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(54) **Title:** NOVEL CATIONIC OXIDATION BASES, THEIR USE FOR DYEING KERATIN FIBRES, DYEING COMPOSITIONS AND DYEING METHODS

(54) **Titre:** NOUVELLES BASES D'OXYDATION CATIONIQUES, LEUR UTILISATION POUR LA TEINTURE D'OXYDATION DES FIBRES KERATINIQUES, COMPOSITIONS TINCTORIALES ET PROCEDES DE TEINTURE

(57) **Abstract**

The invention concerns novel pyrazole derivatives comprising at least a cationic group Z, Z being selected among the quaternized aliphatic chains, aliphatic chains comprising at least a saturated quaternized cycle, and aliphatic chains comprising at least an unsaturated quaternized cycle, their use as oxidation base for dyeing keratin fibres, dyeing compositions containing them, and dyeing methods using them.

(57) **Abrégé**

L'invention a pour objet de nouveaux dérivés pyrazoliques comportant au moins un groupement cationique Z, Z étant choisi parmi des chaînes aliphatiques quaternisées, des chaînes aliphatiques comportant au moins un cycle saturé quaternisé, et des chaînes aliphatiques comportant au moins un cycle insaturé quaternisé, leur utilisation à titre de base d'oxydation pour la teinture d'oxydation des fibres kératiniques, les compositions tinctoriales les contenant, ainsi que les procédés de teinture d'oxydation les mettant en oeuvre.

NOVEL CATIONIC OXIDATION BASES, THEIR USE FOR THE OXIDATION DYEING OF KERATIN FIBRES, DYE COMPOSITIONS AND DYEING PROCESSES

The invention relates to novel pyrazole derivatives containing at least one cationic group Z, Z being chosen from quaternized aliphatic chains, aliphatic chains containing at least one quaternized saturated ring and aliphatic chains containing at least one quaternized unsaturated ring, to their use as oxidation base for the oxidation dyeing of keratin fibres, to dye compositions containing them and to oxidation dyeing processes using them.

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

It is also known that the shades obtained with these oxidation bases can be varied by combining them with couplers or coloration modifiers, the latter being chosen in particular from aromatic meta-diamines,

meta-aminophenols, meta-diphenols and certain heterocyclic compounds.

The variety of molecules used as oxidation bases and couplers makes it possible to obtain a wide range of colours.

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

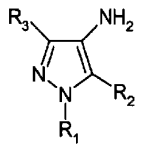
The dyes must also allow white hairs to be covered, and, lastly, they must be as unselective as possible, i.e. they must allow the smallest possible differences in coloration to be produced over the entire length of the same keratin fibre, which may indeed be differently sensitized (i.e. damaged) between its tip and its root.

Now, the Applicant has just discovered, entirely surprisingly and unexpectedly, that novel pyrazole derivatives of formula (I) defined below, containing at least one cationic group Z, Z being chosen from quaternized aliphatic chains, aliphatic chains containing at least one quaternized saturated ring and aliphatic chains containing at least one quaternized unsaturated ring, are not only suitable for use as oxidation base, but also allow dye compositions

to be obtained which lead to strong colorations, in a wide range of colours, and which have excellent properties of resistance to the various treatments to which keratin fibres may be subjected.

These discoveries form the basis of the present invention.

A first subject of the invention is thus novel compounds of formula (I) below, the addition salts thereof with an acid or with a base, and the possible tautomeric forms thereof:



(I)

in which:

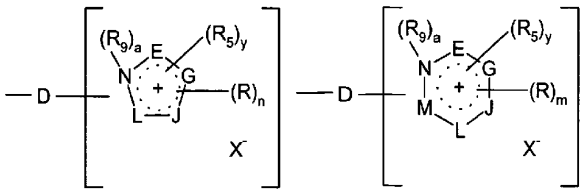
- R_1 represents a hydrogen atom; a group Z as defined below; a C_1-C_6 alkyl radical; a C_1-C_6 trifluoroalkyl radical; a C_1-C_6 monohydroxyalkyl radical; a C_2-C_6 polyhydroxyalkyl radical; an aryl(C_1-C_6)alkyl radical in which the aryl radical may be in particular a phenyl radical or a 5- or 6-membered aromatic heterocycle such as, for example, a pyridyl ring, an imidazolyl ring, a furyl ring or an oxazolyl ring; a (C_1-C_6)alkoxy(C_1-C_6)alkyl radical; a (C_1-C_6)alkylthio-(C_1-C_6)alkyl radical; an amino(C_1-C_6)alkylcarbonyl-(C_1-C_6)alkyl radical; an N-Z-amino(C_1-C_6)alkylcarbonyl-(C_1-C_6)alkyl radical; an N-(C_1-C_6)alkylamino(C_1-C_6)-alkylcarbonyl(C_1-C_6)alkyl radical; an N,N-di(C_1-C_6)-

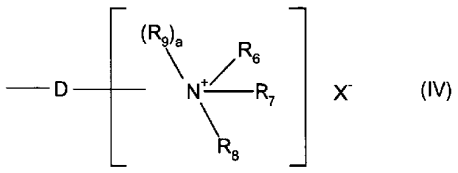
alkylamino(C_1-C_6)alkylcarbonyl(C_1-C_6)alkyl radical; a C_1-C_6 aminosulphonylalkyl radical; a C_1-C_6 N-Z-amino-sulphonylalkyl radical; an N-(C_1-C_6)alkylamino-sulphonyl(C_1-C_6)alkyl radical; an N,N-di(C_1-C_6)alkyl-aminosulphonyl(C_1-C_6)alkyl radical;

- R_2 and R_3, which may be identical or different, represent a group $-NHR_4$; a hydroxyl radical; a halogen atom; a nitro radical; a cyano radical; a carboxyl radical; a C_1-C_6 alkylcarboxyl radical; a carboxyaryl radical; a carbamyl radical; an N-(C_1-C_6)alkylcarbamyl radical; an N,N-di(C_1-C_6)alkylcarbamyl radical; an N-arylcarbamyl radical; a C_1-C_6 alkoxy radical; an aryloxy radical; a C_1-C_6 thioalkyl radical; a thioaryl radical or one of the meanings given above for R_1; it being understood that at least one of the radicals R_2 and R_3 represents a group $-NHR_4$ or a hydroxyl radical;
- R_4 represents a hydrogen atom; a group Z as defined below; a C_1-C_6 alkyl radical; a C_1-C_6 monohydroxyalkyl radical; a C_2-C_6 polyhydroxyalkyl radical; a (C_1-C_6)-alkoxy(C_1-C_6)alkyl radical; an aryl radical; a benzyl radical; a cyano(C_1-C_6)alkyl radical; a carbamyl-(C_1-C_6)alkyl radical; an N-(C_1-C_6)alkylcarbamyl(C_1-C_6)-alkyl radical; an N,N-di(C_1-C_6)alkylcarbamyl(C_1-C_6)-alkyl radical; a thiocarbamyl(C_1-C_6)alkyl radical; a C_1-C_6 trifluoroalkyl radical; a C_1-C_6 sulphoalkyl radical; a (C_1-C_6)alkylcarboxy(C_1-C_6)alkyl radical; a (C_1-C_6)alkylsulphinyl(C_1-C_6)alkyl radical; a C_1-C_6 aminosulphonylalkyl radical; a C_1-C_6 N-Z-amino-

sulphonylalkyl radical; an N-(C_1-C_6)alkylamino-sulphonyl(C_1-C_6)alkyl radical; an N,N-di(C_1-C_6)alkyl-aminosulphonyl(C_1-C_6)alkyl radical; a C_1-C_6 aminoalkyl radical; a C_1-C_6 aminoalkyl radical in which the amine is substituted with one or two radicals, which may be identical or different, chosen from C_1-C_6 alkyl, C_1-C_6 monohydroxyalkyl, C_2-C_6 polyhydroxyalkyl, (C_1-C_6)alkyl-carbonyl, C_1-C_6 alkylsulphonyl, formyl and trifluoro-(C_1-C_6)alkylcarbonyl radicals or with a group Z; the amine of the C_1-C_6 aminoalkyl radical may also be substituted with two radicals forming, together with the nitrogen atom of the said amine, a saturated or unsaturated 5- or 6-membered ring which may contain one or more hetero atoms chosen from nitrogen, oxygen and sulphur, such as, for example, a piperidine, morpholine, imidazole or oxazole ring;

- Z is chosen from the unsaturated cationic groups of formulae (II) and (III) below, and the saturated cationic groups of formula (IV) below:





(IV)

in which:

- D is a linker arm which represents a linear or branched alkyl chain preferably containing from 1 to 14 carbon atoms, which can be interrupted by one or more hetero atoms such as oxygen, sulphur or nitrogen atoms, and which can be substituted with one or more hydroxyl or C_1-C_6 alkoxy radicals, and which can bear one or more ketone functions;
- the ring members E, G, J, L and M, which may be identical or different, represent a carbon, oxygen, sulphur or nitrogen atom;
- n is an integer between 0 and 4 inclusive;
- m is an integer between 0 and 5 inclusive;
- the radicals R, which may be identical or different, represent a second group Z, which is identical to or different from the first group Z, a halogen atom, a hydroxyl radical, a C_1-C_6 alkyl radical, a C_1-C_6 monohydroxyalkyl radical, a C_2-C_6 polyhydroxyalkyl radical, a nitro radical, a cyano radical, a cyano(C_1-C_6)alkyl radical, a C_1-C_6 alkoxy radical, a tri(C_1-C_6)alkylsilane(C_1-C_6)alkyl radical, an amido radical, an aldehydo radical, a carboxyl radical, a (C_1-C_6)alkylcarbonyl radical, a thio radical, a C_1-C_6

thioalkyl radical, a C_1-C_6 alkylthio radical, an amino radical, an amino radical protected with a (C_1-C_6)alkylcarbonyl or C_1-C_6 alkylsulphonyl radical; a group NHRO or NROR in which RO and R, which may be identical or different, represent a C_1-C_6 alkyl radical, a C_1-C_6 monohydroxyalkyl radical or a C_2-C_6 polyhydroxyalkyl radical;

- R_5 represents a C_1-C_6 alkyl radical, a C_1-C_6 monohydroxyalkyl radical, a C_2-C_6 polyhydroxyalkyl radical, a cyano(C_1-C_6)alkyl radical, a tri(C_1-C_6)alkylsilane(C_1-C_6)alkyl radical, a (C_1-C_6)alkoxy(C_1-C_6)alkyl radical, a carbamyl(C_1-C_6)-alkyl radical, a (C_1-C_6)alkylcarboxy(C_1-C_6)alkyl radical, a benzyl radical or a second group Z, which is identical to or different from the first group Z;
- R_6, R_7 and R_8, which may be identical or different, represent a C_1-C_6 alkyl radical, a C_1-C_6 monohydroxyalkyl radical, a C_2-C_6 polyhydroxyalkyl radical, a (C_1-C_6)alkoxy(C_1-C_6)alkyl radical, a cyano(C_1-C_6)alkyl radical, an aryl radical, a benzyl radical, a C_1-C_6 amidoalkyl radical, a tri(C_1-C_6)alkylsilane(C_1-C_6)alkyl radical or a C_1-C_6 aminoalkyl radical in which the amine is protected with a (C_1-C_6)alkylcarbonyl or C_1-C_6 alkylsulphonyl radical; two of the radicals R_6, R_7 and R_8 can together also form, with the nitrogen atom to which they are attached, a saturated 5- or 6-membered carbon ring or a ring containing one or more hetero

atoms such as, for example, a pyrrolidine ring, a piperidine ring, a piperazine ring or a morpholine ring, it being possible for the said ring to be unsubstituted or substituted with a halogen atom, a hydroxyl radical, a C_1-C_6 alkyl radical, a C_1-C_6 monohydroxyalkyl radical, a C_2-C_6 polyhydroxyalkyl radical, a nitro radical, a cyano radical, a cyano(C_1-C_6)alkyl radical, a C_1-C_6 alkoxy radical, a tri(C_1-C_6)alkylsilane(C_1-C_6)alkyl radical, an amido radical, an aldehydo radical, a carboxyl radical, a keto(C_1-C_6)alkyl radical, a thio radical, a C_1-C_6 thioalkyl radical, a C_1-C_6 alkylthio radical, an amino radical or an amino radical protected with a (C_1-C_6)alkylcarbonyl or C_1-C_6 alkylsulphonyl radical; one of the radicals R_6, R_7 and R_8 can also represent a second group Z which is identical to or different from the first group Z;

- R_9 represents a C_1-C_6 alkyl radical; a C_1-C_6 monohydroxyalkyl radical; a C_2-C_6 polyhydroxyalkyl radical; an aryl radical; a benzyl radical; a C_1-C_6 aminoalkyl radical, a C_1-C_6 aminoalkyl radical in which the amine is protected with a (C_1-C_6)alkylcarbonyl or C_1-C_6 alkylsulphonyl radical; a carboxy-(C_1-C_6)alkyl radical; a cyano(C_1-C_6)alkyl radical; a carbamyl(C_1-C_6)alkyl radical; a C_1-C_6 trifluoroalkyl radical; a tri(C_1-C_6)alkylsilane(C_1-C_6)alkyl radical; a C_1-C_6 sulphonamidoalkyl radical; a (C_1-C_6)alkylcarboxy-(C_1-C_6)alkyl radical; a (C_1-C_6)alkylsulphinyl-

(C_1-C_6)alkyl radical; a (C_1-C_6)alkylsulphonyl-(C_1-C_6)alkyl radical; a (C_1-C_6)alkylketo(C_1-C_6)alkyl radical; an N-(C_1-C_6)alkylcarbamyl(C_1-C_6)alkyl radical; an N-(C_1-C_6)alkylsulphonamido(C_1-C_6)alkyl radical;

- a and y are integers equal to 0 or 1; with the following conditions:
  - in the unsaturated cationic groups of formula (II):
    - when a = 0, the linker arm D is attached to the nitrogen atom,
    - when a = 1, the linker arm D is attached to one of the ring members E, G, J or L,
    - y can take the value 1 only:
      1) when the ring members E, G, J and L simultaneously represent a carbon atom and when the radical R_5 is borne by the nitrogen atom of the unsaturated ring; or alternatively
      2) when at least one of the ring members E, G, J and L represents a nitrogen atom to which the radical R_5 is attached;
  - in the unsaturated cationic groups of formula (III):
    - when a = 0, the linker arm D is attached to the nitrogen atom,
    - when a = 1, the linker arm D is attached to one of the ring members E, G, J, L or M,
    - y can take the value 1 only when at least one of the ring members E, G, J, L and M represents a

divalent atom and when the radical R_5 is borne by the nitrogen atom of the unsaturated ring;

- in the cationic groups of formula (IV):
  - when a = 0, then the linker arm is attached to the nitrogen atom bearing the radicals R_6 to R_8,
  - when a = 1, then two of the radicals R_6 to R_8 form, together with the nitrogen atom to which they are attached, a saturated 5- or 6-membered ring as defined above, and the linker arm D is borne by a carbon atom of the said saturated ring;

- X^- represents a monovalent or divalent anion and is preferably chosen from a halogen atom such as chlorine, bromine, fluorine or iodine, a hydroxide, a hydrogenosulphate or a C_1-C_6 alkyl sulphate such as, for example, a methyl sulphate or an ethyl sulphate;

it being understood that the number of cationic groups Z is at least equal to 1.

As mentioned above, the colorations obtained with the oxidation dye composition containing one or more compounds of formula (I) in accordance with the invention are strong and produce a wide range of colours. They moreover have excellent properties of resistance to the action of various external agents (light, bad weather, washing, permanent-waving, perspiration, friction). These properties are particularly noteworthy, in particular as regards the

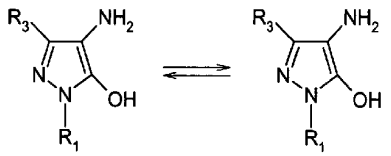
resistance of the colorations obtained to the action of light, washings, permanent-waving and perspiration.

In formula (I) above, the alkyl and alkoxy radicals can be linear or branched.

Among the rings of the unsaturated groups Z of formula (II) above, mention may be made in particular, for example, of pyrrole, imidazole, pyrazole, oxazole, thiazole and triazole rings.

Among the rings of the unsaturated groups Z of formula (III) above, mention may be made in particular, for example, of pyridine, pyrimidine, pyrazine, oxazine and triazine rings.

When the compounds of formula (I) are such that they contain an OH group on one of the positions 3 or 5, α of a nitrogen atom, there is a tautomeric equilibrium which may be represented, for example, by the following scheme:



Among the compounds of formula (I) above which may be mentioned in particular are:

- [3-(4-amino-2,5-dimethyl-2H-pyrazol-3-ylamino)propyl]-trimethylammonium chloride;
- [3-(4-amino-2,5-dimethyl-2H-pyrazol-3-ylamino)propyl]-(2-hydroxyethyl)dimethylammonium chloride;

- 3-[3-(4-amino-2,5-dimethyl-2H-pyrazol-3-ylamino)-propyl]-1-(2-hydroxyethyl)-3H-imidazol-1-ium chloride;
- 3-[(4-amino-2H-pyrazol-3-ylcarbamoyl)methyl]-1-methyl-3H-imidazol-1-ium chloride;
- 3-[2-(4,5-diamino-3-methylpyrazol-1-yl)ethyl]-1-methyl-3H-imidazol-1-ium chloride;
- 3-[2-(4,5-diaminopyrazol-1-yl)ethyl]-1-methyl-3H-imidazol-1-ium chloride;
- [2-(4,5-diamino-3-methylpyrazol-1-yl)ethyl]trimethyl-ammonium chloride;
- [2-(4,5-diaminopyrazol-1-yl)ethyl]trimethylammonium chloride;
- [2-(4-amino-5-hydroxypyrazol-1-yl)ethyl]trimethyl-ammonium chloride;
- [2-(4-amino-5-hydroxy-3-methylpyrazol-1-yl)ethyl]-trimethylammonium chloride;
- 3-[2-(4-amino-5-hydroxy-3-methylpyrazol-1-yl)ethyl]-1-methyl-3H-imidazol-1-ium chloride;
- 3-[2-(4-amino-5-hydroxypyrazol-1-yl)ethyl]-1-methyl-3H-imidazol-1-ium chloride;
- 3-[2-(4,5-diamino-1-methyl-1H-pyrazol-3-yl)ethyl]-1-methyl-3H-imidazol-1-ium chloride,

and the addition salts thereof with an acid or with a base, and the possible tautomeric forms thereof.

Among these compounds of formula (I) that are preferred more particularly are:

- [3-(4-amino-2,5-dimethyl-2H-pyrazol-3-ylamino)propyl]-trimethylammonium chloride;

- [3-(4-amino-2,5-dimethyl-2H-pyrazol-3-ylamino)propyl]-(2-hydroxyethyl)dimethylammonium chloride;
- 3-[3-(4-amino-2,5-dimethyl-2H-pyrazol-3-ylamino)-propyl]-1-(2-hydroxyethyl)-3H-imidazol-1-ium chloride;
- 3-[(4-amino-2H-pyrazol-3-ylcarbamoyl)methyl]-1-methyl-3H-imidazol-1-ium chloride;
- 3-[2-(4,5-diamino-3-methylpyrazol-1-yl)ethyl]-1-methyl-3H-imidazol-1-ium chloride;
- 3-[2-(4,5-diamino-1-methyl-1H-pyrazol-3-yl)ethyl]-1-methyl-3H-imidazol-1-ium chloride;

and the addition salts thereof with an acid or with a base, and the possible tautomeric forms thereof.

The compounds of formula (I) in accordance with the invention may be readily obtained according to methods that are well known in the prior art:

- either by reducing the corresponding cationic nitro or nitroso compounds. In this case, the reduction to the corresponding primary aromatic amine is carried out according to conventional methods (J. Lehmman in Houben-Weyl, "Methoden der Organischen Chemie", Volume IV/1c: Reduction I pages 491 to 537, 1980). The methods that are preferred according to the invention involve metals such as Zn, Sn or Fe in acidic medium, for instance aqueous hydrochloric acid or aqueous acetic acid in the presence or absence of a co-solvent such as methanol, ethanol or tetrahydrofuran. Catalytic hydrogenation is a reduction method that is preferred according to the invention.

This catalytic hydrogenation uses metals such as palladium, platinum or nickel. It is even more particularly preferred to use palladium-on-charcoal or Raney nickel, or alternatively oxides such as PtO_2 in solvents such as methanol, ethanol, tetrahydrofuran or ethyl acetate, in the presence or absence of an acid, for example acetic acid. These catalytic reductions may also be carried out with formic acid in the presence of a trialkylamine such as triethylamine or with an ammonium formate instead of hydrogen gas (S. Ram, R.E. Ehrenkaufer, Synthesis, 1988, 91).

- or by reducing the corresponding cationic azo compounds (reductive cleavage). The reduction to the corresponding primary aromatic amine is carried out according to conventional methods (J. Lehmman in Houben-Weyl, "Methoden der Organischen Chemie", Volume IV/1c: Reduction I pages 551 to 553, 1980; E.C. Taylor & Coll., J. Amer. Chem. Soc., 80, 421, 1958).

This reduction step (production of a primary aromatic amine) which gives the synthesized compound its nature as an oxidizable compound (oxidation base), which may or may not be followed by a salification, is generally, for convenience, the final step of the synthesis.

This reduction can take place earlier in the sequence of reactions leading to the preparation of the

compounds of formula (I), and according to well-known processes it is then necessary to "protect" the primary amine created (for example by an acetylation, benzenesulphonation, etc. step), then carry out the desired substitution(s) or modification(s) (including quaternization) and end by "deprotecting" (generally in acidic medium) the amine function.

When the synthesis is complete, the compounds of formula (I) in accordance with the invention can, if necessary, be recovered by methods which are well known in the state of the art, such as crystallization or distillation.

Another subject of the invention is the use of the compounds of formula (I) in accordance with the invention as oxidation bases for the oxidation dyeing of keratin fibres, and in of particular human keratin fibres such as the hair.

The invention also relates to a composition for the oxidation dyeing of keratin fibres, and in particular of human keratin fibres such as the hair, characterized in that it comprises, as an oxidation base, in a medium which is suitable for dyeing, at least one compound of formula (I) in accordance with the invention.

The compound(s) of formula (I) in accordance with the invention 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.

The medium which is suitable for dyeing (or the 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 soluble in water. As organic solvent, mention may be made, for example, of C_1-C_4 lower alkanols, such as ethanol and isopropanol; glycerol; glycols and glycol ethers such as 2-butoxyethanol, propylene glycol, propylene glycol monomethyl ether, diethylene glycol monoethyl ether and monomethyl ether, as well as aromatic alcohols such as benzyl alcohol or phenoxyethanol, similar products and mixtures thereof.

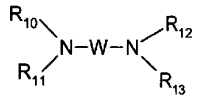
The solvents can be present in proportions preferably of between 1 and 40% by weight approximately relative to the total weight of the dye composition, and even more preferably between 5 and 30% by weight approximately.

The pH of the dye composition in accordance with the invention is generally between 3 and 12 approximately, and preferably between 5 and 11 approximately. It can be adjusted to the desired value using acidifying or basifying agents commonly used to dye 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 and lactic acid, and sulphonic acids.

Among the basifying agents which can 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_{10}, R_{11}, R_{12} and R_{13}, which may be identical or different, represent a hydrogen atom, a C_1-C_6 alkyl radical or a C_1-C_6 hydroxyalkyl radical.

The dye composition in accordance with the invention can also contain, in addition to the compound or compounds of formula (I) defined above, at least one additional oxidation base which can be chosen from the oxidation bases conventionally used in oxidation dyeing and among which mention may be made in particular of para-phenylenediamines, bis(phenyl)alkylenediamines, para-aminophenols, ortho-aminophenols and heterocyclic bases other than the compounds of formula (I).

Among the para-phenylenediamines which can be mentioned more particularly, for example, are para-

phenylenediamine, para-toluylenediamine, 2,6-dimethyl-para-phenylenediamine, 2-•-hydroxyethyl-para-phenylenediamine, 2-n-propyl-para-phenylenediamine, 2-isopropyl-para-phenylenediamine, N-(•-hydroxypropyl)-para-phenylenediamine, N,N-bis(•-hydroxyethyl)-para-phenylenediamine, 4-amino-N-(•-methoxyethyl)aniline and the para-phenylenediamines described in French patent application FR 2,630,438, and the addition salts thereof with an acid.

Among the bis(phenyl)alkylenediamines which can be mentioned more particularly, for example, are N,NN-bis(•-hydroxyethyl)-N,NN-bis(4N-aminophenyl)-1,3-diaminopropanol, N,NN-bis(•-hydroxyethyl)-N,NN-bis(4N-aminophenyl)ethylenediamine, N,NN-bis(4-aminophenyl)-tetramethylenediamine, N,NN-bis(•-hydroxyethyl)-N,NN-bis(4-aminophenyl)tetramethylenediamine, N,NN-bis(4-methylaminophenyl)tetramethylenediamine and N,NN-bis(ethyl)-N,NN-bis(4N-amino-3N-methylphenyl)-ethylenediamine, and the addition salts thereof with an acid.

Among the para-aminophenols which can be mentioned more particularly, for example, are para-aminophenol, 4-amino-3-methylphenol, 4-amino-3-fluorophenol, 4-amino-3-hydroxymethylphenol, 4-amino-2-methylphenol, 4-amino-2-hydroxymethylphenol, 4-amino-2-methoxymethylphenol, 4-amino-2-aminomethylphenol and 4-amino-2-(•-hydroxyethylaminomethyl)phenol, and the addition salts thereof with an acid.

Among the ortho-aminophenols which can be mentioned more particularly, for example, are 2-aminophenol, 2-amino-5-methylphenol, 2-amino-6-methylphenol and 5-acetamido-2-aminophenol, and the addition salts thereof with an acid.

Among the heterocyclic bases which can be mentioned more particularly, for example, are pyridine derivatives, pyrimidine derivatives and non-cationic pyrazole derivatives.

Among the pyridine derivatives which may be mentioned more particularly are the compounds disclosed, for example, in patents GB 1 026 978 and GB 1 153 196, such as 2,5-diaminopyridine, 2-(4-methoxyphenyl)amino-3-aminopyridine, 2,3-diamino-6-methoxypyridine, 2-(β-methoxyethyl)amino-3-amino-6-methoxypyridine and 3,4-diaminopyridine, and the addition salts thereof with an acid.

Among the pyrimidine derivatives which may be mentioned more particularly are the compounds disclosed, for example, in German patent DE 2 359 399 or Japanese patents JP 88-169 571 and JP 91-10659 or patent application WO 96/15765, such as 2,4,5,6-tetra-aminopyrimidine, 4-hydroxy-2,5,6-triaminopyrimidine, 2-hydroxy-4,5,6-triaminopyrimidine, 2,4-dihydroxy-5,6-diaminopyrimidine, 2,5,6-triaminopyrimidine, and pyrazolopyrimidine derivatives such as those mentioned in patent application FR-A-2 750 048, and among which mention may be made of pyrazolo[1,5-a]pyrimidine-3,7-

diamine; 2,5-dimethylpyrazolo[1,5-a]pyrimidine-3,7-diamine; pyrazolo[1,5-a]pyrimidine-3,5-diamine; 2,7-dimethylpyrazolo[1,5-a]pyrimidine-3,5-diamine; 3-aminopyrazolo[1,5-a]pyrimidine-7-ol; 3-aminopyrazolo[1,5-a]-pyrimidin-5-ol; 2-(3-aminopyrazolo[1,5-a]pyrimidin-7-ylamino)ethanol, 2-(7-aminopyrazolo[1,5-a]pyrimidin-3-ylamino)ethanol, 2-[(3-aminopyrazolo[1,5-a]pyrimidin-7-yl)-(2-hydroxyethyl)amino]ethanol, 2-[(7-aminopyrazolo[1,5-a]pyrimidin-3-yl)-(2-hydroxyethyl)amino]-ethanol, 5,6-dimethylpyrazolo[1,5-a]pyrimidine-3,7-diamine, 2,6-dimethylpyrazolo[1,5-a]pyrimidine-3,7-diamine, 2,5,N7,N7-tetramethylpyrazolo[1,5-a]pyrimidine-3,7-diamine and 3-amino-5-methyl-7-imidazolylpropylaminopyrazolo[1,5-a]pyrimidine, the possible tautomeric forms thereof, and the addition salts thereof with an acid.

Among the non-cationic pyrazole derivatives which may be mentioned more particularly are the compounds disclosed in patents DE 3 843 892 and DE 4 133 957 and patent applications WO 94/08969, WO 94/08970, FR-A-2 733 749 and DE 195 43 988, such as 4,5-diamino-1-methylpyrazole, 3,4-diaminopyrazole, 4,5-diamino-1-(4'-chlorobenzyl)pyrazole, 4,5-diamino-1,3-dimethylpyrazole, 4,5-diamino-3-methyl-1-phenyl-pyrazole, 4,5-diamino-1-methyl-3-phenylpyrazole, 4-amino-1,3-dimethyl-5-hydrazinopyrazole, 1-benzyl-4,5-diamino-3-methylpyrazole, 4,5-diamino-3-tert-butyl-1-methylpyrazole, 4,5-diamino-1-tert-butyl-3-methyl-

pyrazole, 4,5-diamino-1-(β-hydroxyethyl)-3-methylpyrazole, 4,5-diamino-1-ethyl-3-methylpyrazole, 4,5-diamino-1-ethyl-3-(4'-methoxyphenyl)pyrazole, 4,5-diamino-1-ethyl-3-hydroxymethylpyrazole, 4,5-diamino-3-hydroxymethyl-1-methylpyrazole, 4,5-diamino-3-hydroxymethyl-1-isopropylpyrazole, 4,5-diamino-3-methyl-1-isopropylpyrazole, 4-amino-5-(2'-aminoethyl)-amino-1,3-dimethylpyrazole, 3,4,5-triaminopyrazole, 1-methyl-3,4,5-triaminopyrazole and 3,5-diamino-1-methyl-4-methylaminopyrazole, 3,5-diamino-4-(β-hydroxyethyl)amino-1-methylpyrazole, and the addition salts thereof with an acid.

When they are used, these additional oxidation bases preferably represent 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.

The oxidation dye compositions in accordance with the invention can also contain at least one coupler and/or at least one direct dye, in particular in order to modify the shades or to enrich them with glints.

The couplers which can be used in the oxidation dye compositions 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 such as, for example, indole derivatives, indolene derivatives, pyridine derivatives and pyrazolones, and the addition salts thereof with an acid.

These couplers are chosen more particularly from 2-methyl-5-aminophenol, 5-N-(•-hydroxyethyl)amino-2-methylphenol, 3-aminophenol, 1,3-dihydroxybenzene, 1,3-dihydroxy-2-methylbenzene, 4-chloro-1,3-dihydroxy-benzene, 2,4-diamino-1-(•-hydroxyethyloxy)benzene, 2-amino-4-(•-hydroxyethylamino)-1-methoxybenzene, 1,3-diaminobenzene, 1,3-bis(2,4-diaminophenoxy)propane, sesamol, •-naphthol, 6-hydroxyindole, 4-hydroxyindole, 4-hydroxy-N-methylindole, 6-hydroxyindoline, 2,6-dihydroxy-4-methylpyridine, 1H-3-methylpyrazol-5-one and 1-phenyl-3-methylpyrazol-5-one, and the addition salts thereof with an acid.

When they are present, these couplers preferably represent 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.

In general, the addition salts with an acid which can be used in the context of the invention (compounds of formula (I), additional oxidation bases and couplers) are chosen in particular from the hydrochlorides, hydrobromides, sulphates, citrates, succinates, tartrates, lactates and acetates. The

addition salts with a base which may be used in the context of the invention (compounds of formula (I)) are in particular those obtained with sodium hydroxide, potassium hydroxide, aqueous ammonia or amines.

The dye composition in accordance with the invention can also contain various adjuvants conventionally used in compositions for dyeing the hair, such as anionic, cationic, nonionic, amphoteric or zwitterionic surfactants or mixtures thereof, anionic, cationic, nonionic, amphoteric or zwitterionic polymers or mixtures thereof, inorganic or organic thickeners, antioxidants, penetration agents, sequestering agents, fragrances, buffers, dispersing agents, conditioners such as, for example, silicones, film-forming agents, preserving agents and opacifiers.

Needless to say, a person skilled in the art will take care to select this or these optional additional compounds such that the advantageous properties intrinsically associated with the oxidation 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, creams or gels or in any other form which is suitable for dyeing keratin fibres, and in particular human hair.

The invention also relates to 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 this process, at least one dye composition as defined above is applied to the fibres, the colour being developed at acidic, neutral or alkaline pH using an oxidizing agent which is added to the dye composition just at the time of use, or which is present in an oxidizing composition which is applied simultaneously or sequentially in a separate manner.

According to a preferred embodiment of the dyeing process of the invention, the dye composition described above is preferably mixed, at the time of use, with an oxidizing composition containing, in a medium which is suitable for dyeing, at least one oxidizing agent present in an amount which is sufficient to develop a coloration. The mixture obtained is then applied to the keratin fibres and is left in place for 3 to 50 minutes approximately, preferably 5 to 30 minutes approximately, after which the fibres are rinsed, washed with shampoo, rinsed again and dried.

The oxidizing agent can be chosen from the oxidizing agents conventionally used for the oxidation dyeing of keratin fibres, and among which mention may be made of hydrogen peroxide, urea peroxide, alkali metal bromates and persalts such as perborates and

persulphates, and enzymes such as peroxidases, laccases, tyrosinases and oxidoreductases, among which mention may be made in particular of pyranose oxidases, glucose oxidases, glycerol oxidases, lactate oxidases, pyruvate oxidases and uricases.

The pH of the oxidizing composition containing the oxidizing agent as defined above is such that, after mixing with the dye composition, the pH of the resultant composition applied to the keratin fibres preferably varies between 3 and 12 approximately, and even more preferably between 5 and 11. It is adjusted to the desired value using acidifying or basifying agents commonly used to dye keratin fibres and as defined above.

The oxidizing composition as defined above can also contain various adjuvants conventionally used in compositions for dyeing the hair and as defined above.

The composition which is finally applied to the keratin fibres can be in various forms, such as in the form of liquids, creams or gels or any other form which is suitable for dyeing keratin fibres, and in particular human hair.

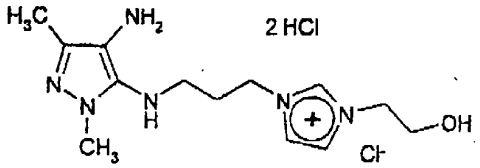
Another subject of the invention is a multi-compartment dyeing device or "kit" or any other multi-compartment packaging system, a first compartment of which contains the dye composition as defined above and a second compartment of which contains the oxidizing

composition as defined above. These devices can be equipped with a 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.

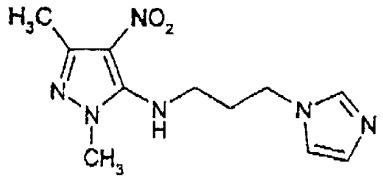
The examples which follow are intended to illustrate the invention without, however, limiting its scope.

PREPARATION EXAMPLES

PREPARATION EXAMPLE 1: Synthesis of 3-[3-(4-amino-2,5-dimethyl-2H-pyrazol-3-ylamino)propyl]-1-(2-hydroxyethyl)-3H-imidazol-1-ium chloride dihydrochloride



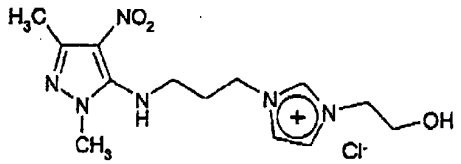
a) Preparation of (2,5-dimethyl-4-nitro-2H-pyrazol-3-yl)(3-imidazol-1-ylpropyl)amine



0.88 g of 5-chloro-1,3-dimethyl-4-nitro-1H-pyrazole (Aldrich), 1 molar equivalent of triethylamine, 1.1 molar equivalents of 3-imidazol-1-ylpropylamine and 5 ml of N,N-dimethylformamide were introduced into a 25 ml three-necked round-bottomed

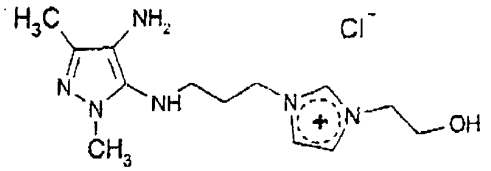
flask equipped with a magnetic stirrer, a thermometer and a condenser. The reaction medium was maintained at a temperature of about 105°C for 6 hours. The solvent was evaporated off under vacuum. A black liquid was obtained, which was purified by chromatography on silica gel (ethyl acetate/methanol = 4/1). 0.75 g of (2,5-dimethyl-4-nitro-2H-pyrazol-3-yl)(3-imidazol-1-yl-propyl)amine was obtained in the form of white crystals in a yield of 56.7%.

b) Preparation of 3-[3-(2,5-dimethyl-4-nitro-2H-pyrazol-3-ylamino)propyl]-1-(2-hydroxyethyl)-3H-imidazol-1-ium chloride



0.57 g of (2,5-dimethyl-4-nitro-2H-pyrazol-3-yl)(3-imidazol-1-ylpropyl)amine and 2.2 g of 2-chloroethanol were introduced into a 10 ml three-necked round-bottomed flask equipped with a magnetic stirrer, a thermometer and a condenser. The reaction medium was refluxed for 2 hours. The solvent was evaporated off under vacuum. 0.7 g of 3-[3-(2,5-dimethyl-4-nitro-2H-pyrazol-3-ylamino)propyl]-1-(2-hydroxyethyl)-3H-imidazol-1-ium chloride was obtained in the form of a viscous liquid, in a yield of 96%.

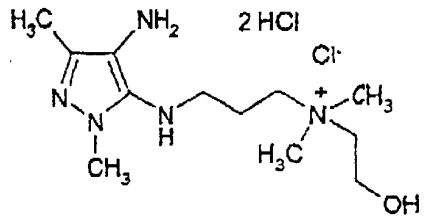
c) Preparation of 3-[3-(4-amino-2,5-dimethyl-2H-pyrazol-3-ylamino)propyl]-1-(2-hydroxyethyl)-3H-imidazol-1-ium chloride dihydrochloride



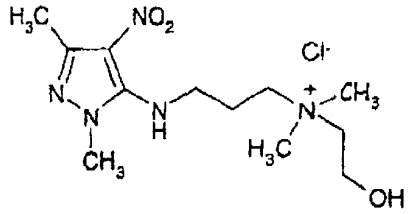
7.9 g of 3-[3-(2,5-dimethyl-4-nitro-2H-pyrazol-3-ylamino)propyl]-1-(2-hydroxyethyl)-3H-imidazol-1-ium chloride obtained above in the preceding step, 150 ml of methanol and 0.97 g of 5% palladium-on-charcoal containing about 50% water were introduced into a 500 ml hydrogenation reactor. A hydrogen pressure of 10 bar was established and the reaction medium was brought to 115°C. After 5 hours, the catalyst was filtered off through Celite over 100 ml of a hydrochloric ethanol solution at a concentration of 5 mol/litre. The solvent was evaporated off under vacuum using a vane pump (0.1 bar). 6.5 g of 3-[3-(4-amino-2,5-dimethyl-2H-pyrazol-3-ylamino)propyl]-1-(2-hydroxyethyl)-3H-imidazol-1-ium chloride dihydrochloride were obtained in the form of a solid, in a yield of 73%.

The ^{1}H NMR analysis (d_6-DMSO + CD_3OD) was as follows: 2.03 (m; 2H); 2.13 (s; 3H); 3.03 (t; 2H); 3.57 (s; 3H); 3.72 (t; 2H); 4.24 (t, 2H); 4.34 (t; 2H); 7.73 (dd; 1H); 9.33 (s; 1H).

PREPARATION EXAMPLE 2: Synthesis of [3-(4-amino-2,5-dimethyl-2H-pyrazol-3-ylamino)propyl](2-hydroxyethyl)-dimethylammonium chloride dihydrochloride



a) Preparation of [3-(2,5-dimethyl-4-nitro-2H-pyrazol-3-ylamino)propyl](2-hydroxyethyl)dimethylammonium chloride



0.5 g of N-(2,5-dimethyl-4-nitro-2H-pyrazol-3-yl)-N',N'-dimethylpropane-1,3-diamine and 2.2 g of 2-chloroethanol were introduced into a 10 ml three-necked round-bottomed flask equipped with a magnetic stirrer, a thermometer and a condenser. The reaction medium was maintained at reflux for 2 hours. The medium was cooled to room temperature and diluted with 50 ml of ethyl acetate. The precipitate was filtered off. 0.55 g of [3-(2,5-dimethyl-4-nitro-2H-pyrazol-3-yl-amino)propyl](2-hydroxyethyl)dimethylammonium chloride

was obtained in the form of yellow crystals, in a yield of 82%.

b) Preparation of [3-(4-amino-2,5-dimethyl-2H-pyrazol-3-ylamino)-propyl](2-hydroxyethyl)dimethylammonium chloride dihydrochloride

3.22 g of dimethylammonium chloride, 150 ml of methanol and 0.42 g of 5% palladium-on-charcoal containing about 50% water were introduced into a 250 ml hydrogenation reactor. The reactor was subjected to a hydrogen pressure of 11.7 bar and the reaction medium was brought to 60°C. After 2 hours, the hydrogen pressure was 8.3 bar. The catalyst was filtered off through Celite. A stream of hydrogen chloride gas was passed through the filtrate and the solvent was evaporated off under vacuum. 3 g of a viscous liquid were obtained, and were diluted in 100 ml of water and then freeze-dried. 1.54 g of [3-(4-amino-2,5-dimethyl-2H-pyrazol-3-ylamino)propyl](2-hydroxyethyl)dimethyl-ammonium chloride dihydrochloride (containing 1.3 mol of water) were obtained in the form of a solid, in a yield of 40%, the elemental analysis of which, calculated for $C_{12}H_{26}N_5O \cdot Cl \cdot 2HCl \cdot 1.3H_2O$ (MW=388.15 g/mol), was as follows:

%	C	H	N	O	Cl
Calculated	37.09	7.88	18.03	9.48	27.43
Found	37.46	7.88	17.79	9.68	26.85

APPLICATION EXAMPLES

EXAMPLES 1 to 8 OF DYEING IN BASIC MEDIUM

The following dye compositions were prepared (contents in grams):

EXAMPLE	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
[3-(4-Amino-2,5-dimethyl-2H-pyrazol-3-yl-amino)propyl](2-hydroxyethyl)dimethyl-ammonium chloride dihydrochloride (compound of formula (I))	1.09	1.09	1.09	1.09	1.09	1.09	1.09	1.09
1,3-Dihydroxybenzene (coupler)	-	0.33	-	-	-	-	-	-
3-Aminophenol (coupler)	-	-	0.327	-	-	-	-	-
6-Hydroxyindole (coupler)	-	-	-	0.399	-	-	-	-
5-N-(β-Hydroxyethyl)amino-2-methylphenol (coupler)	-	-	-	-	0.504	-	-	-
2,4-Diamino-1-(β-hydroxyethyloxy)benzene dihydrochloride (coupler)	-	-	-	-	-	0.723	-	-
4-Hydroxyindole (coupler)	-	-	-	-	-	-	0.399	-
3-Amino-2-chloro-6-methylphenol (coupler)	-	-	-	-	-	-	-	0.48
Common dye support No. 1	(*)	(*)	(*)	(*)	(*)	(*)	(*)	(*)
Demineralized water qs	100 g	100 g	100 g	100 g	100 g	100 g	100 g	100 g

(*) Common dye support No. 1:

- 96E Ethyl alcohol	18 g
- Sodium metabisulphite as an aqueous solution containing 35%	0.68 g
- Pentasodium salt of diethylenetriamino-pentaacetic acid	1.1 g
- 20% Aqueous ammonia	10.0 g

At the time of use, each of the above dye compositions was mixed, weight for weight, with a 20-volumes hydrogen peroxide solution (6% by weight) of pH 3.

The mixture obtained was applied to locks of permanent-waved grey hair containing 90% white hairs, for 30 minutes. The locks were then rinsed, washed with a standard shampoo, rinsed again and then dried.

The shades obtained are given in the table below:

EXAMPLE	**Dyeing pH**	**Shade obtained**
1	10 ± 0.2	Light ash-violet
2	10 ± 0.2	Slightly iridescent golden ash light blond
3	10 ± 0.2	Ash-violet
4	10 ± 0.2	Ash-chestnut dark blond
5	10 ± 0.2	Violet iridescent light chestnut
6	10 ± 0.2	Deep green-blue
7	10 ± 0.2	Violet-ash chestnut
8	10 ± 0.2	Violet

EXAMPLES 9 to 12 OF DYEING IN NEUTRAL MEDIUM

The following dye compositions were prepared (contents in grams):

EXAMPLE	9	10	11	12
[3-(4-Amino-2,5-dimethyl-2H-pyrazol-3-ylamino)-propyl](2-hydroxyethyl)-dimethylammonium chloride dihydrochloride (compound of formula (I))	1.09	1.09	1.09	1.09
5-N-(β-Hydroxyethyl)amino-2-methylphenol (coupler)	0.504	-	-	-
2,4-Diamino-1-(β-hydroxy-ethyloxy)benzene dihydro-chloride (coupler)	-	0.723	-	-
6-Hydroxyindole (coupler)	-	-	0.399	-
4-Hydroxyindole (coupler)	-	-	-	0.399
Common dye support No. 2	(**)	(**)	(**)	(**)
Demineralized water qs	100 g	100 g	100 g	100 g

(**) Common dye support No. 2:

- 96° ethanol 18 g
- K_2HPO_4/KH_2PO_4 buffer (1.5 M/1 M) 10 g
- Sodium metabisulphite 0.68 g
- Pentasodium salt of diethylenetriamine-pentaacetic acid 1.1 g

At the time of use, each of the above dye compositions was mixed, weight for weight, with a 20-volumes hydrogen peroxide solution (6% by weight) of pH 3.

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

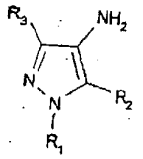
The shades obtained are given in the table below:

EXAMPLE	Dyeing pH	Shade Obtained
9	5.7 ∀ 0.2	Ash-violet
10	5.7 ∀ 0.2	Green
11	5.7 ∀ 0.2	Slightly violet light blonde
12	5.7 ∀ 0.2	Light red-violet

For the purposes of this specification it will be clearly understood that the word "comprising" means "including but not limited to", and that the words "comprise" and "comprises" have a corresponding meaning.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. Compounds of formula (I) below, the addition salts thereof with an acid or with a base, and the possible tautomeric forms thereof:



(I)

in which:

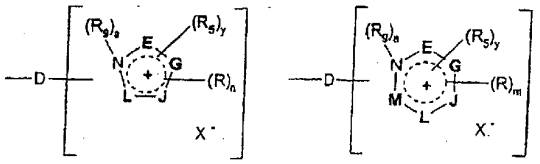
- R_1 represents a hydrogen atom; a group Z as defined below; a C_1-C_6 alkyl radical; a C_1-C_6 trifluoroalkyl radical; a C_1-C_6 monohydroxyalkyl radical; a C_2-C_6 polyhydroxyalkyl radical; an aryl (C_1-C_6) alkyl radical; a (C_1-C_6) alkoxy (C_1-C_6) alkyl radical; a (C_1-C_6) aklylthio (C_1-C_6) alkyl radical; an amino (C_1-C_6)-alkylcarbonyl (C_1-C_6) alkyl radical; an N-Z amino (C_1-C_6) alkylcarbonyl (C_1-C_6) alkyl radical; an N-(C_1-C_6) alkyl amino (C_1-C_6) alkylcarbonyl (C_1-C_6) alkyl radical; an N,N-di (C_1-C_6) alkylamino (C_1-C_6) alkylcarbonyl (C_1-C_6) alkyl radical; a C_1-C_6 aminosulphonylalkyl radical; a C_1-C_6 N-Z-aminosulphonylalkyl radical; an N-(C_1-C_6) alkyl-aminosulphonyl (C_1-C_6) alkyl radical; an N,N-di (C_1-C_6)alkylaminosulphonyl (C_1-C_6) alkyl radical;
- R_2 and R_3, which may be identical or different, represent a group $-NHR_4$; a hydroxyl radical; a halogen atom; a nitro radical; a cyano radical; a carboxyl

radical; a C_1-C_6 alkylcarboxyl radical; a carboxyaryl radical; a carbamyl radical; an N-(C_1-C_6)alkylcarbamyl radical; an N,N-di(C_1-C_6)alkylcarbamyl radical; an N-arylcarbamyl radical; a C_1-C_6 alkoxy radical; an aryloxy radical; a C_1-C_6 thioalkyl radical; a thioaryl radical or one of the meanings given above for R_1; it being understood that at least one of the radicals R_2 and R_3 represents a group $-NHR_4$ or a hydroxyl radical;

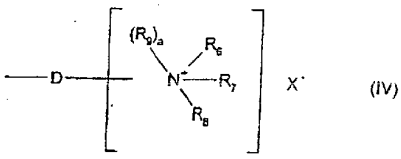
- R_4 represents a hydrogen atom; a group Z as defined below; a C_1-C_6 alkyl radical; a C_1-C_6 monohydroxyalkyl radical; a C_2-C_6 polyhydroxyalkyl radical; a (C_1-C_6)-alkoxy(C_1-C_6)alkyl radical; an aryl radical; a benzyl radical; a cyano(C_1-C_6)alkyl radical; a carbamyl-(C_1-C_6)alkyl radical; an N-(C_1-C_6)alkylcarbamyl(C_1-C_6)-alkyl radical; an N,N-di(C_1-C_6)alkylcarbamyl(C_1-C_6)-alkyl radical; a thiocarbamyl(C_1-C_6)alkyl radical; a C_1-C_6 trifluoroalkyl radical; a C_1-C_6 sulphoalkyl radical; a (C_1-C_6)alkylcarboxy(C_1-C_6)alkyl radical; a (C_1-C_6)alkylsulphinyl(C_1-C_6)alkyl radical; a C_1-C_6 aminosulphonylalkyl radical; a C_1-C_6 N-Z-amino-sulphonylalkyl radical; an N-(C_1-C_6)alkylamino-sulphonyl(C_1-C_6)alkyl radical; an N,N-di(C_1-C_6)alkyl-aminosulphonyl(C_1-C_6)alkyl radical; a C_1-C_6 aminoalkyl radical; a C_1-C_6 aminoalkyl radical in which the amine is substituted with one or two radicals, which may be identical or different, chosen from C_1-C_6 alkyl, C_1-C_6 monohydroxyalkyl, C_2-C_6 polyhydroxyalkyl, (C_1-C_6)alkyl-carbonyl, C_1-C_6 alkylsulphonyl, formyl and trifluoro-

(C_1-C_6) alkylcarbonyl radicals or with a group Z; the amine of the C_1-C_6 aminoalkyl radical may also be substituted with two radicals forming, together with the nitrogen atom of the said amine, a saturated or unsaturated 5- or 6-membered ring which may contain one or more hetero atoms chosen from nitrogen, oxygen and sulphur;

- Z is chosen from the unsaturated cationic groups of formulae (II) and (III) below, or the saturated cationic groups of formula (IV) below:



(II) (III)



(IV)

in which:

- D is a linker arm which represents a linear or branched alkyl chain which can be interrupted by one or more hetero atoms such as oxygen, sulphur or nitrogen atoms, and which can be substituted with one or more hydroxyl or C_1-C_6 alkoxy radicals, and which can bear one or more ketone functions;

- the ring members E, G, J, L and M, which may be identical or different, represent a carbon, oxygen, sulphur or nitrogen atom;
- n is an integer between 0 and 4 inclusive;
- m is an integer between 0 and 5 inclusive;
- the radicals R, which may be identical or different, represent a second group Z, which is identical to or different from the first group Z, a halogen atom, a hydroxyl radical, a C_1-C_6 alkyl radical, a C_1-C_6 monohydroxyalkyl radical, a C_2-C_6 polyhydroxyalkyl radical, a nitro radical, a cyano radical, a cyano(C_1-C_6)alkyl radical, a C_1-C_6 alkoxy radical, a tri(C_1-C_6)alkylsilane(C_1-C_6)alkyl radical, an amido radical, an aldehydo radical, a carboxyl radical, a (C_1-C_6)alkylcarbonyl radical, a thio radical, a C_1-C_6 thioalkyl radical, a C_1-C_6 alkylthio radical, an amino radical, an amino radical protected with a (C_1-C_6)alkylcarbonyl or C_1-C_6 alkylsulphonyl radical; a group NHRO or NROR in which RO and R , which may be identical or different, represent a C_1-C_6 alkyl radical, a C_1-C_6 monohydroxyalkyl radical or a C_2-C_6 polyhydroxyalkyl radical;
- R_5 represents a C_1-C_6 alkyl radical, a C_1-C_6 monohydroxyalkyl radical, a C_2-C_6 polyhydroxyalkyl radical, a cyano(C_1-C_6)alkyl radical, a tri(C_1-C_6)alkylsilane(C_1-C_6)alkyl radical, a (C_1-C_6)alkoxy(C_1-C_6)alkyl radical, a carbamyl(C_1-C_6)-alkyl radical, a (C_1-C_6)alkylcarboxy(C_1-C_6)alkyl

radical, a benzyl radical or a second group Z, which is identical to or different from the first group Z;

- R_6, R_7 and R_8, which may be identical or different, represent a C_1-C_6 alkyl radical, a C_1-C_6 monohydroxyalkyl radical, a C_2-C_6 polyhydroxyalkyl radical, a (C_1-C_6)alkoxy(C_1-C_6)alkyl radical, a cyano(C_1-C_6)alkyl radical, an aryl radical, a benzyl radical, a C_1-C_6 amidoalkyl radical, a tri(C_1-C_6)alkylsilane(C_1-C_6)alkyl radical or a C_1-C_6 aminoalkyl radical in which the amine is protected with a (C_1-C_6)alkylcarbonyl or C_1-C_6 alkylsulphonyl radical; two of the radicals R_6, R_7 and R_8 can together also form, with the nitrogen atom to which they are attached, a saturated 5- or 6-membered carbon ring or a ring containing one or more hetero atoms, it being possible for the said ring to be unsubstituted or substituted with a halogen atom, a hydroxyl radical, a C_1-C_6 alkyl radical, a C_1-C_6 monohydroxyalkyl radical, a C_2-C_6 polyhydroxyalkyl radical, a nitro radical, a cyano radical, a cyano(C_1-C_6)alkyl radical, a C_1-C_6 alkoxy radical, a tri(C_1-C_6)alkylsilane(C_1-C_6)alkyl radical, an amido radical, an aldehydo radical, a carboxyl radical, a keto(C_1-C_6)alkyl radical, a thio radical, a C_1-C_6 thioalkyl radical, a C_1-C_6 alkylthio radical, an amino radical or an amino radical protected with a (C_1-C_6)alkylcarbonyl or C_1-C_6 alkylsulphonyl radical;

one of the radicals R_6, R_7 and R_8 can also represent a second group Z which is identical to or different from the first group Z;

- R_9 represents a C_1-C_6 alkyl radical; a C_1-C_6 monohydroxyalkyl radical; a C_2-C_6 polyhydroxyalkyl radical; an aryl radical; a benzyl radical; a C_1-C_6 aminoalkyl radical, a C_1-C_6 aminoalkyl radical in which the amine is protected with a (C_1-C_6)alkylcarbonyl or C_1-C_6 alkylsulphonyl radical; a carboxy(C_1-C_6)alkyl radical; a cyano(C_1-C_6)alkyl radical; a carbamyl(C_1-C_6)alkyl radical; a C_1-C_6 trifluoroalkyl radical; a tri(C_1-C_6)alkylsilane(C_1-C_6)alkyl radical; a C_1-C_6 sulphonamidoalkyl radical; a (C_1-C_6)alkylcarboxy(C_1-C_6)alkyl radical; a (C_1-C_6)alkylsulphinyl(C_1-C_6)alkyl radical; a (C_1-C_6)alkylsulphonyl(C_1-C_6)alkyl radical; a (C_1-C_6)alkylketo(C_1-C_6)alkyl radical; an N-(C_1-C_6)alkylcarbamyl(C_1-C_6)alkyl radical; an N-(C_1-C_6)alkylsulphonamido(C_1-C_6)alkyl radical;
- a and y are integers equal to 0 or 1; with the following conditions:
  - in the unsaturated cationic groups of formula (II):
    - when a = 0, the linker arm D is attached to the nitrogen atom,
    - when a = 1, the linker arm D is attached to one of the ring members E, G, J or L,
    - y can take the value 1 only:

1) when the ring members E, G, J and L simultaneously represent a carbon atom and when the radical R_5 is borne by the nitrogen atom of the unsaturated ring; or alternatively

2) when at least one of the ring members E, G, J and L represents a nitrogen atom to which the radical R_5 is attached;

- in the unsaturated cationic groups of formula (III):
  - when a = 0, the linker arm D is attached to the nitrogen atom,
  - when a = 1, the linker arm D is attached to one of the ring members E, G, J, L or M,
  - y can take the value 1 only when at least one of the ring members E, G, J, L and M represents a divalent atom and when the radical R_5 is borne by the nitrogen atom of the unsaturated ring;
- in the cationic groups of formula (IV):
  - when a = 0, then the linker arm is attached to the nitrogen atom bearing the radicals R_6 to R_8,
  - when a = 1, then two of the radicals R_6 to R_8 form, together with the nitrogen atom to which they are attached, a saturated 5- or 6-membered ring as defined above, and the linker arm D is borne by a carbon atom of the said saturated ring;

• X^- represents a monovalent or divalent anion;

it being understood that the number of cationic groups Z is at least equal to 1.

2. Compounds according to claim 1, in which the aryl (C_1-C_6) alkyl radical of R_1 is a radical in which the aryl radical is a phenyl radical or a 5- or 6-membered aromatic heterocycle.

3. Compounds according to claim 1 or 2, in which the linear or branched alkyl chain of the linker arm of D contains from 1 to 14 carbon atoms.

4. Compounds according to any one of the preceding claims, in which the rings of the unsaturated groups Z of formula (II) are chosen from pyrrole, imidazole, pyrazole, oxazole, thiazole or triazole rings.

5. Compounds according to any one of claims 1 to 3, in which the rings of the unsaturated groups Z of formula (III) are chosen from pyridine, pyrimidine, pyrazine, oxazine or triazine rings.

6. Compounds according to any one of the preceding claims, in which two of the radicals R_6, R_7 and R_8 form a pyrrolidine ring, a piperidine ring, a piperazine ring or a morpholine ring.

7. Compounds according to any one of the preceding claims, in which X^- is chosen from a halogen atom, a hydroxide, a hydrogenosulphate or a C_1-C_6 alkyl sulphate.

8. Compounds according to any one of the preceding claims, in which the compounds are:

- [3-(4-amino-2,5-dimethyl-2H-pyrazol-3-ylamino)propyl]-trimethylammonium chloride;
- [3-(4-amino-2,5-dimethyl-2H-pyrazol-3-ylamino)propyl]-(2-hydroxyethyl)dimethylammonium chloride;
- 3-[3-(4-amino-2,5-dimethyl-2H-pyrazol-3-ylamino)-propyl]-1-(2-hydroxyethyl)-3H-imidazol-1-ium chloride;
- 3-[(4-amino-2H-pyrazol-3-ylcarbamoyl)methyl)-1-methyl-3H-imidazol-1-ium chloride;

- 3-[2-(4,5-diamino-3-methylpyrazol-1-yl)ethyl]-1-methyl-3H-imidazol-1-ium chloride;
- 3-[2-(4,5-diaminopyrazol-1-yl)ethyl]-1-methyl-3H-imidazol-1-ium chloride;
- [2-(4,5-diamino-3-methylpyrazol-1-yl)ethyl]trimethylammonium chloride;
- [2-(4,5-diaminopyrazol-1-yl)ethyl]trimethylammonium chloride;
- [2-(4-amino-5-hydroxypyrazol-1-yl)ethyl]trimethylammonium chloride;
- [2-(4-amino-5-hydroxy-3-methylpyrazol-1-yl)ethyl]-trimethylammonium chloride;
- 3-[2-(4-amino-5-hydroxy-3-methylpyrazol-1-yl)ethyl]-1-methyl-3H-imidazol-1-ium chloride;
- 3-[2-(4-amino-5-hydroxypyrazol-1-yl)ethyl]-1-methyl-3H-imidazol-1-ium chloride;
- 3-[2-(4,5-diamino-1-methyl-1H-pyrazol-3-yl)ethyl]-1-methyl-3H-imidazol-1-ium chloride;

or the addition salts thereof with an acid or with a base, or the possible tautomeric forms thereof.

9. Compounds according to claim 8, chosen from:

- [3-(4-amino-2,5-dimethyl-2H-pyrazol-3-ylamino)propyl]-trimethylammonium chloride;
- [3-(4-amino-2,5-dimethyl-2H-pyrazol-3-ylamino)propyl]-(2-hydroxyethyl) dimethylammonium chloride;
- 3-[3-(4-amino-2,5-dimethyl-2H-pyrazol-3-ylamino)-propyl]-1-(2-hydroxyethyl)-3H-imidazol-1-ium chloride;
- 3-[(4-amino-2H-pyrazol-3-ylcarbamoyl)methyl]-1-methyl-3H-imidazol-1-ium chloride;
- 3-[2-(4,5-diamino-3-methylpyrazol-1-yl)ethyl]-1-methyl-3H-imidazol-1-ium chloride;
- 3-[2-(4,5-diamino-1-methyl-1H-pyrazol-3-yl)ethyl]-1-methyl-3H-imidazol-1-ium chloride;

or the addition salts thereof with an acid or with a base, or the possible tautomeric forms thereof.

10. Compounds according to any one of the preceding claims, in which the addition salts with an acid are chosen from the hydrochlorides, hydrobromides, sulphates, citrates, succinates, tartrates, lactates or acetates and in which the addition salts with a base are chosen from those obtained with sodium hydroxide, potassium hydroxide, aqueous ammonia or amines.

11. A method of using the compounds of formula (I) as defined in any one of claims 1 to 10, as oxidation bases for the oxidation dyeing of keratin fibres.

12. Composition for the oxidation dyeing of keratin fibres, comprising as an oxidation base, in a medium which is suitable for dyeing, at least one compound of formula (I) as defined in any one of claims 1 to 10.

13. Composition according to claim 12, in which the compound(s) of formula (I) represent(s) from 0.0005 to 12% by weight relative to the total weight of the dye composition.

14. Composition according to claim 13, in which the compound(s) of formula (I) represent(s) from 0.005 to 6% by weight relative to the total weight of the dye composition.

15. Composition according to any one of claims 12 to 14, further comprising at least one additional oxidation base chosen from para-phenylenediamines, bis(phenyl)alkylenediamines, para-aminophenols, ortho-aminophenols or heterocyclic bases other than the compounds of formula (I).

16. Composition according to claim 15, in which the additional oxidation base(s) represent(s) from 0.0005% to 12% by weight relative to the total weight of the dye composition.

17. Composition according to any one of claims 12 to 16, further comprising at least one coupler and/or at least one direct dye.

18. Composition according to claim 17, in which the coupler(s) is (are) chosen from meta-phenylenediamines, meta-aminophenols, meta-diphenols or heterocyclic couplers, or the additional salts thereof with an acid.

19. Composition according to claim 18, in which the coupler(s) is (are) chosen from 2-methyl-5-aminophenol, 5-N-(•-hydroxyethyl) amino-2-methylphenol, 3-aminophenol, 1,3-dihydroxybenzene, 1,3-dihydroxy-2-methylbenzene, 4-chloro-1,3-dihydroxy-benzene, 2,4-diamino-1-(•-hydroxyethyloxy)benzene, 2-amino-4-(•-hydroxyethylamino)-1-methoxybenzene, 1,3-diaminobenzene, 1,3-bis(2,4-diaminophenoxy) propane, sesamol, •-naphthol, 6-hydroxyindole, 4-hydroxyindole, 4-hydroxy-N-methylindole, 6-hydroxyindoline, 2,6-dihydroxy-4-methylpyridine, 1H-3-methylpyrazol-5-one or 1-phenyl-3-methylpyrazol-5-one, or the addition salts thereof with an acid.

20. Composition according to any one of claims 17 to 19, in which the coupler(s) represent(s) from 0.0001 to 10% by weight relative to the total weight of the dye composition.

21. Composition according to any one of claims 12 to 20, in which the addition salts with an acid are chosen from the hydrochlorides, hydrobromides, sulphates, citrates, succinates, tartrates, lactates or acetates.

22. Process for dyeing keratin fibres, in which at least one dye composition as defined in any one of claims 10 to 19 is applied to these fibres and the colour is developed at acidic, neutral or alkaline pH using an oxidising agent which is added to the dye composition just at the time of use, or which is present in an oxidising composition which is applied simultaneously or sequentially in a separate manner.

23. A process according to claim 22, in which the keratin fibres are human keratin fibres.

24. A process according to claim 22 or 23, in which the keratin fibres are hair.

25. Process according to any one of claims 22 to 24, in which the oxidising agent is chosen from hydrogen peroxide, urea peroxide, alkali metal bromates, or persalts or enzymes.

26. A process according to claim 25, in which the persalts are perborates or persulphates.

27. Multi-compartment dyeing device or multi-compartment dyeing "kit", having a first compartment and a second compartment in which the first compartment contains a dye composition as defined in any one of claims 12 to 21, and in which the second compartment contains an oxidising composition.

28. Compounds of formula (I) substantially as hereinbefore described with reference to any one of the foregoing examples.

29. A method of using the compounds of formula (I) substantially as hereinbefore described with reference to any one of the foregoing examples.

30. Composition for the oxidation dyeing of keratin fibres substantially as hereinbefore described with reference to any one of the foregoing examples.

31. Process for dyeing keratin fibres substantially as hereinbefore described with reference to any one of the foregoing examples.

32. Multi-compartment dyeing device or multi-compartment dyeing "kit" substantially as hereinbefore described with reference to any one of the foregoing examples.

Dated this 5th day of August 2003

L'OREAL

By their Patent Attorneys

GRIFFITH HACK

Fellows Institute of Patent and

Trade Mark Attorneys of Australia

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