3 g	ethylenediaminetetraacetic acid disodium salt hydrate
	ad 100.0 g	water, demineralized

10 g of the above coloring solution are mixed directly prior to application with 10 g of a
 10 6 percent strength hydrogen peroxide solution. The mixture is then applied to bleached
 hair. After a contact time of 30 minutes at 40°C, the hair is rinsed with water, washed
 with a standard commercial shampoo and dried. The resulting colorations are summarized
 in table 1.

15

Table 1:

Example No.	Coupler substance of the formula (I)	Developer substance				
		I. 2,5-Diamino--toluene sulfate	II. 2,5-Diamino-phenyl-ethanol sulfate	III. 4,5-Diamino-1-(2'-hydroxy-ethyl)-pyrazole sulfate	IV. 4-Amino-phenol	V. 2,4,5,6-Tetra-amino-pyrimidine sulfate
6	as in example 1	violet	violet	intense raspberry red	weak orange-brown	blue-gray

7	as in example 2	violet	violet	intense raspberry red	weak orange- brown	blue-gray
8	as in example 3	dark violet	violet	intense raspberry red	orange	gray
9	as in example 4	violet	violet	intense raspberry red	weak orange- brown	gray
10	as in example 5	dark violet	violet	intense raspberry red	red- brown	fennel green

Table 1: (continuation)

Example No.	Coupler substance of the formula (I)	Developer substance	
		VI. N,N-Bis(2-hydroxy- ethyl)-p-phenylene- diamine	VII. 4-Hydroxy-o- toluidine
11	as in example 1	dark blue	pale red-brown
12	as in example 2	dark blue	pale red-brown
13	as in example 3	dark blue	pale red-brown
14	as in example 4	dark blue	pale red-brown
15	as in example 5	dark blue	pale red-brown

Examples 16 to 39: Hair colorants

Hair-coloring solutions of the following composition are prepared:

- 5 X g 3-aminophenol derivative of the formula (I) (coupler
substance **K1** to **K5** as in table 4)
- U g developer substance **E8** to **E15** as in table 2
- Y g coupler substance **K12** to **K36** as in table 4
- 10.0 g lauryl ether sulfate (28 percent strength aqueous solution)
- 10 9.0 g ammonia (22 percent strength aqueous solution)
- 7.8 g ethanol
- 0.3 g ascorbic acid
- 0.3 g ethylenediaminetetraacetic acid disodium salt hydrate
- ad 100.0 g water, demineralized

15

30 g of the above coloring solution are mixed directly prior to application with 30 g of a
6 percent strength aqueous hydrogen peroxide solution. The mixture is then applied to
bleached hair. After a contact time of 30 minutes at 40°C, the hair is rinsed with water,
washed with a standard commercial shampoo and dried. The coloring results are
20 summarized in table 5.

Table 2:

Developer substances	
E8	1,4-Diaminobenzene
E9	2,5-Diaminophenylethanol sulfate
E10	3-Methyl-4-aminophenol
E11	4-Amino-2-aminomethylphenol dihydrochloride
E13	N,N-Bis(2'-hydroxyethyl)-p-phenylenediamine sulfate
E14	4,5-Diamino-1-(2'-hydroxyethyl)pyrazole sulfate
E15	2,5-Diaminotoluene sulfate

Table 3:

Direct dyes	
D2	6-Chloro-2-ethylamino-4-nitrophenol
D3	2-Amino-6-chloro-4-nitrophenol

5 **Table 4:**

Coupler substances	
K1	3-Amino-2-(4-morpholinylmethyl)phenol
K2	3-Amino-2-(1-pyrrolidinylmethyl)phenol
K3	3-Amino-2-[(2-furylmethyl)amino]methyl}phenol
K4	3-Amino-2-(1-piperidinylmethyl)phenol
K5	3-Amino-2-[(4-methyl-1-piperazinyl)methyl]phenol
K12	2-Amino-4-(2'-hydroxyethyl)aminoanisoie sulfate
K13	1,3-Diamino-4-(2'-hydroxyethoxy)benzene sulfate
K14	2,4-Diamino-5-fluorotoluene sulfate
K18	N-(3-Dimethylamino)phenylurea
K19	1,3-Bis(2,4-diaminophenoxy)propane tetrahydrochloride
K21	3-Aminophenol
K22	5-Amino-2-methylphenol
K23	3-Amino-2-chloro-6-methylphenol
K24	5-Amino-4-fluoro-2-methylphenol sulfate
K25	1-Naphthol
K31	1,3-Dihydroxybenzene
K32	2-Methyl-1,3-dihydroxybenzene
K33	1-Chloro-2,4-dihydroxybenzene
K34	4-(2'-Hydroxyethyl)amino-1,2-methylenedioxybenzene hydrochloride
K36	2-Amino-5-methylphenol

Table 5: Hair colorants

Example No.	16	17	18	19	20	21
Dyes	(amount of dye in grams)					
K1	0.10	0.12	0.05	0.07	0.10	0.12
E8	0.30					
E9					0.25	0.20
E10						0.10
E15		0.25	0.30	0.25		
K12			0.05			
K13				0.05		
K21	0.05					
K22		0.05				
K23			0.05	0.10	0.10	0.10
K25					0.10	
K31	0.20			0.15	0.10	0.10
K32		0.20		0.10		
K33			0.20			
K36						0.10
Coloring result	blonde	blonde	blonde	blonde	blonde	blonde

Table 5 (continuation)

Example No.	22	23	24	25	26	27
Dyes	(amount of dye in grams)					
K2	0.10	0.12	0.05	0.07	0.10	0.12
E8	0.30					
E9					0.25	0.20
E10						0.10
E15		0.25	0.30	0.25		
K12			0.05			
K13				0.05		
K21	0.05					
K22		0.05				
K23			0.05	0.10	0.10	0.10
K25					0.10	
K31	0.20			0.15	0.10	0.10
K32		0.20		0.10		
K33			0.20			
K36						0.10
Coloring result	blonde	blonde	blonde	blonde	blonde	blonde

Table 5 (continuation)

Example No.	28	29	30	31	32	33
Dyes	(amount of dye in grams)					
K3	0.10	0.12	0.05	0.07	0.10	0.12
E8	0.30					
E9					0.25	0.20
E10						0.10
E15		0.25	0.30	0.25		
K12			0.05			
K13				0.05		
K21	0.05					
K22		0.05				
K23			0.05	0.10	0.10	0.10
K25					0.10	
K31	0.20			0.15	0.10	0.10
K32		0.20		0.10		
K33			0.20			
K36						0.10
Coloring result	blonde	blonde	blonde	blonde	blonde	blonde

Table 5 (continuation)

Example No.	34	35	36	37	38	39
Dyes	(amount of dye in grams)					
K4	0.10	0.06	0.05		0.10	0.12
K5		0.06		0.07		
E8	0.30					
E9					0.25	0.20
E10						0.10
E15		0.25	0.30	0.25		
K12			0.05			
K13				0.05		
K21	0.05					
K22		0.05				
K23			0.05	0.10	0.10	0.10
K25					0.10	
K31	0.20			0.15	0.10	0.10
K32		0.20		0.10		
K33			0.20			
K36						0.10
Coloring result	blonde	blonde	blonde	blonde	blonde	blonde

Examples 40 to 63: Hair colorants

Hair-coloring solutions of the following composition are prepared:

	X g	3-aminophenol derivative of the formula (I) (coupler
5	substance K1 to K4 as in table 4)	
	U g	developer substance E8 to E15 as in table 2
	Y g	coupler substance K12 to K34 as in table 4
	Z g	direct dyes D2 and/or D3 as in table 3
	10.0 g	lauryl ether sulfate (28 percent strength aqueous solution)
10	9.0 g	ammonia (22 percent strength aqueous solution)
	7.8 g	ethanol
	0.3 g	ascorbic acid
	0.3 g	ethylenediaminetetraacetic acid disodium salt hydrate
	ad 100.0 g	water, demineralized
15		
	30 g of the above coloring cream are mixed directly prior to application with 30 g of a	
	6 percent strength aqueous hydrogen peroxide solution. The mixture is then applied to the	
	hair. After a contact time of 30 minutes at	
	40 °C, the hair is rinsed with water, washed with a standard commercial shampoo and	
20	dried. The coloring results are summarized in table 6.	

Table 6: Hair colorants

Example No.	40	41	42	43	44	45
Dyes	(amount of dye in grams)					
K1	0.60	1.30	1.15	0.15	0.15	0.15
E8	1.50					
E11	0.10					
E13		1.60				0.70
E14				0.10	0.10	
E15			1.80	0.70	0.70	
K12	0.50					
K14	0.10					
K18	0.05					
K19	0.10					
K23			0.05	0.10	0.10	0.10
K24	0.15					
K31	0.90	1.10	1.10	0.40	0.40	0.40
K34	0.10					
D2				0.10	0.10	0.10
D3				0.05	0.05	0.05
Coloring result	black	black	black	brown	brown	brown

Table 6: (continuation)

Example No.	46	47	48	49	50	51
Dyes	(amount of dye in grams)					
K2	0.60	1.30	1.15	0.15	0.15	0.15
E8	1.50					
E11	0.10					
E13		1.60				0.70
E14				0.10	0.10	
E15			1.80	0.70	0.70	
K12	0.50					
K14	0.10					
K18	0.05					
K23			0.05	0.10	0.10	0.10
K24	0.15					
K31	0.90	1.10	1.10	0.40	0.40	0.40
K34	0.10					
D2				0.10	0.10	0.10
D3				0.05	0.05	0.05
Coloring result	black	black	black	brown	brown	brown

Table 6: (continuation)

Example No.	52	53	54	55	56	57
Dyes	(amount of dye in grams)					
K3	0.60	1.30	1.15	0.15	0.15	0.15
E8	1.50					
E11	0.10					
E13		1.60				0.70
E14				0.10	0.10	
E15			1.80	0.70	0.70	
K12	0.50					
K14	0.10					
K18	0.05					
K23			0.05	0.10	0.10	0.10
K24	0.15					
K31	0.90	1.10	1.10	0.40	0.40	0.40
K34	0.10					
D2				0.10	0.10	0.10
D3				0.05	0.05	0.05
Coloring result	black	black	black	brown	brown	brown

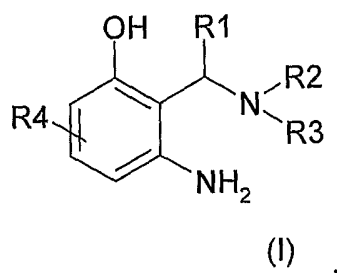
Table 6: (continuation)

Example No.	58	59	60	61	62	63
Dyes	(amount of dye in grams)					
K4	0.60	1.30	1.15	0.15	0.15	0.15
E8	1.50					
E11	0.10					
E13		1.60				0.70
E14				0.10	0.10	
E15			1.80	0.70	0.70	
K12	0.50					
K14	0.10					
K18	0.05					
K23			0.05	0.10	0.10	0.10
K24	0.15					
K31	0.90	1.10	1.10	0.40	0.40	0.40
K34	0.10					
D2				0.10	0.10	0.10
D3				0.05	0.05	0.05
Coloring result	black	black	black	brown	Brown	brown

- 5 Unless stated otherwise, all of the percentages given in the present application are percentages by weight.

What is claimed is:

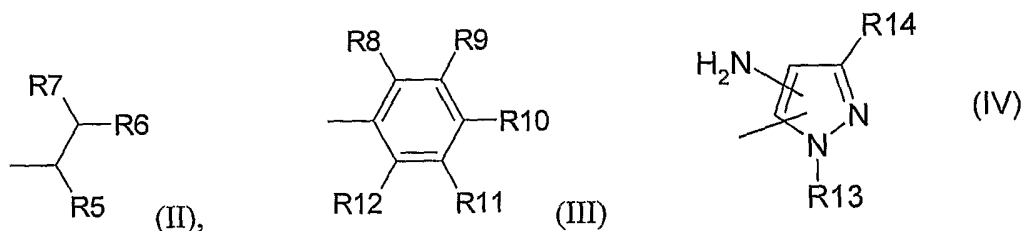
1. Agent for the oxidative coloring of keratin fibers based on a developer substance-coupler substance combination, characterized in that it comprises at least one 3-amino-2-aminomethylphenol derivative of the formula (I) or its physiologically compatible, water-soluble salt,



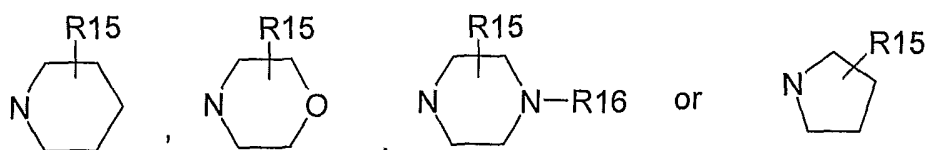
in which

R1 is hydrogen or a C₁-C₆-alkyl group;

R2 and **R3**, independently of one another, are hydrogen, a saturated C₁-C₆-alkyl group, an unsaturated C₂-C₆-alkyl group, a C₂-C₄-hydroxyalkyl group, a C₃-C₄-dihydroxyalkyl group, a C₂-C₄-aminoalkyl group, a C₁-C₄-dimethylaminoalkyl group, a C₂-C₄-acetylaminoalkyl group, a C₁-C₄-methoxyalkyl group, a C₁-C₄-ethoxyalkyl group, a C₁-C₄-cyanoalkyl group, a C₁-C₄-carboxyalkyl group, a C₁-C₄-aminocarbonylalkyl group, a pyridylmethyl group, a furfuryl group, a hydrogenated furfuryl group, a substituted pyridyl group or a radical of the formula (II), (III) or (IV),



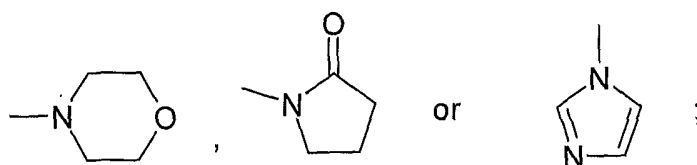
or **R2** and **R3**, together with the nitrogen atom, form a heterocyclic ring of the formula;



R4 is hydrogen, a halogen atom, a C₁-C₄-alkyl group, a C₁-C₄-hydroxyalkyl group or a C₁-C₄-alkoxy group;

R5 is hydrogen, a carboxyl group, or an aminocarbonyl group;

R6 and **R7**, independently of one another, are hydrogen, a hydroxyl group, an aminocarbonyl group, a methylthiomethyl group, a phenyl radical substituted by a phenyl group or hydroxyl group or a radical of the formula



R8, R9, R10, R11 and **R12**, independently of one another, are hydrogen, a halogen atom, a cyano group, a hydroxyl group, a C₁-C₄-alkoxy group, a C₁-C₄-hydroxyalkoxy group, a C₁-C₆-alkyl group, a C₁-C₄-alkyl thioether group, a mercapto group, a nitro group, an amino group, an alkylamino group, a hydroxyalkylamino group, a dialkylamino group, a di(hydroxyalkyl)amino group, a (dihydroxyalkyl)amino group, a (hydroxyalkyl)alkylamino group, a trifluoromethane group, a -C(O)H- group, a -C(O)CH₃- group, a -C(O)CF₃- group, a -Si(CH₃)₃- group, a C₁-C₄-hydroxyalkyl group or a C₃-C₄-dihydroxyalkyl group or two adjacent radicals **R8** to **R12** form an -O-CH₂-O-bridge;

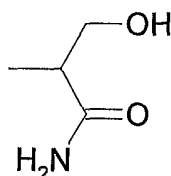
R13 is a C₁-C₄-alkyl group or a C₁-C₄-hydroxyalkyl group;

R14 is hydrogen or a C₁-C₆-alkyl group;

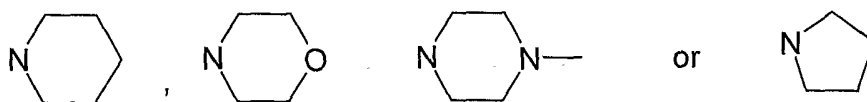
R15 is one or more hydrogen atoms, hydroxyl groups, carboxyl groups, aminocarbonyl groups or hydroxymethyl groups;

R16 is hydrogen or a C₁-C₆-alkyl group; where at least one of the radicals **R2** and **R3** is different from hydrogen.

2. Agent according to claim 1, characterized in that the compound of the formula (I) is chosen from compounds in which (i) **R1** and/or **R4** is hydrogen, and/or (ii) **R2** is a methyl group or a C₁-C₄-hydroxyalkyl group and **R3** is a C₁-C₄-hydroxyalkyl group and/or (iii) **R2** is hydrogen and **R3** is a C₁-C₄-hydroxyalkyl group, a substituted pyridyl radical, a furfuryl radical, a hydrogenated furfuryl radical, a substituted phenyl radical, a substituted pyrazoyl radical or a radical of the following formula



and/or (iv) **R2** and **R3** form an aliphatic ring of the formula



3. Agent according to claim 1 or 2, characterized in that the compound of the formula (I) is chosen from the group consisting of 3-amino-2-[(2,3-dihydroxypropyl)-aminomethyl]phenol; 3-amino-2-[(2-aminoethylamino)methyl]phenol; 3-amino-2-[(2-hydroxyethylamino)-methyl]phenol; 3-amino-2-(4-morpholinylmethyl)phenol; 2-[(2-hydroxy-6-aminobenzyl)methylamino]ethanol; 3-amino-2-(1-pyrrolidinylmethyl)phenol, 3-amino-2-[[2-(2-furylmethyl)amino]methyl]phenol, 2-(2-hydroxy-6-amino-benzylamino)propan-1-ol; 2-[(2-hydroxy-6-aminobenzyl)-(2-hydroxyethyl)amino]ethanol; [1-(2-hydroxy-6-amino-benzyl)pyrrolidin-2-yl]methanol; 1-(2-hydroxy-6-aminobenzyl)pyrrolidine-2-carboxamide; 3-amino-2-[(4-methylpyridin-2-ylamino)methyl]phenol; 3-amino-2-(1-piperidinylmethyl)phenol, 3-amino-2-[(4-methyl-1-piperazinyl)methyl]phenol, 3-amino-2-[(2-aminophenylamino)methyl]phenol; 3-amino-2-[(2-chloro-phenylamino)methyl]phenol; 3-amino-2-[(2-dimethylaminophenylamino)methyl]phenol; 3-amino-2-[(2-

fluorophenylamino)methyl]phenol; 3-amino-2-{[2-(2-hydroxyethylamino)phenylamino]methyl}phenol; 3-amino-2-{[2-N,N-bis(2-hydroxyethyl)aminophenylamino]methyl}phenol; 3-amino-2-[(2-pyrrolidinephenylamino)methyl]phenol; 3-amino-2-[(3-aminophenylamino)methyl]phenol; 3-amino-2-[(3-chlorophenylamino)methyl]phenol; 3-amino-2-[(3-dimethylaminophenylamino)methyl]phenol; 3-amino-2-[(3-fluorophenylamino)methyl]phenol; 3-amino-2-{[3-(2-hydroxyethylamino)phenylamino]methyl}phenol; 3-amino-2-{[3-N,N-bis(2-hydroxyethyl)aminophenylamino]methyl}phenol; 3-amino-2-[(3-pyrrolidinephenylamino)methyl]phenol; 3-amino-2-[(4-aminophenylamino)methyl]phenol; 3-amino-2-[(4-chlorophenylamino)methyl]phenol; 3-amino-2-[(4-dimethylaminophenylamino)methyl]phenol; 3-amino-2-[(4-fluorophenylamino)methyl]phenol; 3-amino-2-{[4-(2-hydroxyethylamino)phenylamino]methyl}phenol; 3-amino-2-{[4-N,N-bis(2-hydroxyethyl)aminophenylamino]methyl}phenol; 3-amino-2-[(4-pyrrolidinephenylamino)methyl]phenol; 3-amino-2-{[2-(2-hydroxyethoxy)-4-aminophenylamino]methyl}phenol; 3-amino-2-[(2,4-diaminophenylamino)methyl]phenol; 3-amino-2-[(2-chloro-4-aminophenylamino)methyl]phenol; 3-amino-2-[(4-amino-2-hydroxyphenylamino)methyl]phenol; 3-amino-2-[(2-hydroxyethylamino-4-aminophenylamino)methyl]phenol; 3-amino-2-[(2-methyl-4-aminophenylamino)methyl]phenol; 3-amino-2-{[3-(2-hydroxyethoxy)-4-aminophenylamino]methyl}phenol; 3-amino-2-[(3-amino-4-aminophenylamino)methyl]phenol; 3-amino-2-[(3-chloro-4-aminophenylamino)methyl]phenol; 3-amino-2-[(3-hydroxy-4-aminophenylamino)methyl]phenol; 3-amino-2-{[3-(2-hydroxyethylamino)-4-aminophenylamino]methyl}phenol; 3-amino-2-[(3-methyl-4-aminophenylamino)methyl]phenol; 3-amino-2-{[2-(2-hydroxyethoxy)phenylamino]methyl}phenol; 3-amino-2-[(2-hydroxyphenylamino)methyl]phenol; 3-amino-2-{[3-(2-hydroxyethoxy)phenylamino]methyl}phenol; 3-amino-2-[(3-hydroxyphenylamino)methyl]phenol; 3-amino-2-{[4-(2-hydroxyethoxy)phenylamino]methyl}phenol; 3-amino-2-[(4-hydroxyphenylamino)methyl]phenol; 3-amino-2-(phenylaminomethyl)phenol and 2-[5-

amino-4-(2-hydroxy-6-aminobenzylamino)pyrazol-1-yl]ethanol.

4. Agent according to one of claims 1 to 3, characterized in that it comprises the 3-amino-2-aminomethylphenol derivative of the formula (I) in an amount of from 0.005 to 20 percent by weight.

5. Agent according to one of claims 1 to 4, characterized in that the developer substance is chosen from the group consisting of

1,4-diaminobenzene (p-phenylenediamine), 1,4-diamino-2-methylbenzene (p-tolylenediamine), 1,4-diamino-2,6-dimethylbenzene, 1,4-diamino-3,5-diethylbenzene, 1,4-diamino-2,5-dimethylbenzene, 1,4-diamino-2,3-dimethylbenzene, 2-chloro-1,4-diaminobenzene, 1,4-diamino-2-(thiophen-2-yl)benzene, 1,4-diamino-2-(thiophen-3-yl)benzene, 4-(2,5-diaminophenyl)-2-((diethylamino)methyl)thiophene, 2-chloro-3-(2,5-diaminophenyl)thiophene, 1,4-diamino-2-(pyridin-3-yl)benzene, 2,5-diaminobiphenyl, 2,5-diamino-4'-(1-methylethyl)-1,1'-biphenyl, 2,3',5'-triamino-1,1'-biphenyl, 1,4-diamino-2-methoxymethylbenzene, 1,4-diamino-2-aminomethylbenzene, 1,4-diamino-2-((phenylamino)methyl)benzene, 1,4-diamino-2-((ethyl-(2-hydroxyethyl)amino)methyl)benzene, 1,4-diamino-2-hydroxymethylbenzene, 1,4-diamino-2-(2-hydroxyethoxy)benzene, 2-(2-(acetylaminomethyl)ethoxy)-1,4-diaminobenzene, 4-phenylaminoaniline, 4-dimethylaminoaniline, 4-diethylaminoaniline, 4-dipropylaminoaniline, 4-[ethyl(2-hydroxyethyl)amino]aniline, 4-[di(2-hydroxyethyl)amino]aniline, 4-[di(2-hydroxyethyl)amino]-2-methylaniline, 4-[(2-methoxyethyl)amino]aniline, 4-[(3-hydroxypropyl)amino]aniline, 4-[(2,3-dihydroxypropyl)amino]aniline, 4-(((4-aminophenyl)methyl)amino)aniline, 4-[(4-aminophenylamino)methyl]phenol, 1,4-diamino-N-(4-pyrrolidin-1-yl-benzyl)benzene, 1,3-dihydroxy-2-((2-furylmethyl)aminomethyl)benzene, 1,4-diamino-N-thiophen-2-ylmethylbenzene, 1,4-diamino-N-furan-2-ylmethylbenzene, 1,4-diamino-N-thiophen-3-ylmethylbenzene, 1,4-diamino-N-benzylbenzene, 1,4-diamino-2-(1-hydroxyethyl)benzene, 1,4-diamino-2-(2-hydroxyethyl)benzene, 1,4-diamino-2-(1-methylethyl)benzene, 1,3-bis[(4-aminophenyl)(2-hydroxyethyl)amino]-

2-propanol, 1,4-bis[(4-aminophenyl)amino]butane, 1,8-bis(2,5-diaminophenoxy)-3,6-dioxaoctane, 2,5-diamino-4'-hydroxy-1,1'-biphenyl, 2,5-diamino-2'-trifluoromethyl-1,1'-biphenyl, 2,4',5-triamino-1,1'-biphenyl, 4-aminophenol, 4-amino-3-methylphenol, 4-amino-3-(hydroxymethyl)phenol, 4-amino-3-fluorophenol, 4-methylaminophenol, 4-amino-2-(aminomethyl)phenol, 4-amino-2-(hydroxymethyl)phenol, 4-amino-2-fluorophenol, 4-amino-2-[(2-hydroxyethyl)amino]methylphenol, 4-amino-2-methylphenol, 4-amino-2-(methoxymethyl)phenol, 4-amino-2-(2-hydroxyethyl)phenol, 5-aminosalicylic acid, 2,5-diaminopyridine, 2,4,5,6-tetraaminopyrimidine, 2,5,6-triamino-4-(1H)-pyrimidone, 4,5-diamino-1-(2-hydroxyethyl)-1H-pyrazole, 4,5-diamino-1-(1-methylethyl)-1H-pyrazole, 4,5-diamino-1-[(4-methylphenyl)methyl]-1H-pyrazole, 1-[(4-chlorophenyl)methyl]-4,5-diamino-1H-pyrazole, 4,5-diamino-1-methyl-1H-pyrazole, 4,5-diamino-1-pentyl-1H-pyrazole, 4,5-diamino-1-(phenylmethyl)-1H-pyrazole, 4,5-diamino-1-[(4-methoxyphenyl)methyl]-1H-pyrazole, 2-aminophenol, 2-amino-6-methylphenol, 2-amino-5-methylphenol, 1,2,4-trihydroxybenzene, 2,4-diaminophenol, 1,4-dihydroxybenzene, 2-(((4-aminophenyl)amino)methyl)-1,4-diaminobenzene.

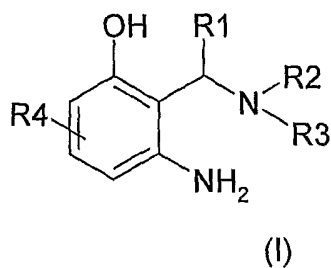
6. Agent according to one of claims 1 to 5, characterized in that the developer substances and coupler substances, based on the total amount of the colorant, are present in each case in a total amount of from 0.005 to 20 percent by weight.

7. Agent according to one of claims 1 to 6, characterized in that it additionally comprises at least one additional coupler substance and/or at least one direct dye.

8. Agent according to one of claims 1 to 7, characterized in that it is a hair colorant.

9. 3-Amino-2-aminomethylphenol derivative of the formula (I) or physiologically compatible, water-soluble salt thereof,

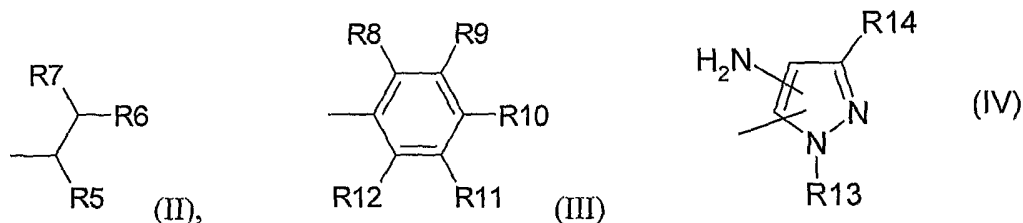
37



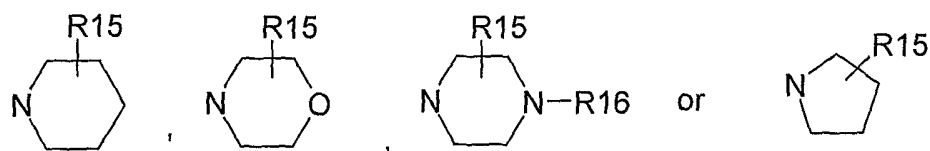
in which

R1 is hydrogen or a C₁-C₆-alkyl group;

R2 and **R3**, independently of one another, are hydrogen, a saturated C₁-C₆-alkyl group, an unsaturated C₂-C₆-alkyl group, a C₂-C₄-hydroxyalkyl group, a C₃-C₄-dihydroxyalkyl group, a C₂-C₄-aminoalkyl group, a C₁-C₄-dimethylaminoalkyl group, a C₂-C₄-acetaminoalkyl group, a C₁-C₄-methoxyalkyl group, a C₁-C₄-ethoxyalkyl group, a C₁-C₄-cyanoalkyl group, a C₁-C₄-carboxyalkyl group, a C₁-C₄-aminocarbonylalkyl group, a pyridylmethyl group, a furfuryl group, a hydrogenated furfuryl group, a substituted pyridyl group or a radical of the formula (II), (III) or (IV),



or **R2** and **R3**, together with the nitrogen atom, form a heterocyclic ring of the formula;

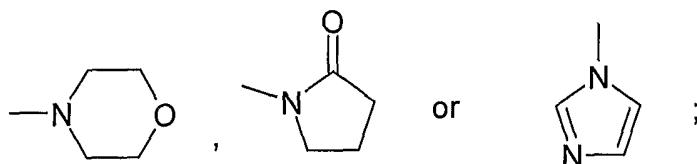


R4 is hydrogen, a halogen atom, a C₁-C₄-alkyl group, a C₁-C₄-hydroxyalkyl group or a C₁-C₄-alkoxy group;

R5 is hydrogen, a carboxyl group, or an aminocarbonyl group;

R6 and **R7**, independently of one another, are hydrogen, a hydroxyl group, an

aminocarbonyl group, a methylthiomethyl group, a phenyl radical substituted by a phenyl group or hydroxyl group or a radical of the formula



R8, R9, R10, R11 and **R12**, independently of one another, are hydrogen, a halogen atom, a cyano group, a hydroxyl group, a C₁-C₄-alkoxy group, a C₁-C₄-hydroxyalkoxy group, a C₁-C₆-alkyl group, a C₁-C₄-alkyl thioether group, a mercapto group, a nitro group, an amino group, an alkylamino group, a hydroxyalkylamino group, a dialkylamino group, a di(hydroxyalkyl)amino group, a (dihydroxyalkyl)amino group, a (hydroxyalkyl)alkylamino group, a trifluoromethane group, a -C(O)H- group, a -C(O)CH₃- group, a -C(O)CF₃- group, a -Si(CH₃)₃- group, a C₁-C₄-hydroxyalkyl group or a C₃-C₄-dihydroxyalkyl group or two adjacent radicals **R8** to **R12** form an -O-CH₂-O- bridge;

R13 is a C₁-C₄-alkyl group or a C₁-C₄-hydroxyalkyl group;

R14 is hydrogen or a C₁-C₆-alkyl group;

R15 is one or more hydrogen atoms, hydroxyl groups, carboxyl groups, aminocarbonyl groups or hydroxymethyl groups;

R16 is hydrogen or a C₁-C₆-alkyl group; where at least one of the radicals **R2** and **R3** is different from hydrogen, and **R1** and **R4** are not hydrogen at the same time if **R2** and **R3** are a methyl group or **R2** and **R3**, together with the nitrogen atom, form a pyrrolidine ring or piperidine ring.