COMPOSITION FOR THE OXIDATION DYEING OF KERATIN FIBRES AND DYEING PROCESS USING THIS COMPOSITION

The invention relates to a composition for the oxidation dyeing of keratin fibres, and in particular human keratin fibres such as the hair, comprising, in a medium which is suitable for dyeing, at least one oxidation base, at least one cationic direct dye and at least one enzyme of 2-electron oxidoreductase type in the presence of at least one donor for the said enzyme, and to the dyeing process using this composition.

It is known to dye keratin fibres, and in particular human hair, with dye compositions containing oxidation dye precursors, in particular ortho- or para-phenylenediamines, ortho- or para-aminophenols and heterocyclic bases, which are generally referred to as oxidation bases. Oxidation dye precursors, or oxidation bases, are colourless or weakly coloured compounds which, when combined with oxidizing products, can give rise to coloured compounds and dyes by a process of oxidative condensation.

It is also known that the shades obtained with these oxidation bases can be varied by combining them with couplers or colour modifiers, the latter being chosen in particular from aromatic meta-diamines, meta-aminophenols, meta-diphenols and certain heterocyclic compounds.

The variety of molecules used as oxidation

bases and couplers allows a wide range of colours to be obtained.

It is also known that, in order to further vary the shades obtained and to give them glints, direct dyes, i.e. coloured substances which provide a coloration in the absence of an oxidizing agent, can be used in combination with the oxidation dye precursors and couplers.

The vast majority of these direct dyes belong to the family of compounds of the nitrobenzene series and have the drawback, when they are incorporated into dye compositions, of leading to colorations with insufficient staying power, in particular with regard to shampooing.

The so-called "permanent" coloration obtained by means of these oxidation dyes must moreover satisfy a certain number of requirements. Thus, it must have no toxicological drawbacks, it must be able to give shades of the desired intensity and it must be able to withstand external agents (light, bad weather, washing, permanent-waving, perspiration, rubbing).

The dyes must also be able to cover white hair and, lastly, they must be as unselective as possible, i.e. they must give the smallest possible colour differences along the same length of keratin fibre, which may in fact be differently sensitized (i.e. damaged) between its tip and its root.

The oxidation dyeing of keratin fibres is

generally carried out in alkaline medium, in the presence of hydrogen peroxide. However, the use of alkaline media in the presence of hydrogen peroxide have the drawback of causing appreciable degradation of the fibres, as well as considerable bleaching of the keratin fibres, which is not always desirable.

The oxidation dyeing of keratin fibres can also be carried out using oxidizing systems other than hydrogen peroxide, such as enzymatic systems. Thus, it has already been proposed to dye keratin fibres, in particular in patent application EP-A-0,310,675, with compositions comprising an oxidation base and optionally a coupler, in combination with enzymes such as pyranose oxidase, glucose oxidase or uricase, in the presence of a donor for the said enzymes. Although being used under conditions which do not result in a degradation of the keratin fibres which is comparable to that caused by the dyes used in the presence of hydrogen peroxide, these dyeing processes nevertheless lead to colorations which are not entirely satisfactory, in particular as regards their intensity, chromaticity and resistance to the various attacking factors to which the hair may be subjected.

The Applicant has now discovered that it is possible to obtain new dyes, which are capable of leading to intense and chromatic colorations, without giving rise to any significant degradation of the keratin fibres, and which are relatively unselective

and show good resistance to the various attacking factors to which the hair may be subjected, by combining at least one oxidation base, at least one cationic direct dye and at least one enzyme of 2-electron oxidoreductase type in the presence of at least one donor for the said enzyme.

This discovery forms the basis of the present invention.

A first subject of the invention is thus a ready-to-use composition for the oxidation dyeing of keratin fibres, and in particular human keratin fibres such as the hair, characterized in that it comprises, in a medium which is suitable for dyeing:

- at least one oxidation base,
- at least one cationic direct dye,
- at least one enzyme of 2-electron oxidoreductase type, and
- at least one donor for the said enzyme.

The ready-to-use dye composition in accordance with the invention leads to intense, chromatic, relatively unselective colorations with excellent properties of resistance both to atmospheric agents such as light and bad weather and to perspiration and the various treatments to which the hair may be subjected (washing, permanent-waving).

A subject of the invention is also a process for the oxidation dyeing of keratin fibres using this ready-to-use dye composition.

The 2-electron oxidoreductase(s) used in the ready-to-use dye composition in accordance with the invention can be chosen in particular from pyranose oxidases, glucose oxidases, glycerol oxidases, lactate oxidases, pyruvate oxidases and uricases.

According to the invention, the 2-electron oxidoreductase is preferably chosen from uricases of animal, microbiological or biotechnological origin.

By way of example, mention may be made of uricase extracted from boar liver, uricase from Arthrobacter globiformis, as well as uricase from Aspergillus flavus.

The 2-electron oxidoreductase(s) can be used in pure crystalline form or in a form diluted in a diluent which is inert with respect to the said 2-electron oxidoreductase.

The 2-electron oxidoreductase(s) in accordance with the invention preferably represent(s) from 0.01 to 20% by weight approximately relative to the total weight of the ready-to-use dye composition, and even more preferably from 0.1 to 5% by weight approximately relative to this weight.

According to the invention, the term donor is understood to refer to the various substrates involved in the functioning of the said 2-electron oxidoreductase(s).

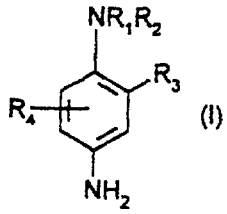
The nature of the donor (or substrate) for the said enzyme varies depending on the nature of the

2-electron oxidoreductase used. For example, as donors for the pyranose oxidases, mention may be made of D-glucose, L-sorbose and D-xylose; as a donor for the glucose oxidases, mention may be made of D-glucose; as donors for the glycerol oxidases, mention may be made of glycerol and dihydroxyacetone; as donors for the lactate oxidases, mention may be made of lactic acid and its salts; as donors for the pyruvate oxidases, mention may be made of pyruvic acid and its salts; and lastly, as donors for the uricases, mention may be made of uric acid and its salts.

The donor(s) (or substrate(s)) used in accordance with the invention preferably represent(s) from 0.01 to 20% by weight approximately relative to the total weight of the ready-to-use dye composition in accordance with the invention, and even more preferably from 0.1 to 5% by approximately relative to this weight.

The nature of the oxidation base(s) used in the ready-to-use dye composition is not a critical factor. They can be chosen, in particular, from para-phenylenediamines, double bases, para-aminophenols, ortho-aminophenols and heterocyclic oxidation bases.

Among the para-phenylenediamines which can be used as oxidation bases in the dye compositions in accordance with the invention, mention may be made in particular of the compounds of formula (I) below, and the addition salts thereof with an acid:



(I)

in which:

- R_1 represents a hydrogen atom, a C_1-C_4 alkyl radical, a C_1-C_4 monohydroxyalkyl radical, a C_2-C_4 polyhydroxyalkyl radical, a (C_1-C_4)alkoxy(C_1-C_4)alkyl radical, a C_1-C_4 alkyl radical substituted with a nitrogenous group, a phenyl radical or a 4'-aminophenyl radical;
- R_2 represents a hydrogen atom, a C_1-C_4 alkyl radical, a C_1-C_4 monohydroxyalkyl radical, a C_2-C_4 polyhydroxyalkyl radical, a (C_1-C_4)alkoxy(C_1-C_4)alkyl radical or a C_1-C_4 alkyl radical substituted with a nitrogenous group;
- R_3 represents a hydrogen atom, a halogen atom such as a chlorine, bromine, iodine or fluorine atom, a C_1-C_4 alkyl radical, a C_1-C_4 monohydroxyalkyl radical, a C_1-C_4 hydroxyalkoxy radical, an acetylamino(C_1-C_4)-alkoxy radical, a C_1-C_4 mesylaminoalkoxy radical or a carbamoylamino(C_1-C_4)alkoxy radical,
- R_4 represents a hydrogen or halogen atom or a C_1-C_4 alkyl radical.

Among the nitrogenous groups of formula (I) above, mention may be made in particular of amino, mono(C_1-C_4)alkylamino, di(C_1-C_4)alkylamino, tri(C_1-C_4)-alkylamino, monohydroxy(C_1-C_4)alkylamino, imidazolinium and ammonium radicals.

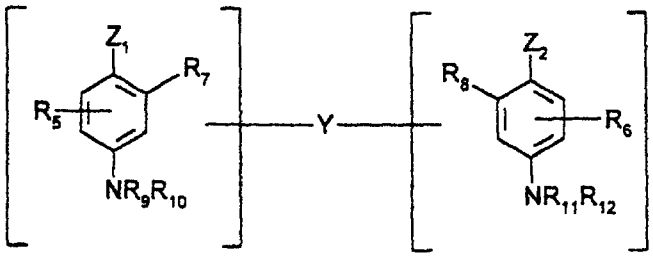
Among the para-phenylenediamines of formula (I) above, mention may be made more particularly of para-phenylenediamine, para-toluylenediamine, 2-chloro-para-phenylenediamine, 2,3-dimethyl-para-phenylene-diamine, 2,6-dimethyl-para-phenylenediamine, 2,6-diethyl-para-phenylenediamine, 2,5-dimethyl-para-phenylenediamine, N,N-dimethyl-para-phenylenediamine, N,N-diethyl-para-phenylenediamine, N,N-dipropyl-para-phenylenediamine, 4-amino-N,N-diethyl-3-methylaniline, N,N-bis(β-hydroxyethyl)-para-phenylenediamine, 4-amino-N,N-bis(β-hydroxyethyl)-2-methylaniline, 4-amino-2-chloro-N,N-bis(β-hydroxyethyl)aniline, 2-β-hydroxy-ethyl-para-phenylenediamine, 2-fluoro-para-phenylene-diamine, 2-isopropyl-para-phenylenediamine, N-(β-hydroxypropyl)-para-phenylenediamine, 2-hydroxy-methyl-para-phenylenediamine, N,N-dimethyl-3-methyl-para-phenylenediamine, N,N-(ethyl-β-hydroxyethyl)-para-phenylenediamine, N-(β,γ-dihydroxypropyl)-para-phenylene-diamine, N-(4'-aminophenyl)-para-phenylenediamine, N-phenyl-para-phenylenediamine, 2-β-hydroxyethyloxy-para-phenylenediamine, 2-β-acetylaminoethyloxy-para-phenylenediamine and N-(β-methoxyethyl)-para-phenylenediamine, and the addition salts thereof with an acid.

Among the para-phenylenediamines of formula (I) above, para-phenylenediamine, para-toluylenediamine, 2-isopropyl-para-phenylenediamine, 2-β-hydroxyethyl-para-phenylenediamine, 2-β-hydroxyethyloxy-para-phenylenediamine, 2,6-dimethyl-para-phenylenediamine,

2,6-diethyl-para-phenylenediamine, 2,3-dimethyl-para-phenylenediamine, N,N-bis(β-hydroxyethyl)-para-phenylenediamine, 2-chloro-para-phenylenediamine and 2-β-acetylaminoethyloxy-para-phenylenediamine and the addition salts thereof with an acid are most particularly preferred.

According to the invention, the term double bases is understood to refer to the compounds containing at least two aromatic rings bearing amino and/or hydroxyl groups.

Among the double bases which can be used as oxidation bases in the dye compositions in accordance with the invention, mention may be made in particular of the compounds corresponding to formula (II) below, and the addition salts thereof with an acid:



(II)

in which:

- Z_1 and Z_2, which may be identical or different, represent a hydroxyl or $-NH_2$ radical which may be substituted with a C_1-C_4 alkyl radical or with a linker arm Y;

- the linker arm Y represents a linear or branched alkylene chain containing from 1 to 14 carbon atoms, which may be interrupted by or terminated with one or

more nitrogenous groups and/or one or more hetero atoms such as oxygen, sulphur or nitrogen atoms, and optionally substituted with one or more hydroxyl or C_1-C_6 alkoxy radicals;

- R_5 and R_6 represent a hydrogen or halogen atom, a C_1-C_4 alkyl radical, a C_1-C_4 monohydroxyalkyl radical, a C_2-C_4 polyhydroxyalkyl radical, a C_1-C_4 aminoalkyl radical or a linker arm Y;

- R_7, R_8, R_9, R_{10}, R_{11} and R_{12}, which may be identical or different, represent a hydrogen atom, a linker arm Y or a C_1-C_4 alkyl radical;

it being understood that the compounds of formula (II) contain only one linker arm Y per molecule.

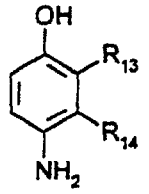
Among the nitrogenous groups of formula (II) above, mention may be made in particular of amino, mono(C_1-C_4)alkylamino, di(C_1-C_4)alkylamino, tri(C_1-C_4)-alkylamino, monohydroxy(C_1-C_4)alkylamino, imidazolinium and ammonium radicals.

Among the double bases of formula (II) above, mention may be made more particularly of N,N'-bis-(β-hydroxyethyl)-N,N'-bis(4'-aminophenyl)-1,3-diamino-propanol, N,N'-bis(β-hydroxyethyl)-N,N'-bis(4'-amino-phenyl)ethylenediamine, N,N'-bis(4-aminophenyl)-tetramethylenediamine, N,N'-bis(β-hydroxyethyl)-N,N'-bis(4-aminophenyl)tetramethylenediamine, N,N'-bis(4-methylaminophenyl)tetramethylenediamine, N,N'-bis(ethyl)-N,N'-bis(4'-amino-3'-methylphenyl)-ethylenediamine and 1,8-bis(2,5-diaminophenoxy)-

3,5-dioxaoctane, and the addition salts thereof with an acid.

Among these double bases of formula (II), N,N'-bis(β-hydroxyethyl)-N,N'-bis(4'-aminophenyl)-1,3-diaminopropanol and 1,8-bis(2,5-diaminophenoxy)-3,5-dioxaoctane, or one of the addition salts thereof with an acid, are particularly preferred.

Among the para-aminophenols which can be used as oxidation bases in the dye compositions in accordance with the invention, mention may be made in particular of the compounds corresponding to formula (III) below, and the addition salts thereof with an acid:



(III)

in which:

- R_{13} represents a hydrogen or halogen atom or a C_1-C_4 alkyl, C_1-C_4 monohydroxyalkyl, (C_1-C_4)alkoxy(C_1-C_4)alkyl, C_1-C_4 aminoalkyl or hydroxy(C_1-C_4)alkylamino(C_1-C_4)alkyl radical,
- R_{14} represents a hydrogen or halogen atom or a C_1-C_4 alkyl, C_1-C_4 monohydroxyalkyl, C_2-C_4 polyhydroxyalkyl, C_1-C_4 aminoalkyl, C_1-C_4 cyanoalkyl or (C_1-C_4)alkoxy-(C_1-C_4)alkyl radical,

it being understood that at least one of the radicals R_{13} or R_{14} represents a hydrogen atom.

Among the para-aminophenols of formula (III) above, mention may be made more particularly of para-aminophenol, 4-amino-3-methylphenol, 4-amino-3-fluorophenol, 4-amino-3-hydroxymethylphenol, 4-amino-2-methylphenol, 4-amino-2-hydroxymethylphenol, 4-amino-2-methoxymethylphenol, 4-amino-2-aminomethylphenol, 4-amino-2-(β-hydroxyethylaminomethyl)phenol and 4-amino-2-fluorophenol, and the addition salts thereof with an acid.

Among the ortho-aminophenols which can be used as oxidation bases in the dye compositions in accordance with the invention, mention may be made more particularly of 2-aminophenol, 2-amino-5-methylphenol, 2-amino-6-methylphenol and 5-acetamido-2-aminophenol, and the addition salts thereof with an acid.

Among the heterocyclic bases which can be used as oxidation bases in the dye compositions in accordance with the invention, mention may be made more particularly of pyridine derivatives, pyrimidine derivatives, pyrazole derivatives and pyrazolo-pyrimidine derivatives, and the addition salts thereof with an acid.

Among the pyridine derivatives, mention may be made more particularly of the compounds described, for example, in patents GB 1,026,978 and GB 1,153,196, such as 2,5-diaminopyridine, 2-(4-methoxyphenyl)amino-3-aminopyridine, 2,3-diamino-6-methoxypyridine, 2-(β-methoxyethyl)amino-3-amino-6-methoxypyridine and

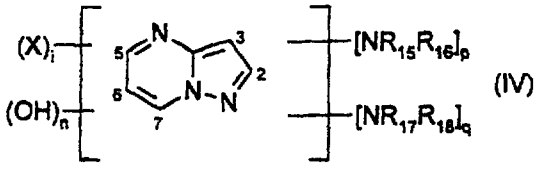
3,4-diaminopyridine, and the addition salts thereof with an acid.

Among the pyrimidine derivatives, mention may be made more particularly of the compounds described, for example, in German patent DE 2,359,399 or Japanese patents JP 88-169,571 and JP 91-10659 or patent applications WO 96/15765, such as 2,4,5,6-tetraaminopyrimidine, 4-hydroxy-2,5,6-triaminopyrimidine, 2-hydroxy-4,5,6-triaminopyrimidine, 2,4-dihydroxy-5,6-diaminopyrimidine and 2,5,6-triaminopyrimidine, and the addition salts thereof with an acid.

Among the pyrazole derivatives, mention may be made more particularly of the compounds described in patents DE 3,843,892, DE 4,133,957 and patent applications WO 94/08969, WO 94/08970, FR-A-2,733,749 and DE 195 43 988, such as 4,5-diamino-1-methylpyrazole, 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-tert-butyl-1-methylpyrazole, 4,5-diamino-1-tert-butyl-3-methylpyrazole, 4,5-diamino-1-(β-hydroxyethyl)-3-methylpyrazole, 4,5-diamino-1-ethyl-3-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-(2'-aminoethyl)amino-1,3-dimethylpyrazole, 3,4,5-triaminopyrazole, 1-methyl-3,4,5-triaminopyrazole, 3,5-diamino-1-methyl-4-methylaminopyrazole and 3,5-diamino-4-(β-hydroxyethyl)amino-1-methylpyrazole, and the addition salts thereof with an acid.

Among the pyrazolopyrimidine derivatives, mention may be made more particularly of the pyrazolo[1,5-a]pyrimidines of formula (IV) below, and the addition salts thereof with an acid or with a base and the tautomeric forms thereof, when a tautomeric equilibrium exists:



(IV)

in which:

- R_{15}, R_{16}, R_{17} and R_{18}, which may be identical or different, denote a hydrogen atom, a C_1-C_4 alkyl radical, an aryl radial, a C_1-C_4 hydroxyalkyl radical, a C_2-C_4 polyhydroxyalkyl radical, a (C_1-C_4)alkoxy(C_1-C_4)-alkyl radical, a C_1-C_4 aminoalkyl radical (it being possible for the amine to be protected with an acetyl, ureido or sulphonyl radical), a (C_1-C_4)alkylamino(C_1-C_4)-alkyl radical, a di[(C_1-C_4)alkyl]amino(C_1-C_4)alkyl radical (it being possible for the dialkyl radicals to form a 5- or 6-membered carbon-based ring or a

heterocycle), a hydroxy(C_1-C_4)alkyl- or di[hydroxy-(C_1-C_4)alkyl]amino(C_1-C_4)alkyl radical;

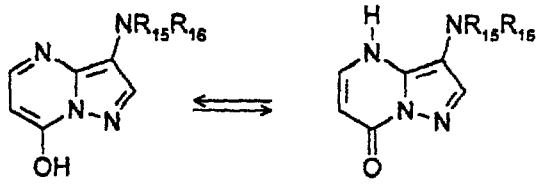
- the radicals X, which may be identical or different, denote a hydrogen atom, a C_1-C_4 alkyl radical, an aryl radical, a C_1-C_4 hydroxyalkyl radical, a C_2-C_4 polyhydroxyalkyl radical, a C_1-C_4 aminoalkyl radical, a (C_1-C_4)alkylamino(C_1-C_4)alkyl radical, a di[(C_1-C_4)-alkyl]amino(C_1-C_4)alkyl radical (it being possible for the dialkyls to form a 5- or 6-membered carbon-based ring or a heterocycle), a hydroxy(C_1-C_4)alkyl- or di-[hydroxy(C_1-C_4)alkyl]amino(C_1-C_4)alkyl radical, an amino radical, a (C_1-C_4)alkyl- or di[(C_1-C_4)alkyl]amino radical; a halogen atom, a carboxylic acid group, a sulphonic acid group;
- i is equal to 0, 1, 2 or 3;
- p is equal to 0 or 1;
- q is equal to 0 or 1;
- n is equal to 0 or 1;

with the proviso that:

- the sum p + q is other than 0;
- when p + q is equal to 2, then n is equal to 0 and the groups $NR_{15}R_{16}$ and $NR_{17}R_{18}$ occupy the (2,3); (5,6); (6,7); (3,5) or (3,7) positions;
- when p + q is equal to 1, then n is equal to 1 and the group $NR_{15}R_{16}$ (or $NR_{17}R_{18}$) and the OH group occupy the (2,3); (5,6); (6,7); (3,5) or (3,7) positions.

When the pyrazolo[1,5-a]pyrimidines of formula (IV) above are such that they contain a hydroxyl group

on one of the positions 2, 5 or 7 α to a nitrogen atom, a tautomeric equilibrium exists represented, for example, by the following scheme:



Among the pyrazolo[1,5-a]pyrimidines of formula (IV) above, mention may be made in particular of:

- pyrazolo[1,5-a]pyrimidine-3,7-diamine;
- 2,5-dimethylpyrazolo[1,5-a]pyrimidine-3,7-diamine;
- pyrazolo[1,5-a]pyrimidine-3,5-diamine;
- 2,7-dimethylpyrazolo[1,5-a]pyrimidine-3,5-diamine;
- 3-aminopyrazolo[1,5-a]pyrimidin-7-ol;
- 3-aminopyrazolo[1,5-a]pyrimidin-5-ol;
- 2-(3-aminopyrazolo[1,5-a]pyrimidin-7-ylamino)ethanol;
- 2-(7-aminopyrazolo[1,5-a]pyrimidin-3-ylamino)ethanol;
- 2-[(3-aminopyrazolo[1,5-a]pyrimidin-7-yl)-(2-hydroxyethyl)amino]ethanol;
- 2-[(7-aminopyrazolo[1,5-a]pyrimidin-3-yl)-(2-hydroxyethyl)amino]ethanol;
- 5,6-dimethylpyrazolo[1,5-a]pyrimidine-3,7-diamine;
- 2,6-dimethylpyrazolo[1,5-a]pyrimidine-3,7-diamine;
- 2,5,N7,N7-tetramethylpyrazolo[1,5-a]pyrimidine-3,7-diamine;

and the addition salts thereof and the tautomeric forms thereof, when a tautomeric equilibrium exists.

The pyrazolo[1,5-a]pyrimidines of formula (IV)

above can be prepared by cyclization starting with an aminopyrazole, according to the syntheses described in the following references:

- EP 628559 Beiersdorf-Lilly.
- R. Vishdu, H. Navedul, Indian J. Chem., 34b (6), 514, 1995.
- N.S. Ibrahim, K.U. Sadek, F.A. Abdel-Al, Arch. Pharm., 320, 240, 1987.
- R.H. Springer, M.B. Scholten, D.E. O'Brien, T. Novinson, J.P. Miller, R.K. Robins, J. Med. Chem., 25, 235, 1982.
- T. Novinson, R.K. Robins, T.R. Matthews, J. Med. Chem., 20, 296, 1977.
- US 3907799 ICN Pharmaceuticals.

The pyrazolo[1,5-a]pyrimidines of formula (IV) above can also be prepared by cyclization starting from hydrazine, according to the syntheses described in the following references:

- A. McKillop and R.J. Kobilecki, Heterocycles, 6(9), 1355, 1977.
- E. Alcade, J. De Mendoza, J.M. Marcia-Marquina, C. Almera, J. Elguero, J. Heterocyclic Chem., 11(3), 423, 1974.
- K. Saito, I. Hori, M. Higarashi, H. Midorikawa, Bull. Chem. Soc. Japan, 47(2), 476, 1974.

The oxidation base(s) preferably represent(s) from 0.0005 to 12% by weight approximately relative to the total weight of the dye composition in accordance

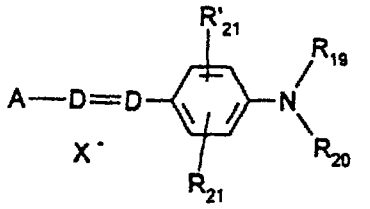
with the invention, and even more preferably from 0.005 to 6% by weight approximately relative to this weight.

The cationic direct dye(s) which can be used in the ready-to-use dye composition in accordance with the invention is (are) preferably chosen from cationic aminoanthraquinone dyes, cationic monoazo or diazo dyes and cationic naphthoquinone dyes.

By way of example, mention may be made in particular of [8-[(p-aminophenyl)azol]-7-hydroxy-2-naphthyl]trimethylammonium chloride (also known as Basic Brown 16 or Arianor Mahogany 306002 in the Color Index), 3-[(4-amino-6-bromo-5,8-dihydro-1-hydroxy-8-imino-5-oxo-2-naphthalenyl)amino]-N,N,N-trimethyl-benzenaminium chloride (also known as Basic Blue 99 or Arianor Steel Blue 306004 in the Color Index), 7-hydroxy-8-[(2-methoxyphenyl)azo]-N,N,N-trimethyl-2-naphthalenaminium chloride (also known as Basic Red 76 or Arianor Madder Red in the Color Index), [8-[(4-amino-2-nitrophenyl)azo]-7-hydroxy-2-naphthyl]-trimethylammonium chloride (also known as Basic Brown 17 or Arianor Sienna Brown 306001 in the Color Index) and 3-[(4,5-dihydro-3-methyl-5-oxo-1-phenyl-1H-pyrazol-4-yl)azo]-N,N,N-trimethylbenzenaminium chloride (also known as Basic Yellow 57 or Arianor Straw Yellow 306005 in the Color Index).

The cationic direct dye(s) can also be chosen from:

a) the compounds of formula (V) below:



(V)

in which:

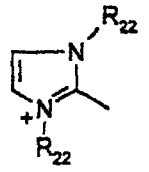
D represents a nitrogen atom or a -CH group,

R_{19} and R_{20}, which may be identical or different, represent a hydrogen atom; a C_1-C_4 alkyl radical which can be substituted with a -CN, -OH or $-NH_2$ radical or form, with a carbon atom of the benzene ring, an optionally oxygenated or nitrogenous heterocycle, which can be substituted with one or more C_1-C_4 alkyl radicals; a 4'-aminophenyl radical,

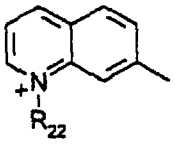
R_{21} and R'_{21}, which may be identical or different, represent a hydrogen atom, a halogen atom chosen from chlorine, bromine, iodine and fluorine, or a cyano, C_1-C_4 alkoxy or acetyloxy radical,

X^- represents an anion preferably chosen from chloride, methyl sulphate and acetate,

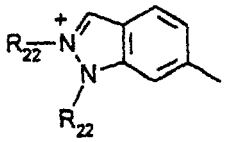
A represents a group chosen from structures A1 to A19 below:



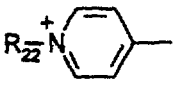
A_1 ;



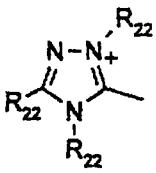
A_2 ;



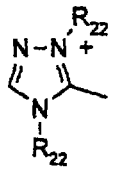
A_3 ;



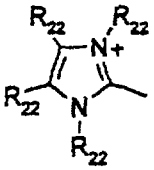
A_4 ;



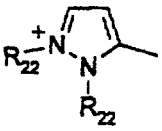
A_5 ;



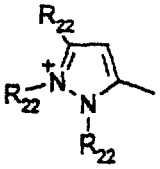
A_6 ;



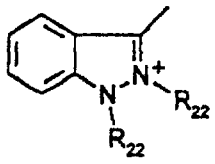
A_7 ;



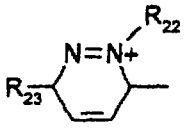
A_8 ;



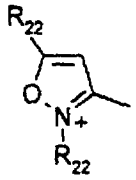
A_9 ;



;

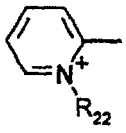


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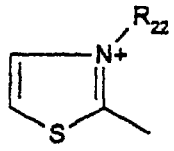


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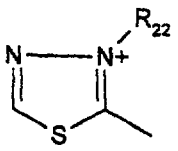
A_{10} A_{11} A_{12}



;

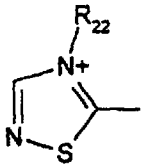


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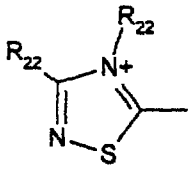


;

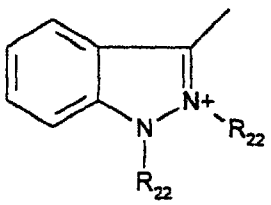
A_{13} A_{14} A_{15}



;

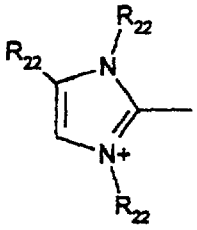


;



A_{16} A_{17} A_{18}

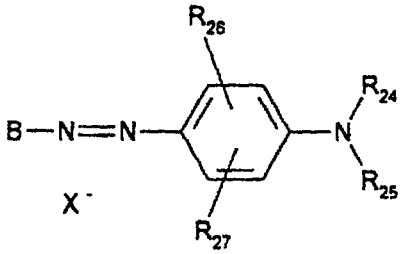
and



A_{19} ;

in which R_{22} represents a C_1-C_4 alkyl radical which can be substituted with a hydroxyl radical and R_{23} represents a C_1-C_4 alkoxy radical;

b) the compounds of formula (VI) below:



(IV)

in which:

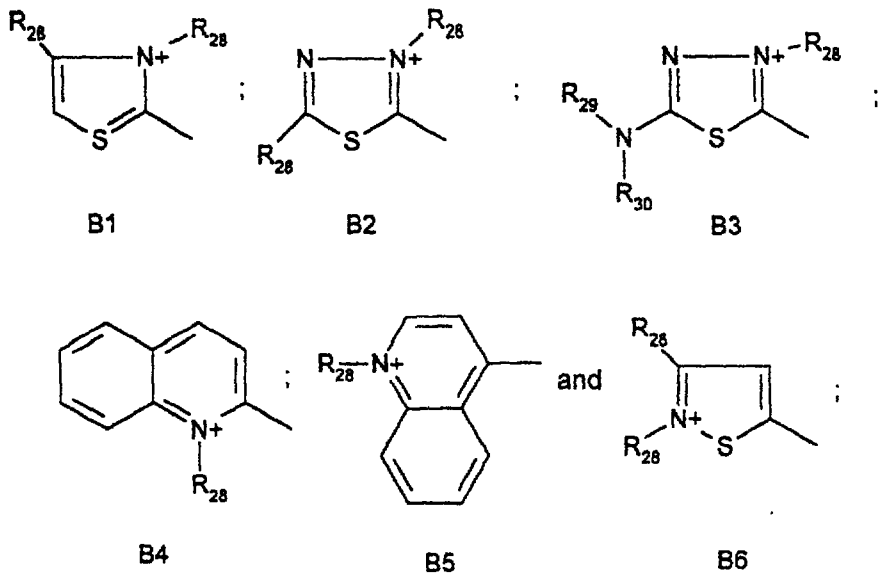
R_{24} represents a hydrogen atom or a C_1-C_4 alkyl radical,

R_{25} represents a hydrogen atom, an alkyl radical which can be substituted with a -CN radical or with an amino group, a 4'-aminophenyl radical or forms, with R_{24}, an optionally oxygenated and/or nitrogenous heterocycle which can be substituted with a C_1-C_4 alkyl radical,

R_{26} and R_{27}, which may be identical or different, represent a hydrogen atom, a halogen atom such as bromine, chlorine, iodine or fluorine, a C_1-C_4 alkyl or C_1-C_4 alkoxy radical or a -CN radical,

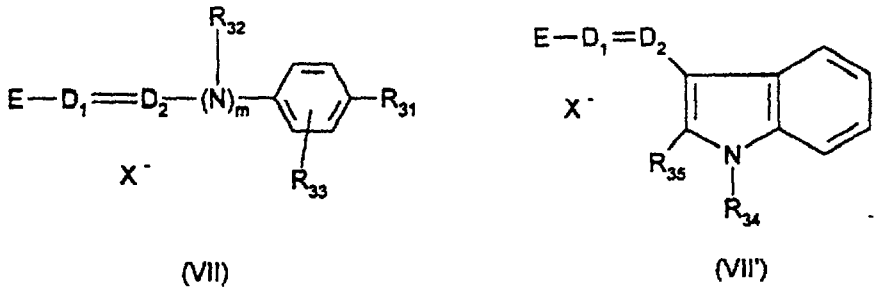
X^- represents an anion preferably chosen from chloride, methyl sulphate and acetate,

B represents a group chosen from structures B1 to B6 below:



in which R_{28} represents a C_1-C_4 alkyl radical, R_{29} and R_{30}, which may be identical or different, represent a hydrogen atom or a C_1-C_4 alkyl radical;

c) the compounds of formulae (VII) and (VII') below:



in which:

R_{31} represents a hydrogen atom, a C_1-C_4 alkoxy radical, a halogen atom such as bromine, chlorine, iodine or fluorine, or an amino radical,

R_{32} represents a hydrogen atom, a C_1-C_4 alkyl radical or forms, with a carbon atom of the benzene ring, a heterocycle which is optionally oxygenated and/or

substituted with one or more C_1-C_4 alkyl groups,

R_{33} represents a hydrogen atom or a halogen atom such as bromine, chlorine, iodine or fluorine,

R_{34} and R_{35}, which may be identical or different, represent a hydrogen atom or a C_1-C_4 alkyl radical,

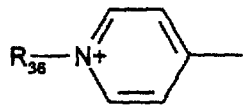
D_1 and D_2, which may be identical or different, represent a nitrogen atom or a -CH group,

m = 0 or 1,

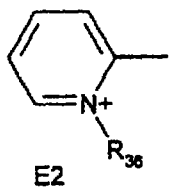
it being understood that when R_{31} represents an unsubstituted amino group, then D_1 and D_2 simultaneously represent a -CH group and m = 0,

X^- represents an anion preferably chosen from chloride, methyl sulphate and acetate,

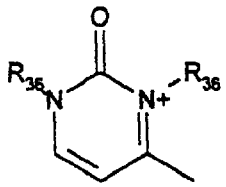
E represents a group chosen from structures E1 to E8 below:



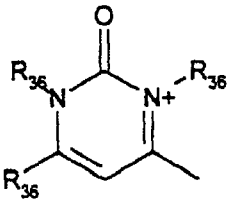
E1 ;



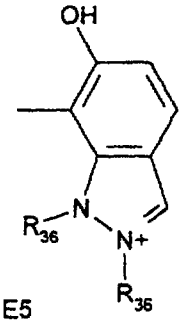
E2 ;



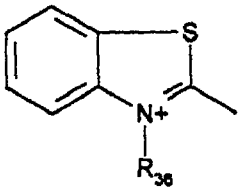
E3 ;



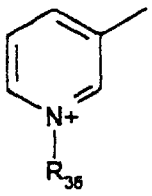
E4 ;



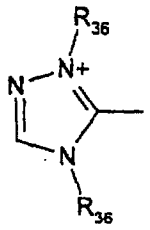
E5 ;



E6 ;



E7 and



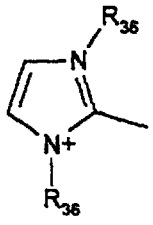
E8

;

in which R_{36} represents a C_1-C_4 alkyl radical;

when m = 0 and when D_1 represents a nitrogen atom, then E can also denote a group of structure E9 below:

E9

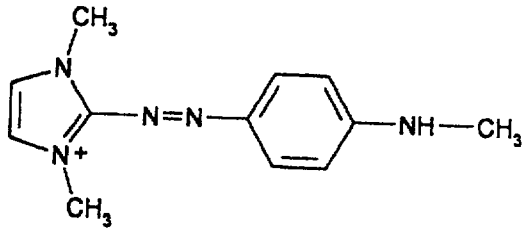


;

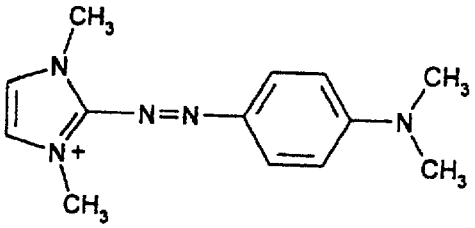
in which R_{36} represents a C_1-C_4 alkyl radical.

The cationic direct dyes of formulae (V), (VI), (VII) and (VII') which can be used in the ready-to-use dye composition in accordance with the invention are known compounds and are described, for example, in patent applications WO 95/01772, WO 95/15144 and EP-A-0,714,954.

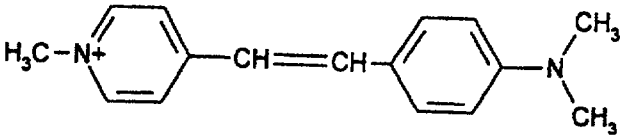
Among the cationic direct dyes of formula (V) which can be used in the ready-to-use dye compositions in accordance with the invention, mention may be made more particularly of the compounds corresponding to structures (V1) to (V52) below:



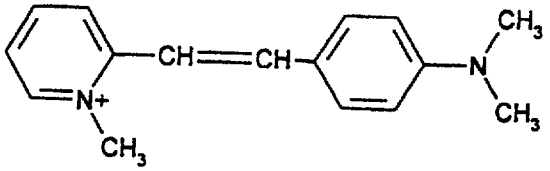
(V1)



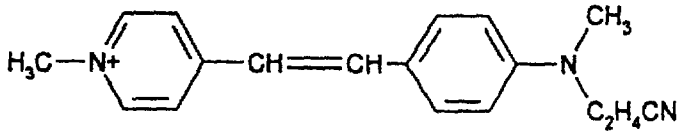
(V2)



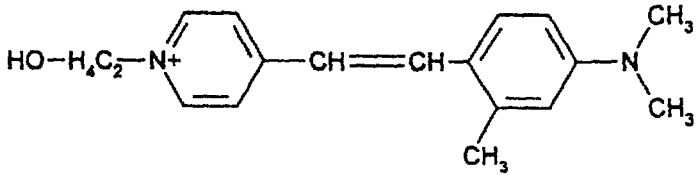
(V3)



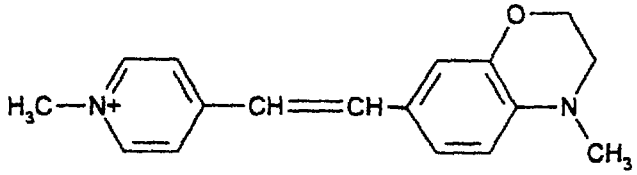
(V4)



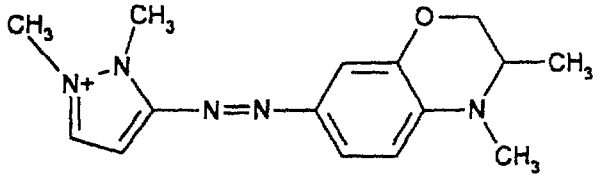
Cl^- (V5)



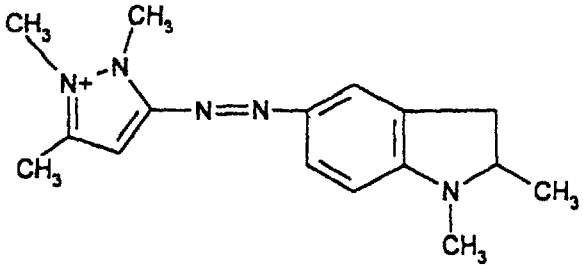
Cl^- (V6)



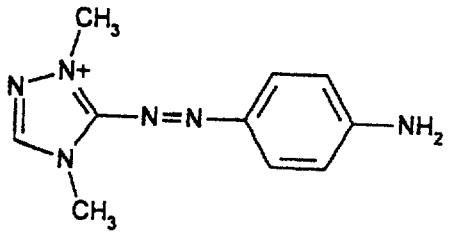
Cl^- (V7)



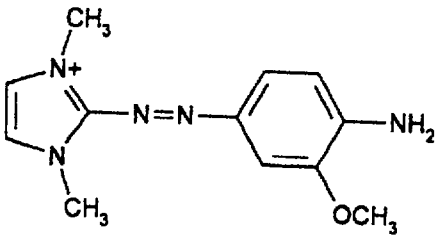
Cl^- (V8)



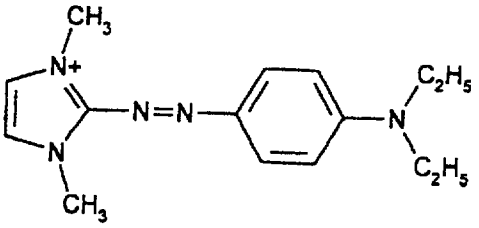
Cl^- (V9)



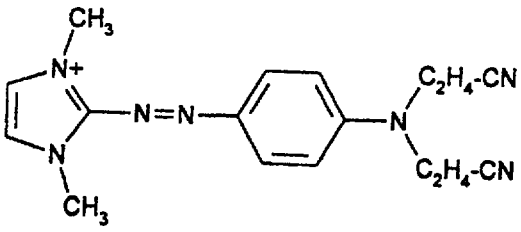
Cl^- (V10)



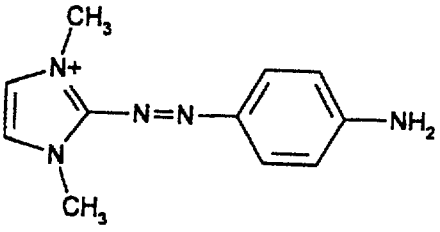
Cl^- (V11)



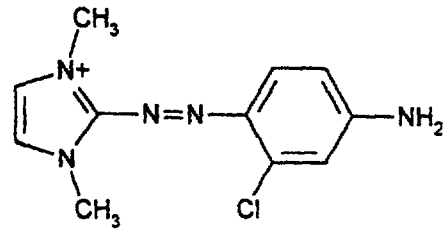
Cl^- (V12)



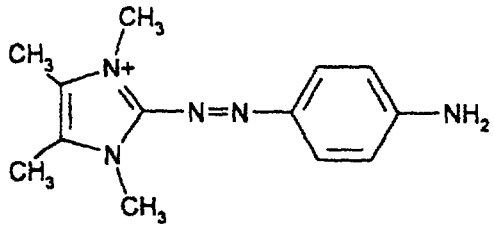
Cl^- (V13)



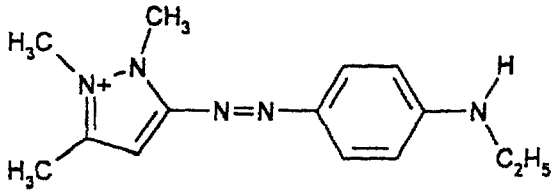
Cl^- (V14)



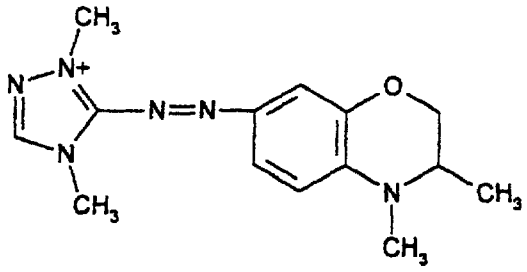
Cl^- (V15)



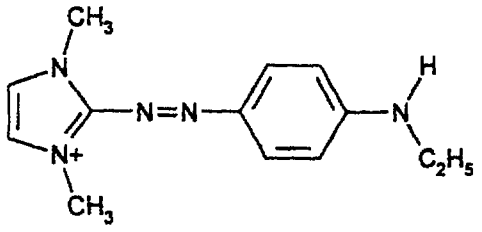
Cl^- (V16)



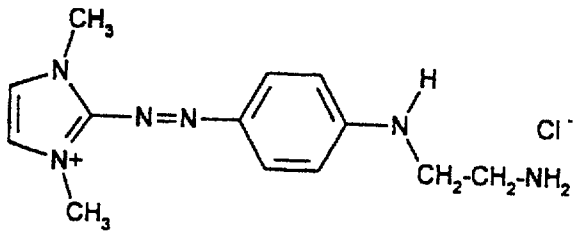
Cl^- (V17)



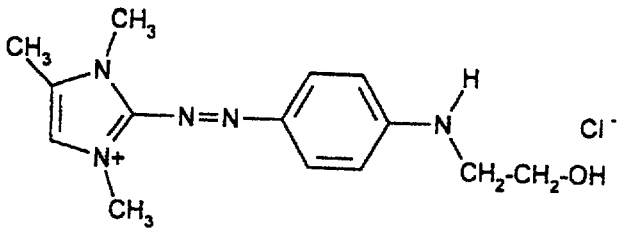
Cl^- (V18)



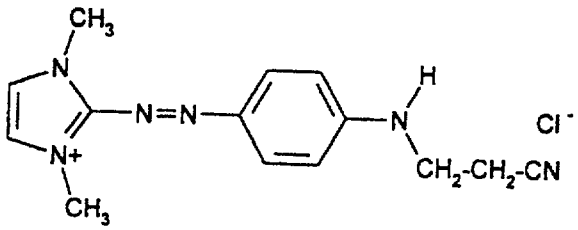
Cl^- (V19)



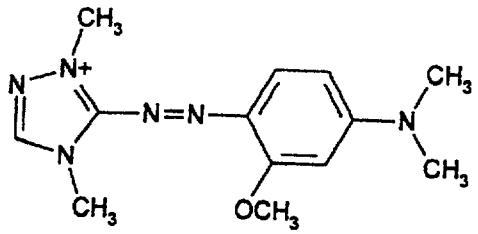
(V20)



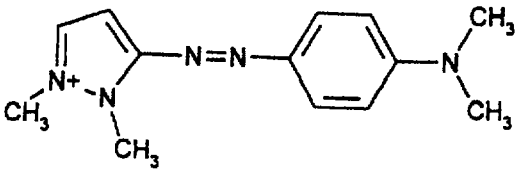
(V21)



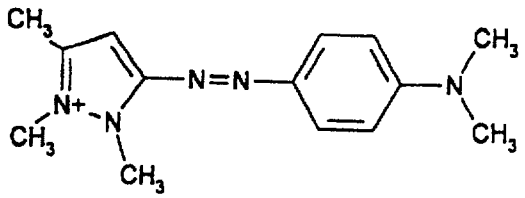
(V22)



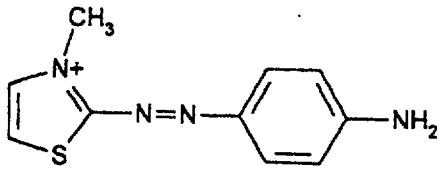
(V23)



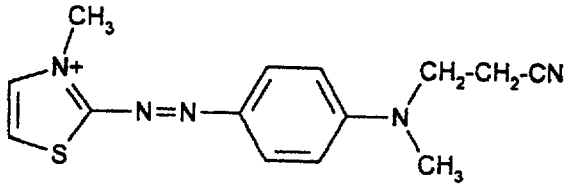
(V24)



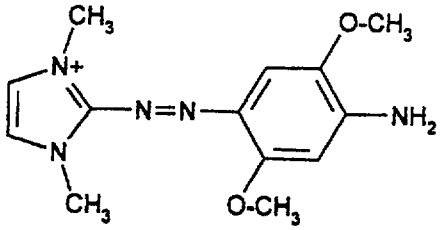
Cl^- (V25)



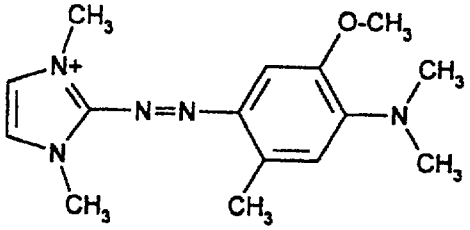
Cl^- (V26)



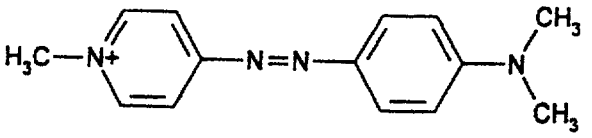
Cl^- (V27)



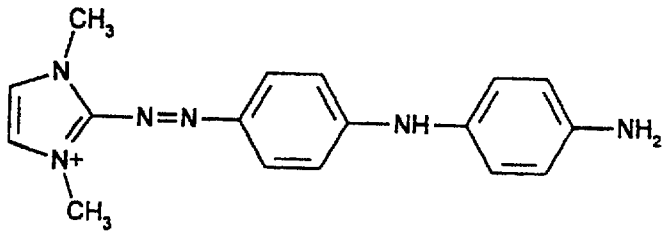
Cl^- (V28)



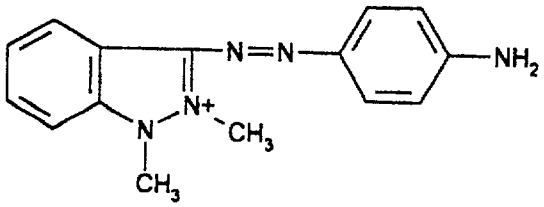
Cl^- (V29)



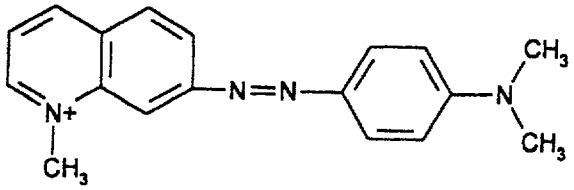
Cl^- (V30)



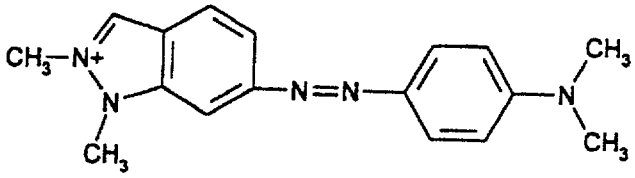
Cl⁻ (V31)



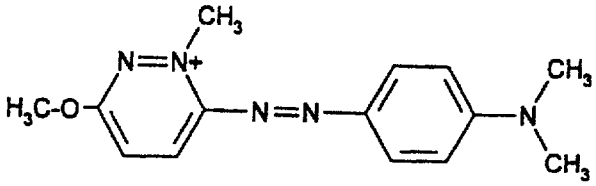
Cl⁻ (V32)



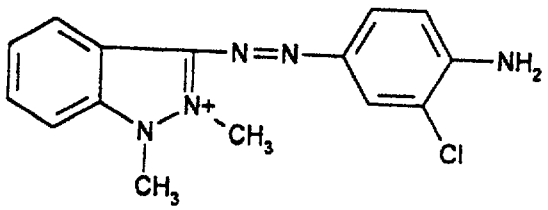
Cl⁻ (V33)



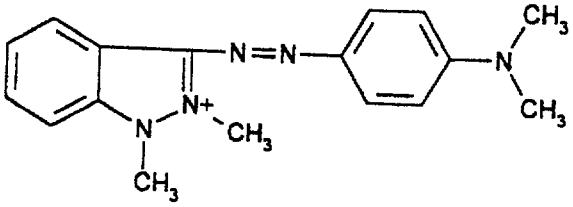
Cl⁻ (V34)



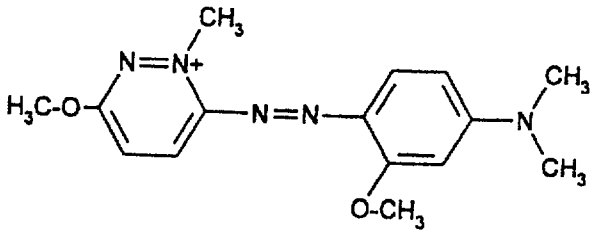
Cl⁻ (V35)



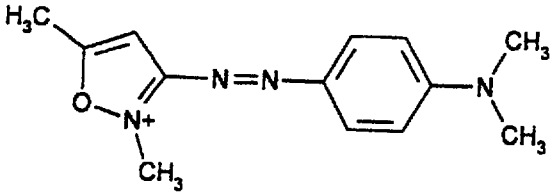
Cl^- (V36)



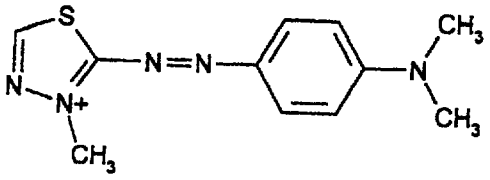
Cl^- (V37)



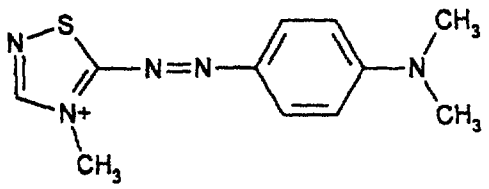
Cl^- (V38)



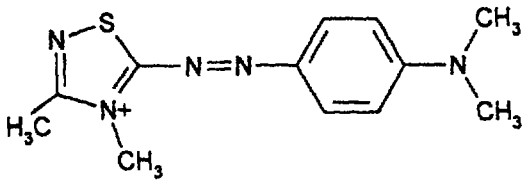
Cl^- (V39)



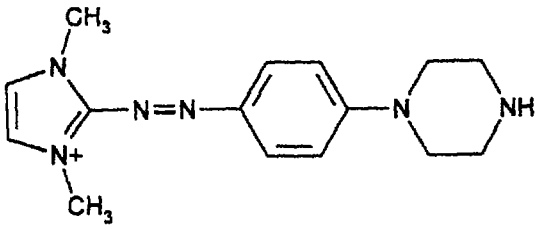
Cl^- (V40)



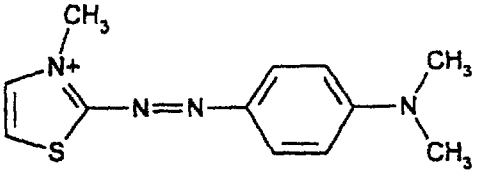
Cl⁻ (V41)



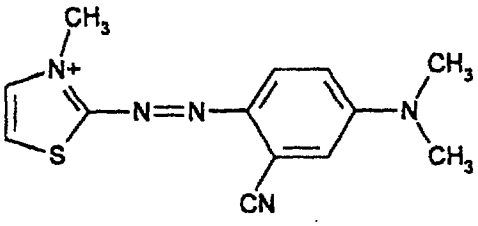
Cl⁻ (V42)



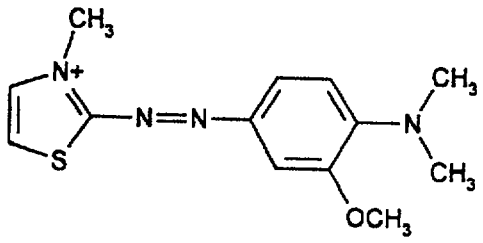
Cl⁻ (V43)



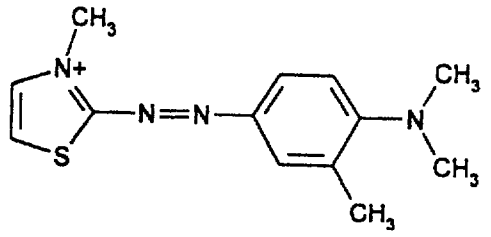
Cl⁻ (V44)



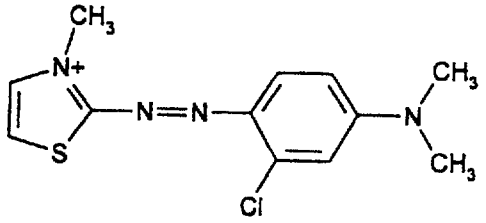
Cl⁻ (V45)



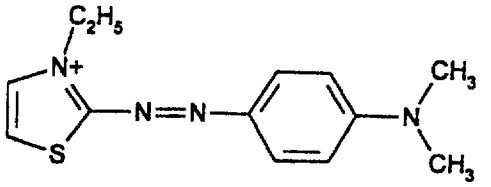
(V46)



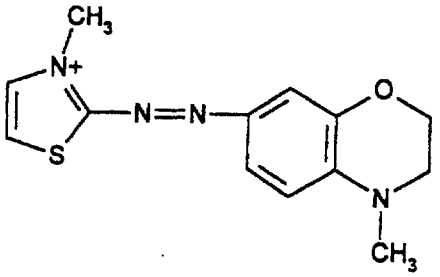
(V47)



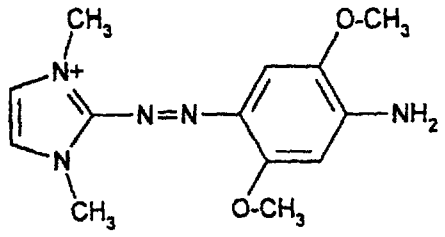
(V48)



(V49)

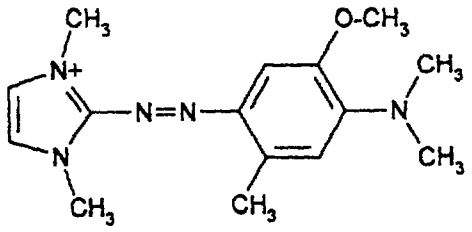


(V50)



(V51)

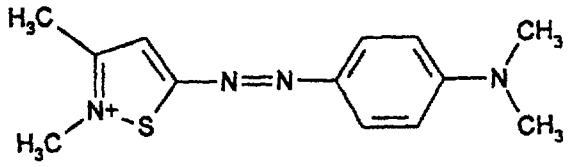
and



(V52)

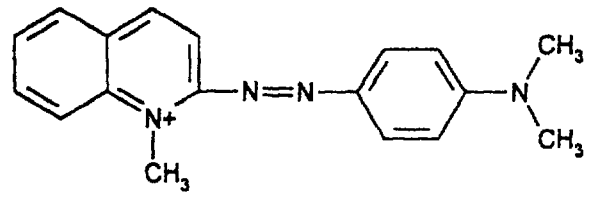
Among the compounds of structures (V1) to (V52) described above, the ones most particularly preferred are the compounds corresponding to structures (V1), (V2), (V4), (V14) and (V31).

Among the cationic direct dyes of formula (VI) which can be used in the ready-to-use dye compositions in accordance with the invention, mention may be made more particularly of the compounds corresponding to structures (VI1) to (VI12) below:



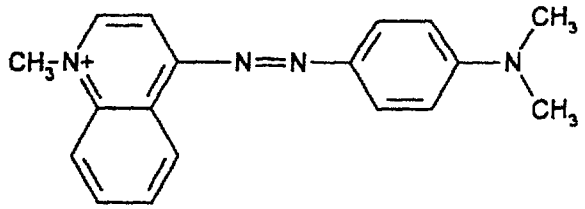
(VI1)

;



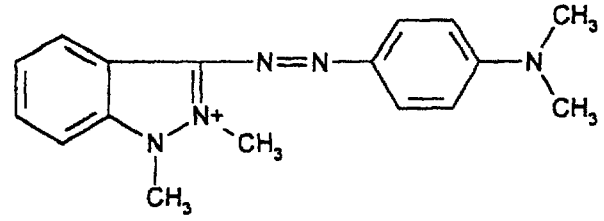
(VI2)

;



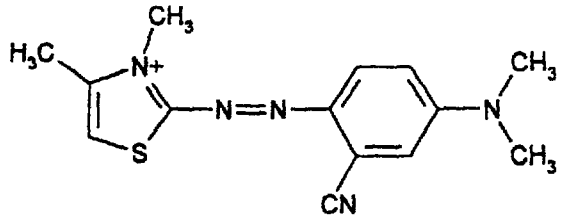
(VI3)

;



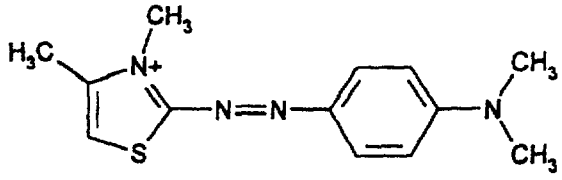
(VI4)

;



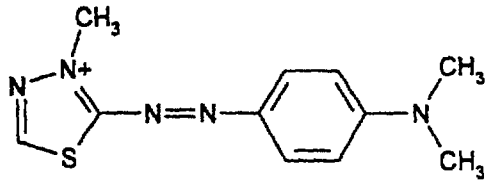
(VI5)

;



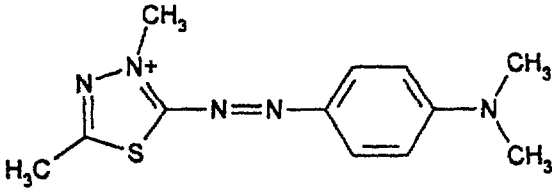
(VI6)

;



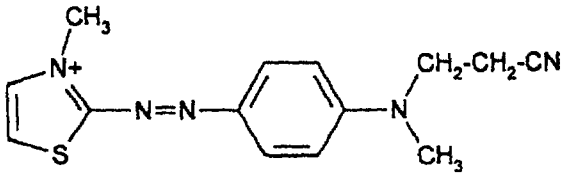
$CH_3SO_4^-$ (VI7)

;



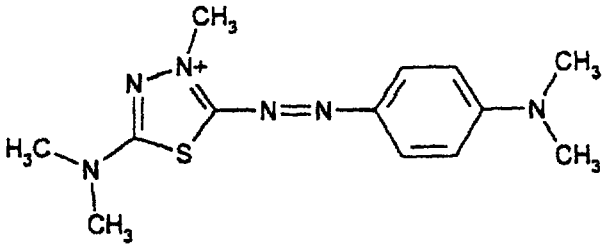
$CH_3SO_4^-$ (VI8)

;



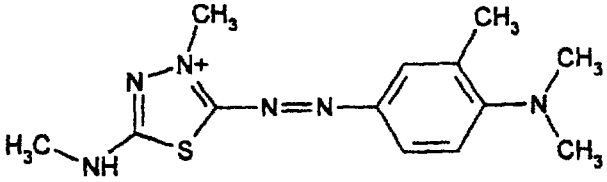
Cl^- (VI9)

;



$CH_3SO_4^-$ (VI10)

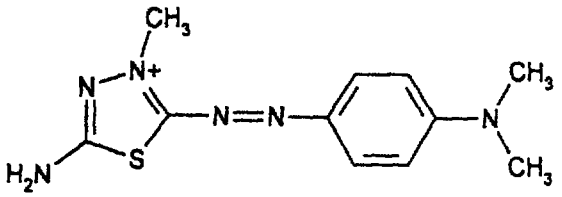
- ;



$CH_3SO_4^-$ (VI11)

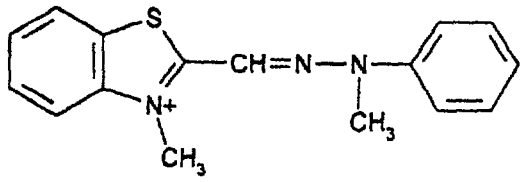
;

and



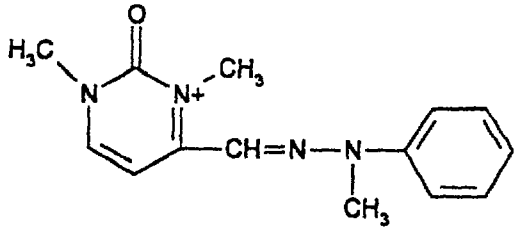
$CH_3SO_4^-$ (VII12)

Among the cationic direct dyes of formula (VII) which can be used in the ready-to-use dye compositions in accordance with the invention, mention may be made more particularly of the compounds corresponding to structures (VII1) to (VII18) below:



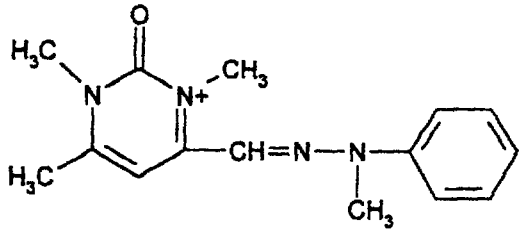
Cl^- (VII1)

;



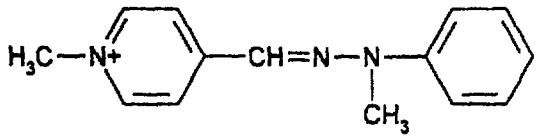
Cl^- (VII2)

;

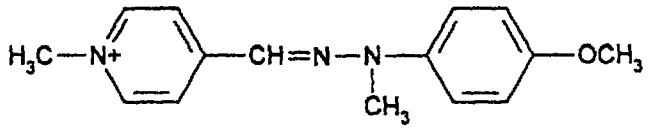


Cl^- (VII3)

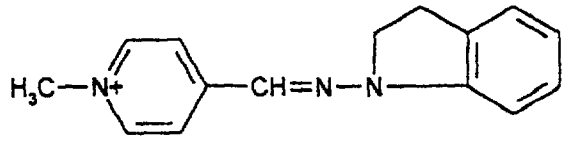
;


$CH_3SO_4^-$ (VII4)

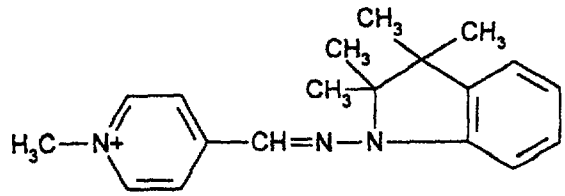
;


Cl^- (VII5)

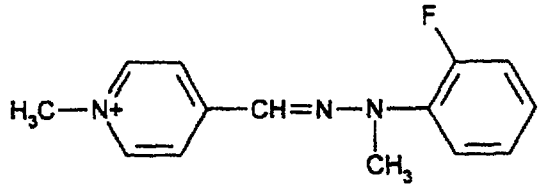
;


$CH_3SO_4^-$ (VII6)

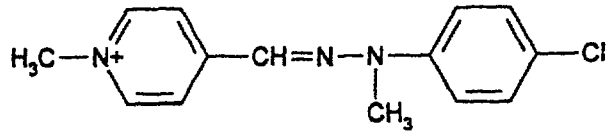
;


$CH_3SO_4^-$ (VII7)

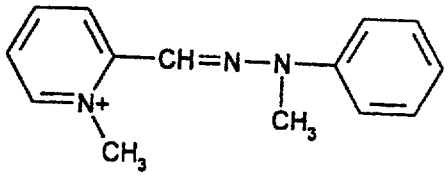
;


Cl^- (VII8)

;

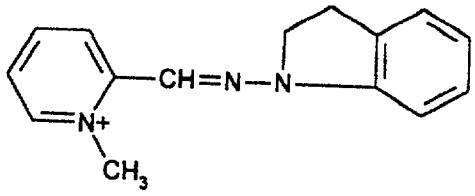

Cl^- (VII9)

;



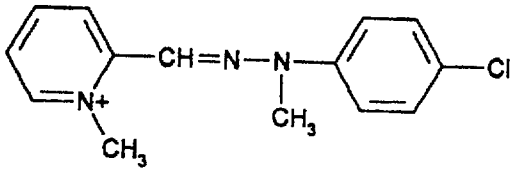
$CH_3SO_4^-$ (VII10)

;



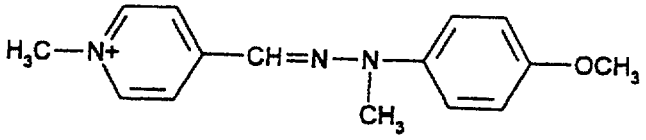
$CH_3SO_4^-$ (VII11)

;



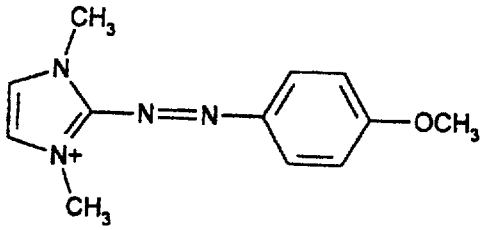
$CH_3SO_4^-$ (VII12)

;



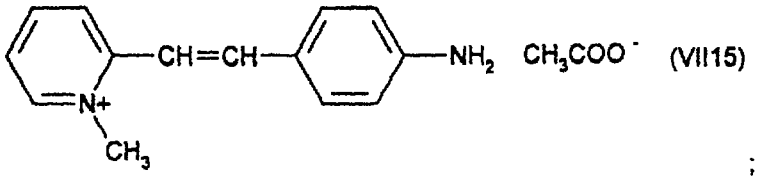
$CH_3SO_4^-$ (VII13)

;

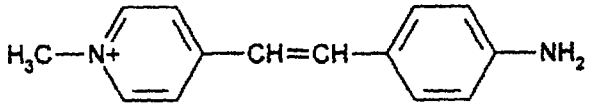


Cl^- (VII14)

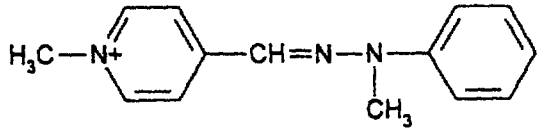
;


(VII15)

;

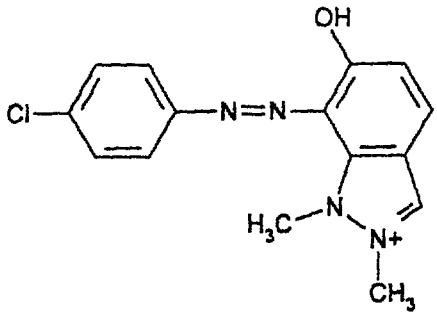

(VII16)

;


(VII17)

;

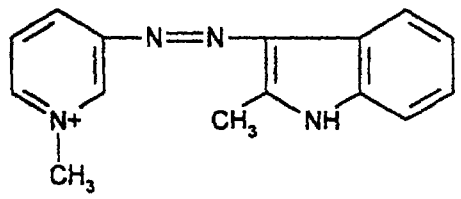
and


(VII18)

.

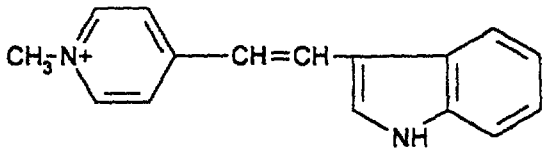
Among the specific compounds of structures (VII1) to (VII18) described above, the ones most particularly preferred are the compounds corresponding to structures (VII4), (VII5) and (VII13).

Among the cationic direct dyes of formula (VII') which can be used in the ready-to-use dye compositions in accordance with the invention, mention may be made more particularly of the compounds corresponding to structures (VII'1) to (VII'3) below:



Cl⁻ (VII'1)

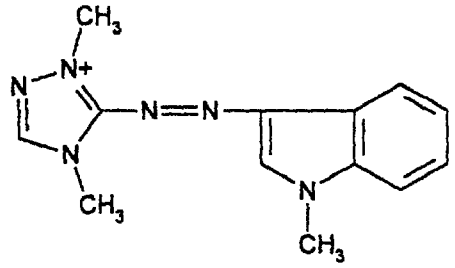
;



Cl⁻ (VII'2)

;

and



Cl⁻ (VII'3)

.

The cationic direct dye(s) used according to the invention preferably represent(s) from 0.001 to 10% by weight approximately relative to the total weight of the ready-to-use dye composition, and even more preferably from 0.05 to 5% by weight approximately relative to this weight.

The dye composition in accordance with the invention can also contain one or more couplers and/or non-cationic direct dyes, in particular in order to modify the shades or to enrich them with glints.

Among the couplers which can be present in the ready-to-use dye composition in accordance with the invention, mention may be made in particular of

meta-phenylenediamines, meta-aminophenols, meta-diphenols and heterocyclic couplers, and the addition salts thereof with an acid.

When they are present, these additional couplers preferably represent from 0.0001 to 10% by weight approximately relative to the total weight of the ready-to-use dye composition, and even more preferably from 0.005 to 5% by weight approximately relative to this weight.

In general, the addition salts with an acid which can be used in the context of the dye compositions of the invention (oxidation bases and couplers) are chosen in particular from the hydrochlorides, hydrobromides, sulphates, tartrates, lactates and acetates.

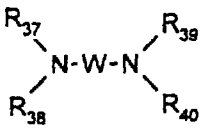
The medium which is suitable for dyeing (or support) for the ready-to-use dye composition in accordance with the invention generally consists of water or a mixture of water and at least one organic solvent to dissolve the compounds which would not be sufficiently soluble in water. By way of organic solvents, mention may be made, for example, of C_1-C_4 alkanols, such as ethanol and isopropanol; glycerol; glycols and glycol ethers such as 2-butoxyethanol, propylene glycol, propylene glycol monomethyl ether, diethylene glycol monoethyl ether and monomethyl ether, and aromatic alcohols such as benzyl alcohol or phenoxyethanol, similar products and mixtures thereof.

The solvents can be present in proportions preferably of between 1 and 40% by weight approximately relative to the total weight of the dye composition, and even more preferably between 5 and 30% by weight approximately.

The pH of the ready-to-use composition in accordance with the invention is chosen such that the enzymatic activity of the 2-electron oxidoreductase is sufficient. It is generally between 5 and 11 approximately, and preferably between 6.5 and 10 approximately. It can be adjusted to the desired value using acidifying or basifying agents usually used for dyeing keratin fibres.

Among the acidifying agents, mention may be made, by way of example, of inorganic or organic acids such as hydrochloric acid, orthophosphoric acid, sulphuric acid, carboxylic acids such as acetic acid, tartaric acid, citric acid or lactic acid, and sulphonic acids.

Among the basifying agents, mention may be made, by way of example, of aqueous ammonia, alkaline carbonates, alkanolamines such as mono-, di- and triethanolamines, 2-methyl-2-aminopropanol and derivatives thereof, sodium hydroxide, potassium hydroxide and the compounds of formula (VIII) below:



(VIII)

in which W is a propylene residue optionally substituted with a hydroxyl group or a C_1-C_4 alkyl radical; R_{37}, R_{38}, R_{39} and R_{40}, which may be identical or different, represent a hydrogen atom or a C_1-C_4 alkyl or C_1-C_4 hydroxyalkyl radical.

The ready-to-use dye composition in accordance with the invention can also contain various adjuvants used conventionally in compositions for the dyeing of the hair, such as anionic, cationic, nonionic, amphoteric or zwitterionic surfactants or mixtures thereof, anionic, cationic, nonionic, amphoteric or zwitterionic polymers or mixtures thereof, inorganic or organic thickeners, antioxidants, enzymes other than the 2-electron oxidoreductases used in accordance with the invention, such as, for example, peroxidases, penetration agents, sequestering agents, fragrances, buffers, dispersing agents, conditioners such as, for example, silicones which may or may not be volatile or modified, film-forming agents, ceramides, preserving agents and opacifiers.

Needless to say, a person skilled in the art will take care to select this or these optional complementary compound(s) such that the advantageous properties intrinsically associated with the ready-to-use dye composition in accordance with the invention are not, or are not substantially, adversely affected by the addition or additions envisaged.

The ready-to-use dye composition in accordance

with the invention can be in various forms, such as in the form of liquids, creams or gels, which may be pressurized, or in any other form which is suitable for dyeing keratin fibres, and in particular human hair. In this case the oxidation dye(s) and the 2-electron oxidoreductase(s) are present in the same ready-to-use composition, and consequently the said composition must be free of gaseous oxygen, so as to avoid any premature oxidation of the oxidation dye(s).

A subject of the invention is also a process for dyeing keratin fibres, and in particular human keratin fibres such as the hair, using the ready-to-use dye composition as defined above.

According to this process, at least one ready-to-use dye composition as defined above is applied to the fibres, for a period which is sufficient to develop the desired coloration, after which the fibres are rinsed, optionally washed with shampoo, rinsed again and dried.

The time required to develop the coloration on the keratin fibres is usually between 3 and 60 minutes and even more precisely between 5 and 40 minutes.

According to one specific embodiment of the invention, the process includes a preliminary step which consists in separately storing, on the one hand, a composition (A) comprising, in a medium which is suitable for dyeing, at least one oxidation base and at least one cationic direct dye, and, on the other hand,

a composition (B) comprising, in a medium which is suitable for dyeing, at least one enzyme of 2-electron oxidoreductase type in the presence of at least one donor for the said enzyme, and then in mixing them together at the time of use, after which this mixture is applied to the keratin fibres.

Another subject of the invention is a multi-compartment dyeing device or "kit" or any other multi-compartment packaging system, a first compartment of which comprises composition (A) as defined above and a second compartment of which comprises composition (B) as defined above. These devices can be equipped with means for delivering the desired mixture onto the hair, such as the devices described in patent FR-2,586,913 in the name of the Applicant.

The examples which follow are intended to illustrate the invention without, however, limiting its scope.

EXAMPLES

DYEING EXAMPLES 1 to 3

The ready-to-use dye compositions below were prepared (contents in grams):

COMPOSITION	1	2	3
para-Phenylenediamine (oxidation base)	0.7	-	0.36
Red cationic direct dye of structure (V1)	0.6	-	-
para-Aminophenol (oxidation base)	-	0.187	-
5-N-(β-Hydroxyethyl)amino-2-methyl-phenol (coupler)	-	0.21	0.36
Orange cationic direct dye of structure (V4)	-	0.065	-
Cationic direct dye: Basic Red 76 (Arianor Madder Red)	-	-	0.12
Uricase from Arthrobacter globiformis, at 20 international units (I.U.)/mg, sold by the company Sigma	1.5	1.5	1.5
Uric acid	1.5	1.5	1.5
Common dye support (*)	(*)	(*)	(*)
Demineralized water qs	100 g	100 g	100 g

(*): Common dye support:

- Ethanol 20.0 g
- Hydroxyethylcellulose sold under the name Natrosol 250 HR® by the company Aqualon 1.0 g
- Poly(C_8-C_{10})alkylglucoside as an aqueous solution containing 60% active material (A.M.)

buffered with ammonium citrate (0.5%), sold under the name Oramix CG110® by the company SEPPIC 8.0 g

- Monoethanolamine qs pH = 9.5

Each of the ready-to-use dye compositions described above was applied to locks of natural grey hair containing 90% white hairs, for 30 minutes. The hair was then rinsed, washed with a standard shampoo and then dried.

The hair was dyed in the shades given in the table below:

EXAMPLE	Shade obtained
1	Intense red
2	Red-copper light blonde
3	Red-purple blonde

CLAIMS

1. Ready-to-use composition for the oxidation dyeing of keratin fibres, and in particular human keratin fibres such as the hair, characterized in that it comprises, in a medium which is suitable for dyeing:

- at least one oxidation base,
- at least cationic direct dye,
- at least one enzyme of 2-electron oxidoreductase type, and
- at least one donor for the said enzyme.

2. Composition according to Claim 1, characterized in that the 2-electron oxidoreductase is chosen from pyranose oxidases, glucose oxidases, glycerol oxidases, lactate oxidases, pyruvate oxidases and uricases.

3. Composition according to either of Claims 1 and 2, characterized in that the 2-electron oxidoreductase is chosen from uricases of animal, microbiological or biotechnological origin.

4. Composition according to any one of the preceding claims, characterized in that the 2-electron oxidoreductase(s) represent(s) from 0.01 to 20% by weight relative to the total weight of the ready-to-use dye composition.

5. Composition according to Claim 4, characterized in that the 2-electron oxidoreductase(s) represent(s) from 0.1 to 5% by weight relative to the



total weight of the ready-to-use dye composition.

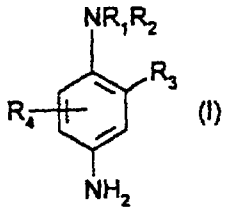
6. Composition according to Claim 3, characterized in that the donor (or substrate) for the said 2-electron oxidoreductase is chosen from uric acid and its salts.

7. Composition according to any one of the preceding claims, characterized in that the donor(s) represent(s) from 0.01 to 20% by weight relative to the total weight of the ready-to-use dye composition.

8. Composition according to Claim 7, characterized in that the donor(s) represent(s) from 0.1 to 5% by weight relative to the total weight of the ready-to-use dye composition.

9. Composition according to any one of the preceding claims, characterized in that the oxidation base(s) is (are) chosen from para-phenylenediamines, double bases, para-aminophenols, ortho-aminophenols and heterocyclic oxidation bases.

10. Composition according to Claim 9, characterized in that the para-phenylenediamines are chosen from the compounds of formula (I) below, and the addition salts thereof with an acid:



(I)

in which:

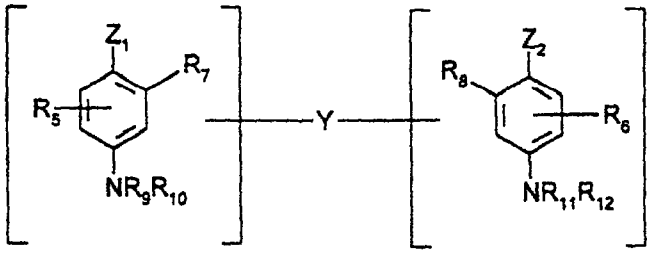
- R_1 represents a hydrogen atom, a C_1-C_4 alkyl radical, a C_1-C_4 monohydroxyalkyl radical, a C_2-C_4 polyhydroxyalkyl radical, a (C_1-C_4)alkoxy(C_1-C_4)alkyl radical, a C_1-C_4 alkyl radical substituted with a nitrogenous group, a phenyl radical or a 4'-aminophenyl radical;
- R_2 represents a hydrogen atom, a C_1-C_4 alkyl radical, a C_1-C_4 monohydroxyalkyl radical, a C_2-C_4 polyhydroxyalkyl radical, a (C_1-C_4)alkoxy(C_1-C_4)alkyl radical or a C_1-C_4 alkyl radical substituted with a nitrogenous group;
- R_3 represents a hydrogen atom, a halogen atom such as a chlorine, bromine, iodine or fluorine atom, a C_1-C_4 alkyl radical, a C_1-C_4 monohydroxyalkyl radical, a C_1-C_4 hydroxyalkoxy radical, an acetylamino(C_1-C_4)-alkoxy radical, a C_1-C_4 mesylaminoalkoxy radical or a carbamoylamino(C_1-C_4)alkoxy radical,
- R_4 represents a hydrogen or halogen atom or a C_1-C_4 alkyl radical.

11. Composition according to Claim 10, characterized in that the para-phenylenediamines of formula (I) are chosen from para-phenylenediamine, para-toluylenediamine, 2-chloro-para-phenylenediamine, 2,3-dimethyl-para-phenylenediamine, 2,6-dimethyl-para-phenylenediamine, 2,6-diethyl-para-phenylenediamine, 2,5-dimethyl-para-phenylenediamine, N,N-dimethyl-para-phenylenediamine, N,N-diethyl-para-phenylenediamine, N,N-dipropyl-para-phenylenediamine, 4-amino-N,N-diethyl-3-methylaniline, N,N-bis(β-hydroxyethyl)-

* C L M S *

para-phenylenediamine, 4-amino-N,N-bis(β-hydroxyethyl)-2-methylaniline, 4-amino-2-chloro-N,N-bis(β-hydroxyethyl)aniline, 2-β-hydroxyethyl-para-phenylenediamine, 2-fluoro-para-phenylenediamine, 2-isopropyl-para-phenylenediamine, N-(β-hydroxypropyl)-para-phenylenediamine, 2-hydroxymethyl-para-phenylenediamine, N,N-dimethyl-3-methyl-para-phenylenediamine, N,N-(ethyl-β-hydroxyethyl)-para-phenylenediamine, N-(β,γ-dihydroxypropyl)-para-phenylenediamine, N-(4'-aminophenyl)-para-phenylenediamine, N-phenyl-para-phenylenediamine, 2-β-hydroxyethyloxy-para-phenylenediamine, 2-β-acetylaminoethyloxy-para-phenylenediamine and N-(β-methoxyethyl)-para-phenylenediamine, and the addition salts thereof with an acid.

12. Composition according to Claim 9, characterized in that the double bases are chosen from the compounds of formula (II), and the addition salts thereof with an acid:



(II)

in which:

- Z_1 and Z_2, which may be identical or different, represent a hydroxyl or $-NH_2$ radical which may be

* C L M S *

substituted with a C_1-C_4 alkyl radical or with a linker arm Y;

- the linker arm Y represents a linear or branched alkylene chain containing from 1 to 14 carbon atoms, which may be interrupted by or terminated with one or more nitrogenous groups and/or one or more hetero atoms such as oxygen, sulphur or nitrogen atoms, and optionally substituted with one or more hydroxyl or C_1-C_6 alkoxy radicals;

- R_5 and R_6 represent a hydrogen or halogen atom, a C_1-C_4 alkyl radical, a C_1-C_4 monohydroxyalkyl radical, a C_2-C_4 polyhydroxyalkyl radical, a C_1-C_4 aminoalkyl radical or a linker arm Y;

- R_7, R_8, R_9, R_{10}, R_{11} and R_{12}, which may be identical or different, represent a hydrogen atom, a linker arm Y or a C_1-C_4 alkyl radical;

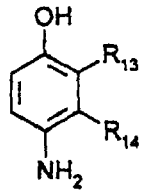
it being understood that the compounds of formula (II) contain only one linker arm Y per molecule.

13. Composition according to Claim 12, characterized in that the double bases of formula (II) are chosen from N,N'-bis(β-hydroxyethyl)-N,N'-bis(4'-aminophenyl)-1,3-diaminopropanol, N,N'-bis(β-hydroxyethyl)-N,N'-bis(4'-aminophenyl)ethylenediamine, N,N'-bis(4-aminophenyl)tetramethylenediamine, N,N'-bis(β-hydroxyethyl)-N,N'-bis(4-aminophenyl)-tetramethylenediamine, N,N'-bis(4-methylaminophenyl)-tetramethylenediamine, N,N'-bis(ethyl)-N,N'-bis(4'-amino-3'-methylphenyl)ethylenediamine and



1,8-bis(2,5-diaminophenoxy)-3,5-dioxaoctane, and the addition salts thereof with an acid.

14. Composition according to Claim 9, characterized in that the para-aminophenols are chosen from the compounds of formula (III), and the addition salts thereof with an acid:



(III)

in which:

- R_{13} represents a hydrogen or halogen atom or a C_1-C_4 alkyl, C_1-C_4 monohydroxyalkyl, (C_1-C_4)alkoxy(C_1-C_4)alkyl, C_1-C_4 aminoalkyl or hydroxy(C_1-C_4)alkylamino(C_1-C_4)alkyl radical,

- R_{14} represents a hydrogen or halogen atom or a C_1-C_4 alkyl, C_1-C_4 monohydroxyalkyl, C_2-C_4 polyhydroxyalkyl, C_1-C_4 aminoalkyl, C_1-C_4 cyanoalkyl or (C_1-C_4)alkoxy-(C_1-C_4)alkyl radical,

it being understood that at least one of the radicals R_{13} or R_{14} represents a hydrogen atom.

15. Composition according to Claim 14, characterized in that the para-aminophenols of formula (III) are chosen from para-aminophenol, 4-amino-3-methylphenol, 4-amino-3-fluorophenol, 4-amino-3-hydroxymethylphenol, 4-amino-2-methylphenol, 4-amino-2-hydroxymethylphenol, 4-amino-2-methoxymethylphenol, 4-amino-2-aminomethylphenol,

4-amino-2-(β-hydroxyethylaminomethyl)phenol and 4-amino-2-fluorophenol, and the addition salts thereof with an acid.

16. Composition according to Claim 9, characterized in that the ortho-aminophenols are chosen from 2-aminophenol, 2-amino-5-methylphenol, 2-amino-6-methylphenol and 5-acetamido-2-aminophenol, and the addition salts thereof with an acid.

17. Composition according to Claim 9, characterized in that the heterocyclic oxidation bases are chosen from pyridine derivatives, pyrimidine derivatives, pyrazole derivatives and pyrazolo-pyrimidine derivatives, and the addition salts thereof with an acid.

18. Composition according to any one of the preceding claims, characterized in that the oxidation base(s) represent(s) from 0.0005 to 12% by weight relative to the total weight of the dye composition.

19. Composition according to Claim 18, characterized in that the oxidation base(s) represent(s) from 0.005 to 6% by weight relative to the total weight of the dye composition.

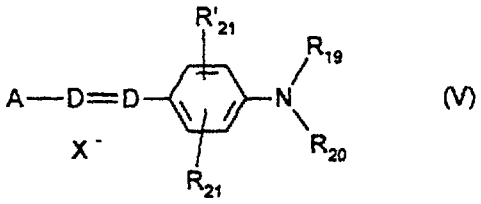
20. Composition according to any one of the preceding claims, characterized in that the cationic direct dye(s) is (are) chosen from cationic aminoanthraquinone dyes, cationic monoazo or diazo dyes and cationic naphthoquinone dyes.



21. Composition according to Claim 20, characterized in that the cationic direct dye(s) is (are) chosen from [8-[(p-aminophenyl)azol]-7-hydroxy-2-naphthyl]trimethylammonium chloride, 3-[(4-amino-6-bromo-5,8-dihydro-1-hydroxy-8-imino-5-oxo-2-naphthalenyl)amino]-N,N,N-trimethylbenzenaminium chloride, 7-hydroxy-8-[(2-methoxyphenyl)azo]-N,N,N-trimethyl-2-naphthalenaminium chloride, [8-[(4-amino-2-nitrophenyl)azo]-7-hydroxy-2-naphthyl]-trimethylammonium chloride and 3-[(4,5-dihydro-3-methyl-5-oxo-1-phenyl-1H-pyrazol-4-yl)azo]-N,N,N-trimethylbenzenaminium chloride.

22. Composition according to any one of Claims 1 to 19, characterized in that the cationic direct dye(s) is (are) chosen from:

a) the compounds of formula (V) below:



(V)

in which:

D represents a nitrogen atom or a -CH group,

R_{19} and R_{20}, which may be identical or different, represent a hydrogen atom; a C_1-C_4 alkyl radical which can be substituted with a -CN, -OH or -NH_2 radical or form, with a carbon atom of the benzene ring, an optionally oxygenated or nitrogenous heterocycle, which

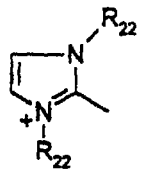
can be substituted with one or more C_1-C_4 alkyl radicals; a 4'-aminophenyl radical,

R_{21} and R'_{21}, which may be identical or different, represent a hydrogen atom, a halogen atom chosen from chlorine, bromine, iodine and fluorine, or a cyano, C_1-C_4 alkoxy or acetyloxy radical,

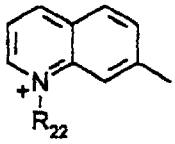
X^- represents an anion preferably chosen from chloride, methyl sulphate and acetate,

A represents a group chosen from structures A1 to A19 below:

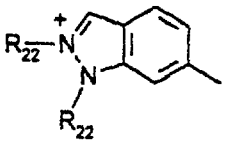
* C L M S *



A_1 ;



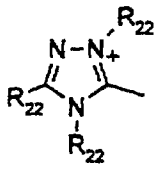
A_2 ;



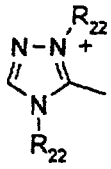
A_3 ;



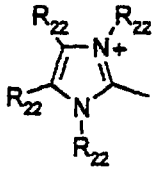
A_4 ;



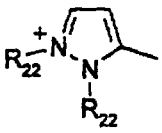
A_5 ;



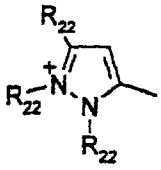
A_6 ;



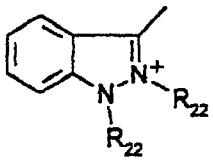
A_7 ;



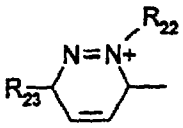
A_8 ;



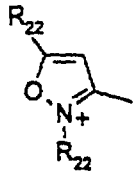
A_9 ;



A_{10} ;

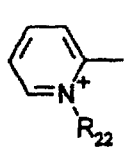


A_{11} ;

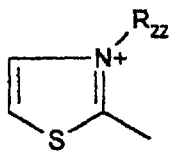


A_{12} ;

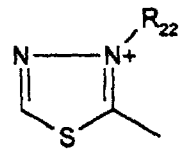
* C L M S *



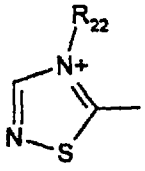
A_{13} ;



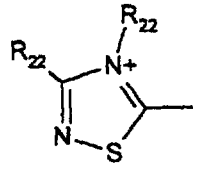
A_{14} ;



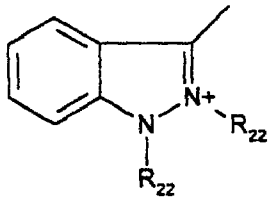
A_{15} ;



A_{16} ;

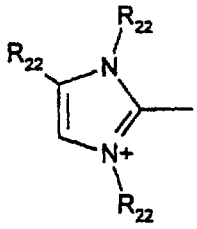


A_{17} ;



A_{18}

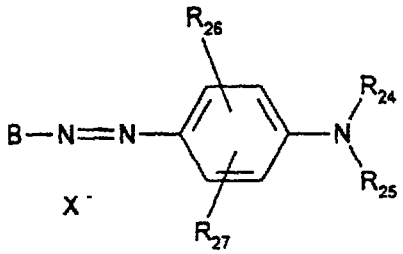
and



A_{19} ;

in which R_{22} represents a C_1-C_4 alkyl radical which can be substituted with a hydroxyl radical and R_{23} represents a C_1-C_4 alkoxy radical;

b) the compounds of formula (VI) below:



(IV)

in which:

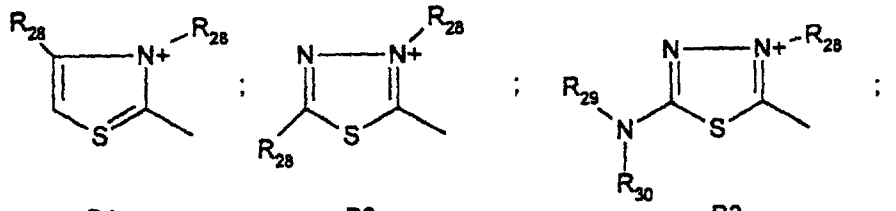
R_{24} represents a hydrogen atom or a C_1-C_4 alkyl radical,

R_{25} represents a hydrogen atom, an alkyl radical which can be substituted with a -CN radical or with an amino group, a 4'-aminophenyl radical or forms, with R_{24}, an optionally oxygenated and/or nitrogenous heterocycle which can be substituted with a C_1-C_4 alkyl radical,

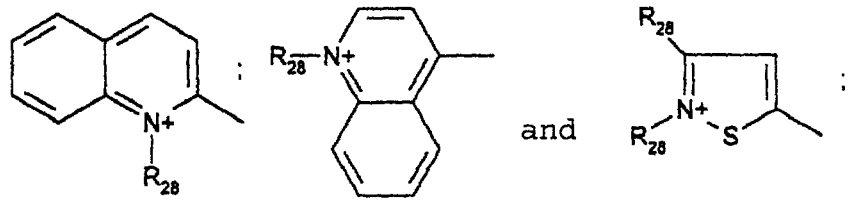
R_{26} and R_{27}, which may be identical or different, represent a hydrogen atom, a halogen atom such as bromine, chlorine, iodine or fluorine, a C_1-C_4 alkyl or C_1-C_4 alkoxy radical or a -CN radical,

X^- represents an anion preferably chosen from chloride, methyl sulphate and acetate,

B represents a group chosen from structures B1 to B6 below:



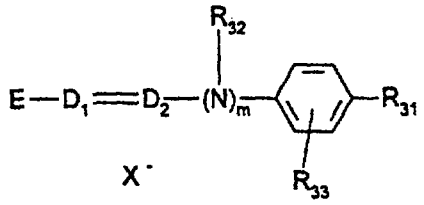
B1 B2 B3



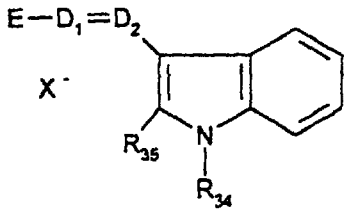
B4 B5 and B6

in which R_{28} represents a C_1-C_4 alkyl radical, R_{29} and R_{30}, which may be identical or different, represent a hydrogen atom or a C_1-C_4 alkyl radical;

c) the compounds of formulae (VII) and (VII') below:



(VII)



(VII')

in which:

R_{31} represents a hydrogen atom, a C_1-C_4 alkoxy radical, a halogen atom such as bromine, chlorine, iodine or fluorine, or an amino radical,

R_{32} represents a hydrogen atom, a C_1-C_4 alkyl radical or forms, with a carbon atom of the benzene ring, a heterocycle which is optionally oxygenated and/or substituted with one or more C_1-C_4 alkyl groups,

R_{33} represents a hydrogen atom or a halogen atom such as bromine, chlorine, iodine or fluorine,

R_{34} and R_{35}, which may be identical or different, represent a hydrogen atom or a C_1-C_4 alkyl radical,

D_1 and D_2, which may be identical or different, represent a nitrogen atom or a -CH group,

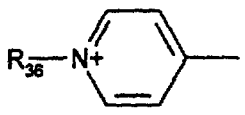
m = 0 or 1,

it being understood that when R_{31} represents an unsubstituted amino group, then D_1 and D_2 simultaneously represent a -CH group and m = 0,

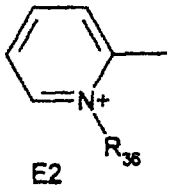
X^- represents an anion preferably chosen from chloride, methyl sulphate and acetate,

E represents a group chosen from structures E1 to E8 below:

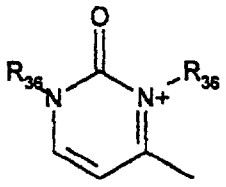
CLMS



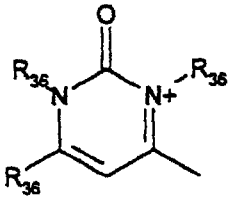
E1 ;



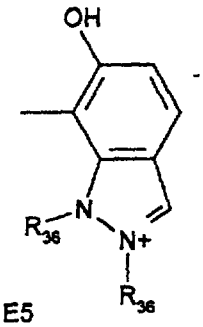
E2 ;



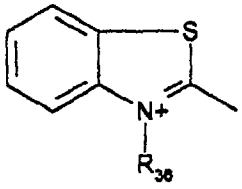
E3 ;



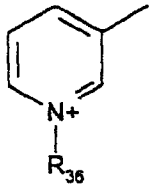
E4 ;



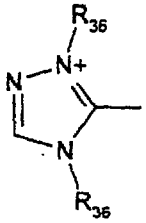
E5 ;



E6 ;



E7 and

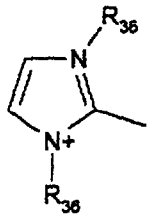


E8 ;

in which R_{36} represents a C_1-C_4 alkyl radical;

when m = 0 and when D_1 represents a nitrogen atom, then E can also denote a group of structure E9 below:

E9



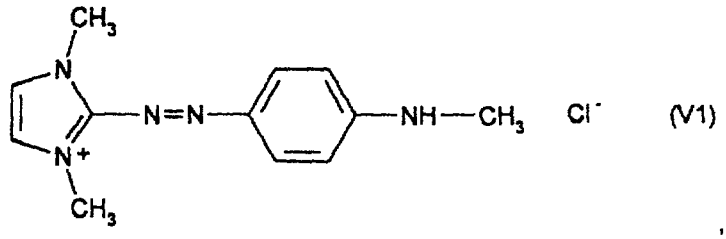
;

in which R_{36} represents a C_1-C_4 alkyl radical.

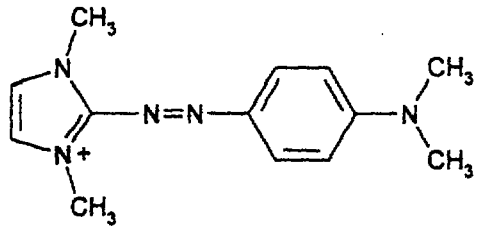
23. Composition according to Claim 22, characterized in that the cationic direct dyes of

* C L M S *

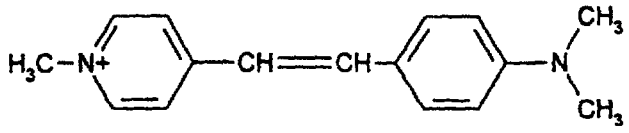
formula (V) are chosen from the compounds corresponding to structures (V1) to (V52) below:



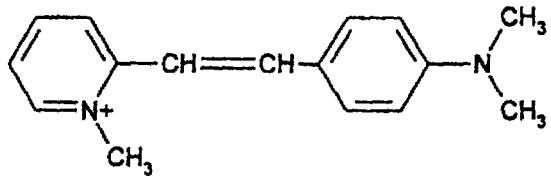
(V1)



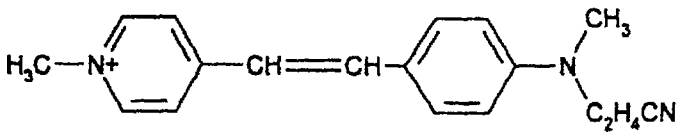
(V2)



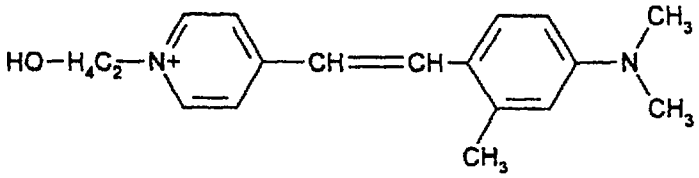
(V3)



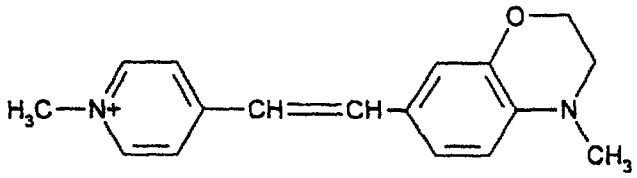
(V4)



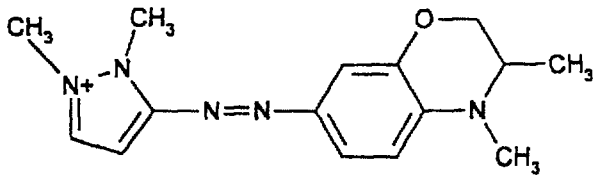
Cl^- (V5)



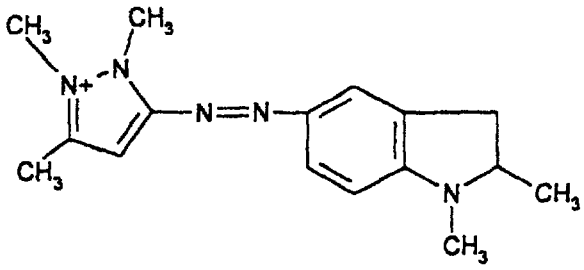
Cl^- (V6)



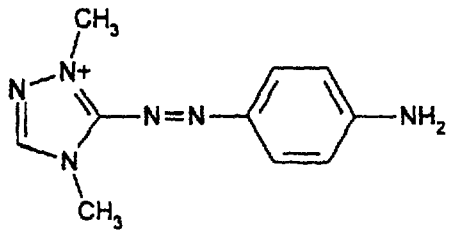
Cl^- (V7)



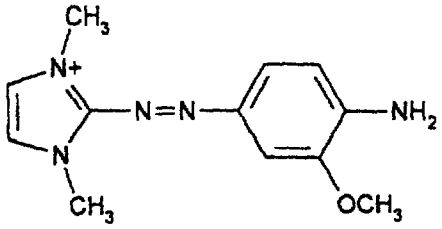
Cl^- (V8)



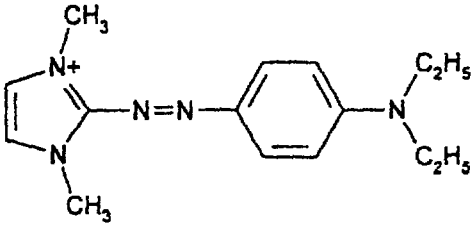
Cl^- (V9)



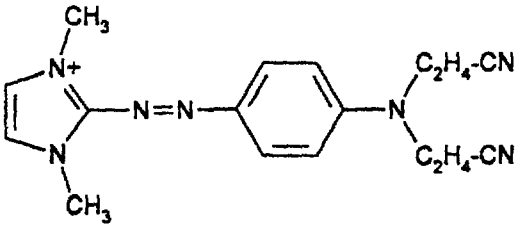
Cl^- (V10)



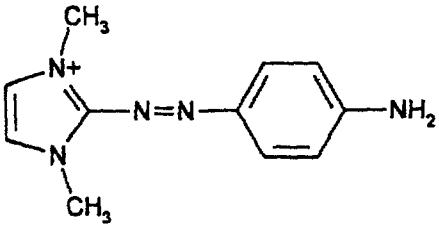
Cl^- (V11)



Cl^- (V12)

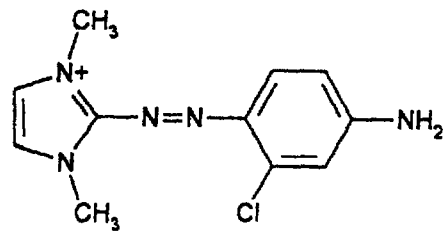


Cl^- (V13)

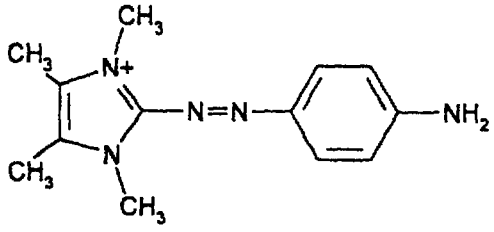


Cl^- (V14)

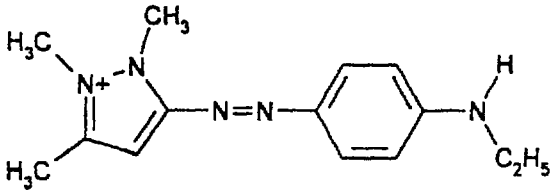
* C L M S *



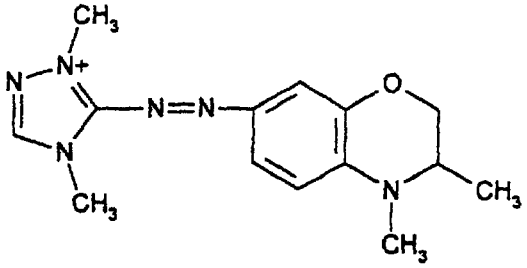
Cl^- (V15)



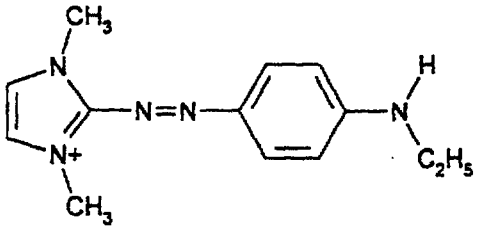
Cl^- (V16)



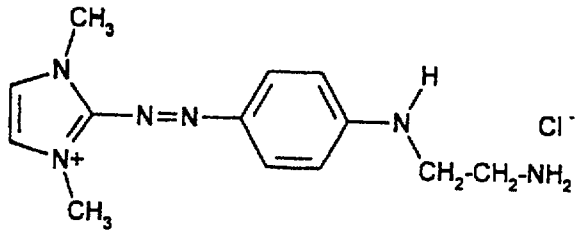
Cl^- (V17)



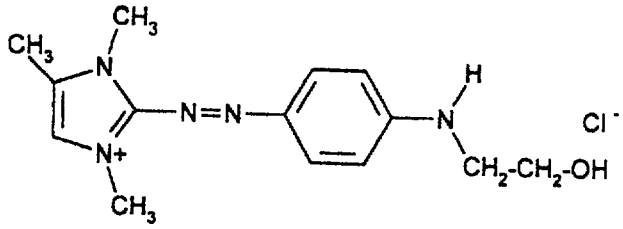
Cl^- (V18)



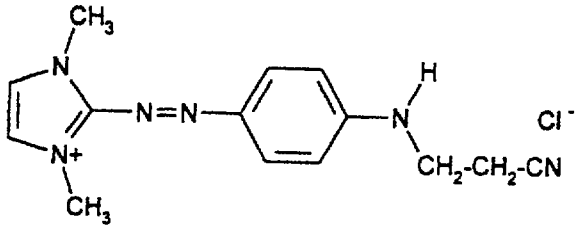
Cl^- (V19)



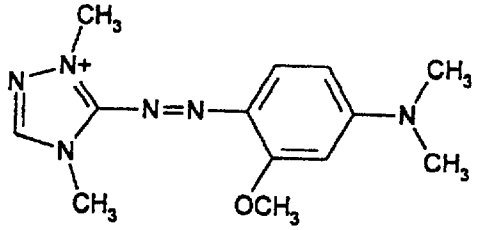
(V20)



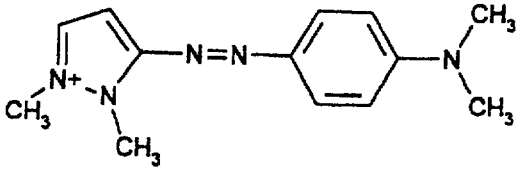
(V21)



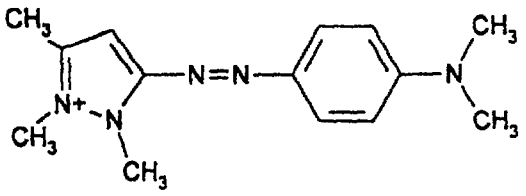
(V22)



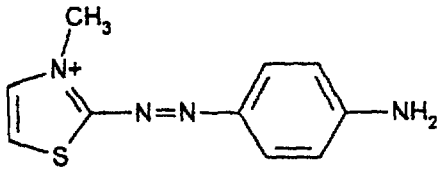
(V23)



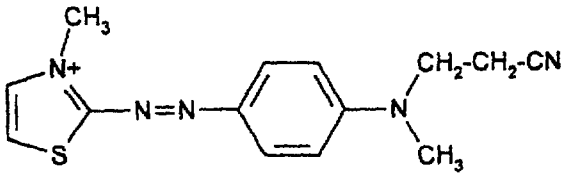
(V24)



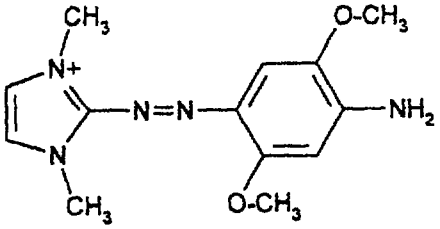
Cl^- (V25)



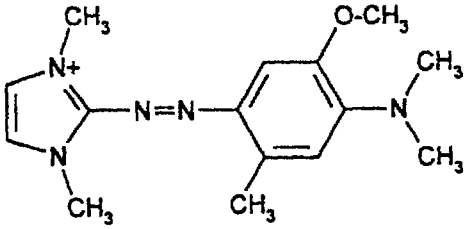
Cl^- (V26)



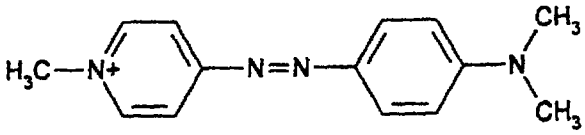
Cl^- (V27)



Cl^- (V28)

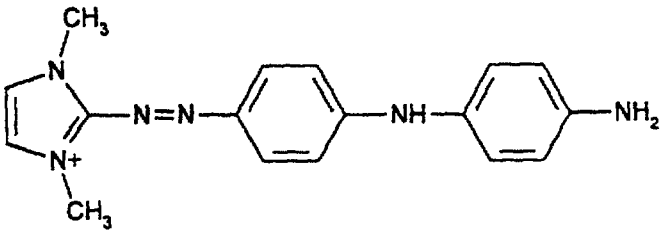


Cl^- (V29)

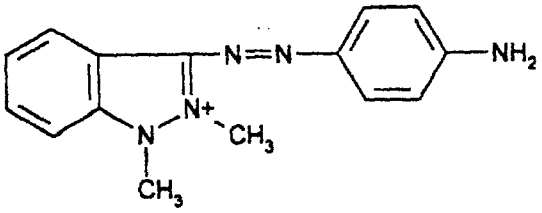


Cl^- (V30)

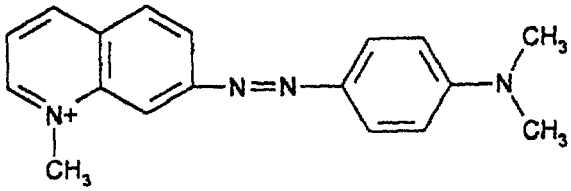
* C L M S *



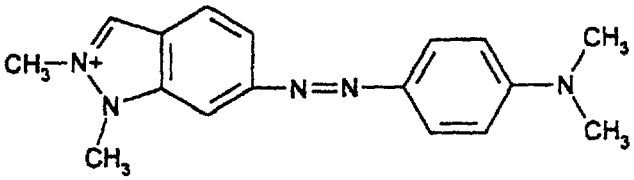
Cl^- (V31)



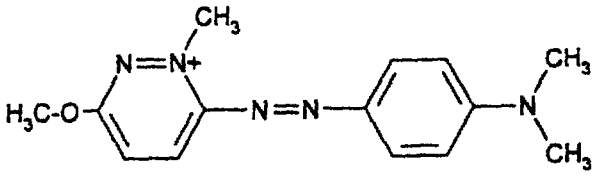
Cl^- (V32)



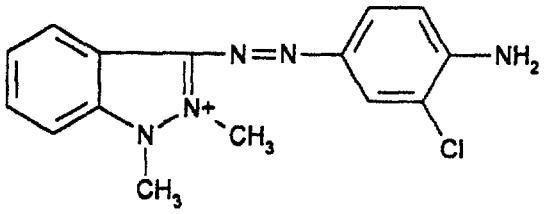
Cl^- (V33)



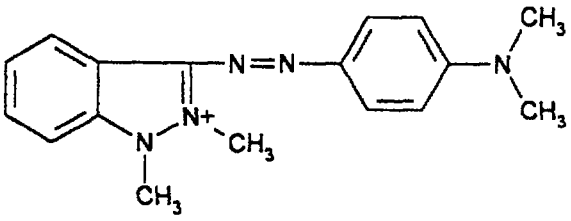
Cl^- (V34)



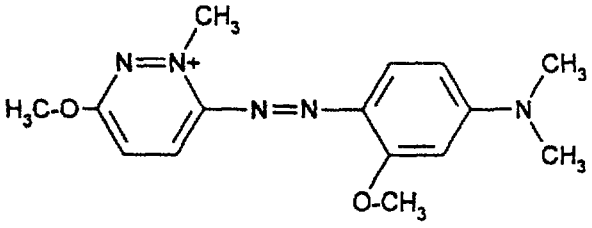
Cl^- (V35)



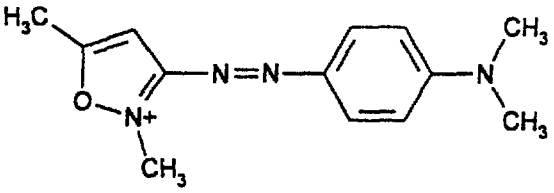
Cl⁻ (V36)



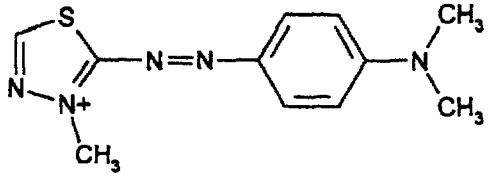
Cl⁻ (V37)



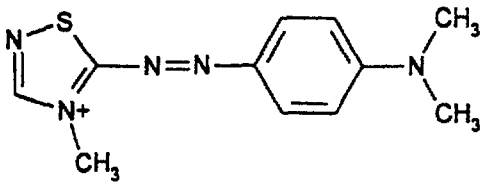
Cl⁻ (V38)



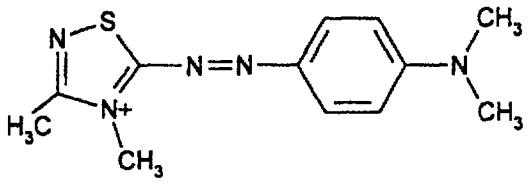
Cl⁻ (V39)



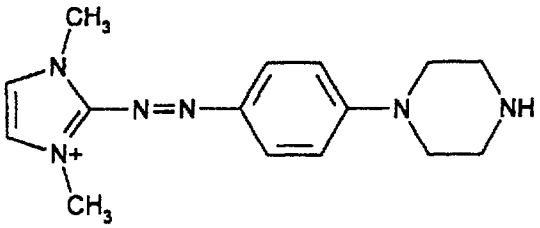
Cl⁻ (V40)



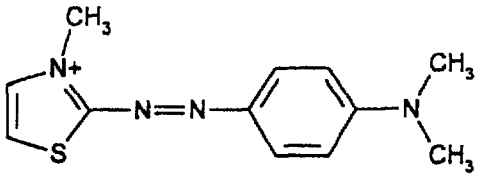
Cl⁻ (V41)



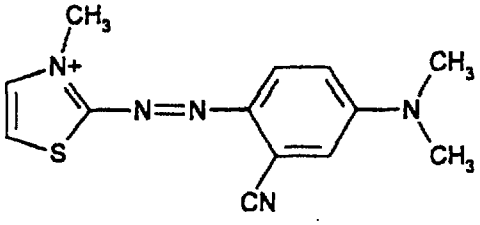
Cl⁻ (V42)



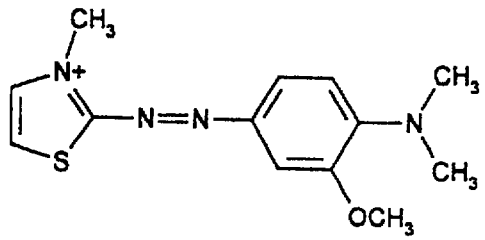
Cl⁻ (V43)



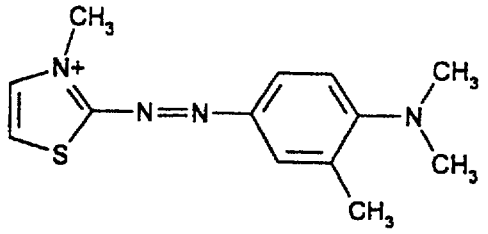
Cl⁻ (V44)



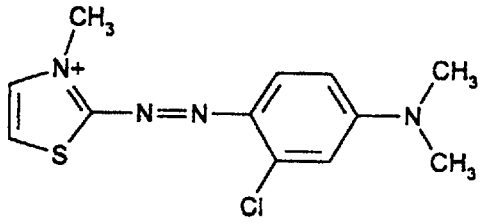
Cl⁻ (V45)



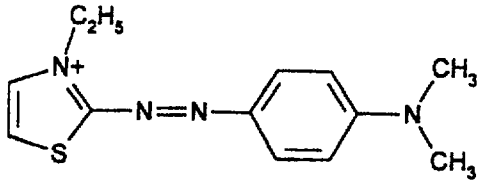
Cl^- (V46)



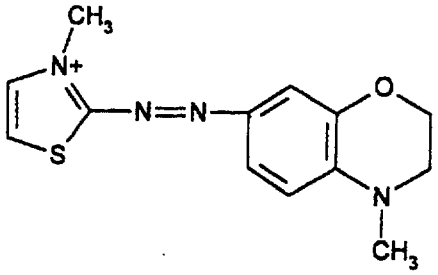
Cl^- (V47)



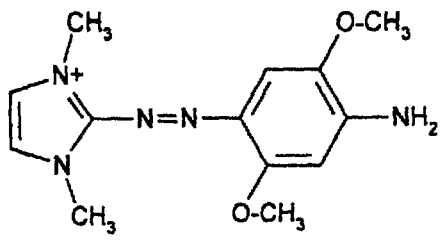
$CH_3SO_4^-$ (V48)



$CH_3SO_4^-$ (V49)

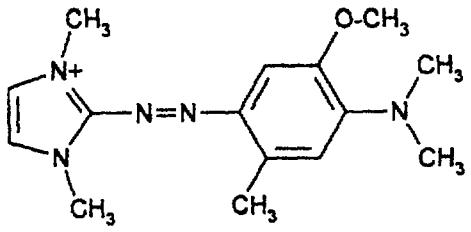


Cl^- (V50)



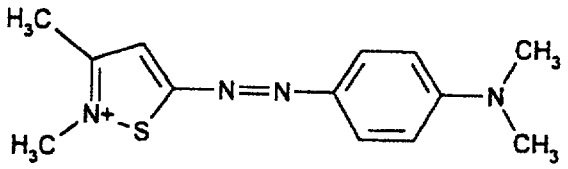
Cl⁻ (V51)

and



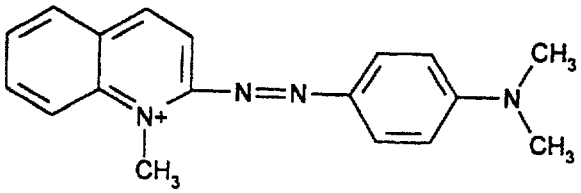
Cl⁻ (V52)

24. Composition according to Claim 22, characterized in that the cationic direct dyes of formula (VI) are chosen from the compounds corresponding to structures (VI1) to (VI12) below:



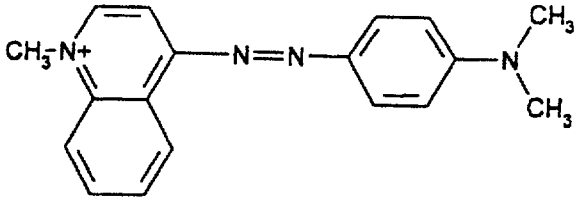
(VI1)

;



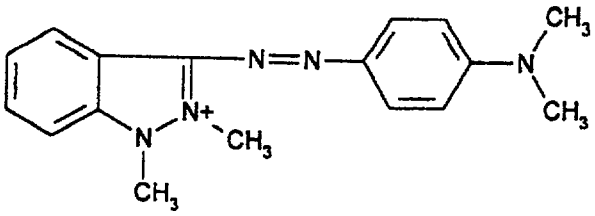
(VI2)

;



(VI3)

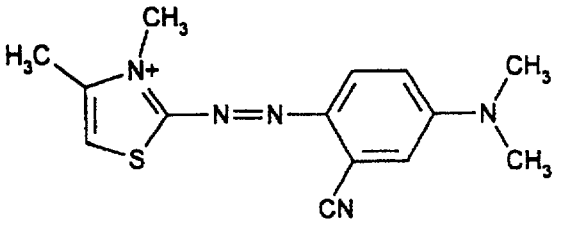
;



(VI4)

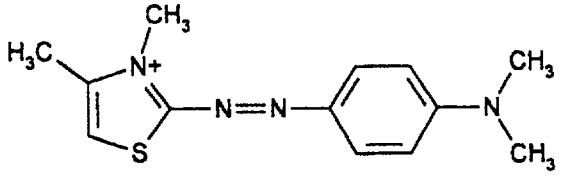
;





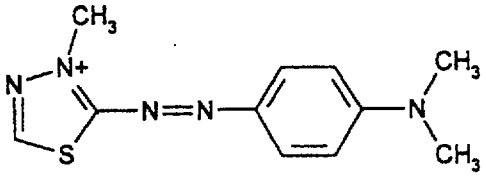
Cl^- (VI5)

;



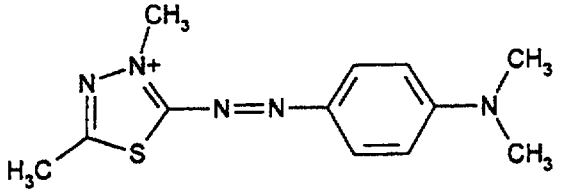
$CH_3SO_4^-$ (VI6)

;



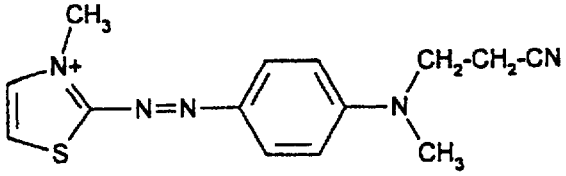
$CH_3SO_4^-$ (VI7)

;



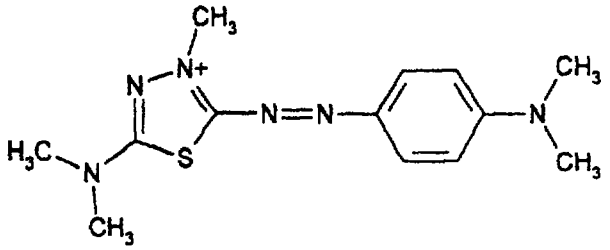
$CH_3SO_4^-$ (VI8)

;



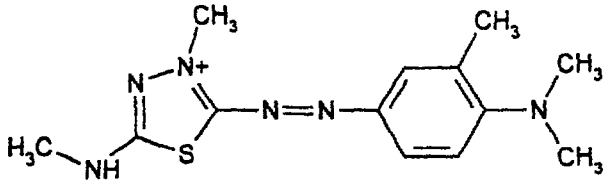
Cl^- (VI9)

;



$CH_3SO_4^-$ (VI10)

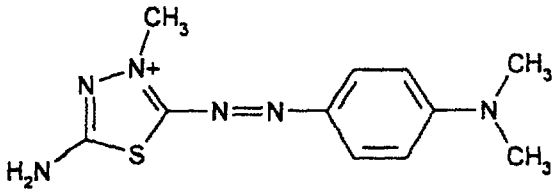
;



$CH_3SO_4^-$ (VI11)

;

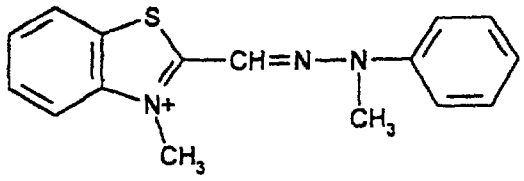
and



$CH_3SO_4^-$ (VI12)

.

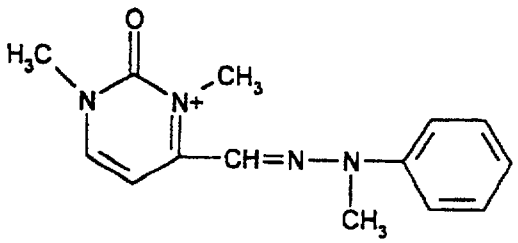
25. Composition according to Claim 22, characterized in that the cationic direct dyes of formula (VII) are chosen from the compounds corresponding to structures (VII1) to (VII18) below:



Cl^- (VII1)

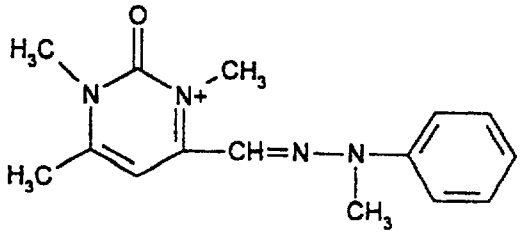
;





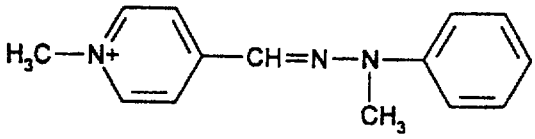
Cl⁻ (VII2)

;



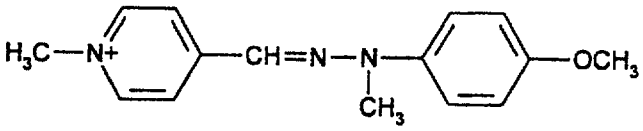
Cl⁻ (VII3)

;



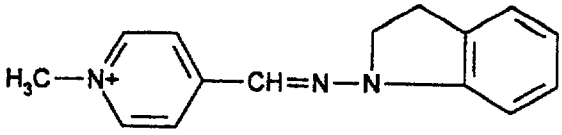
$CH_3SO_4^-$ (VII4)

;



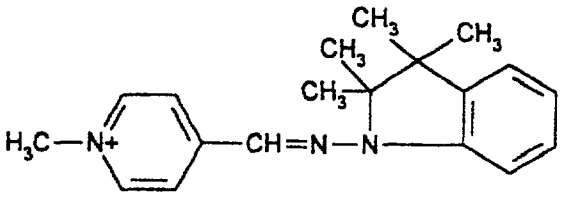
Cl⁻ (VII5)

;



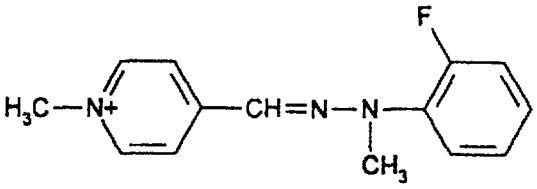
$CH_3SO_4^-$ (VII6)

;



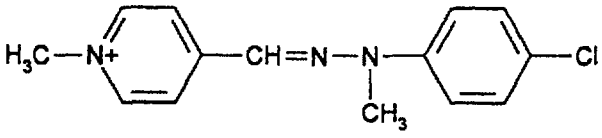
$CH_3SO_4^-$ (VII7)

;



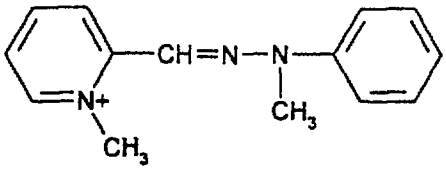
Cl^- (VII8)

;



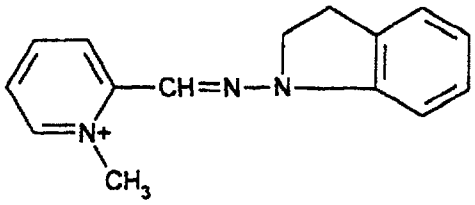
Cl^- (VII9)

;



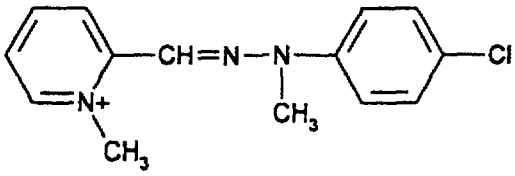
$CH_3SO_4^-$ (VII10)

;



$CH_3SO_4^-$ (VII11)

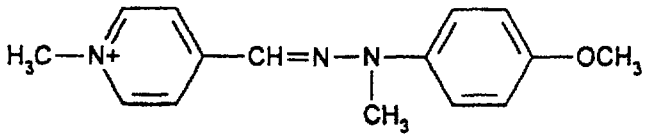
;



$CH_3SO_4^-$ (VII12)

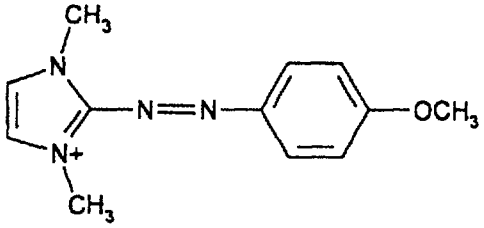
;

CLMS



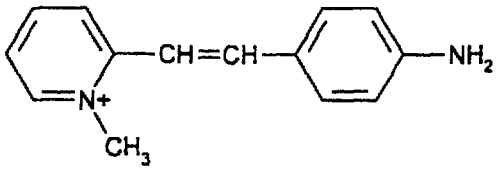
(VII13)

;



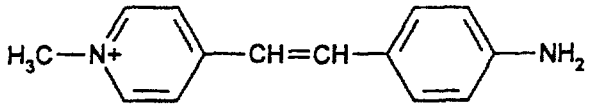
(VII14)

;



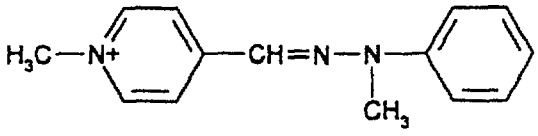
(VII15)

;



(VII16)

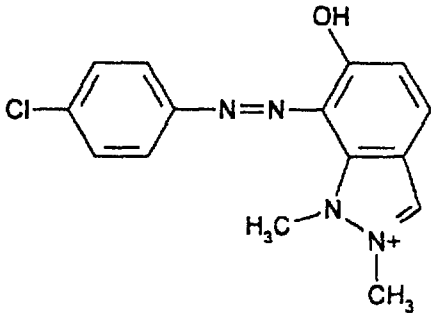
;



(VII17)

;

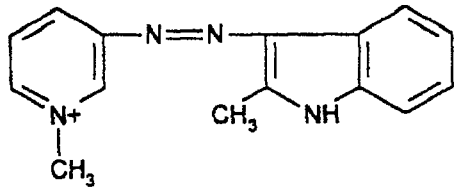
and



(VII18)

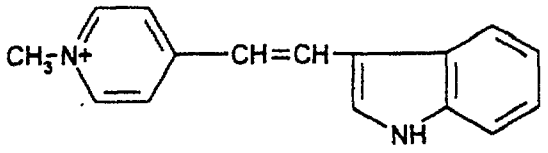
.

26. Composition according to Claim 22, characterized in that the cationic direct dyes of formula (VII') are chosen from the compounds corresponding to structures (VII'1) to (VII'3) below:



Cl⁻ (VII'1)

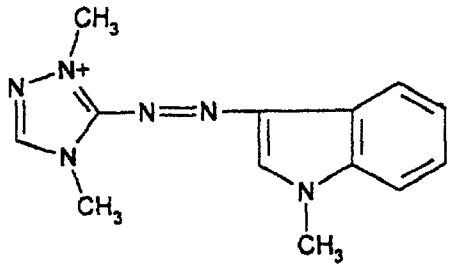
;



Cl⁻ (VII'2)

;

and



Cl⁻ (VII'3)

.

27. Composition according to any one of the preceding claims, characterized in that the cationic direct dye(s) represent(s) from 0.001 to 10% by weight relative to the total weight of the ready-to-use dye composition.

28. Composition according to Claim 27, characterized in that the cationic direct dye(s) represent(s) from 0.05 to 5% by weight relative to the total weight of the ready-to-use dye composition.

29. Composition according to any one of the

preceding claims, characterized in that the addition salts with an acid are chosen from the hydrochlorides, hydrobromides, sulphates, tartrates, lactates and acetates.

30. Composition according to any one of the preceding claims, characterized in that the medium which is suitable for dyeing consists of water or a mixture of water and at least one organic solvent.

31. Composition according to any one of the preceding claims, characterized in that it has a pH of between 5 and 11.

32. Composition according to any one of the preceding claims, characterized in that it contains at least one peroxidase.

33. Process for dyeing keratin fibres, and in particular human keratin fibres such as the hair, characterized in that at least one ready-to-use dye composition as defined in any one of the preceding claims is applied to the said fibres, for a period which is sufficient to develop the desired coloration.

34. Process according to Claim 33, characterized in that it includes a preliminary step which consists in separately storing, on the one hand, a composition (A) comprising, in a medium which is suitable for dyeing, at least one oxidation base and at least one cationic direct dye, and, on the other hand, a composition (B) comprising, in a medium which is suitable for dyeing, at least one enzyme of 2-electron

oxidoreductase type in the presence of at least one donor for the said enzyme, and then in mixing them together at the time of use, after which this mixture is applied to the keratin fibres.

35. Multi-compartment dyeing device or "kit", characterized in that it includes a first compartment comprising composition (A) as defined in Claim 34 and a second compartment comprising composition (B) as defined in Claim 34.

