UK Patent Application (19) GB (11) 2 111 490 A

- (21) Application No 8233090
- (22) Date of filing 19 Nov 1982
- (30) Priority data
- (31) 3145811
- (32) 19 Nov 1981
- (33) Fed. Rep. of Germany (DE)
- (43) Application published 6 Jul 1983
- (51) INT CL3
- C07C 91/44 A61K 7/13
- (52) Domestic classification
 C2C 220 227 22Y 29X
 29Y 30Y 321 32Y 332 360
 361 364 365 36Y 453 45Y
 500 502 50Y 610 620 621
 623 624 633 634 652 660
 661 662 AA LG MK
 D1B 2A4
 U1S 1399 C2C
- (56) Documents cited None
- (58) Field of search C2C
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- (54) New 2-hydroxy-4aminobenzenes and hair colouring media containing these compounds
- (57) Compounds of formula

in which R represents a hydrogen atom, a methyl group or a hydroxyethyl group, are used as coupler substances for the oxidative colouring of hair in combination with developer substances which are known in the hair colouring art as well as optionally further known coupler substances.

ERRATA

SPECIFICATION No. 2 111 490 A

Page 2, line 76, for methylphenyl read methylphenol

Page 5, line 74, delete whole line insert (2'hydroxyethoxy) - 2 - hydroxy - 4-aminobenzene.

THE PATENT OFFICE 11th November, 1983

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(57) Compounds of formula

in which R represents a hydrogen atom, a methyl group or a hydroxyethyl group, are used as coupler substances for the oxidative colouring of hair in combination with developer substances which are known in the hair colouring art as well as optionally further known coupler substances.

15

SPECIFICATION

New 2-hydroxy-4-aminobenzenes, processes for their preparation and hair colouring media containing these compounds

The present invention concerns new 2-5 hydroxy-4-aminobenzenes of the general formula

in which R stands for a hydrogen atom, a methyl group or a hydroxyethyl group.

The present invention also concerns the salts 10 formed from the compounds of the general formula with inorganic or organic acids, such as the hydrochloride, hydrobromide or sulphate or the corresponding phenolate.

The new compounds according to the invention are prepared starting from 4-nitro-1,2methylenedioxybenzene, wherein this is heated at a temperature of 120°C in a solution of sodium in dry ethyleneglycol (a), or diethyleneglycol (b), or 20 2-methoxyethanol (c) for several hours, preferably 3 hours, the resulting solution, after cooling, is dissolved in water and filtered, the filtrate is acidified and the resulting and optionally-purified 2-hydroxy-4-nitrobenzene derivative of the 25 formula

in which R stands for a hydrogen atom, a methyl group or a hyroxyethyl group, is hydrogenated in the presence of a catalyst, preferably palladium, in 30 a manner known per se to form:

1(2'-hydroxyethoxy)-2-hydroxy-4-aminobenzene (a), or

1-(hydroxy-bis-ethoxy)2-hydroxy-4-aminobenzene (b), or

1-(2'-methoxy-ethoxy-2-hydroxy-4-amino-35

The new compounds according to the invention represent precursors for oxidative dyes, which are exceptionally suitable for the colouring 40 of hair.

For the colouring of hair, the so-called oxidative dyes, which are formed by the oxidative coupling of a developer component with a coupler component, play a favoured role owing to their 45 intense dyeing and very good fastness properties. As developer substances, 2,5-diaminotoluene, 4aminophenol and 1,4-diaminobenzene are usually employed; however, 2,5-diaminoamisole, 3methyl-4-aminophenol, 2,5-diaminobenzyl

50 alcohol and 2-(β-hydroxyethyl)-1,4-diaminobenzene have also attained a certain significance. Tetraaminopyridine can also be employed as the developer.

As preferred coupler substances, resorcinol, 4-55 chlorresorcinol, m-aminophenol, 5-amino-2methylphenol, 1-naphthol as well as derivatives of m-phenylenediamine, such as for example 2amino-4-(β-hydroxyethylamino)-anisole or 2,4diaminophenoxyethanol, are known. Furthermore, 4-hydroxy-1,2-methylenedioxybenzene and 4-(βhydroxyethylamino)1,2,methylenedioxybenzene can also be used as coupler substances.

There are numerous special requirements for oxidative dyes, which are to be employed for the colouring of human hair. Thus, they must be beyond criticism in toxicological and dermatological respects and must permit the achievement of colours in the desired intensity. Furthermore it is required, that by combination of suitable developer and coupler components, a broad pallette of varying colour tones can be created. Apart from this, good fastness towards light, permanent waving, acids, and friction is required of the hair colours which can be attained. However in any event such hair colours must remain stable for a period of at least 4 to 6 weeks without being affected by light, chemical media, and friction.

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In addition to the above-mentioned preliminary 80 colouring steps, dyes which can be directly absorbed onto the hair are significant as components of oxidative hair colouring media. With these directly absorbed dyes, especially aromatic nitro dyes, yellow, orange, red, and 85 violet tones can be achieved.

For the creation of the natural tones, resorcinol and m-aminophenol are preferably used as couplers in combination with p-phenylenediamines or 2,5-diaminotoluenes as developers. 90 By the addition of m-aminophenol, the yellow tinge caused by resorcinol is covered up and in this way the colour tone is in general made somewhat warmer. In contrast, if it is desired to create fashion tones, the application of m-amino-95 phenol is for this purpose of little benefit, because it creates in combination with p-aminophenol a colour tone which is only very weak and with the usual p-diamines, such as for example 2,5diaminotoluene or 2,5-diaminobenzyl alcohol, no 100 red tone, but rather a voilet tone, results.

The object of the invention is to make available new colour-effective compounds as coupler substances, which largely overcome the disadvantages of m-aminophenols and give rise 105 to colouring media, which fulfill in an optimal manner the requirements set out above.

The invention further concerns hair colouring media, which contain the new compounds as well as processes for dyeing hair.

Furthermore, the compounds according to the 110 invention should be as kind as possible to the skin of the hands and the scalp.

The object is achieved by means of 2-hydroxy-4-aminobenzenes of the general formula

in which R stands for a hydrogen atom, a methyl group or a hydroxyethyl group, as well as its acid addition salts with inorganic or organic acids or its phenolates.

It has thus been shown, that the aboveindicated disadvantages of m-aminophenol can
be overcome in a simple manner by the use of the
compounds according to the invention, especially
10 by use of 1-(2'-hydroxyethyl)-2-hydroxy-4-aminobenzene as the coupler substance. For example,
1-(2'-hydroxyethyl)-2-hydroxy-4-aminobenzene
forms together with p-aminophenol as the
developer substance a very intensive fashionable
copper tone, which can be suitably modified as
desired.

Furthermore, it is apparent that the new couplers according to the invention create clearly less strongly violet tinged tones in comparison 20 with m-aminophenol with the common p-diamines, such as for example the known 2,5-diaminotoluene, and therefore the coupler substances according to the invention give improved opportunities for the attainment of red 25 tones.

As a result of the above-depicted new oppurtunities for the creation of red tones, it is furthermore possible to replace the red-colouring nitro dyes and at the same time to attain similar and improved colours. The replacement of nitro dyes is therefore also of great significance, for these lead to uneven colouring of unevenly-damaged hair and often dye porous hair ends only insufficiently.

As well as the abovementioned preferred fields of use of the new coupler substances, these can also be used in combination with the developer substances 2,5-diaminoanisole and tetraaminopyridine, whereby advantageous violet tones result.

The new coupler substances according to the invention can either be employed as such or in the form of their salts with inorganic or organic acids, such as for example the chloride, sulphate,

45 phosphate, acetate, proprionate, lactate, citrate or in the form of salts with bases, for example as alkali phenolates.

The coupler substances according to the invention are in general employed in roughly 50 molar amounts, relative to the developer substances used. However even when molar application is expedient, it is not disadvantageous to employ a certain excess or deficiency of the coupler substance. It is furthermore not necessary for the developer components and the coupler components to be single products, but rather the developer components can be a mixture of known developer substances, and also the coupler

components can be a mixture of compounds 60 according to the invention with known coupler substances.

In the hair colouring media, the new coupler substances according to the invention, of which 1-(2'-hydroxyethoxy)-2-hydroxy-4-amino-benzene is preferred, should be present in a concentration from about 0.1 to 5.0 weight %, especially 0.3 to 3.0 weight %.

Besides, in the hair colouring media there can additionally be present known coupler

70 substances, especially 1-naphthol,4-methoxy-1-naphthol, resorcinol, 4-chlorresorcinol, 4,6-dichlorresorcinol, 2-methylresorcinol, 2-amino-4-(β-hydroxyethylamino)-anisole, 2,4-diamino-phenylethanol, 2,4-diaminophenoxyethanol, 1,5-

75 dihydroxytetralin, m-aminophenol, 3-amino-2-methylphenol, 5-amino-2-methylphenyl, 4-hydroxy-1,2, methylene-dioxybenzene, 4-amino-1, 2-methylenedioxybenzene, 4-(β-hydroxy-ethylamino)-1, 2-methylenedioxybenzene, 2,4-

80 diaminoanisole, 5-amino-2-methylphenol, 2-(γ-hydroxypropyl)-5-methylphenol and 2,4-diamino-phenetol. Of the known developer substances, 1,4-diaminobenzene, 2,5-diaminotoluene, 2,5-diaminoanisole, 2,5-diaminobenzyl alcohol, 3-

85 methyl-4-aminophenol, $2-(\beta-hydroxyethyl)-1$, 4-diaminobenzene and 4-aminophenol come particularly into consideration as components of the hair colouring media according to the invention.

90 The total quantity of the developer substance-coupler substance combination present in the hair colouring media described herein should amount to about 0.1 to 6.0 weight %, particularly 0.5 to 3.0 weight %.

For the achievement of certain colour tones, conventional direct dyes, for example triphenylmethane dyes such as Diamond Fuchsin (C.I.42 510) and Leather Ruby HF (C.I.42 520), aromatic nitro dyes such as 2-amino-4, 6-nitro-phenol, 2-nitro-4-(β-hydroxyethylamino)-aniline and 2-

amino-4-nitrophenol, azo-dyes such as Acid Brown 4 (C.I.14 805) and Acid Blue 135 (C.I.13 385), anthraquinone dyes such as Disperse Violet 4 (C.I.61 105), Disperse Blue 1 (C.I.64 500),

105 Disperse Red 15 (C.I.60 710), Disperse Violet 1 (C.I.61 100), as well as 1,4,5,8-tetraamino-anthraquinone and 1,4-diaminoanthraquinone can furthermore be present.

The claimed hair colouring media may

110 furthermore contain colouring precursors which
couple with themselves, such as for example 2amino-5-methylphenol, 2-amino-6-methylphenol, 2-amino-5-ethoxyphenol or even 2-(βhydroxyethylamino)-5-pyridine and 2-propyl
115 amino-5-aminopyridine.

Still further, common cosmetic additives can also be used, for example antioxidants such as ascorbic acid or sodium sulphite, perfume oils, complex formers, wetting agents, emulsifiers, thickeners, care components, and others.

The form of the preparation may for example be a solution, especially an aqueous or aqueousalcoholic solution. The particularly preferred preparative forms are however a creme, a gel, or an emulsion.

Their composition represents a mixture of colouring components with the conventional additives for such preparations.

Conventional additives for solutions, cremes, emulsions or gels are for example, solvents such as water, lower aliphatic alcohols, for example ethanol, propanol and isopropanol, or glycols such 10 as glycerol and glycol ethers such as propylene glycol, furthermore wetting agents or emulsifiers from the class of anionic, cationic, amphoteric, or non-ionic surface active agents such as fatty alcohol sulphates, alkyl sulphonates, alkyl 15 benzene sulphonates, alkyltrimethylammonium salts, alkylbetaines, oxyethylated fatty alcohols, oxyethylated nonylphenols, fatty acid alkanol amides, oxyethylated fatty acid esters, also thickeners such as higher fatty alcohols, 20 stiffeners, cellulose derivatives, Vaseline, paraffin oils and fatty acids as well as care components such as lanoline derivatives, cholesterol, pantothenic acid and betain. The abovementioned components are used in the usual 25 quantities for such purposes, for example the wetting agents and emulsifiers can be present in concentrations from about 0.5 to 30 weight % while the thickeners can be present in the quantity from about 0.1 to 25 weight % in the 30 compositions.

According to the preparation, the hair colouring media according to the invention may be weakly acidic, neutral or alkaline. They particularly display a pH value in the alkaline region between 8.0 and 35 11.5, which is preferably attained using ammonia. However organic amines, such as for example monoethanolamine and triethanolamine, or also inorganic bases such as sodium hydroxide and potassium hydroxide, may be used.

In the process according to the invention for 40 the oxidative colouring of hair, the hair colouring medium, which contains a combination of developer substances which are known in the hair 100 which melts at 159—161 °C, is 5.85 g (29 colouring art with at least one 2-hydroxy-4-45 aminobenzene of the formula (I) as coupler substance, as well as optionally additional known coupler substances, is mixed shortly before use with an oxidative medium, and this mixture is applied to the hair. As oxidative media for the 50 development of the hair colouring, hydrogen peroxide, for example as a 6% aqueous solution or as an addition compound with urea, melamine, or sodium borate, come particularly into consideration. The mixture is allowed to act on 55 the hair at 15 to 50°C for about 10 to 45 minutes, preferably 30 minutes, then the hair is rinsed out with water and dried. In connection with this rinsing, the hair is optionally washed with a shampoo and possibly with a weak organic 60 acid, such as for example citric acid or tartaric

acid. By their application, the new coupler substances according to Claim 1, together with the developer substances which are in general 65 used for the oxidative colouring of hair, provide

very intense fashionable colour tones extending from copper to red, and thus represent a substantial enlargement of the oxidative hair colouring possibilities. In addition, 2-hydroxy-4-70 aminobenzenes of the general formula (I) are distinguished by very good fastness properties of the colours thereby obtained, by very good solubility in water and good storage stability.

The coupler substances according to the 75 invention of Formula (I) are particularly suitable for the creation of fashionable tones such as a hazelnut brown, titian red, as well as mahogany or violet tones.

The following examples are to more precisely 80 explain the subject matter of the invention.

Examples for the preparation of the new compounds Example 1

Preparation of 1-(2'-hydroxyethoxy)-2-85 hydroxy-4-amino-benzene of the formula.

1.7 g (74 mMol) of sodium are dissolved in 80 ml of dry ethyleneglycol and the solution is added to 6.8 g (40 mMol) of 4-nitro-1, 2-methylenedioxybenzene. Afterwards, the mixture was heated for 3 hours at 120°C, and the cooled, dark red solution dissolved in 400 ml of water, filtered, and the filtrate acidified with 2N hydrochloric acid. The 1-(2'-hydroxyethoxy)-2-hydroxy-4nitrobenzene is thus precipitated. The product is filtered with suction, washed with water and dried. The crude product is crystallised out with an ethanol-water mixture and dried for 24 hours in a vacuum. The yield of the product, mMol),=about 72%, with respect to the 4-nitro-1,2-methylenedioxybenzene used.

For the manufacture of the 1-(2'-hydroxyethyoxy)-2-hydroxy-4-aminobenzene, 1.8 g (9 105 mMol) of the nitrobenzene derivative is dissolved in 220 ml of ethanol and hydrogenated with 0.12 g of palladium supported on active carbon (10% palladium). After absorption of hydrogen has stopped, the product is filtered off from the 110 catalyst and the filtrate concentrated. The remaining oil distils in a bulb-tube at 225°C/0.07 mbar.

> Yield: 1.2 g (7 mMol; 77%). CHN-Analysis: C₈H₁₁NO₃

H% N% 115 6.55 8.28 56.80 Calculated: 56.72 6.59 8.18 Found:

To permit easier handling of the substance, it is advantageous to convert it to its hydrochloride or 120 sulphate.

(a) Hydrochloride

1.2 g (7 mMol) of the free base are dissolved in 50 ml isopropanol and mixed with 5 drops of a 37% aqueous hydrochloric acid solution. The hydrochloride precipitates out on addition of diethylether, as a white finely-crystalline powder.

Yield: 118 g (5.7 mMol; 63% based on the nitro precursor) decomposes at 190°C.

CHNCI—Analysis: C₈H₁₂CINO₃

10		C%	Н%	N%	CI%
	Calculated:	46.73	5.88	6.81	17.24
	Found:	46.62	5.91	6.73	17.40

(b) Sulphate

2.3 g (13 mMol) of free base are dissolved in
80 ml of isopropanol. The sulphate precipitates out on addition of a few millilitres of 2N sulphuric acid. The product is suction filtered, washed with isopropanol and dried. The yield is 2.0 g (9 mMol) which equals about 70%, based on the free base used).

Titration:

Weighed portion 41.2 mg Discharge 0.01 n-NaOH (C₈H₁₁NO₃×1/2H₂SO₄)

Calculated: Found: 18.90 ml 18.25 ml

Example 2

Preparation of 1(hydroxy-bis-ethoxy)-2-hydroxy-4-aminobenzene of the formula:

40

25

The procedure is analogous to that in Example I, with the difference, that instead of ethylene glycol, 80 ml of diethyleneglycol are used.

a) 1-(hydroxy-bis-ethoxy)-2-hydroxy-4-35 nitrobenzene

Melting point: 115—116°C

CHN-Analysis:(C₁₀H₁₃NO₆)

Calculated:

Found:

%C %H %N 49.38 5.39 5.76 49.28 5.35 5.72

b) 1-(hydroxy-bis-ethoxy)-2-hydroxy-4aminobenzene

boiling point in ball-pipe: 220—230°C/0.08 mbar. The oil solidifies like glass.

45 CHN-Analysis of the sulphate: $(C_{10}H_{15}NO_4X1/2H_2SO_4)$

	%C	%Н	%N
Calculated:	45.80	6.15	5.34
Found:	44.36	6.17	5.32

50 Example 3

Preparation of 1-(2'-methoxyethoxy)-2-hydroxy-4-aminobenzene of the formula.

Preparation proceeds analogously to the method of Example I, with the difference that instead of ethyleneglycol, 80 ml of 2-methoxyethanol are used.

a) 1-(methoxyethoxy)-2-hydroxy-4nitrobenzene

60 Melting point: 90—91°C CHN-Analysis (C₉H₁₁NO₅)

%C %H %N Calculated: 50.71 5.20 6.57 Found: 50.80 5.23 6.73

65 b Hydrochloride

The hydrochloride of the 1-(2'-methoxy-ethoxy)-2-hydroxy-4-aminobenzene obtained melts with decomposition at a temperature of 153°C.

70 CHN-Analysis: (C₉H₁₄CINO₃)

%C %H %N Calculated: 46.21 6.42 6.38 Found: 46.30 6.36 6.48

Examples of use

75 Example A

Hair colouring medium in creme form. 1-(2'-hydroxyethoxy)-2-hydroxy-4aminobenzenehydrochloride 0.30 g1,4-diaminobenzene 80 0.30 g 2-amino-4, 6-dinitrophenol (Picramic acid) 0.30 gSodium sulphate, anhydrous 3.50 g laurylalcohol-diglycolethersulphate, sodium salt (28% aqueous solution) 85 15.0 g cetyl alcohol

85 15.0 g cetyl alcohol 4.0 g ammonia, 25% 76.2 g water

100.0 g.

50 g of the above-mentioned hair colouring 90 medium is, shortly before use, mixed with 50 g of a 6% hydrogen peroxide solution. The mixture is allowed to act for 30 minutes at 40°C on blonde natural hair. Afterwards the colouring medium is rinsed out, the hair shampooed and dried. It has 95 acquired an intense mahogany colour.

Example B

Hair colouring solution.

	1.00 g	1-(2'-hydroxyethoxy)-2-hydroxy-4- aminobenzene hydrochloride
5	0.50 g	p-aminophenol
	10.0 g	lauryl alcohol-diglycolethersulphate Sodium salt (28% aqueous solution)
	10.0 g	isopropanol
	0.3 g	Sodium sulphate, anhydrous
10	10.0 g	ammonia 25%
	68.2 g	water

100.0 g

50 g of the hair colouring medium identified overleaf are, shortly before use, mixed with 50 g of a 6% hydrogen peroxide solution, and applied to blonde natural hair. After a time of action of 30 minutes at 40°C, the hair has, after rinsing, shampooing and drying, received a full titian red colouring.

20 Example C

Hair colouring gel

114.1 00.041.119 90.				
0.70 g	1-(2'-hydroxyethoxy)-2-hydroxy-4-			
	aminobenzene hydrochloride			
0.50 g	tetraaminopyrimidine			
15.0 g	oleic acid			
7.0 g	isopropanol			
0.3 g	ascorbic acid			
9.0 g	ammonia 25%			
67.5 g	water			

30 100.0 g

25

50 g of the hair colouring media are, shortly before use, mixed with 50 g of a 6% hydrogen peroxide solution, and applied to blonde natural hair for 30 minutes at 40°C for action. After 35 rinsing, shampooing and drying, the hair is coloured an intense purple.

All percentages given in the preceding application represent percentages by weight.

Claims

40 1. 2-hydroxy-4-aminobenzenes of the general formula:

in which R stands for a hydrogen atom, a methyl group or a hydroxyethyl group, as well as its acid 45 addition salts with inorganic or organic acids or its phenolates.

2. 1-(2'-hydroxyethoxy)-2-hydroxy-4-amino-benzene.

3. Process for the manufacture of compounds 50 according to formula (I), characterised in that 4nitro-1,2-methylenedioxybenzene is heated to 120°C in a solution of sodium in dry ethylene glycol (a), or diethyleneglycol (b), or 2-methoxyethanol (c) for several hours, preferably 3 hours, 55 the resulting solution is, after cooling, mixed with water and filtered, the filtrate is acidified and the resulting and optionally-purified 2-hydroxy-4nitro-benzene derivative of the formula

60 in which R stands for a hydrogen atom, a methyl group or a hydroxyethyl group, is hydrogenated in the presence of a catalyst in a manner known per se to form 1-(2'-hydroxyethoxy)-2-hydroxy-4-aminobenzene (a), or 1-(hydroxy-bis-ethoxy)-2-hydroxy-4-aminobenzene (b), or 1-(2'-methoxyethoxy)-2-hydroxy-4-aminobenzene (c).

4. Hair colouring medium, characterised in that it contains a combination of developer substances known in the hair colouring art with at least one
70 of the compounds according to Claim 1 as coupler substance.

Medium according to Claim 4, characterised in that it contains as coupler substance 1-2-(β-hydroxyethyl)-1 4-diaminobenzene, 4-

75 6. Medium according to Claim 4 or 5, characterised in that it contains the compounds according to Claim 1 in a concentration from about 0.1 to 5.0 weight %, preferably 0.3 to 3.0 weight %.

7. Medium according to any one of Claims 4 to 6, characterised in that it contains at least one of the developer substances 1,4-diaminobenzene, 2,5-diaminotoluene, 2,5-diaminobenzylalcohol, 2-(β-hydroxyethyl)-1-4-diaminobenzene, 4aminophenol, 3-methyl-4-aminophenol, 2,5-diaminoanisole and tetraaminopyrimidine.

Medium according to any one of Claims 4 to 7, characterised in that it contains at least one of the coupler substances 1-naphthol, 4-methoxy-1-naphthol, resorcinol, 4-chlorresorcinol, 4,6-dichlorresorcinol, 2-methylresorcinol, 4-hydroxy-1,2-methylenedioxybenzene, 4-(β-hydroxyethylamino)-1, 2-methylenedioxybenzene, 4-amino-1, 2-methylene-dioxybenzene, 5-amino-2-methylphenol, 2,4-diaminophenoxyethanol, 2-amino-4-(β-hydroxyethylamino)-anisole and 2-(γ-hydroxy-propyl)-5-methylphenol.

9. Medium according to any one of claims 4 to 8, characterised in that the total amount of
100 developer substance-coupler substance combination present amounts to 0.1 to 6.0 weight %, preferably 0.5 to 3.0 weight %.

10. Medium according to any one of claims 4 to 9, characterised in that it additionally contains
 105 as colouring components 2-amino-5-methylphenol, 2-amino-6-methylphenol, 2-amino-5-ethoxyphenol, 2-(β-hydroxyethylamino)-5-amino-pyridine or 2-propylamino-5-aminopyridine.

11. Medium according to any one of Claims 4
110 to 10, characterised in that it additionally contains

at least one of the direct dyes Diamond Fuchsin (C.I.42 510), Leather Ruby HF (C.I.42 520), 2-amino-4, 6-dinitrophenol, 2-nitro-4-(β-hydroxyethylamino)-aniline, 2-amino-4-nitrophenol, Acid Brown 4 (C.I. 14 805), Acid Blue 135 (C.I. 13 385), Disperse Red 15 (C.I. 60 710), Disperse Violet 1 (C.I. 61 100), 1,4,5,8-tetraaminoanthraquinone and 1,4-diamino-anthraquinone.

- 10 12. Medium according to any one of Claims 4 to 11, characterised in that it additionally contains antioxidants, preferably ascorbic acid or sodium sulphite.
- 13. Medium according to any one of Claims 415 to 12, characterised in that it additionally contains

wetting agents, emulsifiers and/or thickeners.

14. Process for the oxidative colouring of hair, characterised in that, after addition of an oxidative medium, especially hydrogen peroxide, a hair
20 colouring medium containing a combination of developer substances known in the hair colouring art with at least one compound according to Claim 1 as coupler substance as well as additionally if desired known coupler substances
25 according to Claim 8, is applied to the hair, the mixture is allowed to act for about 10 to 45 minutes at a temperature of 15 to 50°C, the hair is then rinsed, optionally washed and further rinsed, and then dried.

Printed for Her Majesty's Stationery Office by the Courier Press, Learnington Spa, 1983. Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained