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DYE COMPOSITION FOR KERATIN FIBRES, WITH A CATIONIC DIRECT DYE AND A SUBSTANTIVE POLYMER

The invention relates to a dye composition for keratin fibres, in particular for human keratin fibres such as the hair, comprising, in a medium which is suitable for dyeing, at least one cationic direct dye of given formula, and which is characterized in that it also contains at least one specific cationic or amphoteric substantive polymer.

The invention also relates to the dyeing processes and devices using the said composition.

AUSTRALIA

Patents Act 1990

COMPLETE SPECIFICATION

STANDARD PATENT

Applicant:

L'ORÉAL

Invention Title:

DYE COMPOSITION FOR KERATIN FIBRES, WITH A CATIONIC DIRECT DYE AND A SUBSTANTIVE POLYMER

The following statement is a full description of this invention, including the best method of performing it known to me/us:

DYE COMPOSITION FOR KERATIN FIBRES, WITH A CATIONIC DIRECT DYE AND A SUBSTANTIVE POLYMER

The invention relates to a dye composition for keratin fibres, in particular for human keratin fibres such as the hair, comprising, in a medium which is suitable for dyeing, at least one cationic direct dye of given formula, and at least one specific cationic or amphoteric substantive polymer.

The invention also relates to the dyeing processes and devices using the said composition.

Two types of coloration can be distinguished in the field of hair treatment.

The first is semi-permanent or temporary dyeing, or direct dyeing, which involves dyes capable of giving the hair's natural colour a more or less pronounced colour change which may withstand shampooing several times. These dyes are known as direct dyes; they can be used with or without an oxidizing agent. In the presence of an oxidizing agent, the aim is to obtain a lightening coloration. The lightening coloration is carried out by applying to the hair the mixture, prepared at the time of use, of a direct dye and an oxidizing agent, and in particular makes it possible to obtain, by lightening the melanin in the hair, an advantageous effect such as a unified colour in the case of grey hair, or to bring out the colour in the case of naturally pigmented hair.

The second is permanent dyeing or oxidation

dyeing. This is carried out with dyes known as "oxidation" dyes comprising oxidation dye precursors and couplers. Oxidation dye precursors, commonly known as "oxidation bases", are initially colourless or weakly coloured compounds which develop their dyeing power on the hair in the presence of oxidizing agents added at the time of use, leading to the formation of coloured compounds and dyes. The formation of these coloured compounds and dyes results either from an oxidative condensation of the "oxidation bases" with themselves or from an oxidative condensation of the "oxidation bases" with coloration modifier compounds commonly known as "couplers", which are generally present in the dye compositions used in oxidation dyeing.

In order to vary the shades obtained with the said oxidation dyes, or to enrich them with glints, it is known to add direct dyes thereto.

Among the cationic direct dyes available in the field of dyeing keratin fibres, in particular human keratin fibres, compounds which are already known are those whose structure is developed in the text which follows; nevertheless, these dyes lead to colorations which have properties that are still insufficient, both as regards the homogeneity of the colour distributed along the fibre ("unison"), in which case it is said that the coloration is too selective, and as regards the staying power, in terms of resistance to the

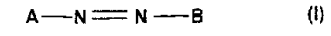
various attacking factors to which the hair may be subjected (light, bad weather, shampooing).

After considerable research conducted in this matter, the Applicant has now discovered that it is possible to obtain novel compositions for dyeing keratin fibres, which are capable of leading to less selective colorations which are particularly resistant to the various attacking factors to which the hair may be subjected, by combining at least one specific cationic or amphoteric substantive polymer with at least one cationic direct dye known in the prior art, and of formula (I) defined below.

This discovery forms the basis of the present invention.

A first subject of the present invention is thus a composition for dyeing keratin fibres, and in particular human keratin fibres such as the hair, containing, in a medium which is suitable for dyeing, **(i)** at least one cationic direct dye whose structure corresponds to formula (I) below, characterized in that it also contains **(ii)** at least one specific cationic or amphoteric substantive polymer.

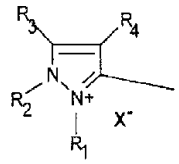
(i) The cationic direct dye which can be used according to the present invention is a compound of formula (I) below:



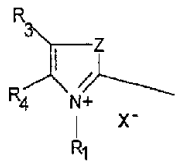
(I)

in which:

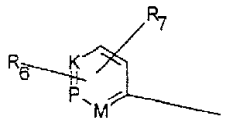
the symbol A represents a group chosen from structures A1 to A3 below:



A_1



A_2



A_3

in which structures A1 to A3,

R_1 denotes a C_1-C_4 alkyl radical, a phenyl radical which can be substituted with a C_1-C_4 alkyl radical or a halogen atom chosen from chlorine, bromine, iodine and fluorine;

R_2 denotes a C_1-C_4 alkyl radical or a phenyl radical;

R_3 and R_4, which may be identical or different, represent a C_1-C_4 alkyl radical, a phenyl radical or, in the case of structure A1, can together form a substituted benzene ring, and in the case of structure A2, can together form a benzene ring optionally substituted with one or more C_1-C_4 alkyl, C_1-C_4 alkoxy or NO_2 radicals;

R_3 can also denote a hydrogen atom;

Z denotes an oxygen or sulphur atom or a group $-NR_2$;

M represents a group -CH, -CR (R denoting C_1-C_4 alkyl) or $-NR_5(X^-)_r$;

K represents a group -CH, -CR (R denoting C_1-C_4 alkyl) or $-NR_5(X^-)_r$;

P represents a group -CH, -CR (R denoting C_1-C_4 alkyl) or $-NR_5(X^-)_r$; r denotes 0 or 1;

R_5 represents an atom O^-, a C_1-C_4 alkoxy radical or a C_1-C_4 alkyl radical;

R_6 and R_7, which may be identical or different, represent a hydrogen atom or a halogen atom chosen from chlorine, bromine, iodine and fluorine, a C_1-C_4 alkyl or C_1-C_4 alkoxy radical or an $-NO_2$ radical;

X^- represents an anion preferably chosen from chloride, iodide, methyl sulphate, ethyl sulphate, acetate and perchlorate;

with the proviso that,

if R_4 denotes a C_1-C_4 alkyl radical and Z denotes a sulphur atom, R_3 does not denote a hydrogen atom;

if R_5 denotes O^-, then r denotes zero;

if K or P or M denote -N-(C_1-C_4)alkyl X^-, then R_6 or R_7 is other than a hydrogen atom;

if K denotes $-NR_5(X^-)_r$, then M=P=-CH; -CR;

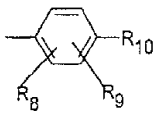
if M denotes $-NR_5(X^-)_r$, then K=P=-CH; -CR;

if P denotes $-NR_5(X^-)_r$, then K=M and denote -CH or -CR;

if Z denotes $-NR_2$ and R_2 denotes a C_1-C_4 alkyl radical, then at least one of the radicals R_1, R_3 or R_4 of $\mathbf{A_2}$ is other than a C_1-C_4 alkyl radical;

the symbol B represents:

-(a) a group of structure B1 below:



B_1

in which structure B1,

R_8 represents a hydrogen atom, a halogen atom chosen from chlorine, bromine, iodine and fluorine, a C_1-C_4 alkyl or C_1-C_4 alkoxy radical, a radical -OH, $-NO_2$, $-NHR_{11}$, $-NR_{12}R_{13}$ or $-NHCO(C_1-C_4)$alkyl radical or forms, with R_9, a 5- or 6-membered ring which may or may not contain one or more hetero atoms chosen from nitrogen, oxygen and sulphur;

R_9 represents a hydrogen atom, a halogen atom chosen from chlorine, bromine, iodine and fluorine, or a C_1-C_4 alkyl or C_1-C_4 alkoxy radical,

or forms, with R_{10} or R_{11}, a 5- or 6-membered ring which may or may not contain one or more hetero atoms chosen from nitrogen, oxygen and sulphur;

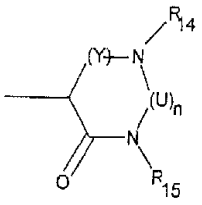
R_{10} represents a hydrogen atom, an -OH radical, a radical $-NHR_{11}$ or a radical $-NR_{12}R_{13}$;

R_{11} represents a hydrogen atom, a C_1-C_4 alkyl radical, a C_1-C_4 monohydroxyalkyl or C_2-C_4 polyhydroxyalkyl radical or a phenyl radical;

R_{12} and R_{13}, which may be identical or different, represent a C_1-C_4 alkyl radical or a C_1-C_4 monohydroxyalkyl or C_2-C_4 polyhydroxyalkyl radical;

-(b) a 5- or 6-membered nitrogenous heterocyclic group

which can contain other hetero atoms and/or carbonyl groups and which can be substituted with one or more C_1-C_4 alkyl, amino or phenyl radicals, and in particular a group of structure B2 below:



B_2

in which structure B2,

R_{14} and R_{15}, which may be identical or different, represent a hydrogen atom, a C_1-C_4 alkyl radical or a phenyl radical;

Y denotes a -CO- radical or a radical  ;

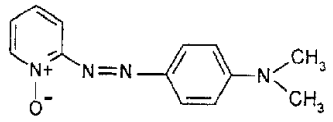
n = 0 or 1, where, when n denotes 1, U denotes a -CO- radical.

In the structures defined above, the C_1-C_4 alkyl or alkoxy group preferably denotes methyl, ethyl, butyl, methoxy or ethoxy.

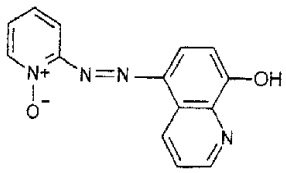
The cationic direct dyes of formula (I) which can be used in the dye compositions in accordance with the invention are known compounds and are described, for example, in patent applications FR-2,189,006, FR-2,285,851 and FR-2,140,205 and its Certificates of Addition.

Among the cationic direct dyes of formula (I) which can be used in the dye compositions in accordance with the invention, those of formula (I) in which the symbol A denotes structure A3 while the symbol B denotes structure B1 or B2 are particularly preferred.

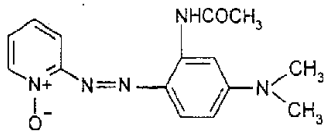
Among these compounds, mention may especially be made more particularly of the compounds of structures $(I)_1$ to $(I)_{77}$ below:



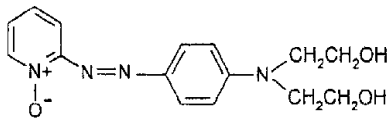
$(I)_1$



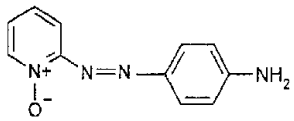
$(I)_2$



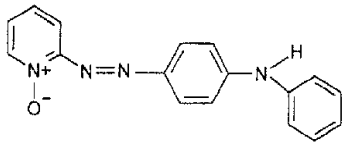
(I)3



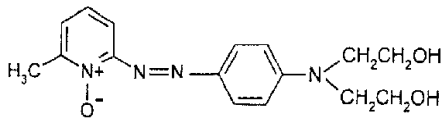
(I)4



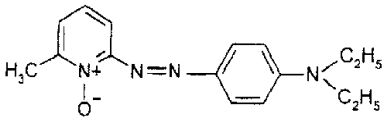
(I)5



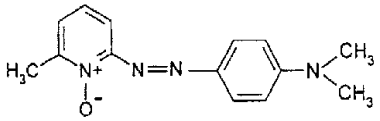
(I)6



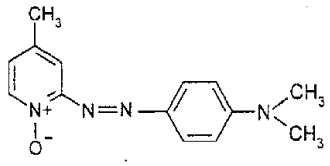
(I)7



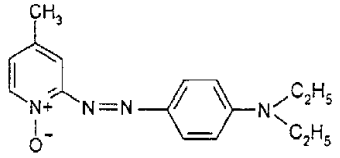
(I)8



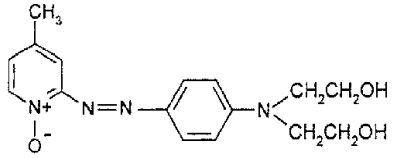
$(I)_9$



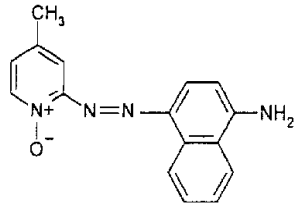
$(I)_{10}$



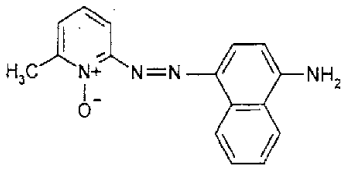
$(I)_{11}$



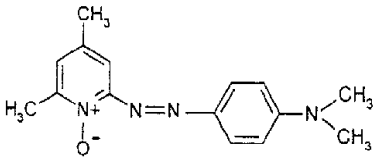
$(I)_{12}$



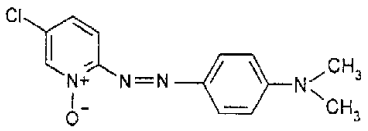
$(I)_{13}$



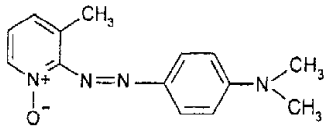
$(I)_{14}$



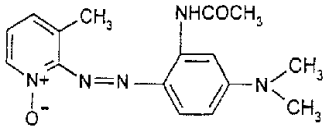
$(I)_{15}$



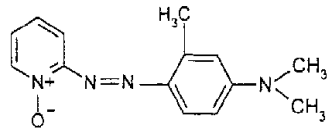
$(I)_{16}$



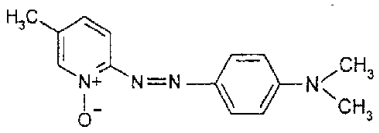
$(I)_{17}$



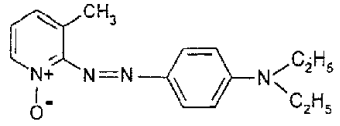
$(I)_{18}$



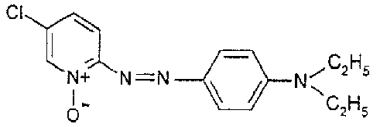
$(I)_{19}$



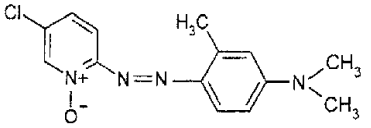
$(I)_{20}$



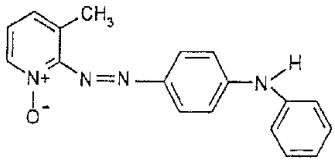
$(I)_{21}$



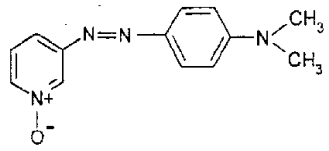
$(I)_{22}$



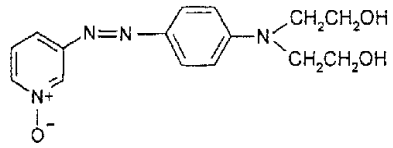
$(I)_{23}$



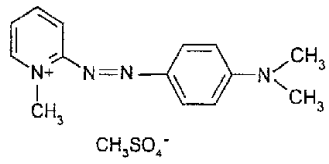
$(I)_{24}$



$(I)_{25}$

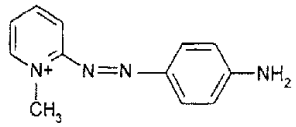


$(I)_{26}$



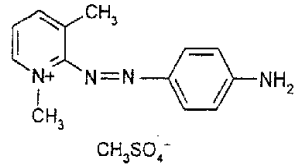
$CH_3SO_4^-$

$(I)_{27}$



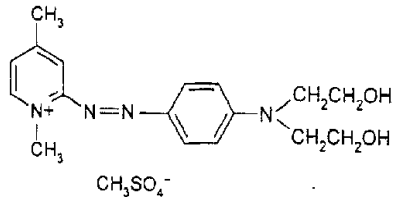
$CH_3SO_4^-$

$(I)_{28}$

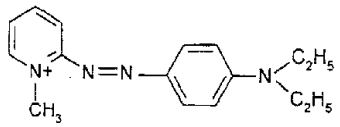


$CH_3SO_4^-$

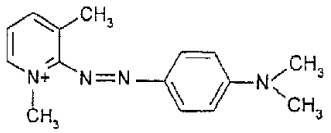
$(I)_{29}$



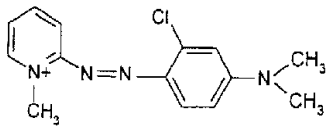
$CH_3SO_4^-$ (I)$_{30}$



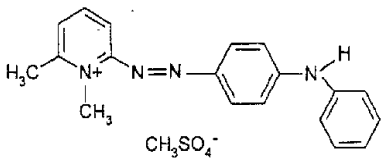
$CH_3SO_4^-$ (I)$_{31}$



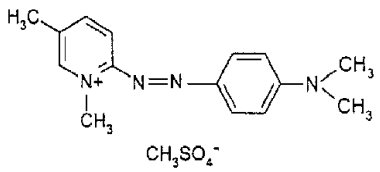
$CH_3SO_4^-$ (I)$_{32}$



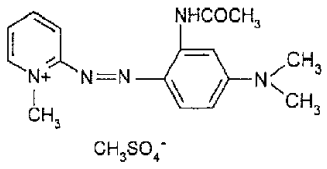
$CH_3SO_4^-$ (I)$_{33}$



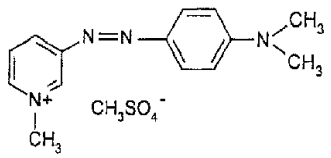
$(I)_{34}$



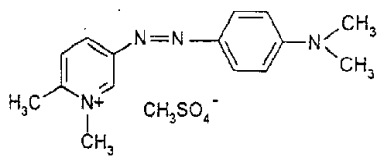
$(I)_{35}$



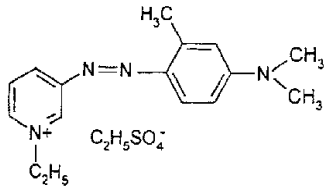
$(I)_{36}$



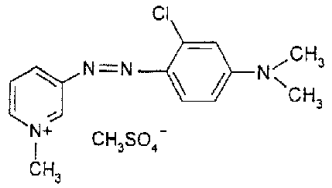
$(I)_{37}$



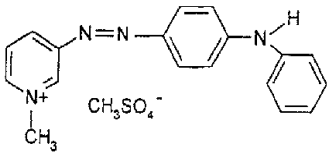
$(I)_{38}$



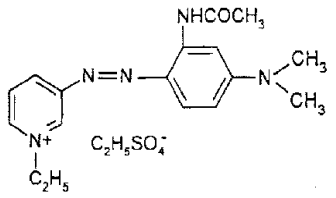
$(I)_{39}$



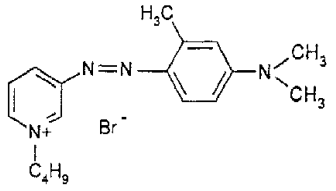
$(I)_{40}$



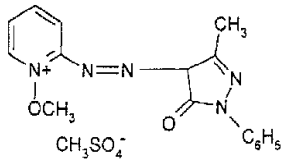
$(I)_{41}$



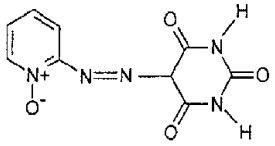
$(I)_{42}$



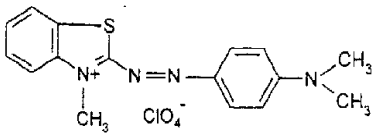
$(I)_{43}$



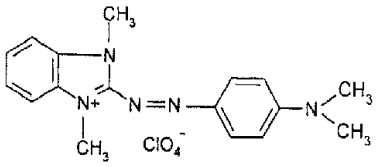
$(I)_{44}$



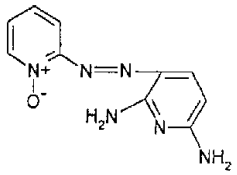
$(I)_{45}$



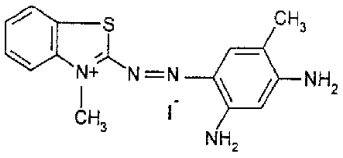
$(I)_{46}$



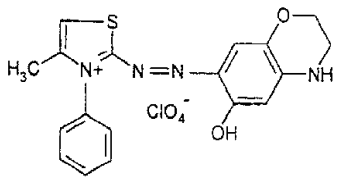
$(I)_{47}$



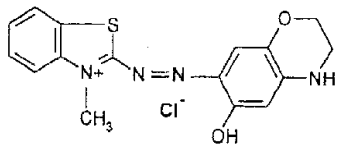
$(I)_{48}$



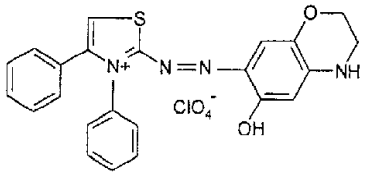
$(I)_{49}$



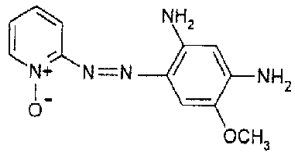
$(I)_{50}$



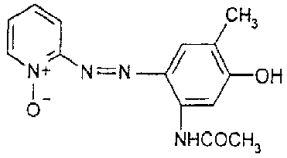
$(I)_{51}$



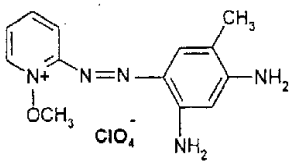
$(I)_{52}$



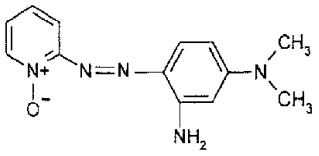
$(I)_{53}$



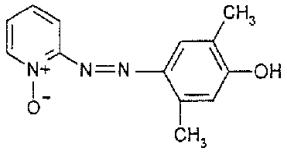
$(I)_{54}$



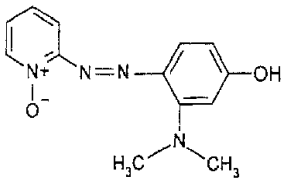
$(I)_{55}$



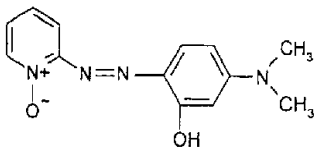
$(I)_{56}$



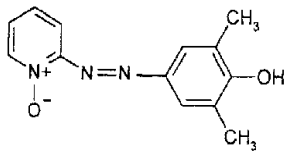
$(I)_{57}$



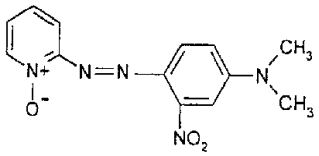
$(I)_{58}$



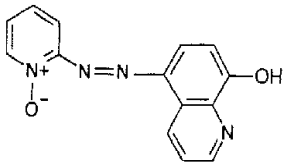
$(I)_{59}$



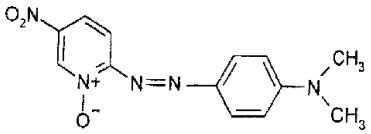
$(I)_{60}$



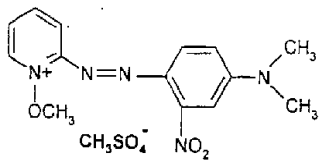
$(I)_{61}$



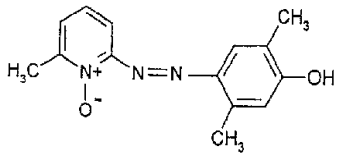
$(I)_{62}$



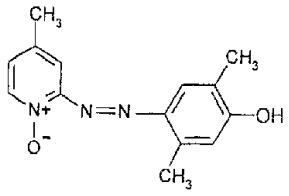
$(I)_{63}$



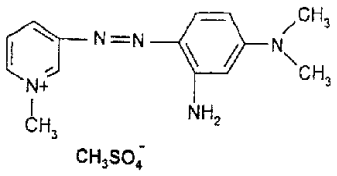
(I)$_{64}$



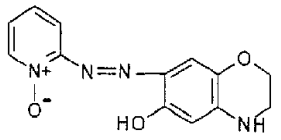
(I)$_{65}$



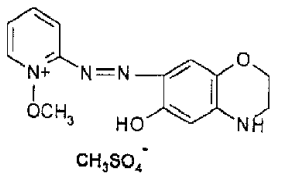
(I)$_{66}$



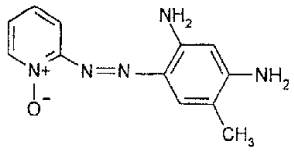
(I)$_{67}$



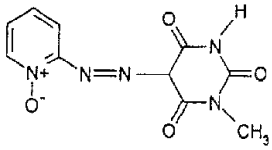
$(I)_{68}$



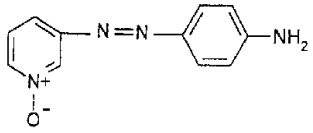
$(I)_{69}$



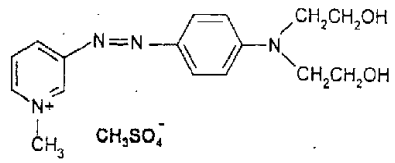
$(I)_{70}$



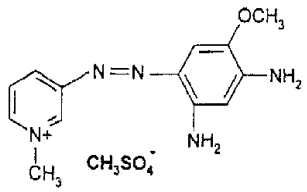
$(I)_{71}$



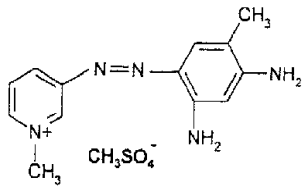
$(I)_{72}$



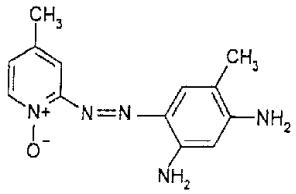
$(I)_{73}$



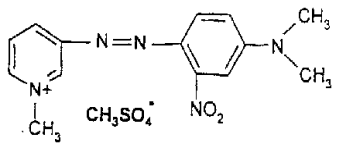
$(I)_{74}$



$(I)_{75}$



$(I)_{76}$



(I)$_{77}$

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 dye composition, and even more preferably from 0.005 to 5% by weight approximately relative to this weight.

(ii) The cationic or amphoteric substantive polymer which can be used according to the present invention is chosen from the group consisting of:

1/- dimethyldiallylammonium halide homopolymers and copolymers;

2/- methacryloyloxyethyltrimethylammonium halide homopolymers and copolymers;

3/- polyquaternary ammonium polymers chosen from those described below;

4/- vinylpyrrolidone copolymers containing methacrylamidopropyltrimethylammonium or methylvinylimidazolium units;

5/- mixtures thereof.

The substantive nature (that is to say the ability to be deposited on the hair) of the polymers used in accordance with the invention is determined conventionally using the test described by Richard J. Crawford, Journal of the Society of Cosmetic Chemists,

1980, 31 -(5) - pages 273 to 278 (development by Red 80 acidic dye).

Among the substantive polymers of the methacryloyloxyethyltrimethylammonium halide homopolymer and copolymer type which can be used according to the invention, mention may be made in particular of the products referred to in the CTFA dictionary (5th edition, 1993) as "Polyquaternium 37", "Polyquaternium 32" and "Polyquaternium 35", which correspond respectively, as regards "Polyquaternium 37", to the crosslinked poly(meth-acryloyloxyethyltrimethylammonium chloride) homopolymer, as a 50% dispersion in mineral oil, sold under the name Salcare SC95 by the company Allied Colloids, as regards "Polyquaternium 32", to the crosslinked copolymer of acrylamide and of methacryloyloxyethyltrimethylammonium chloride (20/80 by weight), as a 50% dispersion in mineral oil, sold under the name Salcare SC92 by the company Allied Colloids, and, as regards "Polyquaternium 35", to the methosulphate of the copolymer of methacryloyloxyethyltrimethylammonium and of methacryloyloxyethyldimethylacetylammonium, sold under the name Plex 7525L by the company Rohm GmbH.

Among the substantive polymers of the dimethyldiallylammonium halide polymer type which can be used according to the invention, mention may be made in particular of:

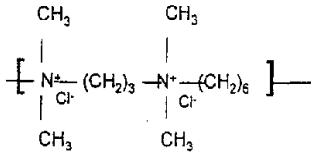
- dimethyldiallylammonium chloride homopolymers such as the one sold under the name "Merquat 100" by the company Merck;

- copolymers of diallyldimethylammonium chloride and of acrylic acid, such as the one in proportions of 80/20 by weight sold under the name Merquat 280 by the company Calgon;

- the copolymers of dimethyldiallylammonium chloride and of acrylamide sold under the names Merquat 550 and Merquat S by the company Merck.

Among the substantive polymers of the poly-quaternary ammonium type which can be used according to the invention, mention may be made of:

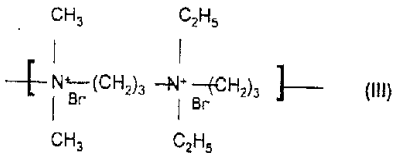
- the polymers prepared and described in French patent 2,270,846, consisting of repeating units corresponding to formula (II) below:



(II)

and in particular those in which the molecular weight, determined by gel permeation chromatography, is between 9500 and 9900;

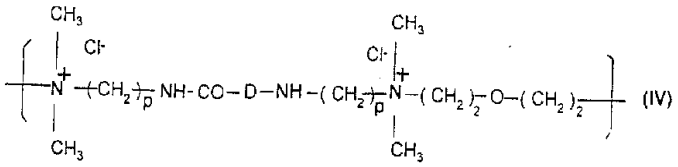
- the polymers prepared and described in French patent 2,270,846, consisting of repeating units corresponding to formula (III) below:



(III)

and in particular those in which the molecular weight, determined by gel permeation chromatography, is about 1200;

- the polymers described and prepared in US patents 4,157,388, 4,390,689, 4,702,906 and 4,719,282 and consisting of repeating units corresponding to formula (IV) below:



(IV)

in which p denotes an integer ranging from 1 to 6 approximately, D can be zero or can represent a group $-(CH_2)_r-CO-$ in which r denotes a number equal to 4 or 7, the molecular mass of the said polymers preferably being less than 100,000, and more preferably less than or equal to 50,000; such polymers are sold in particular by the company Miranol under the names "Mirapol A15", "Mirapol AD1", "Mirapol AZ1" and "Mirapol 175".

Among the vinylpyrrolidone polymers (PVP) containing methacrylamidopropyltrimethylammonium

(MAPTAC) units, mention may be made in particular of those sold under the trade names Gafquat ACP 1011 and Gafquat HS 100 by the company ISP.

Among the vinylpyrrolidone polymers (PVP) containing methylvinylimidazolium units, mention may be made more particularly of:

- the PVP/methylvinylimidazolium chloride copolymers sold under the names Luviquat FC 370, FC 550, FC 905 and HM 552 by the company BASF,
- the PVP/methylvinylimidazolium chloride/vinylimidazole copolymer sold under the name Luviquat 8155 by the company BASF,
- the PVP/methylvinylimidazolium methosulphate copolymer sold under the name Luviquat MS 370 by the company BASF.

The concentration of substantive polymer **(ii)** in the dye composition according to the invention can range between 0.01 and 10% approximately relative to the total weight of the dye composition, and preferably between 0.1 and 5%.

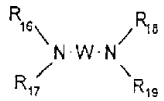
The medium which is suitable for dyeing (or support) generally consists of water or a mixture of water and at least one organic solvent to dissolve the compounds which would not be sufficiently water-soluble. Organic solvents which may be mentioned, for example, are C_1-C_4 lower alkanols such as ethanol and isopropanol; aromatic alcohols such as benzyl alcohol, as well as similar products and mixtures thereof.

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

The pH of the dye composition in accordance with the invention is generally between 2 and 11 approximately, and preferably between 5 and 10 approximately. It can be adjusted to the desired value using acidifying or basifying agents usually used for dyeing keratin fibres.

Among the acidifying agents which may be mentioned, for example, are inorganic or organic acids such as hydrochloric acid, orthophosphoric acid, sulphuric acid, carboxylic acids such as acetic acid, tartaric acid, citric acid or lactic acid, and sulphonic acids.

Among the basifying agents which may be mentioned, for example, are aqueous ammonia, alkaline carbonates, alkanolamines such as mono-, di- and triethanolamine and derivatives thereof, sodium hydroxide, potassium hydroxide and the compounds of formula (V) below:



(V)

in which W is a propylene residue optionally substituted with a hydroxyl group or a C_1-C_6 alkyl

radical; R_{16}, R_{17}, R_{18} and R_{19}, which may be identical or different, represent a hydrogen atom or a C_1-C_6 alkyl or C_1-C_6 hydroxyalkyl radical.

In addition to the cationic direct dye(s) (i) defined above, the dye composition in accordance with the invention can contain one or more additional direct dyes which may be chosen, for example, from nitrobenzene dyes, anthraquinone dyes, naphthoquinone dyes, triarylmethane dyes, xanthene dyes and azo dyes which are non-cationic.

When it is intended for oxidation dyeing, in addition to the cationic direct dye(s) (i), the dye composition in accordance with the invention contains one or more oxidation bases chosen from the oxidation bases conventionally used for oxidation dyeing and among which mention may be made in particular of para-phenylenediamines, bis(phenyl)alkylenediamines, para-aminophenols, ortho-aminophenols and heterocyclic bases.

When it is (they are) used, the oxidation base(s) preferably represent(s) from 0.0005 to 12% by weight approximately relative to the total weight of the dye composition, and even more preferably from 0.005 to 6% by weight approximately relative to this weight.

When it is intended for oxidation dyeing, in addition to the cationic direct dye (i) and the substantive polymer (ii) as well as oxidation bases,

the dye composition in accordance with the invention can also contain one or more couplers so as to modify or enrich with glints the shades obtained using the cationic direct dye(s) (i) and the oxidation bases.

The couplers which can be used in the dye composition in accordance with the invention can be chosen from the couplers used conventionally in oxidation dyeing and among which mention may be made in particular of meta-phenylenediamines, meta-aminophenols, meta-diphenols and heterocyclic couplers.

When it is (they are) present, the coupler(s) preferably represent(s) from 0.0001 to 10% by weight approximately relative to the total weight of the dye composition, and even more preferably from 0.005 to 5% by weight approximately relative to this weight.

The dye composition in accordance with the invention can also contain various adjuvants conventionally used in compositions for dyeing the hair, such as antioxidants, penetrating agents, sequestering agents, fragrances, buffers, dispersing agents, surfactants, film-forming agents, ceramides, preserving agents, screening agents and opacifiers.

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

addition(s) envisaged.

The dye composition according to the invention can be in various forms, such as in the form of liquids, shampoos, creams or gels or any other form which is suitable for dyeing keratin fibres, and in particular human hair. It can be obtained by mixing, at the time of use, a composition, which may be in pulverulent form, containing the cationic dye(s) with a composition containing the specific substantive polymer(s).

When the combination of the cationic direct dye (i) and the substantive polymer (ii) according to the invention is used in a composition intended for oxidation dyeing (one or more oxidation bases are then used, optionally in the presence of one or more couplers), or when it is used in a composition intended for lightening direct dyeing, then the dye composition in accordance with the invention also contains at least one oxidizing agent chosen, for example, from hydrogen peroxide, urea peroxide, alkali metal bromates, persalts such as perborates and persulphates, and enzymes such as peroxidases, laccases and two-electron oxidoreductases. The use of hydrogen peroxide or enzymes is particularly preferred.

Another subject of the invention is a process for dyeing keratin fibres, and in particular human keratin fibres such as the hair, using the dye composition as defined above.

According to a first variant of this dyeing process in accordance with the invention, at least one 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 a second variant of this dyeing process in accordance with the invention, at least one dye composition as defined above is applied to the fibres, for a period which is sufficient to develop the desired coloration, without final rinsing.

According to one specific embodiment of this dyeing process, and when the dye composition in accordance with the invention contains at least one oxidation base and at least one oxidizing agent, the dyeing process includes a preliminary step which consists in separately storing, on the one hand, a composition (A1) comprising, in a medium which is suitable for dyeing, at least one cationic direct dye (i) as defined above and at least one oxidation base, and, on the other hand, a composition (B1) 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, after which this mixture is applied to

the keratin fibres, composition (A1) or composition (B1) containing the cationic or amphoteric substantive polymer (ii) as defined above.

According to another specific embodiment of this dyeing process, and when the dye composition in accordance with the invention contains at least one oxidizing agent, the dyeing process includes a preliminary step which consists in separately storing, on the one hand, a composition (A2) comprising, in a medium which is suitable for dyeing, at least one cationic direct dye (i) as defined above, and, on the other hand, a composition (B2) 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, after which this mixture is applied to the keratin fibres, composition (A2) or composition (B2) containing the cationic or amphoteric substantive polymer as defined above.

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 (A1) or (A2) as defined above and a second compartment of which contains composition (B1) or (B2) as defined above. These devices can be equipped with means for delivering the desired mixture onto the hair, such as the devices described in patent FR-2,586,913 in the name of the Applicant.

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

EXAMPLES

EXAMPLE 1:

The dye composition below was prepared:

Cationic direct dye of formula I(10)		0.12 g
Nonylphenol containing 9 mol of ethylene oxide		8.0 g
Substantive polymer of polyquaternary ammonium type of formula (II)		1.0 g A.M.*
Ethanol		10.0 g
2-Amino-2-methyl-1-propanol	qs	pH 9
Demineralized water	qs	100.0 g

A.M.*: Active material

The above composition was applied for 30 minutes to locks of natural grey hair containing 90% white hairs. The locks of hair were then rinsed, washed with a standard shampoo and then dried.

They were dyed in an intense red shade.

A similar result was obtained with the dye (I)1.

EXAMPLE 2:

The dye composition below was prepared:

Cationic direct dye of formula I(27)	0.10 g
Substantive polymer: diallyldimethyl-ammonium chloride homopolymer sold under the name Merquat 100 by the company	

Calgon		1.0 g A.M.*
Ethanol		10.0 g
Nonylphenol containing 9 mol of ethylene oxide		8.0 g
2-Amino-2-methylpropanol	qs	pH 9
Demineralized water	qs	100 g

A.M.*: Active material

The above composition was applied for 30 minutes to locks of natural grey hair containing 90% white hairs. The locks of hair were then rinsed, washed with a standard shampoo and then dried.

They were dyed in an intense purple shade.

A similar result was obtained with the dye (I)32.

In the claims which follow and in the preceding description of the invention, except where the context requires otherwise due to express language or necessary implication, the word "comprising" is used in the sense of "including", i.e. the features specified may be associated with further features in various embodiments of the invention.

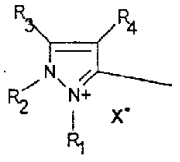
THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. Composition for dyeing keratin fibres, and in particular human keratin fibres such as the hair, containing, in a medium which is suitable for dyeing, **(i)** at least one cationic direct dye of formula (I) below:

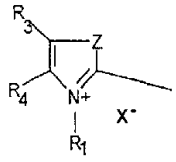
(I)

in which:

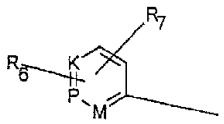
the symbol A represents a group chosen from structures A1 to A3 below:



A_1



A_2



A_3

in which structures A1 to A3,

R_1 denotes a C_1-C_4 alkyl radical, a phenyl radical which can be substituted with a C_1-C_4 alkyl radical or a halogen atom chosen from chlorine, bromine, iodine and fluorine;

R_2 denotes a C_1-C_4 alkyl radical or a phenyl radical;

R_3 and R_4, which may be identical or different, represent a C_1-C_4 alkyl radical, a phenyl radical or, in the case of structure A1, can together form a substituted benzene ring, and in the case of structure A2, can together form a benzene ring optionally substituted with one or more C_1-C_4 alkyl, C_1-C_4 alkoxy or NO_2 radicals;

R_3 can also denote a hydrogen atom;

Z denotes an oxygen or sulphur atom or a group $-NR_2$;

M represents a group -CH, -CR (R denoting C_1-C_4 alkyl) or $-NR_5(X^-)_r$;

K represents a group -CH, -CR (R denoting C_1-C_4 alkyl) or $-NR_5(X^-)_r$;

P represents a group -CH, -CR (R denoting C_1-C_4 alkyl) or $-NR_5(X^-)_r$; r denotes 0 or 1;

R_5 represents an atom O^-, a C_1-C_4 alkoxy radical or a C_1-C_4 alkyl radical;

R_6 and R_7, which may be identical or different, represent a hydrogen atom or a halogen atom chosen from chlorine, bromine, iodine and fluorine, a C_1-C_4 alkyl or C_1-C_4 alkoxy radical or an $-NO_2$ radical;

X^- represents an anion preferably chosen from chloride, iodide, methyl sulphate, ethyl sulphate, acetate and perchlorate;

with the proviso that,

if R_4 denotes a C_1-C_4 alkyl radical and Z denotes a sulphur atom, R_3 does not denote a hydrogen atom;

if R_5 denotes O^-, then r denotes zero;

if K or P or M denote -N-(C_1-C_4)alkyl X^-, then R_6 or R_7 is other than a hydrogen atom;

if K denotes $-NR_5(X^-)_r$, then M=P=-CH; -CR;

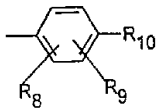
if M denotes $-NR_5(X^-)_r$, then K=P=-CH; -CR;

if P denotes $-NR_5(X^-)_r$, then K=M and denote -CH or -CR;

if Z denotes $-NR_2$ and R_2 denotes a C_1-C_4 alkyl radical, then at least one of the radicals R_1, R_3 or R_4 or A_2 is other than a C_1-C_4 alkyl radical;

the symbol B represents:

-(a) a group of structure B1 below:



B_1

in which structure B1,

R_8 represents a hydrogen atom, a halogen atom chosen from chlorine, bromine, iodine and fluorine, a C_1-C_4 alkyl or C_1-C_4 alkoxy radical, a radical -OH, $-NO_2$, $-NHR_{11}$, $-NR_{12}R_{13}$ or $-NHCO(C_1$-$C_4)$alkyl radical or forms, with R_9, a 5- or 6-membered ring which may or may not contain one or more hetero atoms chosen from nitrogen, oxygen and sulphur;

R_9 represents a hydrogen atom, a halogen atom chosen from chlorine, bromine, iodine and fluorine, or a C_1-C_4 alkyl or C_1-C_4 alkoxy radical,

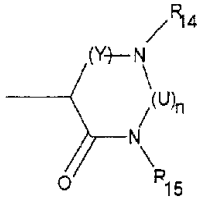
or forms, with R_{10} or R_{11}, a 5- or 6-membered ring which may or may not contain one or more hetero atoms chosen from nitrogen, oxygen and sulphur;

R_{10} represents a hydrogen atom, an -OH radical, a radical $-NHR_{11}$ or a radical $-NR_{12}R_{13}$;

R_{11} represents a hydrogen atom, a C_1-C_4 alkyl radical, a C_1-C_4 monohydroxyalkyl or C_2-C_4 polyhydroxyalkyl radical or a phenyl radical;

R_{12} and R_{13}, which may be identical or different, represent a C_1-C_4 alkyl radical or a C_1-C_4 monohydroxyalkyl or C_2-C_4 polyhydroxyalkyl radical;

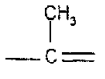
-(b) a 5- or 6-membered nitrogenous heterocyclic group which can contain other hetero atoms and/or carbonyl groups and which can be substituted with one or more C_1-C_4 alkyl, amino or phenyl radicals, and in particular a group of structure B2 below:



B_2

in which structure B2,

R_{14} and R_{15}, which may be identical or different, represent a hydrogen atom, a C_1-C_4 alkyl radical or a phenyl radical;

Y denotes a -CO- radical or a radical  ;

n = 0 or 1, where, when n denotes 1, U denotes a -CO- radical,

the said composition being characterized in that it also contains:

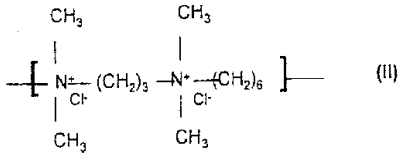
(ii) at least one cationic or amphoteric substantive polymer chosen from the group formed by:

1/- dimethyldiallylammonium halide homopolymers and copolymers;

2/- methacryloyloxyethyltrimethylammonium halide homopolymers and copolymers

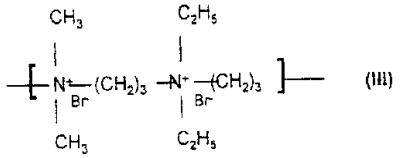
3/- polyquaternary ammonium polymers chosen from the group formed by:

- polymers consisting of repeating units corresponding to formula (II) below:



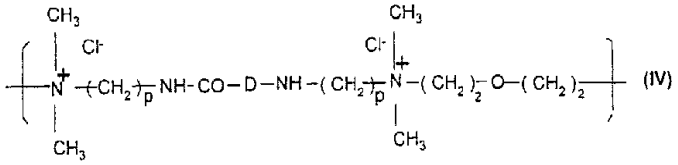
(II)

- polymers consisting of repeating units corresponding to formula (III) below:



(III)

- polymers consisting of repeating units corresponding to formula (IV) below:



(IV)

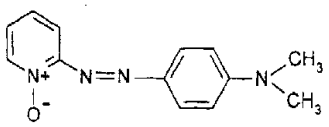
in which p denotes an integer ranging from 1 to 6 approximately, D can be zero or can represent a group $-(CH_2)_r-CO-$ in which r denotes a number equal to 4 or 7;

4/- vinylpyrrolidone copolymers containing methacrylamidopropyltrimethylammonium units or methylvinylimidazolium units;

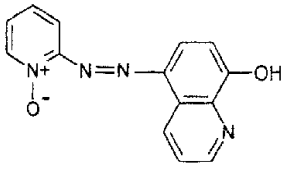
5/- mixtures thereof.

2. Composition according to Claim 1, characterized in that, in formula (I), the C_1-C_4 alkyl radicals and the C_1-C_4 alkoxy radicals are methyl, ethyl, butyl, methoxy and ethoxy radicals.

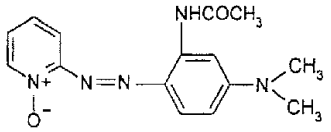
3. Composition according to Claim 2, characterized in that the cationic direct dyes correspond to structures $(I)_1$ to $(I)_{77}$ below:



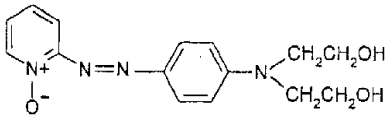
$(I)_1$



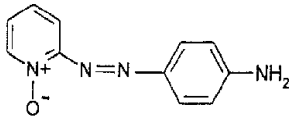
$(I)_2$



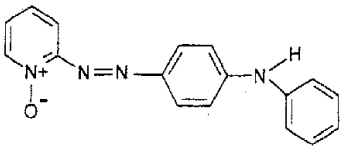
$(I)_3$



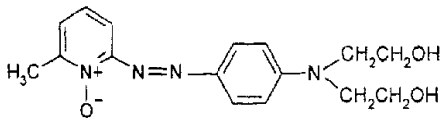
$(I)_4$



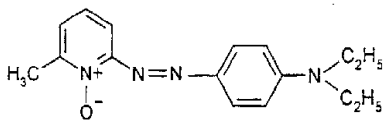
$(I)_5$



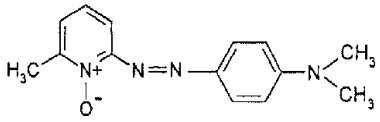
$(I)_6$



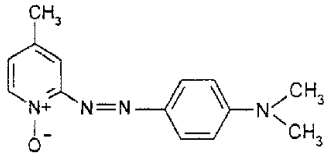
$(I)_7$



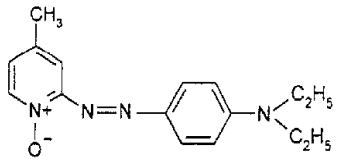
$(I)_8$



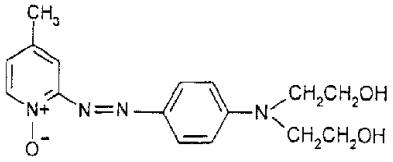
$(I)_9$



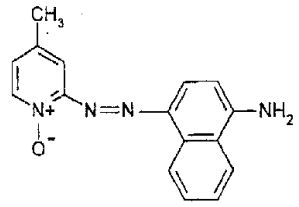
$(I)_{10}$



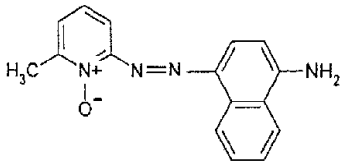
$(I)_{11}$



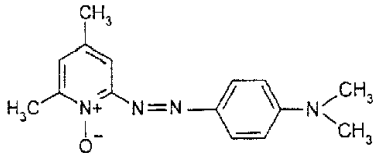
$(I)_{12}$



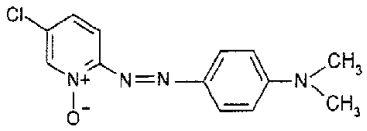
$(I)_{13}$



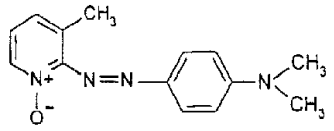
$(I)_{14}$



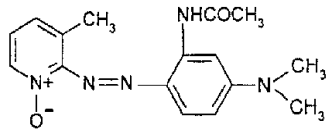
$(I)_{15}$



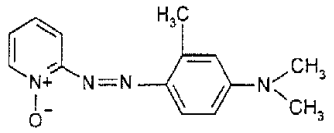
$(I)_{16}$



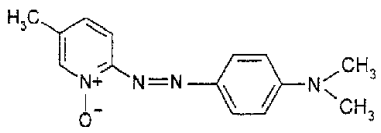
$(I)_{17}$



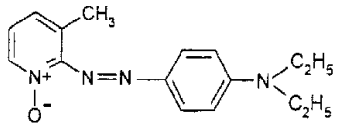
$(I)_{18}$



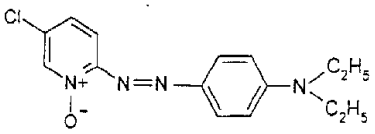
$(I)_{19}$



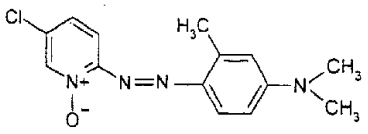
$(I)_{20}$



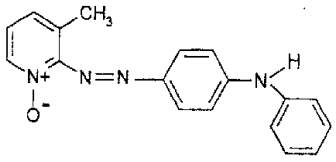
$(I)_{21}$



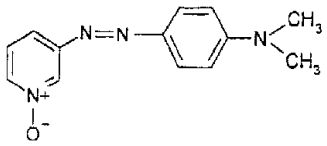
$(I)_{22}$



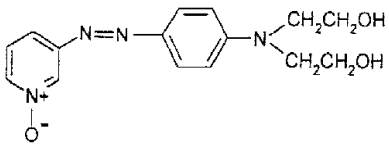
$(I)_{23}$



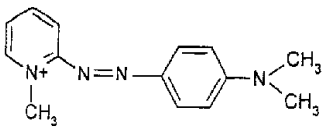
$(I)_{24}$



$(I)_{25}$

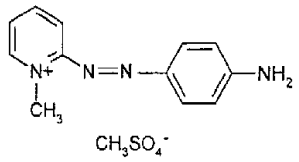


$(I)_{26}$

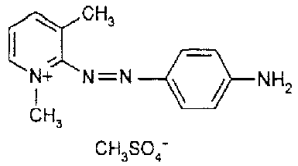


$CH_3SO_4^-$

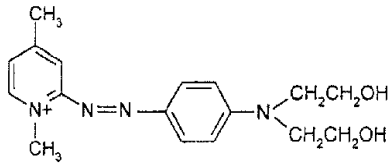
$(I)_{27}$



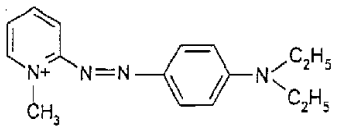
$CH_3SO_4^-$ (I)$_{28}$



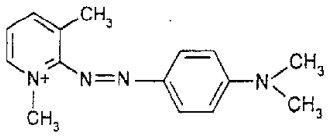
$CH_3SO_4^-$ (I)$_{29}$



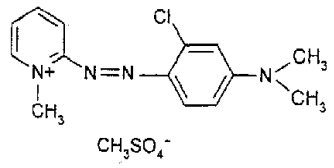
$CH_3SO_4^-$ (I)$_{30}$



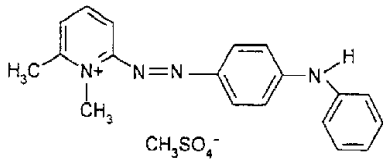
$CH_3SO_4^-$ (I)$_{31}$



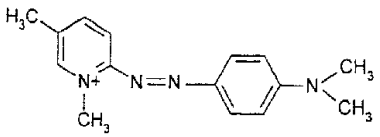
$CH_3SO_4^-$ (I)$_{32}$



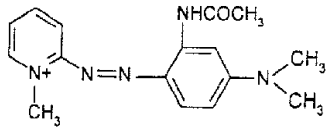
$CH_3SO_4^-$ $(I)_{33}$



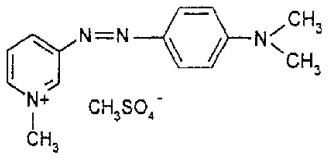
$CH_3SO_4^-$ $(I)_{34}$



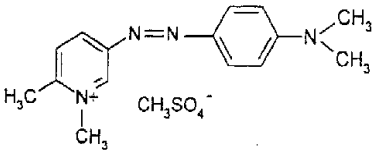
$CH_3SO_4^-$ $(I)_{35}$



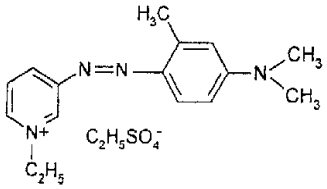
$CH_3SO_4^-$ $(I)_{36}$



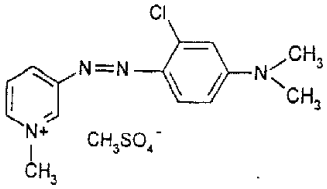
$(I)_{37}$



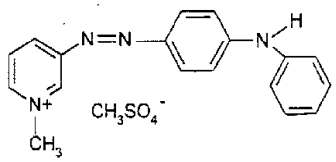
$(I)_{38}$



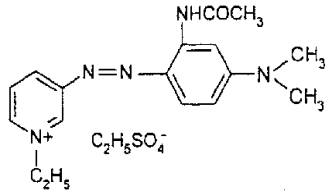
$(I)_{39}$



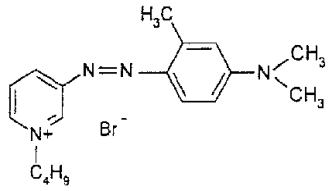
$(I)_{40}$



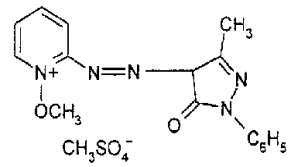
$(I)_{41}$



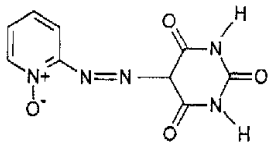
$(I)_{42}$



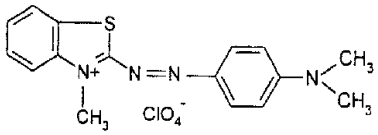
$(I)_{43}$



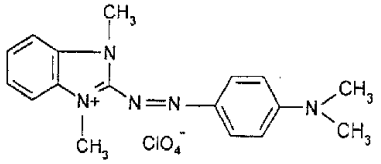
$(I)_{44}$



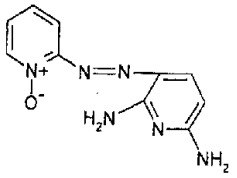
$(I)_{45}$



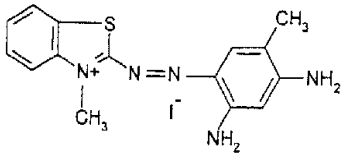
$(I)_{46}$



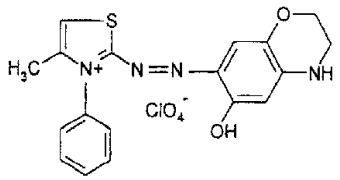
$(I)_{47}$



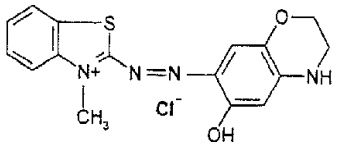
$(I)_{48}$



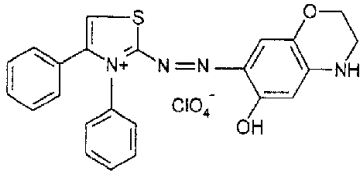
$(I)_{49}$



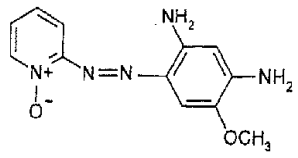
$(I)_{50}$



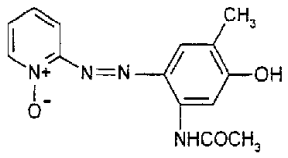
$(I)_{51}$



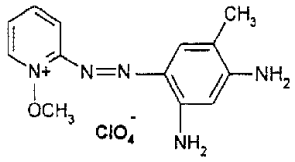
$(I)_{52}$



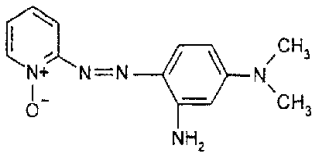
$(I)_{53}$



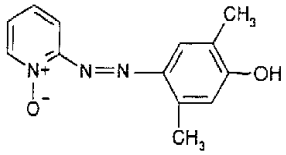
$(I)_{54}$



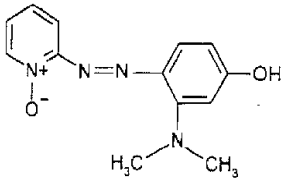
$(I)_{55}$



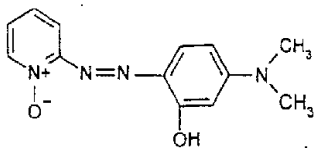
$(I)_{56}$



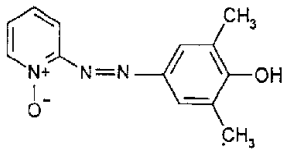
$(I)_{57}$



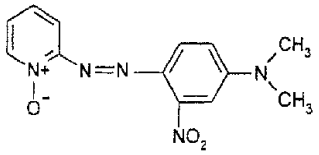
$(I)_{58}$



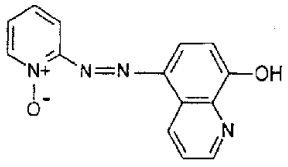
$(I)_{59}$



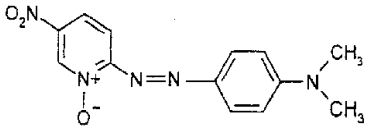
$(I)_{60}$



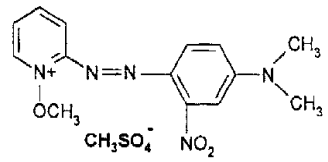
$(I)_{61}$



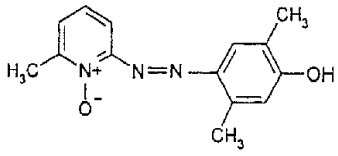
$(I)_{62}$



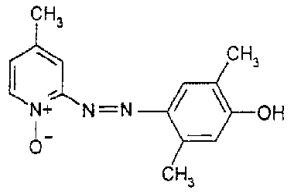
$(I)_{63}$



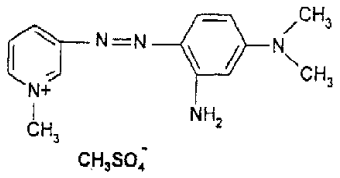
$(I)_{64}$



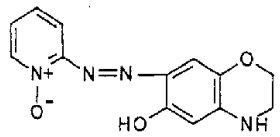
$(I)_{65}$



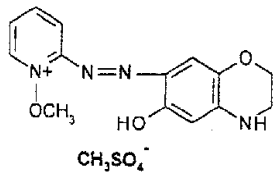
$(I)_{66}$



$(I)_{67}$

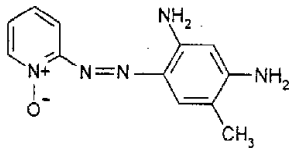


$(I)_{68}$

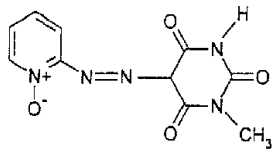


$CH_3SO_4^-$

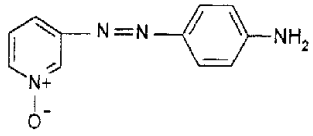
$(I)_{69}$



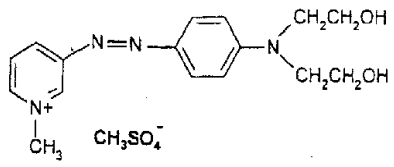
$(I)_{70}$



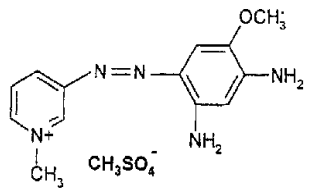
$(I)_{71}$



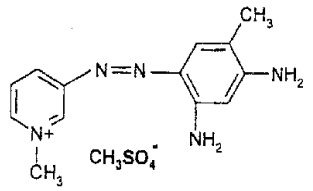
$(I)_{72}$



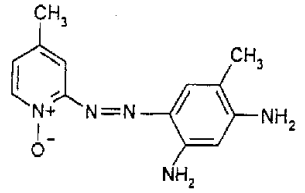
$(I)_{73}$



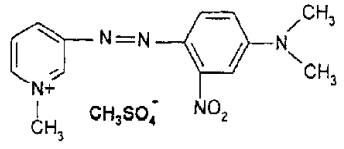
$(I)_{74}$



$(I)_{75}$



$(I)_{76}$



$(I)_{77}$

4. Composition according to any one of the preceding claims, characterized in that the cationic

direct dye(s) of formula (I) represent(s) from 0.001 to 10% by weight relative to the total weight of the composition.

5. Composition according to Claim 4, characterized in that the cationic direct dye(s) of formula (I) represent(s) from 0.005 to 5% by weight relative to the total weight of the composition.

6. Composition according to any one of Claims 1 to 5, characterized in that the substantive polymer is a dimethyldiallylammonium chloride homopolymer.

7. Composition according to any one of Claims 1 to 5, characterized in that the substantive polymer of the dimethyldiallylammonium halide copolymer type is a copolymer of dimethyldiallylammonium chloride and of acrylic acid (80/20 by weight).

8. Composition according to any one of Claims 1 to 5, characterized in that the substantive polymers of the methacryloyloxyethyltrimethylammonium halide homopolymer and copolymer type are chosen from the crosslinked methacryloyloxyethyltrimethylammonium chloride homopolymer, as a 50% dispersion in mineral oil, the crosslinked copolymer of acrylamide and of methacryloyloxyethyltrimethylammonium chloride (20/80 by weight), as a 50% dispersion in mineral oil, and the methosulphate of the copolymer of methacryloyloxyethyltrimethylammonium and of methacryloyloxyethyldimethylacetylammonium.

9. Composition according to any one of the preceding claims, characterized in that the substantive polymer(s) represent(s) from 0.01 to 10% by weight relative to the total weight of the composition.

10. Composition according to Claim 9, characterized in that the substantive polymer(s) represent(s) from 0.1 to 5% by weight relative to the total weight of the composition.

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

12. Composition according to any one of the preceding claims, characterized in that it has a pH of between 2 and 11 and preferably between 5 and 10.

13. Composition according to any one of the preceding claims, characterized in that it is intended for oxidation dyeing and in that it contains one or more oxidation bases chosen from para-phenylenediamines, bis(phenyl)alkylenediamines, para-aminophenols, ortho-aminophenols and heterocyclic bases.

14. Composition according to Claim 13, characterized in that the oxidation base(s) represent(s) from 0.0005 to 12% by weight relative to the total weight of the dye composition.

15. Composition according to Claim 14,

characterized in that the oxidation base(s) represent(s) from 0.005 to 6% by weight relative to the total weight of the dye composition.

16. Composition according to any one of Claims 13 to 15, characterized in that it contains one or more couplers chosen from meta-phenylenediamines, meta-aminophenols, meta-diphenols and heterocyclic couplers.

17. Composition according to Claim 16, characterized in that the coupler(s) represent(s) from 0.0001 to 10% by weight relative to the total weight of the dye composition.

18. Composition according to Claim 17, characterized in that the coupler(s) represent(s) from 0.005 to 5% 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 is intended for oxidation dyeing or lightening direct dyeing and in that it contains at least one oxidizing agent.

20. Process for dyeing keratin fibres, and in particular human keratin fibres such as the hair, characterized in that at least one dye composition as defined in any one of Claims 1 to 19 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.

21. Process for dyeing keratin fibres, and

in particular human keratin fibres such as the hair, characterized in that at least one dye composition as defined in any one of Claims 1 to 19 is applied to the fibres, for a period which is sufficient to develop the desired coloration, without final rinsing.

22. Process for dyeing keratin fibres, and in particular human keratin fibres such as the hair, characterized in that it includes a preliminary step which consists in separately storing, on the one hand, a composition (A1) comprising, in a medium which is suitable for dyeing, at least one cationic direct dye of formula (I) as defined in Claims 1 to 5 and at least one oxidation base, and, on the other hand, a composition (B1) 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, after which this mixture is applied to the keratin fibres, composition (A1) or composition (B1) containing the substantive polymer as defined in Claims 6 to 10.

23. Process for dyeing keratin fibres, and in particular human keratin fibres such as the hair, characterized in that it includes a preliminary step which consists in separately storing, on the one hand, a composition (A2) comprising, in a medium which is suitable for dyeing, at least one cationic direct dye of formula (I) as defined in Claims 1 to 5, and, on the other hand, a composition (B2) 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, after which this mixture is applied to the keratin fibres, composition (A2) or composition (B2) containing the substantive polymer as defined in Claims 6 to 10.

24. Multi-compartment dyeing device or multi-compartment dyeing "kit", characterized in that a first compartment contains composition (A1) or (A2) as defined in Claim 22 or 23 and a second compartment contains composition (B1) or (B2) as defined in Claim 22 or 23.

Dated this 23rd day of April 1999
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By their Patent Attorneys
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