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(54) Title: DYEING COMPOSITION FOR KERATIN FIBRES AND DYEING METHOD USING SAME

(54) Titre: COMPOSITION DE TEINTURE DES FIBRES KERATINIQUES ET PROCEDE DE TEINTURE METTANT EN OEUVRE CETTE COMPOSITION

(57) Abstract

The invention concerns a ready–to–use composition for dyeing keratin fibres, and in particular human keratin fibres such as hair comprising, in an appropriate dyeing medium, at least a cationic direct dye, and at least an auto–oxidizable dye, and the dyeing method using said composition.

(57) Abrégé

L'invention a pour objet une composition prête à l'emploi pour la teinture des fibres kératiniques, et en particulier des fibres kératiniques humaines telles que les cheveux comprenant, dans un milieu approprié pour la teinture, au moins un colorant direct cationique, et au moins un colorant auto–oxydable, ainsi que le procédé de teinture mettant en oeuvre cette composition.

ABSTRACT

COMPOSITION FOR DYEING KERATIN FIBRES AND DYEING PROCESS USING THIS COMPOSITION

The invention relates to a ready-to-use composition for dyeing keratin fibres, and in particular human keratin fibres such as the hair, comprising, in a medium which is suitable for dyeing, at least one cationic direct dye and at least one auto-oxidizable dye, as well as to the dyeing process using this composition.

COMPOSITION FOR DYEING KERATIN FIBRES AND DYEING PROCESS USING THIS COMPOSITION

The invention relates to a composition for dyeing keratin fibres, and in particular human keratin fibres such as the hair, comprising, in a medium which is suitable for dyeing, at least one cationic direct dye and at least one auto-oxidizable dye, as well as to the dyeing process using this composition.

It is known practice to dye keratin fibres, and in particular human hair, with dye compositions containing auto-oxidizable dyes such as benzene derivatives containing at least three hydroxyl and/or amino groups and indole derivatives, such as 5,6-dihydroxyindole. These auto-oxidizable dyes have the particular feature of being able to be oxidized without any oxidizing agent other than atmospheric oxygen, to give rise to coloured and colouring molecules. However, the colorations obtained using these dyes are still not satisfactory, in particular as regards their intensity and their chromaticity.

It is also known practice to dye keratin fibres with direct dyes, and in particular with cationic direct dyes. Direct dyes have the drawback, when they are incorporated into dye compositions, of leading to colorations which are of insufficient staying power, in particular with respect to shampooing.

The Applicant has now discovered that it is

possible to obtain novel compositions for dyeing keratin fibres, which are capable of leading to intense, unselective colorations which show good resistance to the various attacking factors to which the hair may be subjected, by combining at least one cationic direct dye and at least one auto-oxidizable dye.

This discovery forms the basis of the present invention.

A first subject of the invention is thus a ready-to-use composition for dyeing 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 cationic direct dye,
- at least one auto-oxidizable dye.

The ready-to-use dye composition in accordance with the invention leads to intense, chromatic colorations which show low selectivity and excellent properties of resistance both with respect to atmospheric agents such as light and bad weather, and with respect 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 dyeing keratin fibres using this ready-to-use dye composition.

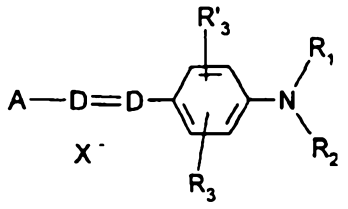
The cationic direct dye(s) which can be used

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)azo]-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-trimethylbenzenaminium 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 (I) below:



(I)

in which:

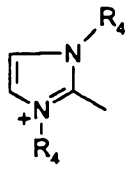
D represents a nitrogen atom or a -CH group,

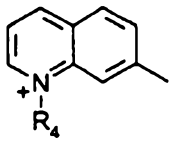
R_1 and R_2, which may be identical or different, represent a hydrogen atom; a C_1-C_4 alkyl radical which can be substituted with a -CN, -OH or $-NH_2$ radical; or form, with a carbon atom of the benzene ring, an optionally oxygenated or nitrogenous heterocycle, which can be substituted with one or more C_1-C_4 alkyl radicals; a 4'-aminophenyl radical,

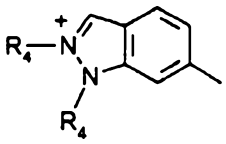
R_3 and R'_3, which may be identical or different, represent a hydrogen or halogen atom chosen from chlorine, bromine, iodine and fluorine, or a cyano, C_1-C_4 alkoxy or acetyloxy radical,

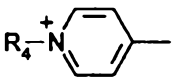
X^- represents an anion preferably chosen from chloride, methyl sulphate and acetate,

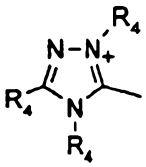
A represents a group chosen by structures A1 to A19 below:

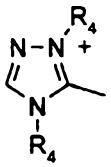

A_1 ;

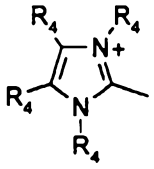

A_2 ;

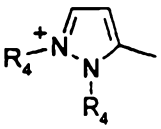

A_3 ;

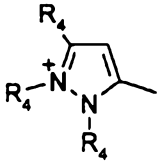

A_4 ;

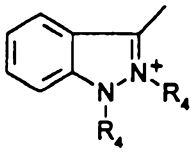

A_5 ;

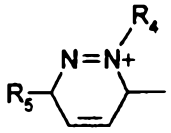

A_6 ;

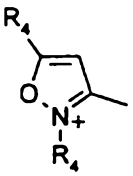

A_7 ;

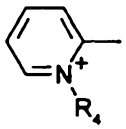

A_8 ;

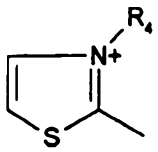

A_9 ;

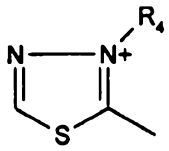

A_{10} ;

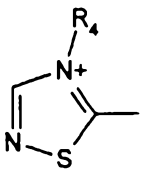

A_{11} ;

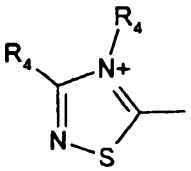

A_{12} ;

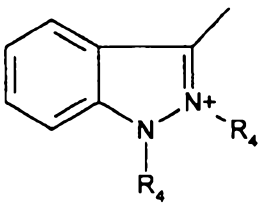

A_{13} ;

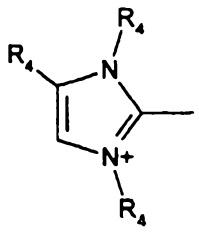

A_{14} ;


A_{15} ;


A_{16} ;

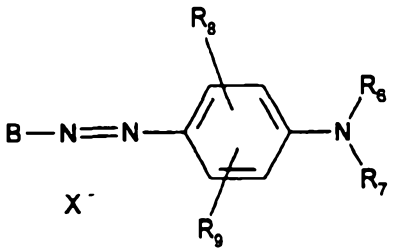

A_{17} ;


A_{18}

and  ;

in which R_4 represents a C_1-C_4 alkyl radical which can be substituted with a hydroxyl radical and R_5 represents a C_1-C_4 alkoxy radical, with the proviso that when D represents -CH, when A represents A_4 or A_{13} and when R_3 is other than an alkoxy radical, then R_1 and R_2 do not simultaneously denote a hydrogen atom;

b) the compounds of formula (II) below:

 (II)

in which:

R_6 represents a hydrogen atom or a C_1-C_4 alkyl radical,

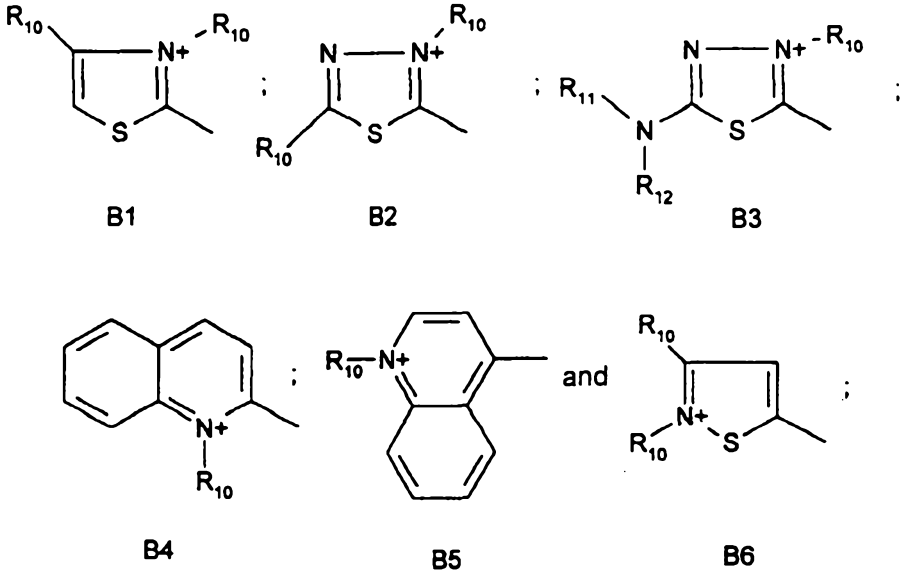
R_7 represents a hydrogen atom, an alkyl radical which can be substituted with a -CN radical or with an amino group, a 4'-aminophenyl radical or forms, with R_6, an optionally oxygenated and/or nitrogenous heterocycle which can be substituted with a C_1-C_4 alkyl radical,

R_8 and R_9, 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,

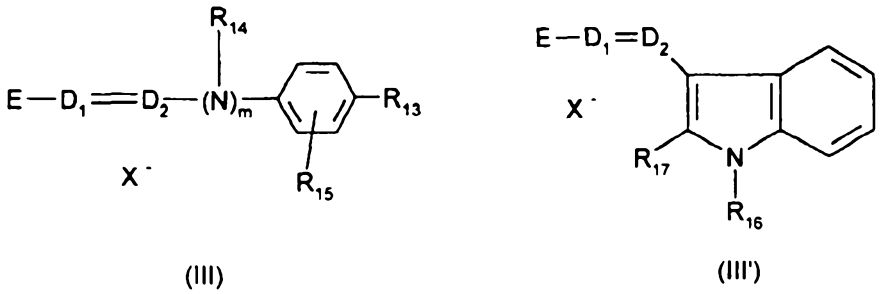
X^- represents an anion preferably chosen from chloride, methyl sulphate and acetate,

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



in which R_{10} represents a C_1-C_4 alkyl radical, R_{11} and R_{12}, which may be identical or different, represent a hydrogen atom or a C_1-C_4 alkyl radical;

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



in which:

R_{13} 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_{14} 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_{15} represents a hydrogen atom or a halogen atom such as bromine, chlorine, iodine or fluorine,

R_{16} and R_{17}, which may be identical or different, represent a hydrogen atom or a C_1-C_4 alkyl radical,

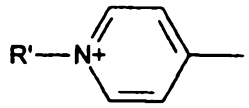
D_1 and D_2, which may be identical or different, represent a nitrogen atom or a -CH group,

m = 0 or 1,

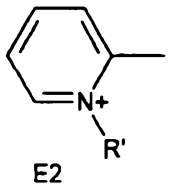
it being understood that when R_{13} represents an unsubstituted amino group, then D_1 and D_2 simultaneously represent a -CH group and m = 0,

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

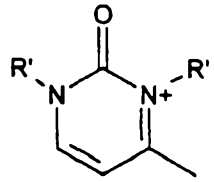
E represents a group chosen by structures E1 to E8 below:



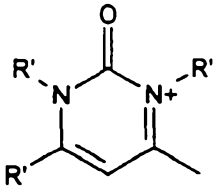
E1 ;



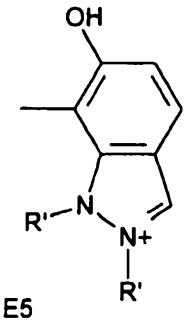
E2 ;



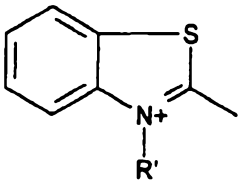
E3 ;



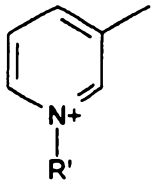
E4 ;



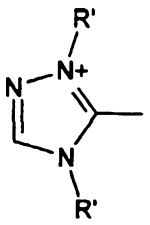
E5 ;



E6 ;



E7 and

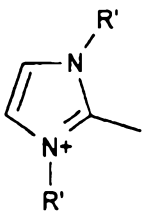


E8 ;

in which R' 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

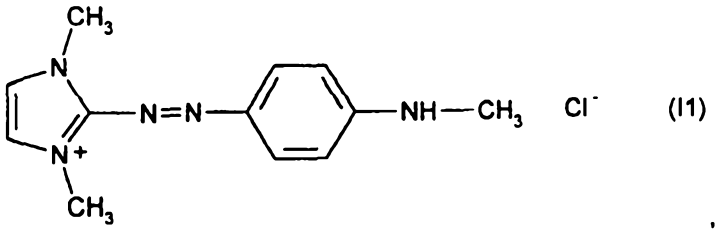


;

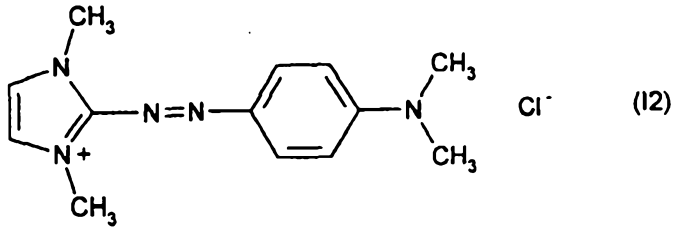
in which R' represents a C_1-C_4 alkyl radical.

The cationic direct dyes of formulae (I), (II), (III) and (III') which can be used in the ready-to-use dye compositions 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.

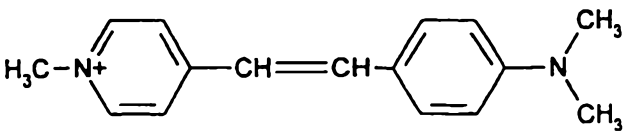
Among the cationic direct dyes of formula (I) which can be used in the ready-to-use dye compositions in accordance with the invention, mention may be made more particularly of the compounds corresponding to structures (I1) to (I52) below:



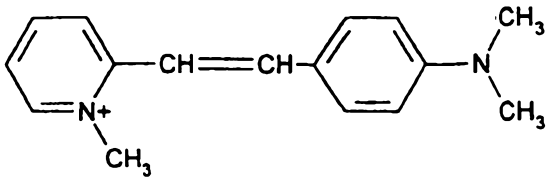
(I1)



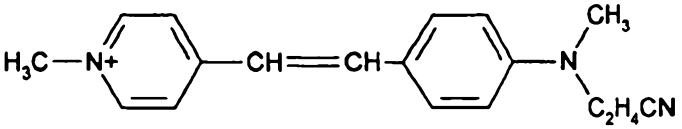
(I2)



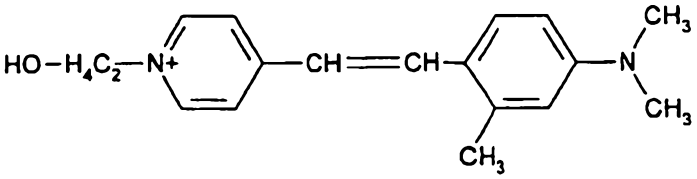
Cl^- (13)



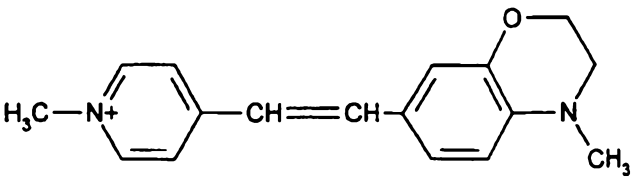
Cl^- (14)



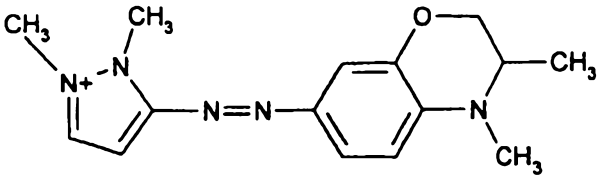
Cl^- (15)



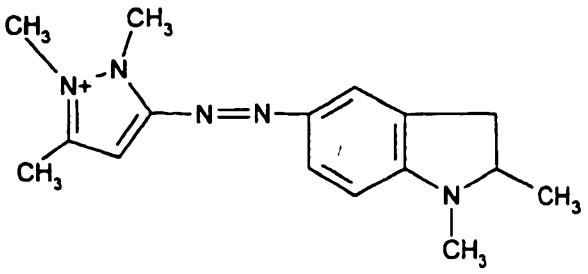
Cl^- (16)



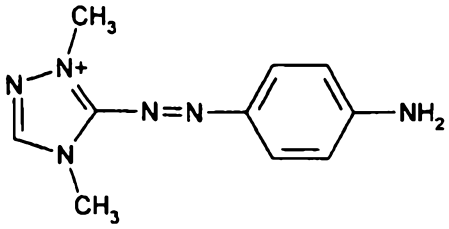
Cl^- (17)



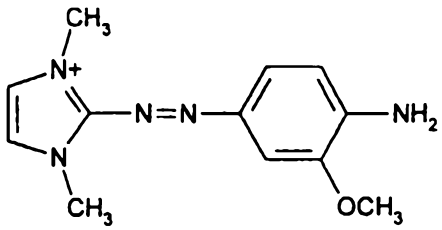
Cl^- (18)



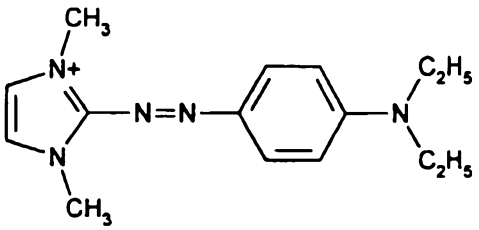
Cl^- (I9)



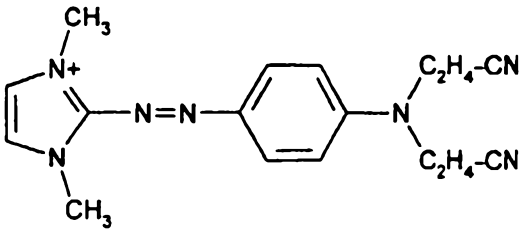
Cl^- (I10)



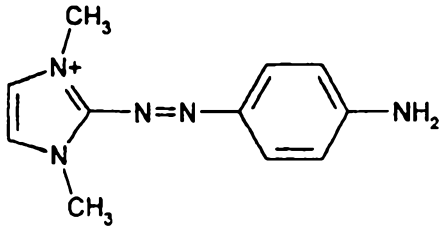
Cl^- (I11)



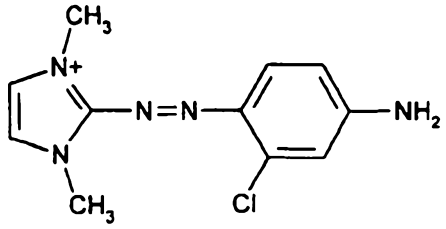
Cl^- (I12)



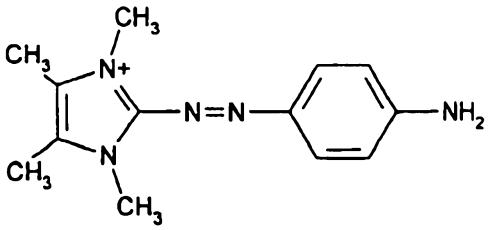
Cl^- (I13)



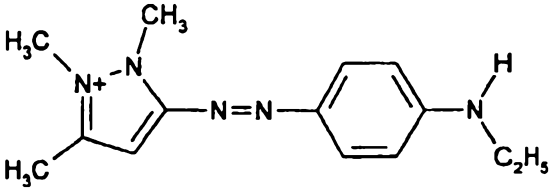
Cl^- (I14)



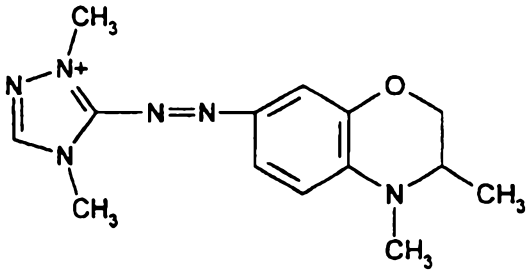
Cl^- (I15)



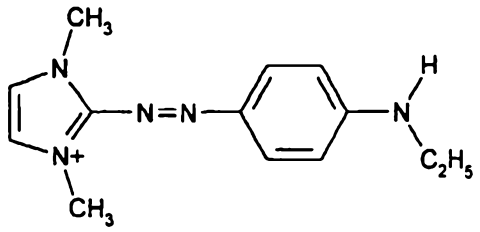
Cl^- (I16)



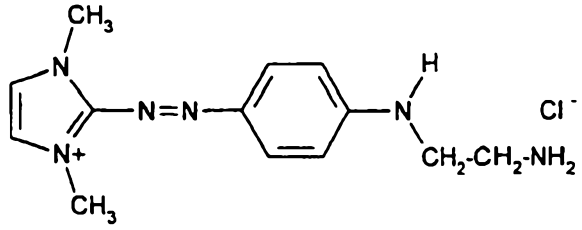
Cl^- (I17)



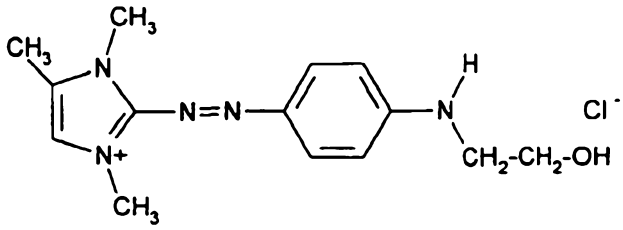
Cl^- (I18)



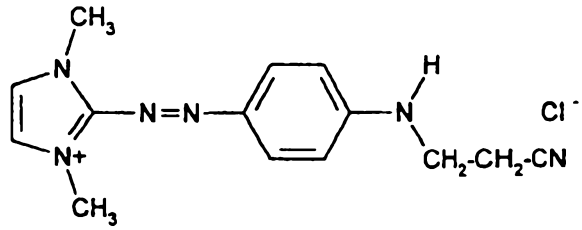
(I19)



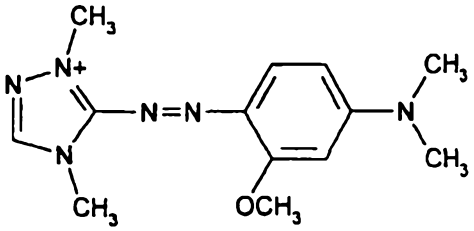
(I20)



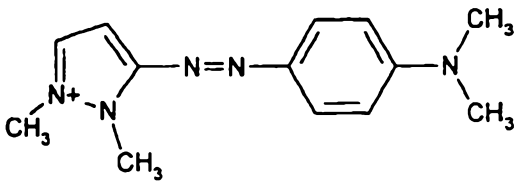
(I21)



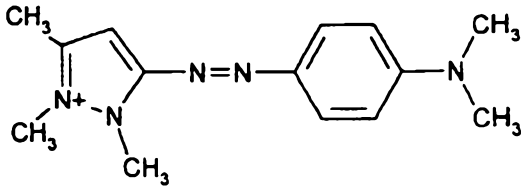
(I22)



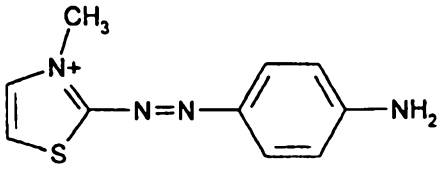
(I23)



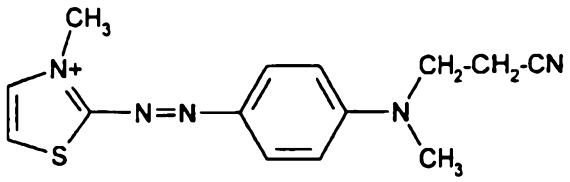
Cl^- (I24)



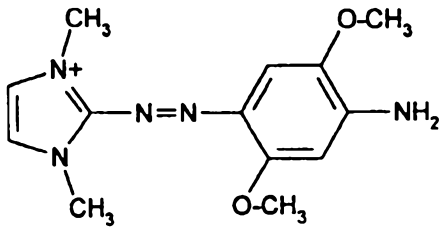
Cl^- (I25)



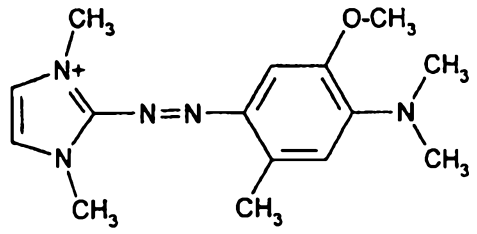
Cl^- (I26)



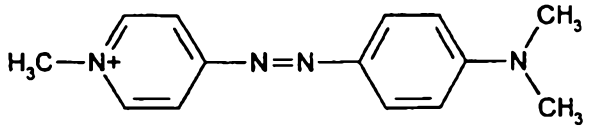
Cl^- (I27)



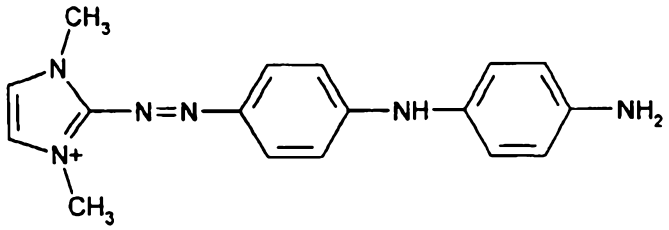
Cl^- (I28)



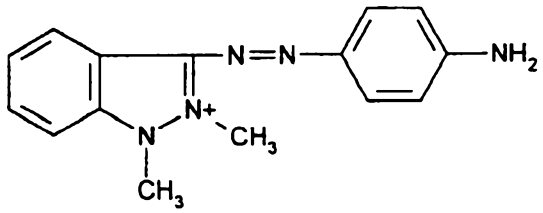
Cl^- (I29)



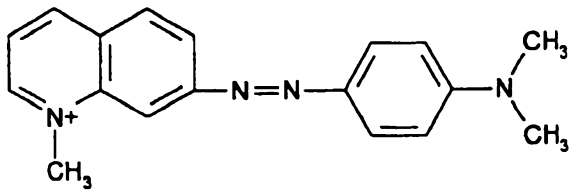
Cl^- (I30)



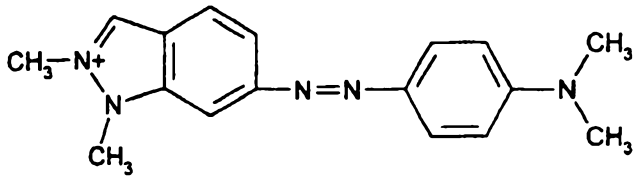
Cl^- (I31)



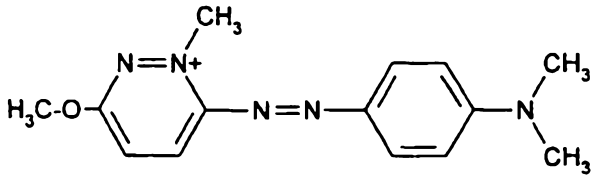
Cl^- (I32)



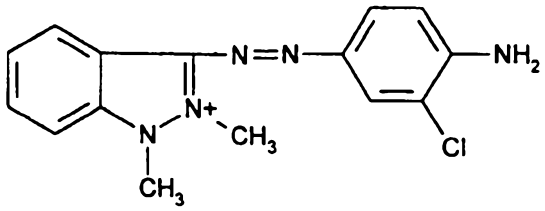
Cl^- (I33)



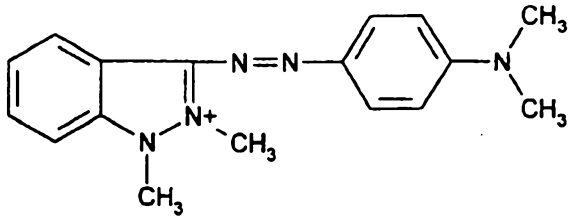
(I34)



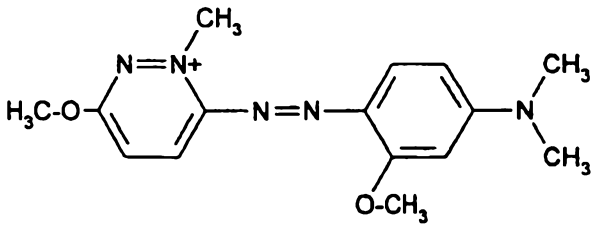
(I35)



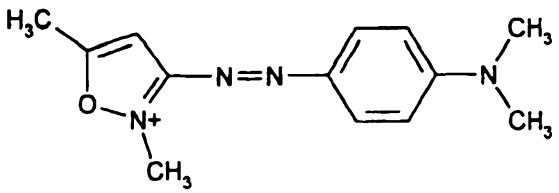
(I36)



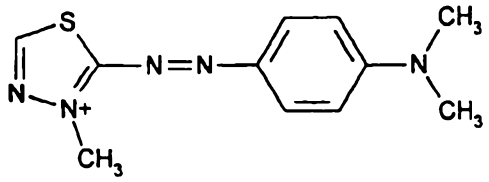
(I37)



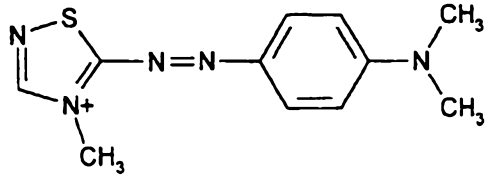
(I38)



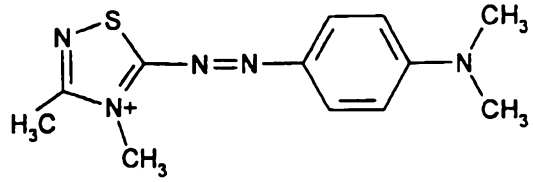
(I39)



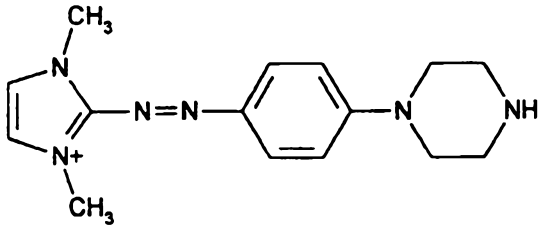
(I40)



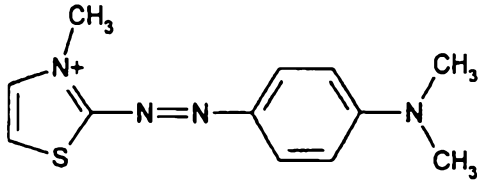
(I41)



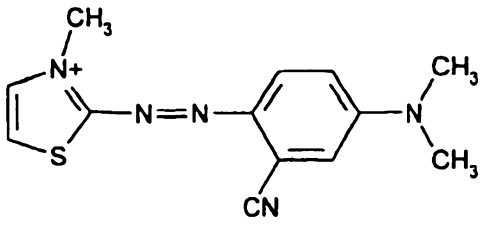
(I42)



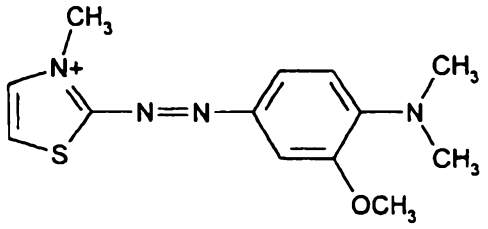
(I43)



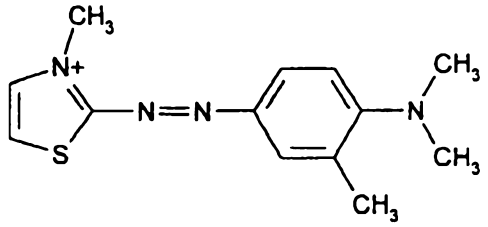
(I44)



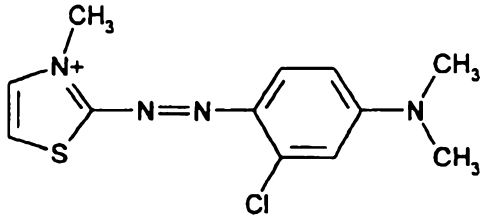
Cl^- (145)



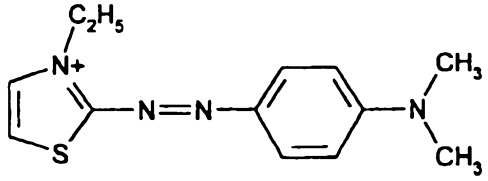
Cl^- (146)



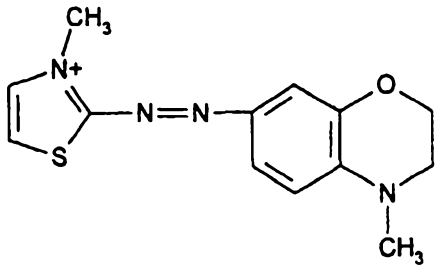
Cl^- (147)



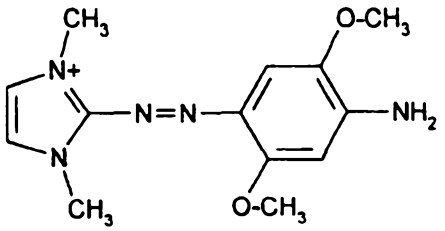
$CH_3SO_4^-$ (148)



$CH_3SO_4^-$ (149)

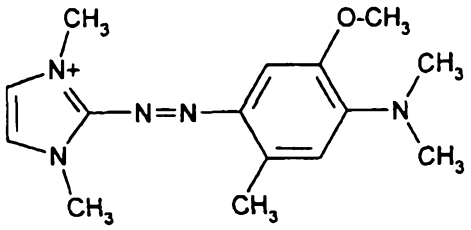


(I50)



(I51)

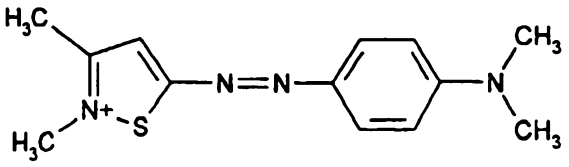
and,



(I52)

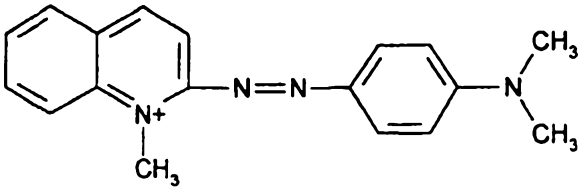
Among the compounds of structures (I1) to (I52) described above, the compounds most particularly preferred are the ones corresponding to structures (I1), (I2), (I14) and (I31).

Among the cationic direct dyes of formula (II) 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 (II1) to (II12) below:



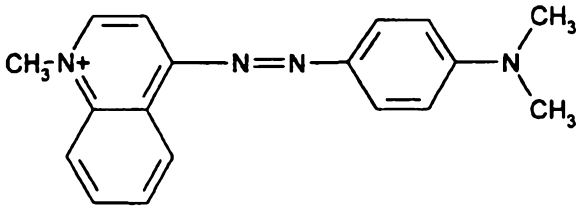
(II1)

;



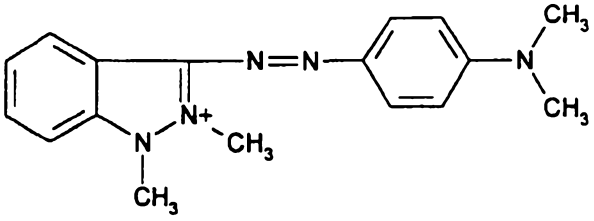
(II2)

;



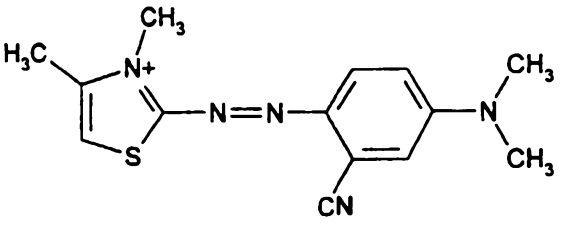
(II3)

;



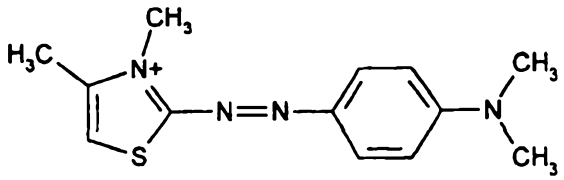
(II4)

;



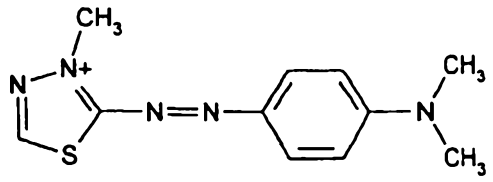
(II5)

;



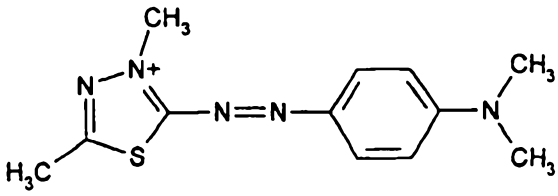
$CH_3SO_4^-$ (II6)

;



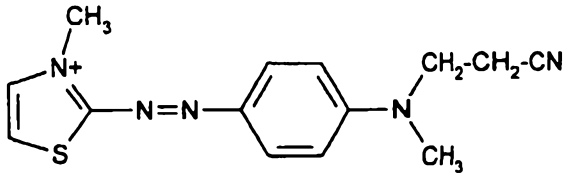
$CH_3SO_4^-$ (II7)

;



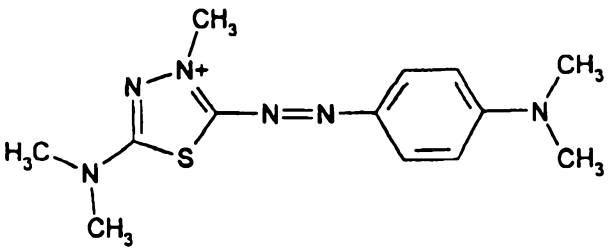
$CH_3SO_4^-$ (II8)

;



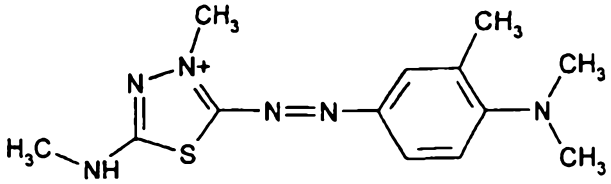
Cl^- (II9)

;



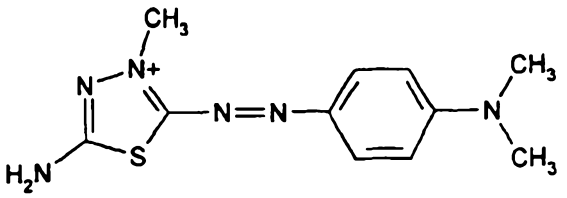
$CH_3SO_4^-$ (II10)

;



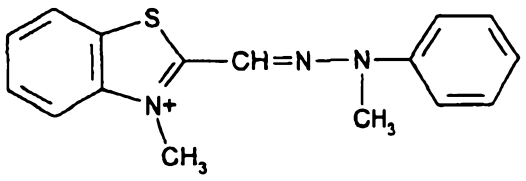
$CH_3SO_4^-$ (II11)

; and



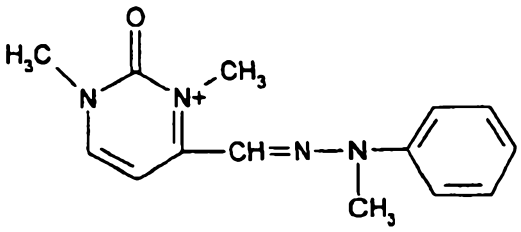
(II12)

Among the cationic direct dyes of formula (III) 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 (III1) to (III18) below:



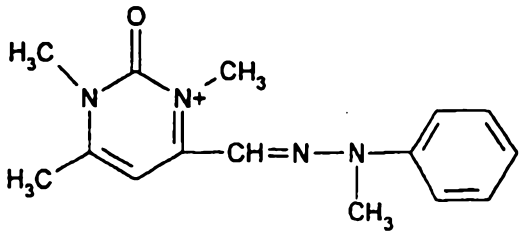
(III1)

;



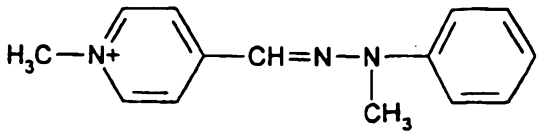
(III2)

;



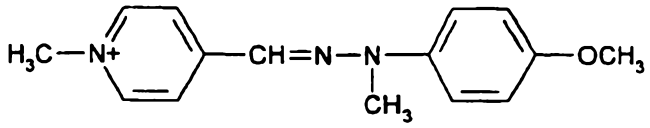
(III3)

;



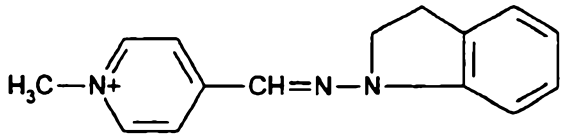
(III4)

;



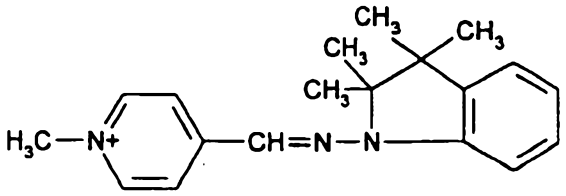
(III5)

;



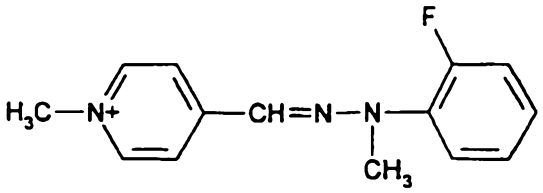
(III6)

;



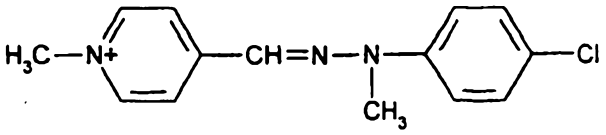
(III7)

;



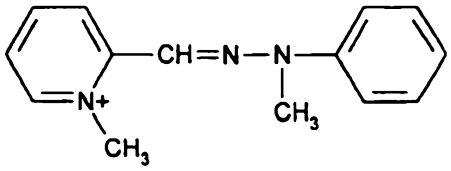
(III8)

;



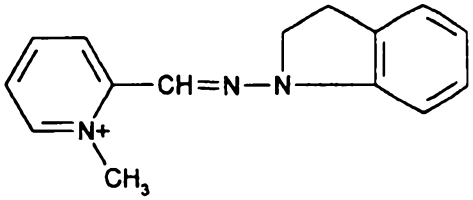
(III9)

;



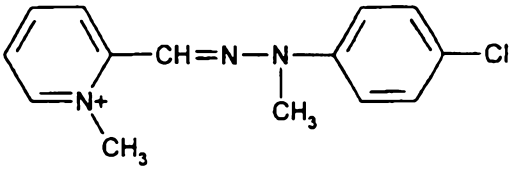
(III10)

;



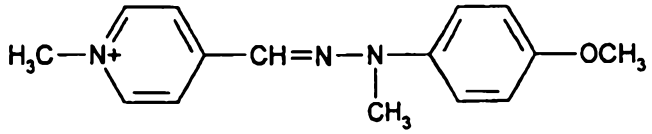
(III11)

;



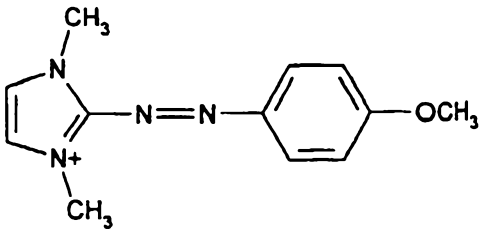
(III12)

;



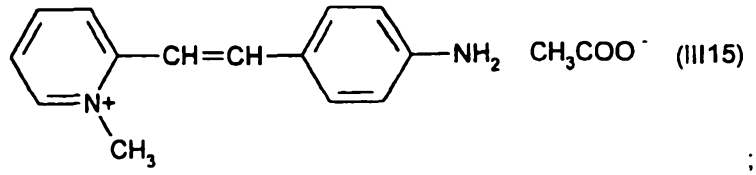
(III13)

;



(III14)

;



(III15)

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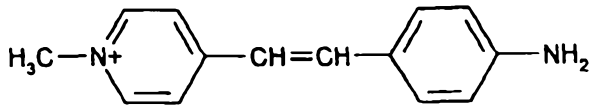
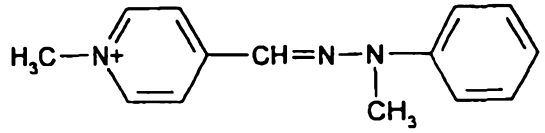


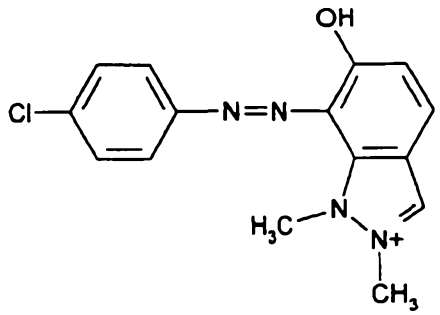
(III16)

;



(III17)

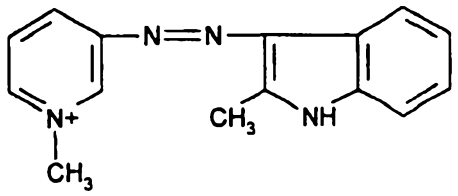
;and



(III18)

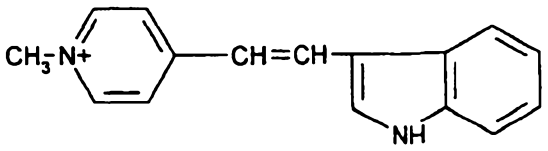
Among the specific compounds of structures (III1) to (III18) described above, the compounds most particularly preferred are the ones corresponding to structures (III4), (III5) and (III13).

Among the cationic direct dyes of formula (III') 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 (III'1) to (III'3) below:



Cl^- (III'1)

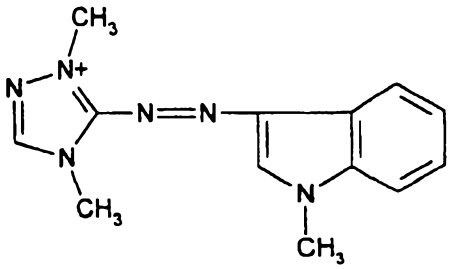
;



Cl^- (III'2)

;

and



Cl^- (III'3)

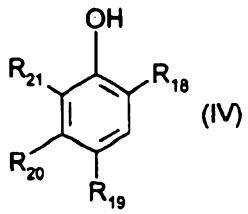
.

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 nature of the auto-oxidizable dye(s) used in the ready-to-use dye composition is not critical. It (they) can be chosen in particular from benzene, indole or indoline auto-oxidizable dyes.

Among the benzene auto-oxidizable dyes which can be used in the dye composition in accordance with the invention, mention may be made more particularly of the compounds of formula (IV) below, and the addition

salts thereof with an acid:



(IV)

in which:

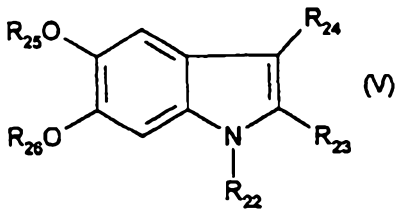
- R_{18} represents a hydrogen atom, a C_1-C_4 alkyl radical or an amino radical,
- R_{19} represents a C_1-C_4 alkyl, hydroxyl, amino, mono(C_1-C_4)alkylamino or di(C_1-C_4)alkylamino radical,
- R_{20} represents a hydrogen atom or a hydroxyl or amino radical,
- R_{21} represents a hydrogen atom or an amino radical;

it being understood that at least two of the radicals R_{19} to R_{21} represent, independently of each other, a hydroxyl, amino, mono(C_1-C_4)alkylamino or di(C_1-C_4)alkylamino radical.

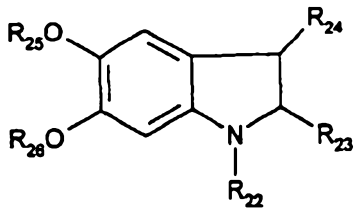
Among the benzene auto-oxidizable dyes of formula (IV) above, mention may be made more particularly of 1,2,4-trihydroxybenzene, 1-methyl-2,4,5-trihydroxybenzene, 2,4-diamino-6-methylphenol, 2-amino-4-methylaminophenol, 2,5-diamino-4-methyl-phenol, 2,6-diamino-4-diethylaminophenol and 2,6-diamino-1,4-dihydroxybenzene, and the addition salts thereof with an acid.

Among the indole and indoline auto-oxidizable dyes which can be used in the dye composition in

accordance with the invention, mention may be made in particular of the compounds of formulae (V) and (VI) below:



(V)



(VI)

in which:

- R_{22}, R_{24}, R_{25} and R_{26}, which may be identical or different, represent a hydrogen atom or a C_1-C_4 alkyl or C_1-C_4 acyl radical,
- R_{23} represents a hydrogen atom, a C_1-C_4 alkyl radical or a carboxyl radical.

Among the auto-oxidizable dyes of formula (V) above, mention may be made more particularly of 5,6-dihydroxyindole, 2-methyl-5,6-dihydroxyindole, 3-methyl-5,6-dihydroxyindole, 1-methyl-5,6-dihydroxyindole, 2,3-dimethyl-5,6-dihydroxyindole, 5-methoxy-6-hydroxyindole, 5-acetoxy-6-hydroxyindole, 5,6-diacetoxyindole and 5,6-dihydroxy-2-indolecarboxylic acid, and the addition salts thereof with an acid.

Among the auto-oxidizable dyes of formula (VI) above, mention may be made more particularly of 5,6-dihydroxyindoline, 1-methyl-5,6-dihydroxyindoline and 1-ethyl-5,6-dihydroxyindoline, and the addition salts thereof with an acid.

The auto-oxidizable dye(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 8% by weight approximately relative to this weight.

In order to facilitate the oxidation of the auto-oxidizable dyes, the ready-to-use dye composition in accordance with the invention can also contain one or more oxidizing agents. These oxidizing agents can be chosen in particular from hydrogen peroxide, urea peroxide, alkali metal bromates, persalts such as perborates and persulphates, and enzymes such as peroxidases and two-electron oxidoreductases.

Among the 2-electron oxidoreductases which can be used as oxidizing agents in the ready-to-use dye composition in accordance with the invention, mention may be made more particularly of pyranose oxidases, glucose oxidases, glycerol oxidases, lactate oxidases, pyruvate oxidases and uricases.

According to the invention, the use of uricases of animal, microbiological or biotechnological origin is particularly preferred.

By way of example, mention may be made in particular of the uricase extracted from boar liver, the uricase from Arthrobacter globiformis and the 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.

When they are used, 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.

When an enzyme of 2-electron oxidoreductase type is used in accordance with the invention, the ready-to-use dye composition can also contain one or more donors.

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

The nature of the donor (or substrate) used varies as a function of the nature of the 2-electron oxidoreductase which is used. For example, D-glucose, L-sorbose and D-xylose may be mentioned as donors for pyranose oxidases; D-glucose may be mentioned as a donor for glucose oxidases; glycerol and dihydroxyacetone may be mentioned as donors for glycerol oxidases; lactic acid and its salts may be mentioned as donors for lactate oxidases; pyruvic acid and its salts may be mentioned as donors for pyruvate oxidases; and lastly, uric acid and its salts may be

mentioned as donors for uricases.

When they are used, 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% approximately relative to this weight.

When the ready-to-use dye composition in accordance with the invention contains an oxidizing agent, it can also contain one or more oxidation bases and/or one or more couplers. These oxidation bases can be chosen in particular from para-phenylenediamines, para-aminophenols, ortho-phenylenediamines and heterocyclic bases such as, for example, pyridine derivatives, pyrimidine derivatives, pyrazole derivatives and pyrazolopyrimidine derivatives. The couplers can be chosen in particular from meta-phenylenediamines, meta-aminophenols, meta-diphenols, heterocyclic couplers such as, for example, indole derivatives, indoline derivatives, benzimidazole derivatives, benzomorpholine derivatives, sesamol derivatives, pyridine, pyrimidine and pyrazole derivatives, and the addition salts thereof with an acid.

When they are present, 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 8% by weight approximately relative to this weight.

When they are present, the coupler(s) preferably represent(s) 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 8% 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 (auto-oxidizable dyes, oxidation bases and couplers) are chosen in particular from the hydrochlorides, hydrobromides, sulphates, tartrates, lactates and acetates.

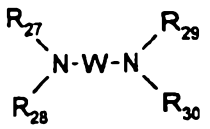
The medium which is suitable for dyeing (or support) for the ready-to-use dye composition in accordance with the invention generally consists of water or of a mixture of water and at least one organic solvent to dissolve the compounds which would not be sufficiently water-soluble. As organic solvents,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

The pH of the ready-to-use composition in accordance with the invention is generally between 5 and 11 approximately and preferably between 6.5 and 10

approximately. It can be adjusted to the desired value by means of acidifying or basifying aids 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 and 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 triethanolamine, 2-methyl-2-amino-1-propanol and derivatives thereof, sodium hydroxide, potassium hydroxide and the compounds of formula (VII) below:



(VII)

in which W is a propylene residue optionally substituted with a hydroxyl group or a C_1-C_4 alkyl radical; R_{27}, R_{28}, R_{29} and R_{30}, 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 conventionally used in compositions for dyeing the hair, such as, for example, antioxidants, penetrating agents, sequestering agents, fragrances,

buffers, dispersing agents, preserving agents and opacifiers.

Needless to say, a person skilled in the art will take care to select this or these optional complementary compounds 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(s) 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. It must be free of gaseous oxygen, so as to avoid any premature oxidation of the auto-oxidizable 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 generally between 3 and 60 minutes and even more precisely between 5 and 40 minutes.

According to one specific embodiment of the invention and when the ready-to-use composition in accordance with the invention contains an oxidizing agent, 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 cationic direct dye, and at least one auto-oxidizable dye, and, on the other hand, a composition (B) containing, in a medium which is suitable for dyeing, at least one oxidizing agent, and then in mixing them together at the time of use, before applying this mixture 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 contains composition (A) as defined above and a second compartment of which contains composition (B) as defined above. These devices can be equipped with a means for applying the desired mixture to 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 following ready-to-use dye compositions were prepared (contents in grams):

COMPOSITION	1	2	3
5,6-Dihydroxyindoline monohydrobromide (auto-oxidizable dye)	0.7	-	-
5,6-Dihydroxyindole (auto-oxidizable dye)	-	0.5	-
1,2,4-Trihydroxybenzene (auto-oxidizable dye)	-	-	1.2
Cationic direct dye Basic Red 76 (Arianor Madder Red)	0.1	-	-
Orange-coloured cationic direct dye of structure (I4)	-	0.07	-
Red cationic direct dye of structure (I1)	-	-	0.05
Common dye support (*)	(*)	(*)	(*)
Demineralized water q.s.	100 g	100 g	100 g

(*): Common dye support:

- Ethanol 20.0 g
- Nonylphenol oxyethylenated with 9 mol of ethylene oxide, sold under the name Igepal NR 9 OR by the company Rhodia Chemie 8.0 g
- 2-Amino-2-methyl-1-propanol q.s. pH = 8.0

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 featured in the table below:

EXAMPLE	Shade obtained
1	Red-blonde
2	Coppery blonde
3	Mahogany blonde

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 featured in the table below:

EXAMPLE	Shade obtained
1	Red-blonde
2	Coppery blonde
3	Mahogany blonde

EXAMPLES 4, 5 AND 6

Examples 4, 5 and 6 are provided as comparative examples to demonstrate the synergy produced by the composition of the invention.

Example 4 illustrates a composition of the prior art employing a cationic direct dye of structural formula I14.

Example 5 illustrates a composition of the prior art employing an auto-oxidisable dye 5,6-dihydroxyindole.

Example 6 illustrates a composition of the invention employing the cationic direct dye of Example 4 and the auto-oxidisable dye of Example 5.

	Example 4 Prior art	Example 5 Prior art	Example 6 Invention
Hydroxypropylguar (JAGUAR HP60 of RHODIA CHIMIE)	1	1	1
APG (ORAMIX CG110 de SEPPIC in aqueous solution 60%)	5 AM*	5 AM*	5 AM*
Ethanol.....	10	10	10
Cationic direct dye of structure (I14).....	0.5		0.25
Auto-oxidisable dye: 5,6-dihydroxyindole.....		0.495	0.2475
Monoethanolamine.....q.s.....pH.....	8	8	8
Preservatives.....q.s.....			
Demineralised water.....q.s.p.....	100	100	100

AM* = Active Material

Each above composition was then applied to hair locks (grey natural hair containing 90% white hairs) for 15 minutes.

The hair was then rinsed, shampooed, rinsed again, and dried.

The colour was then measured within the L* a* b* system wherein L indicates the lightness of the colour (L*=0 is black; L*=100 is white) using a Minolta CM 2002 colorimeter.

Positive values of a* and b* indicate red and yellow respectively, while negative values indicate green and blue respectively.

The dyeing power is represented by L*.

The lower the value of L*, the more intense is the dyeing.

The results are expressed in the following table:

EXAMPLES	l*	a*	b*
4 (prior art)	35.5	36.4	26.7
5 (prior art)	39.8	2.3	7.0
6 (invention)	30.2	24.1	16.8

Conclusion:

The results show that after dyeing using the composition of Example 6 (each dye into the mixture is present in an amount by weight equal to half of the amount of the dye of the Examples 4 and 5) according to the invention, the colour is more intense than by using the compositions of the prior art (Examples 4 and 5 which separately use each dye of the mixture).

Throughout the specification and claims, the words "comprise", "comprises" and "comprising" are used in a non-exclusive sense.

CLAIMS

1. Ready-to-use composition for dyeing 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:

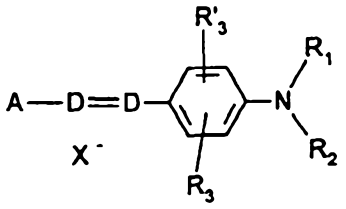
- at least one cationic direct dye and
- at least one auto-oxidizable dye.

2. Composition according to Claim 1, characterized in that the cationic direct dye(s) is (are) chosen from cationic aminoanthraquinone dyes, cationic monoazo or diazo dyes and cationic naphthoquinone dyes.

3. Composition according to Claim 2, characterized in that the cationic direct dye(s) is (are) chosen from [8-[(p-aminophenyl)azo]-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.

4. Composition according to Claim 1, characterized in that the cationic direct dye(s) is (are) chosen from:

a) the compounds of formula (I) below:



(I)

in which:

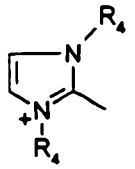
D represents a nitrogen atom or a -CH group,

R_1 and R_2, 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,

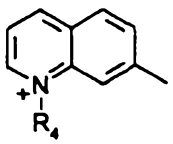
R_3 and R'_3, which may be identical or different, represent a hydrogen or halogen atom chosen from chlorine, bromine, iodine and fluorine, or a cyano, C_1-C_4 alkoxy or acetyloxy radical,

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

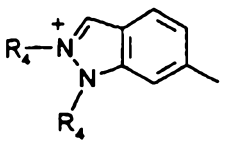
A represents a group chosen by structures A1 to A19 below:



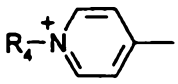
A_1 ;



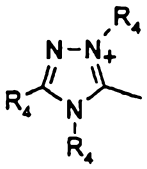
A_2 ;



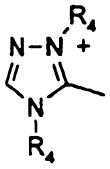
A_3 ;



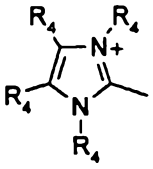
A_4 ;



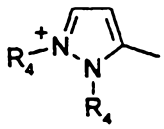
A_5 ;



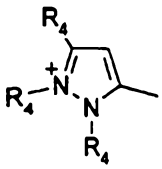
A_6 ;



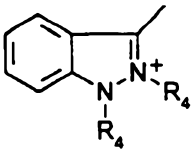
A_7 ;



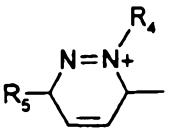
A_8 ;



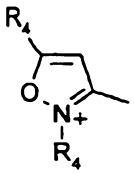
A_9 ;



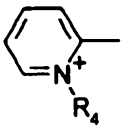
A_{10} ;



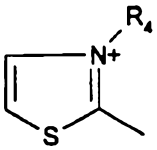
A_{11} ;



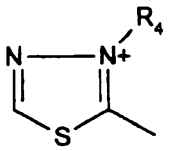
A_{12} ;



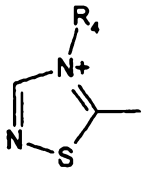
A_{13} ;



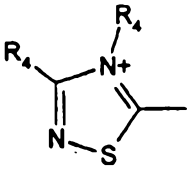
A_{14} ;



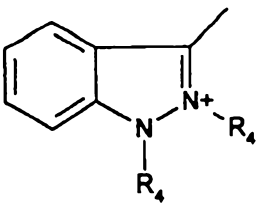
A_{15} ;



A_{16} ;

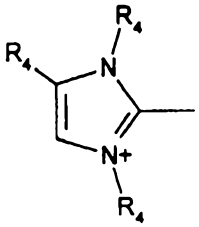


A_{17} ;



A_{18}

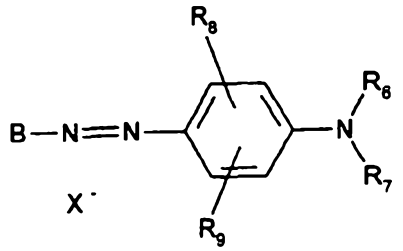
and



A_{19} ;

in which R_4 represents a C_1-C_4 alkyl radical which can be substituted with a hydroxyl radical and R_5 represents a C_1-C_4 alkoxy radical, with the proviso that when D represents -CH, when A represents A_4 or A_{13} and when R_3 is other than an alkoxy radical, then R_1 and R_2 do not simultaneously denote a hydrogen atom;

b) the compounds of formula (II) below:



(II)

in which:

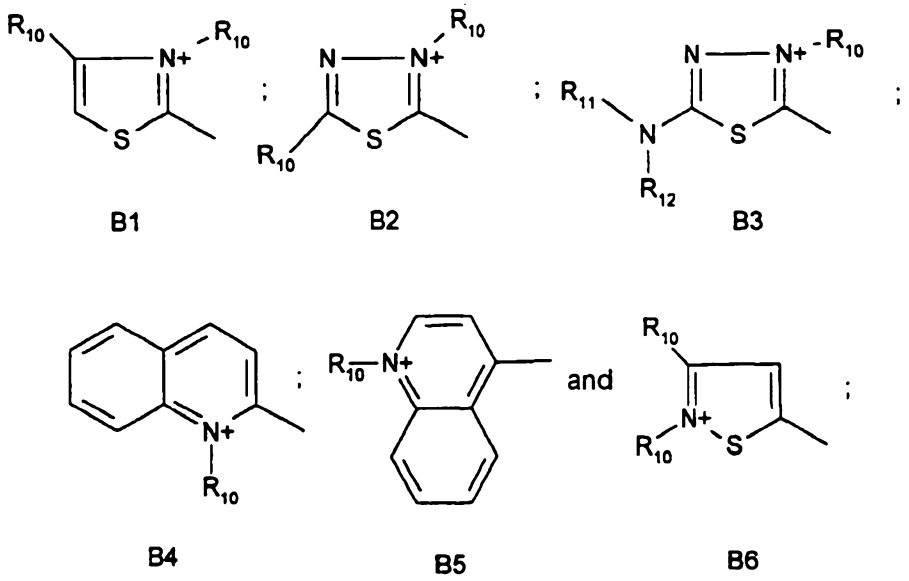
R_6 represents a hydrogen atom or a C_1-C_4 alkyl radical,

R_7 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_6, an optionally oxygenated and/or nitrogenous heterocycle which can be substituted with a C_1-C_4 alkyl radical,

R_8 and R_9, 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,

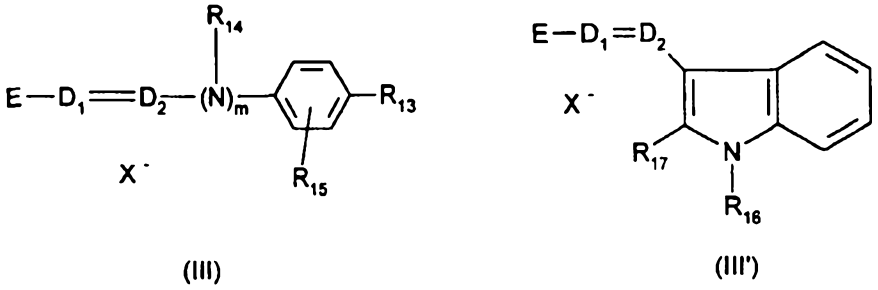
X^- represents an anion preferably chosen from chloride, methyl sulphate and acetate,

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



in which R_{10} represents a C_1-C_4 alkyl radical, R_{11} and R_{12}, which may be identical or different, represent a hydrogen atom or a C_1-C_4 alkyl radical;

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



in which:

R_{13} 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_{14} 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_{15} represents a hydrogen atom or a halogen atom such as bromine, chlorine, iodine or fluorine,

R_{16} and R_{17}, which may be identical or different, represent a hydrogen atom or a C_1-C_4 alkyl radical,

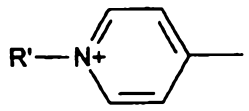
D_1 and D_2, which may be identical or different, represent a nitrogen atom or a -CH group,

m = 0 or 1,

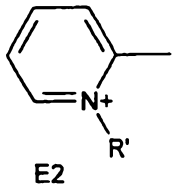
it being understood that when R_{13} represents an unsubstituted amino group, then D_1 and D_2 simultaneously represent a -CH group and m = 0,

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

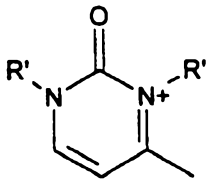
E represents a group chosen by structures E1 to E8 below:



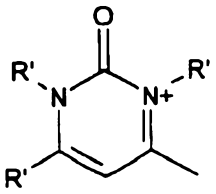
E1 ;



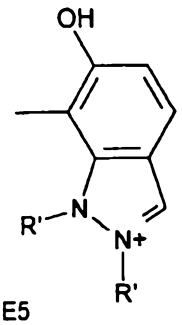
E2 ;



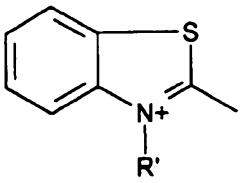
E3 ;



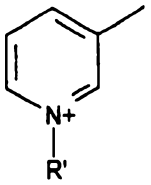
E4 ;



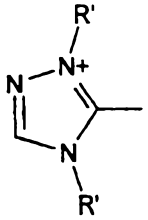
E5 ;



E6 ;



E7 and

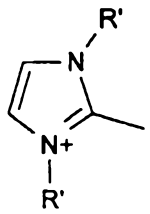


E8 ;

in which R' 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:

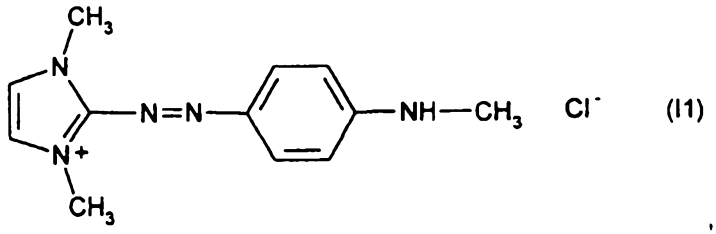
E9



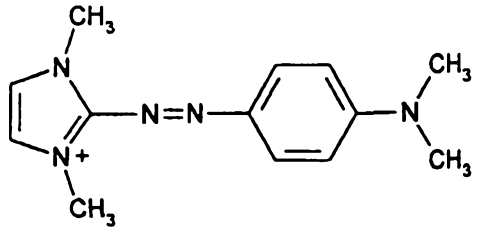
;

in which R' represents a C_1-C_4 alkyl radical.

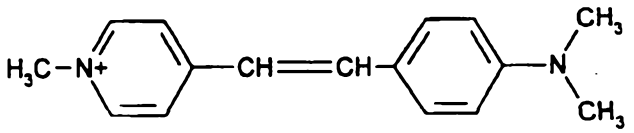
5. Composition according to Claim 4, characterized in that the cationic direct dyes of formula (I) are chosen from the compounds corresponding to structures (I1) to (I52) below:



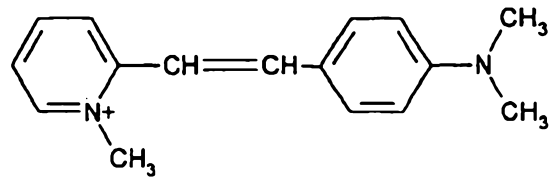
(I1)



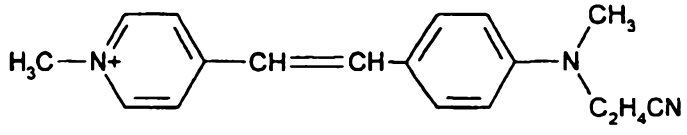
(I2)



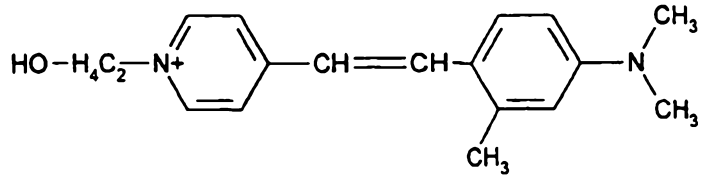
(I3)



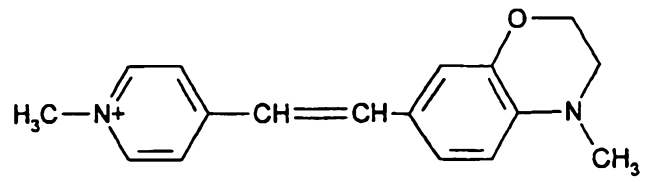
Cl^- (14)



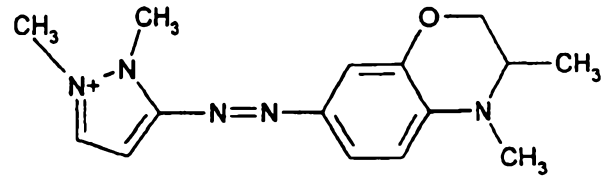
Cl^- (15)



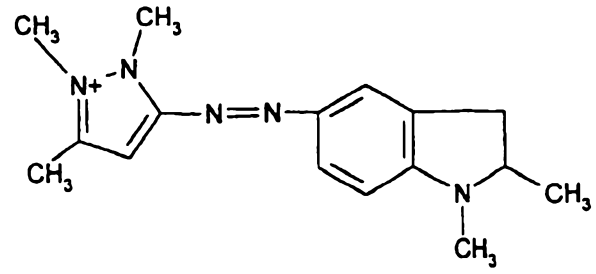
Cl^- (16)



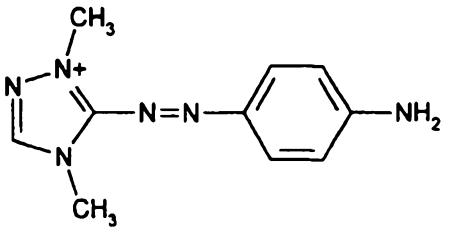
Cl^- (17)



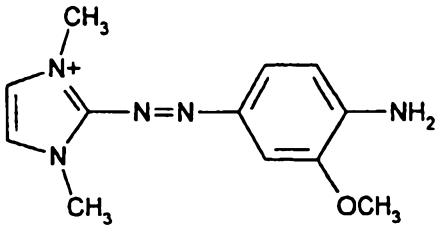
Cl^- (18)



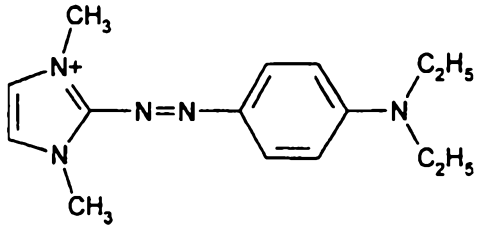
Cl^- (19)



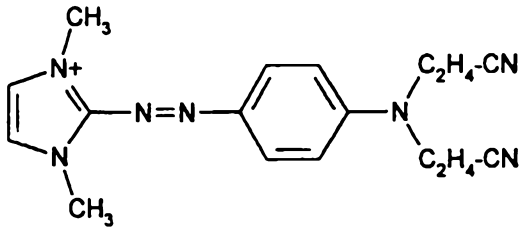
Cl^- (I10)



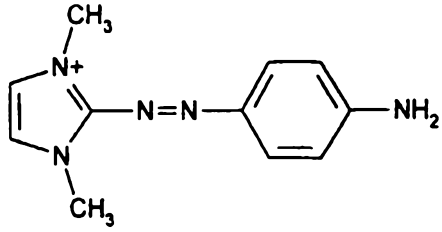
Cl^- (I11)



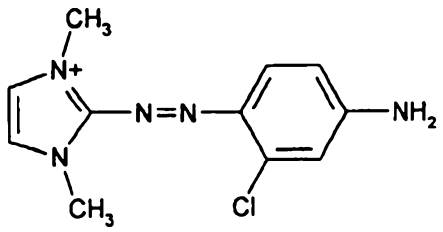
Cl^- (I12)



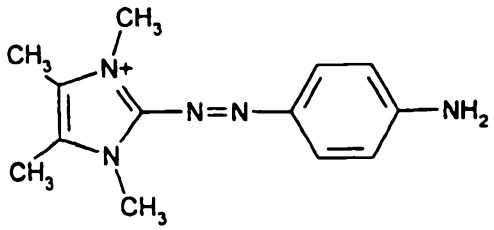
Cl^- (I13)



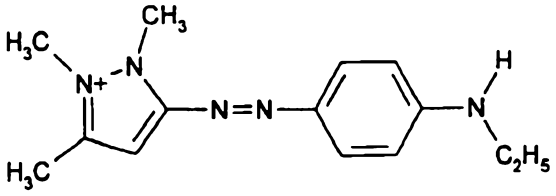
Cl^- (I14)



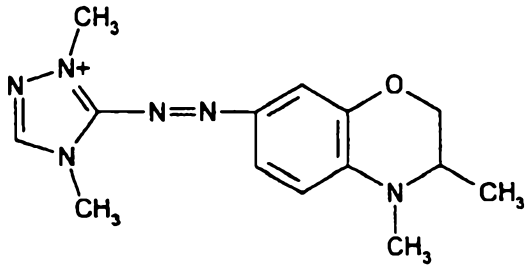
Cl^- (I15)



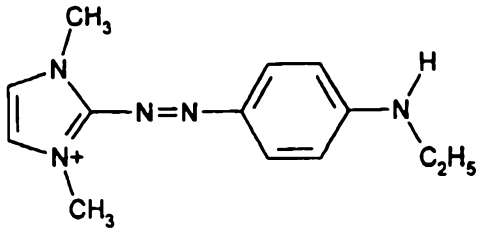
Cl^- (I16)



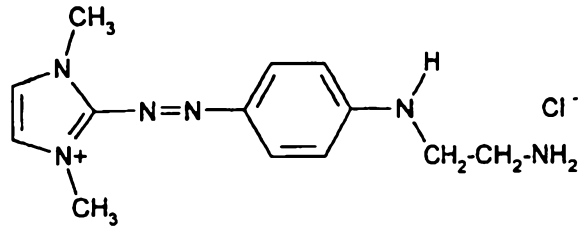
Cl^- (I17)



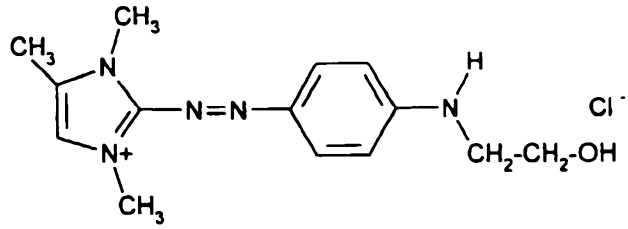
Cl^- (I18)



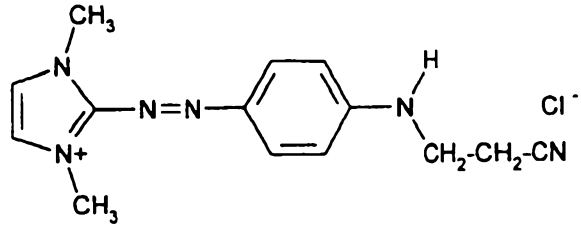
Cl^- (I19)



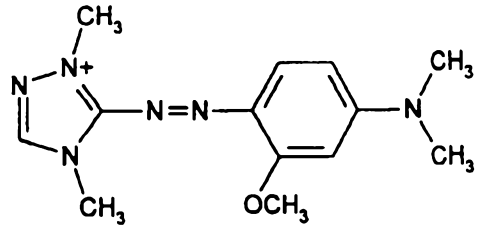
Cl⁻ (I20)



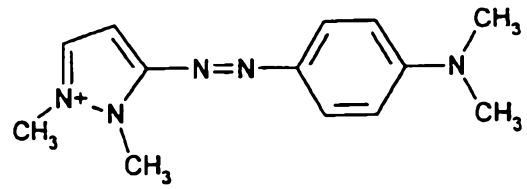
Cl⁻ (I21)



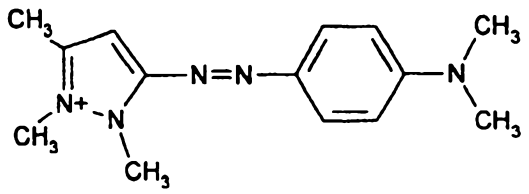
Cl⁻ (I22)



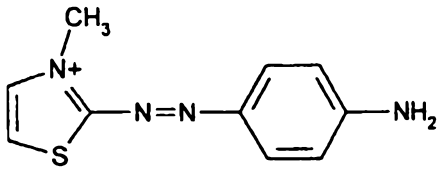
Cl⁻ (I23)



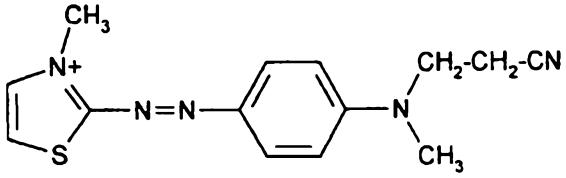
Cl⁻ (I24)



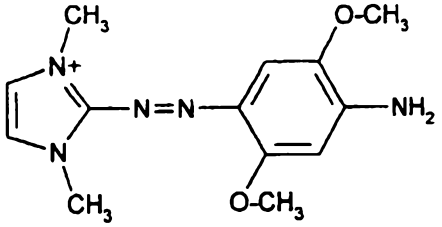
Cl^- (I25)



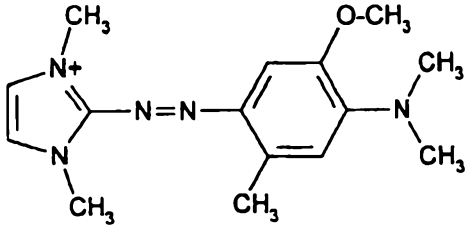
Cl^- (I26)



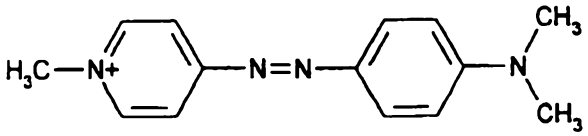
Cl^- (I27)



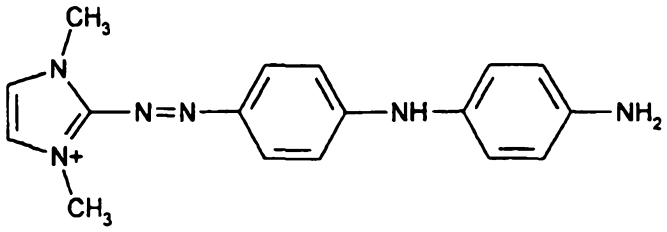
Cl^- (I28)



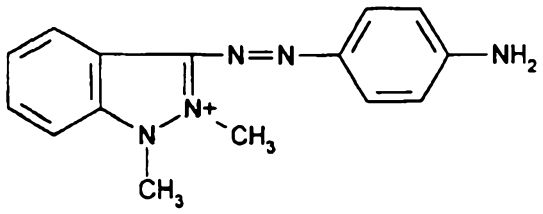
Cl^- (I29)



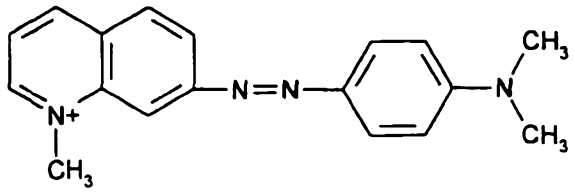
Cl^- (I30)



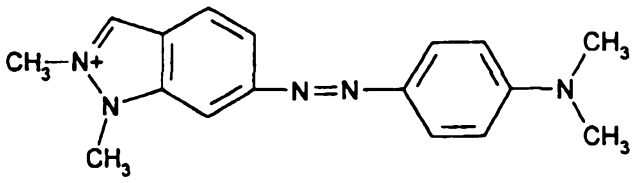
Cl⁻ (I31)



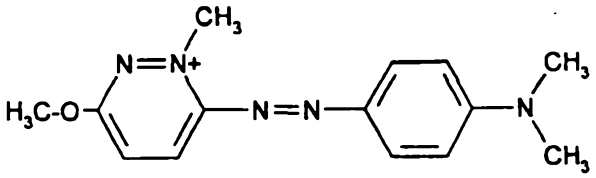
Cl⁻ (I32)



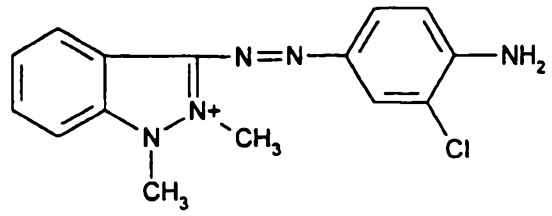
Cl⁻ (I33)



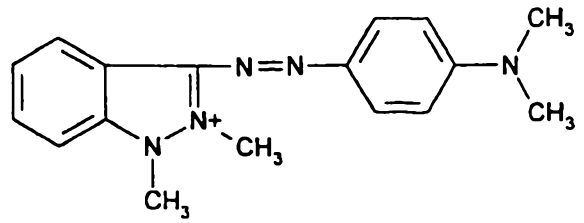
Cl⁻ (I34)



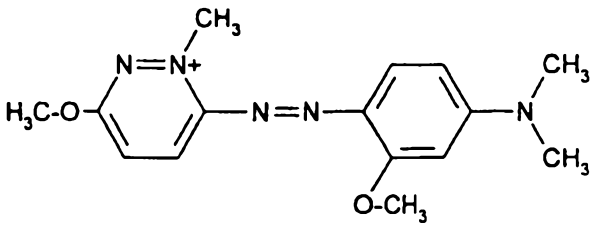
Cl⁻ (I35)



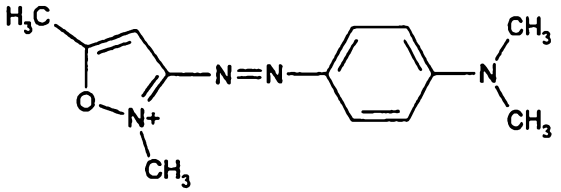
Cl^- (I36)



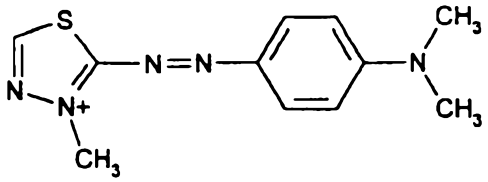
Cl^- (I37)



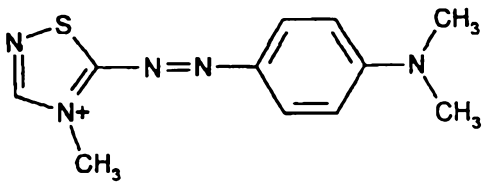
Cl^- (I38)



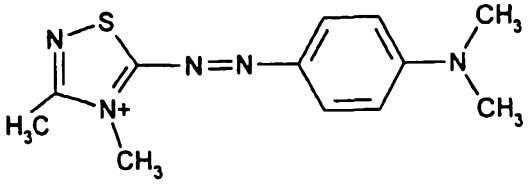
Cl^- (I39)



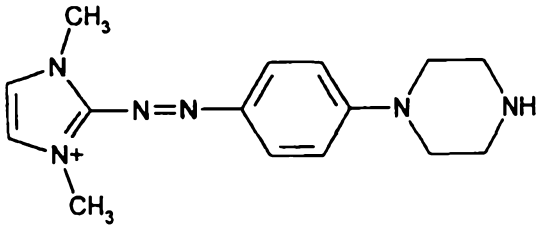
Cl^- (I40)



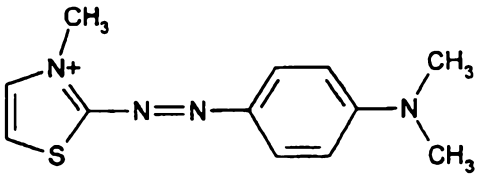
(I41)



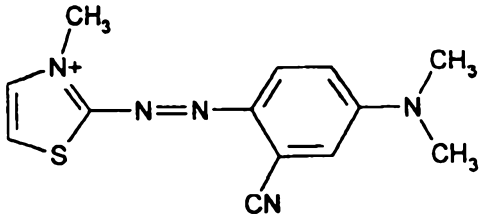
(I42)



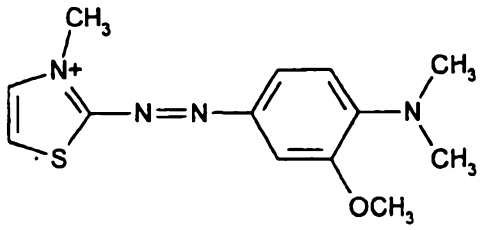
(I43)



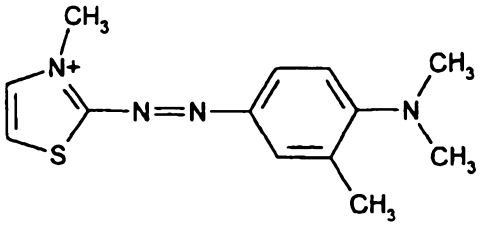
(I44)



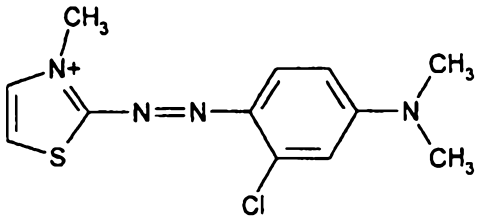
(I45)



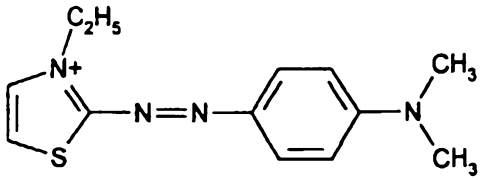
Cl^- (146)



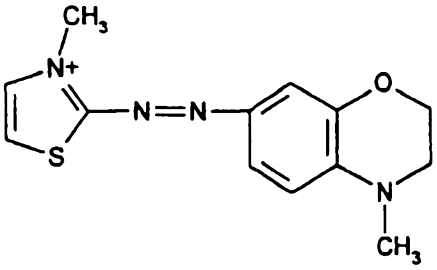
Cl^- (147)



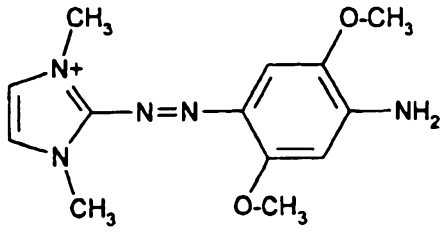
$CH_3SO_4^-$ (148)



$CH_3SO_4^-$ (149)

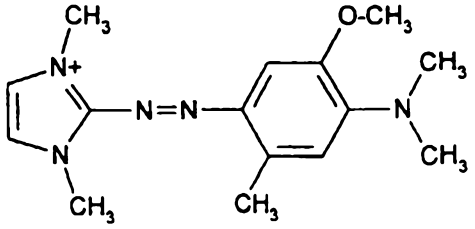


Cl^- (150)



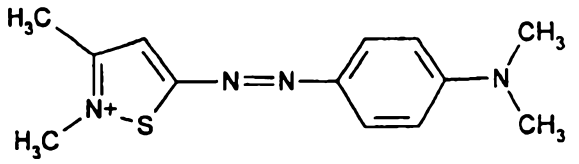
Cl⁻ (I51)

and

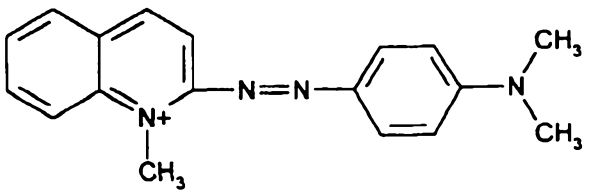


Cl⁻ (I52)

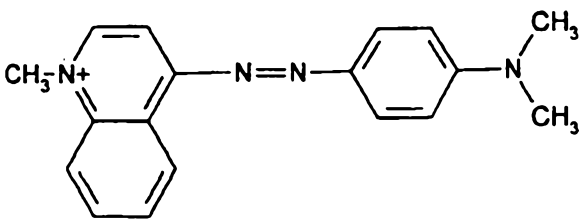
6. Composition according to Claim 4, characterized in that the cationic direct dyes of formula (II) are chosen from the compounds corresponding to structures (II1) to (II12) below:



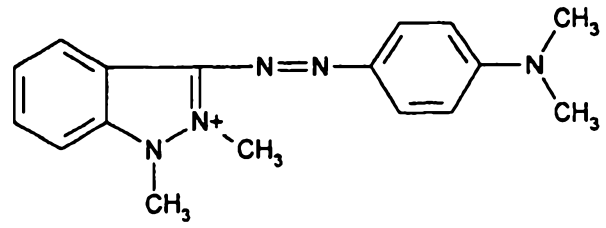
Cl⁻ (II1);



Cl⁻ (II2);

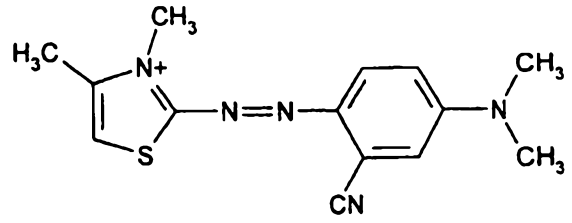


Cl⁻ (II3);



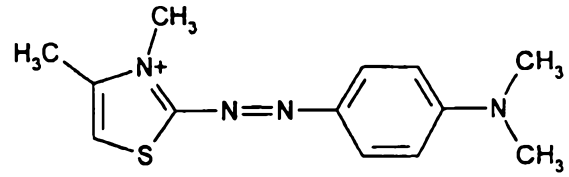
Cl^- (II4)

;



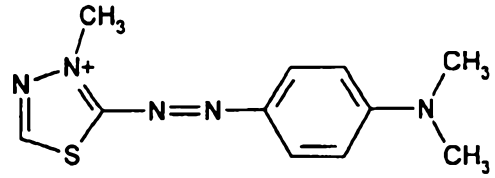
Cl^- (II5)

;



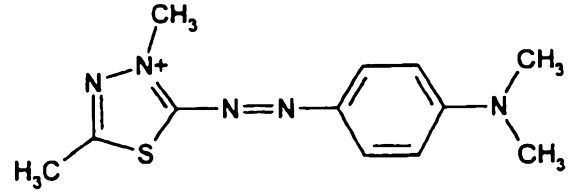
$CH_3SO_4^-$ (II6)

;



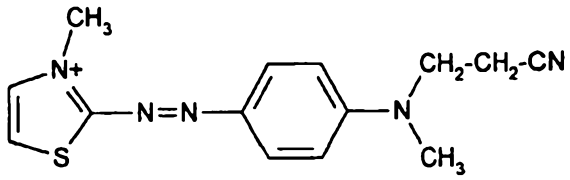
$CH_3SO_4^-$ (II7)

;



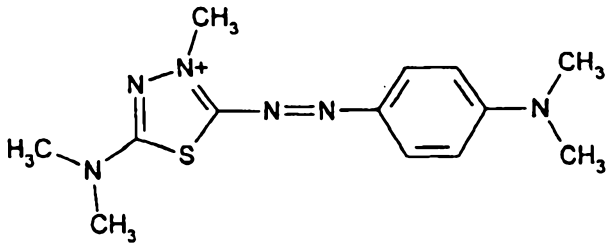
$CH_3SO_4^-$ (II8)

;



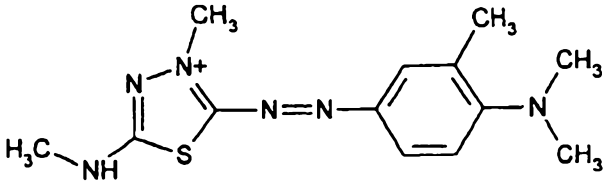
Cl⁻ (II9)

;



$CH_3SO_4^-$ (II10)

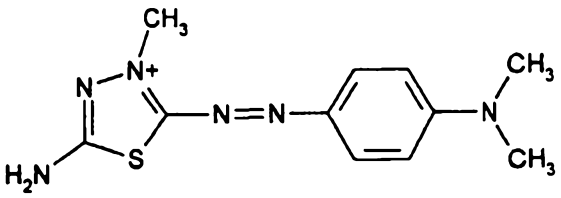
;



$CH_3SO_4^-$ (II11)

;

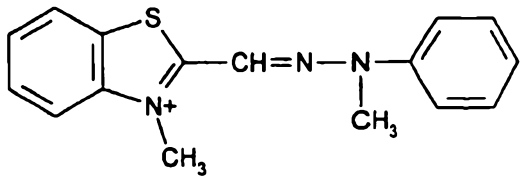
and



$CH_3SO_4^-$ (II12)

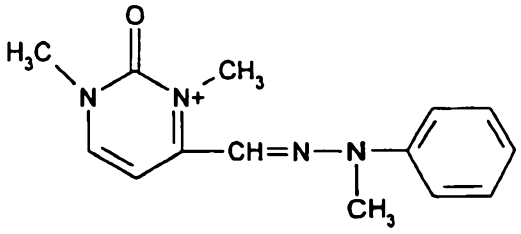
.

7. Composition according to Claim 4, characterized in that the cationic direct dyes of formula (III) are chosen from the compounds corresponding to structures (III1) to (III18) below:



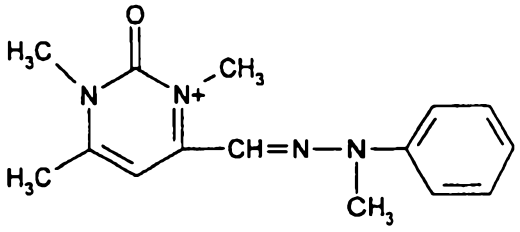
Cl^- (III1)

;



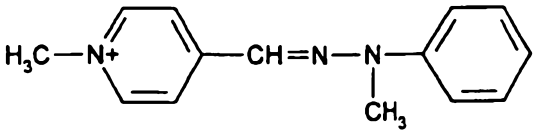
Cl^- (III2)

;



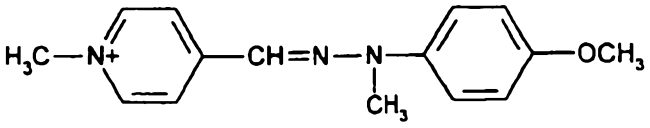
Cl^- (III3)

;



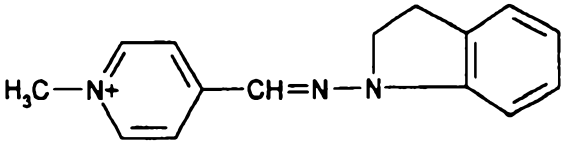
$CH_3SO_4^-$ (III4)

;



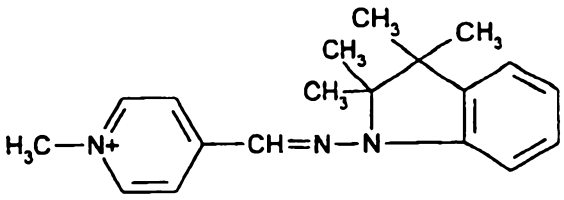
Cl^- (III5)

;



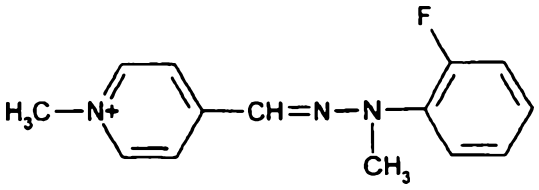
$CH_3SO_4^-$ (III6)

;



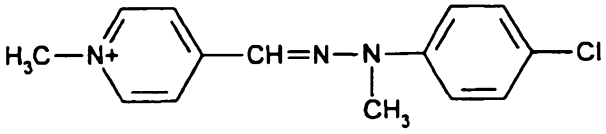
$CH_3SO_4^-$ (III7)

;



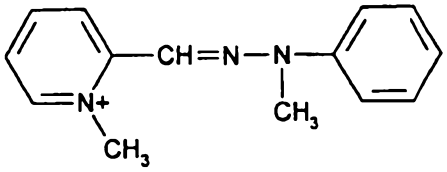
Cl^- (III8)

;



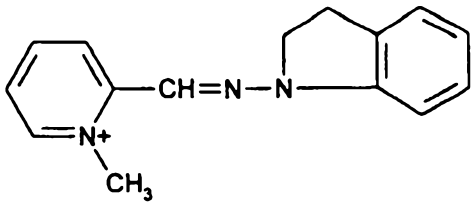
Cl^- (III9)

;



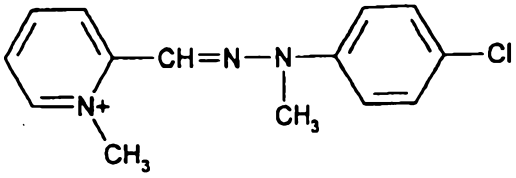
$CH_3SO_4^-$ (III10)

;



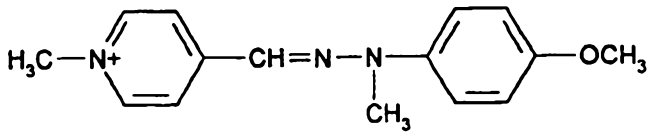
$CH_3SO_4^-$ (III11)

;

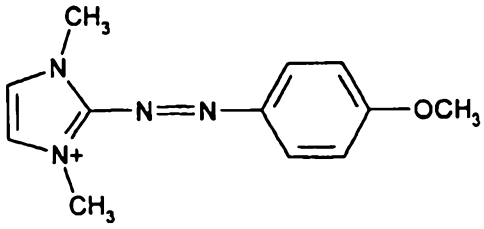


$CH_3SO_4^-$ (III12)

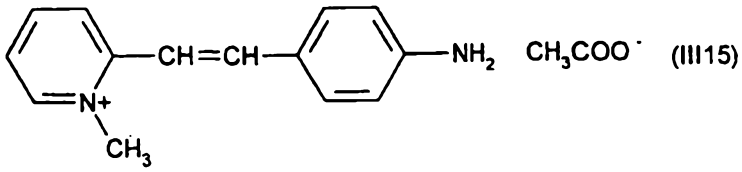
;


(III13)

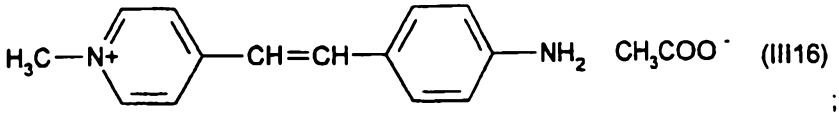
;


(III14)

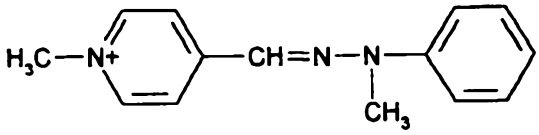
;


(III15)

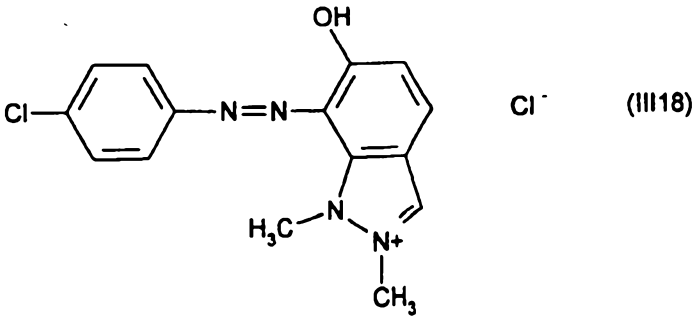
;


(III16)

;

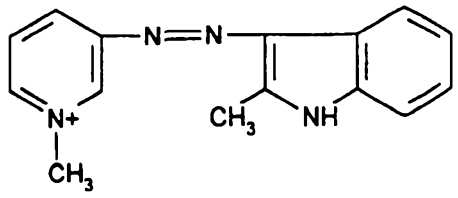

(III17)

; and


(III18)

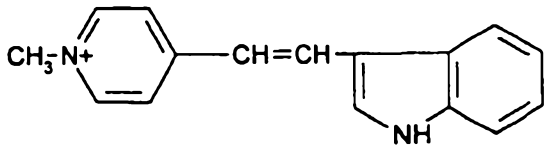
.

8. Composition according to Claim 4, characterized in that the cationic direct dyes of formula (III') are chosen from the compounds corresponding to structures (III'1) to (III'3) below:



(III'1)

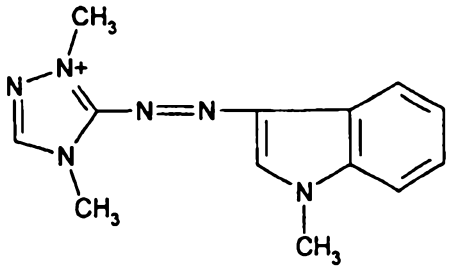
;



(III'2)

;

and



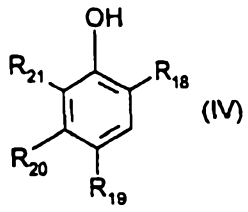
(III'3)

9. 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.

10. Composition according to Claim 9, 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.

11. Composition according to any one of the preceding claims, characterized in that the auto-oxidizable dye(s) is (are) chosen from benzene, indole or indoline auto-oxidizable dyes.

12. Composition according to Claim 11, characterized in that the benzene auto-oxidizable dyes are chosen from the compounds of formula (IV) below, and the addition salts thereof with an acid:



(IV)

in which:

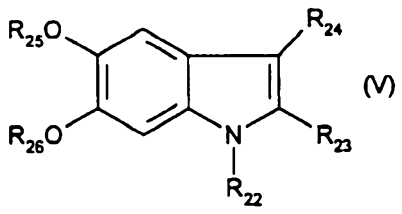
- R_{18} represents a hydrogen atom, a C_1-C_4 alkyl radical or an amino radical,
- R_{19} represents a C_1-C_4 alkyl, hydroxyl, amino, mono(C_1-C_4)alkylamino or di(C_1-C_4)alkylamino radical,
- R_{20} represents a hydrogen atom or a hydroxyl or amino radical,
- R_{21} represents a hydrogen atom or an amino radical;

it being understood that at least two of the radicals R_{19} to R_{21} represent, independently of each other, a hydroxyl, amino, mono(C_1-C_4)alkylamino or di(C_1-C_4)alkylamino radical.

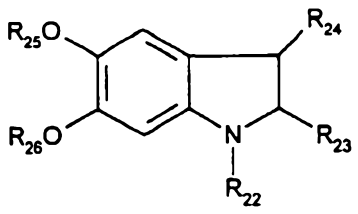
13. Composition according to Claim 12, characterized in that the benzene auto-oxidizable dyes of formula (IV) are chosen from 1,2,4-trihydroxybenzene, 1-methyl-2,4,5-trihydroxybenzene, 2,4-diamino-6-methylphenol, 2-amino-4-methylaminophenol, 2,5-diamino-4-methylphenol, 2,6-diamino-4-diethylaminophenol and 2,6-diamino-1,4-dihydroxybenzene, and

the addition salts thereof with an acid.

14. Composition according to Claim 11, characterized in that the indole and indoline auto-oxidizable dyes are chosen from the compounds of formulae (V) and (VI) below:



(V)



(VI)

in which:

- R_{22}, R_{24}, R_{25} and R_{26}, which may be identical or different, represent a hydrogen atom or a C_1-C_4 alkyl or C_1-C_4 acyl radical,
- R_{23} represents a hydrogen atom, a C_1-C_4 alkyl radical or a carboxyl radical.

15. Composition according to Claim 14, characterized in that the auto-oxidizable dyes of formula (V) are chosen from 5,6-dihydroxyindole, 2-methyl-5,6-dihydroxyindole, 3-methyl-5,6-dihydroxyindole, 1-methyl-5,6-dihydroxyindole, 2,3-dimethyl-5,6-dihydroxyindole, 5-methoxy-6-hydroxyindole, 5-acetoxy-6-hydroxyindole, 5,6-diacetoxyindole and 5,6-dihydroxy-2-indolecarboxylic acid, and the addition salts thereof with an acid.

16. Composition according to Claim 14, characterized in that the auto-oxidizable dyes of formula (VI) are chosen from 5,6-dihydroxyindoline,

1-methyl-5,6-dihydroxyindoline and 1-ethyl-5,6-dihydroxyindoline, and the addition salts thereof with an acid.

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

18. Composition according to Claim 17, characterized in that the auto-oxidizable dye(s) represent(s) from 0.005 to 8% by weight relative to the total weight of the dye composition.

19. Composition according to any one of the preceding claims, characterized in that it contains one or more oxidizing agents chosen from hydrogen peroxide, urea peroxide, alkali metal bromates, persalts such as perborates and persulphates, and enzymes.

20. Composition according to Claim 19, characterized in that the enzymes are chosen from peroxidases and two-electron oxidoreductases.

21. Composition according to Claim 20, characterized in that the two-electron oxidoreductases are chosen from pyranose oxidases, glucose oxidases, glycerol oxidases, lactate oxidases, pyruvate oxidases and uricases.

22. Composition according to Claim 20 or 21, characterized in that the 2-electron oxidoreductases is chosen from uricases of animal, microbiological or

biotechnological origin.

23. Composition according to any one of Claims 20 to 22, characterized in that 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.

24. Composition according to Claim 23, 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.

25. Composition according to any one of Claims 22 to 24, characterized in that it contains a donor (or substrate) for the said 2-electron oxidoreductase, chosen from uric acid and its salts.

26. Composition according to any one of Claims 19 to 25, characterized in that it contains one or more oxidation bases chosen from para-phenylenediamines, para-aminophenols, ortho-phenylenediamines and heterocyclic bases and/or one or more couplers chosen from meta-phenylenediamines, meta-aminophenols, meta-diphenols, heterocyclic couplers such as, for example, indole derivatives, indoline derivatives, benzimidazole derivatives, benzomorpholine derivatives, sesamol derivatives, pyridine, pyrimidine and pyrazole derivatives, and the addition salts thereof with an acid.

27. Composition according to Claim 26, characterized in that the oxidation base(s)

represent(s) from 0.0005 to 12% by weight relative to the total weight of the ready-to-use dye composition and in that the coupler(s) represent(s) from 0.0001 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 oxidation base(s) represent(s) from 0.005 to 8% by weight relative to the total weight of the ready-to-use dye composition and in that the coupler(s) represent(s) from 0.005 to 8% by weight relative to the total weight of the ready-to-use dye composition.

29. Composition according to any one of Claims 12, 13, 15 to 18 and 26 to 28, 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 of 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. 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.

33. Process according to Claim 32, 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 cationic direct dye, and at least one auto-oxidizable dye, and, on the other hand, a composition (B) containing, in a medium which is suitable for dyeing, at least one oxidizing agent, and then in mixing them together at the time of use, before applying this mixture to the keratin fibres.

34. Multi-compartment dyeing "kit" when used to perform the process of claim 33, characterised in that the kit includes a first compartment containing composition (A) and a second compartment containing composition (B).