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# (54) Title: HAIR COMPOSITION

(57) **Abstract:** A hair composition which is characterized in that a substance to be oxidized, an oxidase which utilizes oxygen as a substrate and does not generate hydrogen peroxide, and a cyclodextrin compound are compounded in the said composition.

# DESCRIPTION

# HAIR COMPOSITION

## Technical Field of the Invention

The present invention relates to a hair composition in which a substance to be oxidized, an enzyme which utilizes oxygen as a substrate and does not produce hydrogen peroxide, and a cyclodextrin compound are compounded and, more particularly, it relates to a hair composition having a good stability with a lapse of time and being suitably able to be used as a reactive hairdye (a single preparation type), a permanent-waving preparation of a single preparation type, a depilatory of a single preparation type, etc.

## Background Art

Examples of a composition for hair wherein its property is expressed by oxidizing the substance to be oxidized are hairdye, permanent-waving preparation and depilatory. Conventional hair compositions as such use hydrogen peroxide as an oxidizing agent and, therefore, most of them are in such a type that a substance to be oxidized and an oxidizing agent are placed in separate containers and they are mixed and reacted upon use. Thus, in view of usability such as a troublesome use, there has been a demand for improvement. In addition, hydrogen peroxide has been known to damage the hair and, as the complaints from consumers, damage of the hair has been highlighted.

As a method for solving such a problem, an art where, for example, oxidase is used instead of hydrogen peroxide and a composition of a single preparation type in which a substance to be oxidized and an oxidizing agent are previously mixed so that damage of the hair is reduced has been proposed. Examples of such an art which has been known are that where peroxidase is used (Japanese Laid-Open Patents Sho-47/10400 and Sho-53/32132), laccase is used (U. S. Patent 3,251,742 and Japanese Laid-Open Patent Hei-6/172145), uricase is used (Japanese Laid-Open Patent Sho-63/246313), etc. as an oxidase.

However, in the case where peroxidase is used among the disclosed art as such, hydrogen peroxide is to be added to the preparation because of the characteristics of the said enzyme and it is not possible to give a single preparation type. When uricase is used, a single type preparation can be produced but, because of the use of hydrogen peroxide generated by an enzymatic reaction, that does not solve the problem fundamentally.

On the contrary, when an enzyme which is an oxidase using oxygen as a substrate and does not generate hydrogen peroxide is used, it is possible to prepare a single preparation type and, in addition, because of no generation of hydrogen peroxide, that is useful without anxiety of damage of the hair (cf. Japanese Laid-Open Patent Hei-11/60454). However, when such an enzyme is used, there is a problem due to the unstable property of the enzyme which is a protein that the enzyme reacts in the composition resulting in insoluble aggregates, etc. Therefore, action of the enzyme cannot be fully achieved in actual use and, further, it is a very serious problem as a commercial product that isolated substances as such were generated as the time goes by.

Up to now, as an art for improving the stability of such an enzyme during preservation, catalase (Japanese Laid-Open Patent Hei-8/175935) and uricase (Japanese Laid-Open Patent Hei-8/217652) have been disclosed but they relate to addition of a reducing agent to a composition and there is a possibility of weakening the activity of the enzyme.

## Disclosure of Invention

The present invention has been achieved in view of the above circumstances and an object of the present invention is to offer a hair composition in which there is no damage to the hair, an excellent enzymatic action is achieved by suppression of production of aggregates, etc. by oxidase during preservation and use is simple and easy whereby usability is excellent.

The present inventors have carried out an intensive study for achieving the above-mentioned object and, as a result, have found that, when a cyclodextrin compound is compounded with a hair composition wherein a substance to be oxidized and an oxidase which is an enzyme generating no hydrogen peroxide and utilizes oxygen as substrates are compounded, the said substance to be oxidized and the said oxidase are included in the said cyclodextrin compound whereby generation of insoluble aggregates, etc. as the time goes by is suppressed as shown in the examples mentioned later and stability with a lapse of time of the said hair composition is significantly improved. The present invention has been accomplished consequently.

Thus, the present invention offers a hair composition, characterized in that, a substance to be oxidized, an oxidase which utilizes oxygen as a substrate and does not generate hydrogen peroxide, and a cyclodextrin compound are compounded therein.

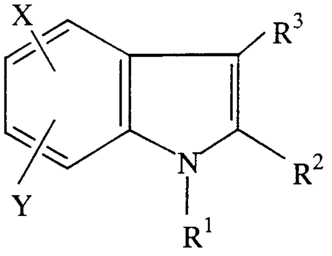
## Best Mode for Carrying Out the Invention

The present invention will now be further illustrated as hereunder. Thus, the hair composition of the present invention is such a composition wherein a substance to be oxidized and an oxidase which utilizes oxygen as a substrate and does not generate hydrogen peroxide are compounded and then a cyclodextrin compound is further compounded therewith.

There is no particular limitation for the hair composition of the present invention in terms of its form as a commercial product but it can be used as various types of hair compositions for hair such as, for example, a hairdye of a reactive type, a permanent-waving preparation of a single preparation type and a depilatory of a single preparation type. In such a form as a commercial product, it is preferred that the enzyme is in a dissolved state in the preparation and, in the case of such a preparation, any of solution and emulsion is acceptable and, further, a propellant may be contained therein. The state upon use may be foams, cream, transparent gel, etc. as well and there is no particular limitation for the product form of the product.

There is no particular limitation for the substance to be oxidized used in the present invention but, depending upon the product forms such as hairdye of a reactive type, permanent-waving preparation of a single preparation type and depilatory of a single preparation type, a substance to be oxidized used therefor may be appropriately selected. For example, when the composition of the present invention is used as a hairdye of a reactive type, coloring substances such as dye precursor, developer and direct dye which are used as substance to be oxidized for hairdye of a reactive type may be used. Specific examples thereof are 5-amino-o-cresol, o-aminophenol, m-aminophenol, p-aminophenol, 2,6-diaminopyridine, 5-(2-hydroxyethylamino)-2-methylphenol, N,N-bis(β-hydroxyl)-p-phenylenediamine, N,N-bis(2-hydroxyethyl)-p-phenylenediamine, p-nitro-o-phenylenediamine, p-phenylenediamine, m-phenylenediamine, N-phenyl-p-phenylenediamine, hydroquinone, 2-hydroxy-5-nitro-2',4'-diaminoazobenzene sodium sulfate, toluene-2,5-diamine, 2-(2'-hydroxyethylamino)-5-aminotoluene, N,N-bis(β-hydroxyl)-p-phenylenediamine sulfate, N,N-bis(2-hydroxyethyl)-p-phenylenediamine sulfate, 5-amino-o-cresol sulfate, p-aminophenol sulfate, o-chloro-p- phenylenediamine sulfate, 2-(2'-hydroxyethylamino)-5-aminotoluene sulfate, 4,4'-diaminodiphenylamine sulfate, p-methylaminophenol sulfate, p-phenylenediamine sulfate, m- phenylenediamine sulfate, toluene-2,5-diamine sulfate, 2,4-diaminophenoxyethanol hydrochloride, toluene-2,5-diamine hydrochloride, m-phenylenediamine hydrochloride, 2,4-diaminophenol hydrochloride, N-phenyl-p-phenylenediamine hydrochloride, N-phenyl-p-phenylenediamine acetate, 1,5-hydroxynaphthalene, toluene-3,4-diamine, p-methylaminophenol, N,N'-bis(4-aminophenyl)-2,5-diamino-1,4-quinonediimine, o-aminophenol sulfate, 2,4-diaminophenol sulfate, m-aminophenol sulfate, 2-amino-4-nitrophenol, 2-amino-5-nitrophenol, 1-amino-4-methylaminoanthraquinone, nitro-p-phenylenediamine hydrochloride, 1,4-diaminoanthraquinone, nitro-p-phenylenediamine, picramic acid, sodium picramate, 2-amino-5-nitrophenol sulfate, resorcinol, nitro-p-phenylenediamine sulfate, p-nitro-o-phenylenediamine sulfate and p-nitro-m-phenylenediamine sulfate. Among them, p-phenylenediamine or salt thereof, toluene-2,5-diamine or salt thereof, p-aminophenol, 5-amino-o-cresol, p-methylaminophenol sulfate, m-aminophenol, p-nitro-o-phenylenediamine, 2,6-diaminopyridine, resorcinol, o-aminophenol and m-phenylenediamine are particularly preferred.

In addition, due to the recent trend of intention to nature, a melanin precursor-like substance represented by the following formula (1) may be appropriately used as well.



(1)

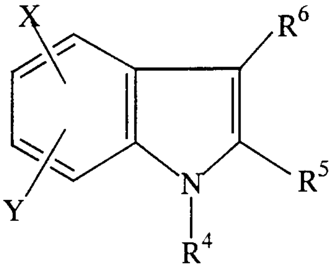
In the above formula, X is a hydrogen atom, $NH_2$, OH or any of $C_{1-6}$ linear or branched alkyl group, alkenyl group and alkoxy group; Y is OH or $NH_2$; and, when X is OH or any of $C_{1-6}$ linear or branched alkyl group, alkenyl group and alkoxy group, X is located at 5-, 6- or 7-position in the ring and is located at ortho-position to Y.

$R^1$ and $R^3$ may be same or different and each of them is a hydrogen atom or any of $C_{1-6}$ linear or branched alkyl group, alkenyl group and alkoxy group; and $R^2$ is a $C_{1-6}$ linear or branched alkyl group, alkenyl group or alkoxy group or a carboxyl group.

Specific examples of the compound represented by the above formula (1) are 4,5-dihydroxyindole, 5,6-dihydroxyindole, 6,7-dihydroxyindole, N-methyl-5,6-dihydroxyindole, N-ethyl-5,6-dihydroxyindole, N-hexyl-5,6-dihydroxyindole, 2-methyl-5,6-dihydroxyindole, 3-methyl-5,6-dihydroxyindole, 4-hydroxyindole, 2,3-dimethyl-5,6-dihydroxyindole, 2-methyl-5-ethyl-6-hydroxyindole, 2-methyl-5-hydroxy-6-β-hydroxyethylindole, 4-hydroxypropylindole, 2,3-dimethyl-5,6-dihydroxyindole, 4-hydroxy-5-methoxyindole, 6-hydroxy-7-

methoxyindole, 6-hydroxy-5-methoxyindole, 6-hydroxyindole, 5-hydroxyindole, 7-hydroxyindole, 7-aminoindole, 5-aminoindole, 4-aminoindole, 5,6-dihydroxyindolecarboxylic acid, 1-methyl-5,6-dihydroxyindole and salts thereof.

Furthermore, a melanin precursor-like substance represented by the following formula (2) may be appropriately used as well.



(2)

In the above formula, K is a hydrogen atom, $NH_2$, OH or any of $C_{1-6}$ linear or branched alkyl group, alkenyl group and alkoxy group; L is OH or $NH_2$; and, when K is OH or any of $C_{1-6}$ linear or branched alkyl group, alkenyl group and alkoxy group, K is located at 5-, 6- or 7-position in the ring and is located at ortho-position to L.

$R^4$ and $R^6$ may be same or different and each of them is a hydrogen atom or any of $C_{1-6}$ linear or branched alkyl group, alkenyl group and alkoxy group; and $R^5$ is a $C_{1-6}$ linear or branched alkyl group, alkenyl group or alkoxy group or a carboxyl group.

Specific examples of the compound represented by the above formula (2) are 4,5-dihydroxyindoline, 5,6-dihydroxyindoline, 6,7-dihydroxyindoline, N-methyl-5,6-dihydroxyindoline, N-ethyl-5,6-dihydroxyindoline, N-hexyl-5,6-dihydroxyindoline, 2-methyl-5,6-dihydroxyindoline, 3-methyl-5,6-dihydroxyindoline, 4-hydroxyindoline, 2,3-dimethyl-5,6-dihydroxyindoline, 2-methyl-5-ethyl-6-hydroxyindoline, 2-methyl-5-hydroxy-6-β-hydroxyethylindoline, 4-hydroxypropylindoline, 2,3-dimethyl-5,6-dihydroxyindoline, 4-hydroxy-5-methoxyindoline, 6-hydroxy-7-methoxyindoline, 6-hydroxy-5-methoxyindoline, 6-hydroxyindoline, 5-hydroxyindoline, 7-hydroxyindoline, 7-aminoindoline, 5-aminoindoline, 4-aminoindoline, 5,6-

dihydroxyindolinecarboxylic acid, 1-methyl-5,6-dihydroxyindoline and salts thereof.

In view of the toning, each of the above-mentioned substances to be oxidized may be used solely or two or more thereof may be used jointly.

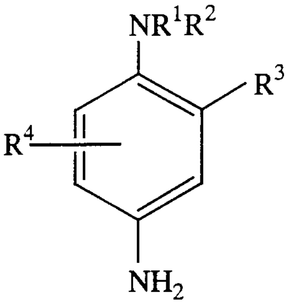
When the hair composition of the present invention is used as a single preparation type permanent-waving preparation or depilatory, examples of a component used as a substance to be oxidized are thioglycolic acid, thioglycolate, cysteine, hydroxycysteine, dihydroxycysteine, acetylated cysteine and sodium sulfite. Each of them may be used solely or two or more thereof may be used jointly. Due to its object for use, the above-mentioned coloring substance is not compounded with those preparations.

There is no particular limitation for the compounding amount of the above substance to be oxidized in the hair composition of the present invention but the amount may be appropriately selected depending upon the product form of the composition and the type of the substance to be oxidized and further depending upon the degree of toning in the case of hairdye of a reactive type and upon the degree of decoloration and the waving effect in the cases of permanent-waving preparation and depilatory. For example, in the case of a hairdye of a reactive type, it is appropriate to compound in an amount of 0.01-10% (% by weight; hereinafter, % will be used in the same sense) or, particularly, 0.1-5% to the total composition. In the case of a permanent-waving preparation, it is appropriate to compound in an amount of 0.01-40% or, particularly, 0.1-20% to the total composition while, in the case of a depilatory, it is appropriate to compound in an amount of 0.01-50% or, particularly, 0.1-30% to the total composition. When the compounding amount of the substance to be oxidized is too small, it may be necessary to use a large amount of the composition for achieving the effect of the compounding sufficiently while, when the amount is too much, the compounding amount of oxidase naturally becomes small whereby the action by oxidation in use is hardly available and, moreover, stabilization may be sometimes difficult.

WO 99/36034, WO 99/36035, WO 99/36036, WO 99/36037, WO 99/36038, WO 99/36039, WO 99/36040, WO 99/36041, WO 99/36042, WO 99/36043, WO 99/36044, WO 99/36045 and WO 99/36046 in the name of L'Oreal discloses different kind of oxidizing dyes (developed substances or oxidation bases) and coupling components (coupling agents) which can also be used according to the present invention and which are hereby incorporated by reference.

The oxidation bases can in particular be selected among para-phenylenediamines, double bases, para-aminophenols, ortho-aminophenols and heterocyclic oxidation bases.

Among the para-phenylenediamines suitable as oxidation bases in the dye compositions according to the invention, the following compounds of the formula (3) and their addition salts with an acid can in particular be mentioned:



(3)

in which

- $R^1$ represents a hydrogen atom, $C_1$-$C_4$-alkyl, $C_1$-$C_4$-monohydroxyalkyl, $C_2$-$C_4$-polyhydroxyalkyl, ($C_1$-$C_4$)alkoxy($C_1$-$C_4$)alkyl, $C_1$-$C_4$-alkyl substituted with a nitrogen-containing group, phenyl or 4'-aminophenyl;
- $R^2$ represents a hydrogen atom, $C_1$-$C_4$-alkyl, $C_1$-$C_4$monohydroxyalkyl, $C_2$-$C_4$polyhydroxyalkyl, ($C_1$-$C_4$)alkoxy($C_1$-$C_4$)alkyl or $C_1$-$C_4$alkyl substituted with a nitrogen-containing group;
- $R^3$ represents a hydrogen atom, a halogen atom such as chlorine, bromine, iodine or fluorine, $C_1$-$C_4$alkyl, $C_1$-$C_4$monohydroxyalkyl, $C_1$-$C_4$hydroxyalkoxy, $C_1$-$C_4$acetylaminoalkoxy, $C_1$-$C_4$mesylaminoalkoxy or $C_1$-$C_4$carbamoylaminoalkoxy,
- $R^4$ represents a hydrogen atom, a halogen atom or $C_1$-$C_4$-alkyl.

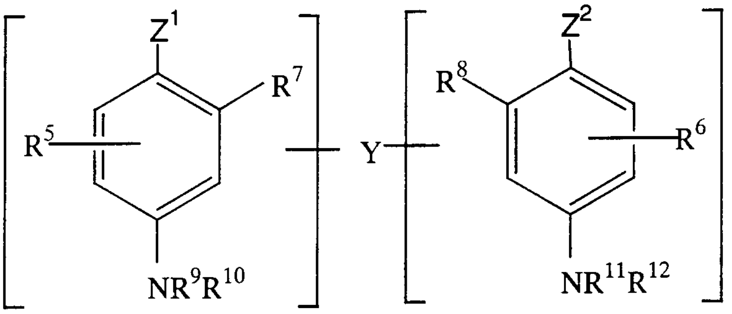
Among the nitrogen-containing groups in the above formula (3), amino, mono($C_1$-$C_4$)alkylamino, di($C_1$-$C_4$)alkylamino, tri($C_1$-$C_4$)alkylamino, monohydroxy($C_1$-$C_4$)alkylamino, imidazolinium and ammonium can in particular be mentioned.

More particularly among the para-phenylenediamines of the above formula (3), the following para-phenylenediamines can be mentioned: para-phenylenediamine, paratoluylenediamine, 2-chloro para-phenylenediamine, 2,3-dimethyl para-phenylenediamine, 2,6-dimethyl para-phenylenediamine, 2,6-diethyl para-phenylenediamine, 2,5-dimethyl para-phenylenediamine, N,N-dimethyl para-phenylenediamine, N,N-diethyl para-phenylenediamine, N,N-dipropyl para-phenylenediamine, 4-amino N,N-diethyl 3-methyl aniline, N,N-bis(β-hydroxyethyl) para-phenylenediamine, 4-N,N-bis-(β-hydroxyethyl)amino 2-methyl aniline, 4-N,N-bis-(β-hydroxyethyl)amino 2-chloro aniline, 2-β-hyroxyethyl para-phenylenediamine, 2-fluoro para-phenylenediamine, 2-isopropyl para-phenylenediamine, N-(β-hydroxypropyl) para-phenylenediamine, 2-hydroxymethyl para-phenylenediamine, N,N-dimethyl 3-methyl para-phenylenediamine, N,N-(ethyl, β-hydroxyethyl) para-phenylenediamine, N-(β,γ-dihydroxypropyl) para-phenylenediamine, N-(4'-aminophenyl) para-phenylenediamine, N-phenyl para-phenylene-diamine, 2-β-hydroxyethyloxy para-phenylenediamine, 2-β-acetylaminoethyloxy para-phenylenediamine, N-(β-methoxyethyl) para-phenylenediamine and their addition salts with an acid.

Among the para-phenylenediamines of the above formula (3), the following are especially preferred: para-phenylenediamine, paratoluylenediamine, 2-isopropyl para-phenylenediamine, 2-β-hydroxyethyl para-phenylenediamine, 2-β-hydroxyethyloxy para-phenylenediamine, 2,6-dimethyl para-phenylenediamine, 2,6-diethyl para-phenylenediamine, 2,3-dimethyl para-phenylenediamine, N,N-bis-(β-hydroxyethyl) para-phenylenediamine, 2-chloro para-phenylenediamine, 2-β-acetylaminoethyloxy para-phenylenediamine and their addition salts with an acid.

By double bases is, according to the invention, meant such compositions which include at least two aromatic nuclei carrying amino and/or hydroxyl groups.

Among the double bases suitable as oxidation bases in the dye compositions according to the invention, the compounds of the following formula (4) and their addition salts with an acid can in particular be mentioned:



(4)

in which

- $Z^1$ and $Z^2$, which are identical or differ, represent a hydroxyl group or $-NH_2$, which can be substituted with a $C_1$-$C_4$alkyl group or with a bridging group Y;
- the bridging group Y is a linear or branched alkylene chain with 1 to 14 carbon atoms, which can be interrupted or terminated by one or more nitrogen-containing groups and/or one or more hetero atoms, such as oxygen, sulphur or nitrogen atoms, and optionally be substituted with one or more hydroxyl groups or $C_1$-$C_6$-alkoxy groups;
- $R^5$ and $R^6$ represents a hydrogen or halogen atom, $C_1$-$C_4$alkyl, $C_1$-$C_4$mono-hydroxyalkyl, $C_2$-$C_4$polyhydroxyalkyl, $C_1$-$C_4$aminoalkyl or a bridging group Y;
- $R^7$, $R^8$, $R^9$, $R^{10}$, $R^{11}$ and $R^{12}$, which are identical or differ, represent a hydrogen atom, a bridging group Y or a $C_1$-$C_4$alkyl group;

whereby it should be understood that the compounds of the formula (4) only include a single bridging group Y per molecule.

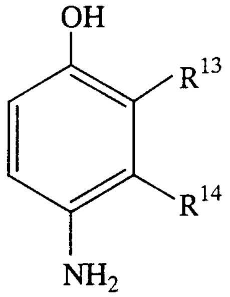
Among nitrogen-containing groups of the above formula (4), the following can in particular be mentioned: amino, mono$(C_1$-$C_4)$alkylamino, di$(C_1$-$C_4)$alkyl-amino, tri$(C_1$-

$C_4$)alkylamino, monohydroxy($C_1$-$C_4$)alkylamino, imidazolinium and ammonium.

Among the double bases of the above formula (4), the following can more particularly be mentioned: N,N=-bis-(β-hydroxyethyl) N,N'-bis-(4'-aminophenyl) 1,3-diamino propanol, N,N=-bis-(β-hydroxyethyl) N,N=-bis-(4'-aminophenyl) ethylenediamine, N,N=-bis-(4-aminophenyl) tetramethylenediamine, N,N'-bis-(β-hydroxyethyl) N,N'-bis-(4-aminophenyl) tetramethylenediamine, N,N'-bis-(4-methylaminophenyl) tetramethylenediamine, N,N'-bis-(ethyl) N,N'-bis-(4'-amino, 3-methylphenyl) ethylenediamine, 1,8-bis-(2,5-diaminophenoxy)-3,5-dioxaoctane and their addition salts with an acid.

Particularly preferred double bases of the formula (4) are N,N'-bis-(β-hydroxyethyl) N,N'-bis-(4'-aminophenyl) 1,3-diamino propanol, 1,8-bis-(2,5-diamino-phenoxy)-3,5-dioxaoctane or one of their addition salts with an acid.

Among the para-aminophenols suitable as oxidation bases in the dye compositions according to the invention, the compounds of the following formula (5) and their addition salts with an acid can especially be mentioned:



(5)

in which

- $R^{13}$ represents a hydrogen or halogen atom, $C_1$-$C_4$alkyl, $C_1$-$C_4$monohydroxyalkyl, ($C_1$-$C_4$)alkoxy($C_1$-$C_4$)alkyl, $C_1$-$C_4$aminoalkyl or ($C_1$-$C_4$)hydroxyalkyl($C_1$-$C_4$)aminoalkyl,
- $R^{14}$ represents a hydrogen or halogen atom, $C_1$-$C_4$alkyl, $C_1$-$C_4$monohydroxyalkyl, $C_2$-$C_4$polyhydroxyalkyl, $C_1$-$C_4$aminoalkyl, $C_1$-$C_4$cyanoalkyl or ($C_1$-$C_4$)alkoxy($C_1$-$C_4$)alkyl,

whereby it should be understood that at least one of the groups $R^{13}$ or $R^{14}$ represents a hydrogen atom.

Among the para-aminophenols of the above formula (5), the following can in particular be mentioned: para-aminophenol, 4-amino 3-methyl phenol, 4-amino 3-fluoro phenol, 4-amino 3-hydroxymethyl phenol, 4-amino 2-methyl phenol, 4-amino 2-hydroxymethyl phenol, 4-amino 2-methoxymethyl phenol, 4-amino 2-aminomethyl phenol, 4-amino 2-(β-hydroxyethyl aminomethyl) phenol, 4-amino 2-fluoro phenol and acid addition salts thereof.

Among the ortho-aminophenols suitable as oxidation bases in the dye compositions according to the invention, the following can in particular be mentioned: 2-amino phenol, 2-amino 5-methyl phenol, 2-amino 6-methyl phenol, 5-acetamido 2-amino phenol and acid addition salts thereof.

Among the heterocyclic bases suitable as oxidation bases in the dye compositions according to the invention, the following can in particular be mentioned: pyridine derivatives, pyrimidine derivatives, pyrazole derivatives, pyrazolo-pyrimidine derivatives and acid addition salts thereof.

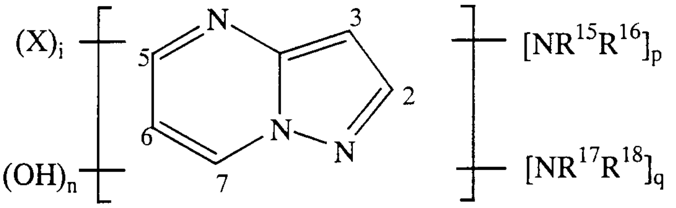
Among the pyridine derivatives, the compositions described for instance in the patents GB-PS 1 026 978 and GB-PS 1 153 196 can in particular be mentioned: 2,5-diamino pyridine, 2-(4-methoxyphenyl)amino 3-amino pyridine, 2,3-diamino 6-methoxy pyridine, 2-(β-methoxyethyl)amino 3-amino 6-methoxy pyridine, 3,4-diamino pyridine and the addition salts thereof.

Among the pyrimidine derivatives, the compositions described for instance in the German patent DE 2 359 399 or the Japanese patents JP 88-169 571 and JP 91-333 495 or in the Patent Application WO 96/15765 can in particular be mentioned: 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 their addition salts with an acid.

Among the pyrazole derivatives, the compounds described for instance in the patents DE 3 843 892 and DE 4 133 957 and in the Patent Applications WO 94/08969, WO 94/08970, FR-A-2 733 749 and DE 195 43 988 can in particular be mentioned: 4,5-diamino

1-methyl pyrazole, 3,4-diamino pyrazole, 4,5-diamino 1-(4'-chlorobenzyl) pyrazole, 4,5-diamino 1,3-dimethyl pyrazole, 4,5-diamino 3-methyl 1-phenyl pyrazole, 4,5-diamino 1-methyl 3-phenyl pyrazole, 4-amino 1,3-dimethyl 5-hydrazino pyrazole, 1-benzyl 4,5-diamino 3-methyl pyrazole, 4,5-diamino 3-tert-butyl 1-methyl pyrazole, 4,5-diamino 1-tert-butyl 3-methyl pyrazole, 4,5-diamino 1-(β-hydroxyethyl) 3-methyl pyrazole, 4,5-diamino 1-ethyl 3-methyl pyrazole, 4,5-diamino 1-ethyl 3-(4'-methoxyphenyl) pyrazole, 4,5-diamino 1-ethyl 3-hydroxymethyl pyrazole, 4,5-diamino 3-hydroxymethyl 1-methyl pyrazole, 4,5-diamino 3-hydroxymethyl 1-isopropyl pyrazole, 4,5-diamino 3-methyl 1-isopropyl pyrazole, 4-amino 5-(2'-aminoethyl)amino 1,3-dimethyl pyrazole, 3,4,5-triamino pyrazole, 1-methyl 3,4,5-triamino pyrazole, 3,5-diamino 1-methyl 4-methylamino pyrazole, 3,5-diamino 4-( β-hydroxyethyl)amino-1-methyl pyrazole and their acid addition salts.

Among the pyrazolo pyrimidine derivatives, the following can in particular be mentioned: the pyrazolo-[1,5-a]-pyrimidines of the formula (6) shown below, their addition salts with an acid or base and their tautomeric forms when a tautomeric equilibrium exists:



(6)

in which

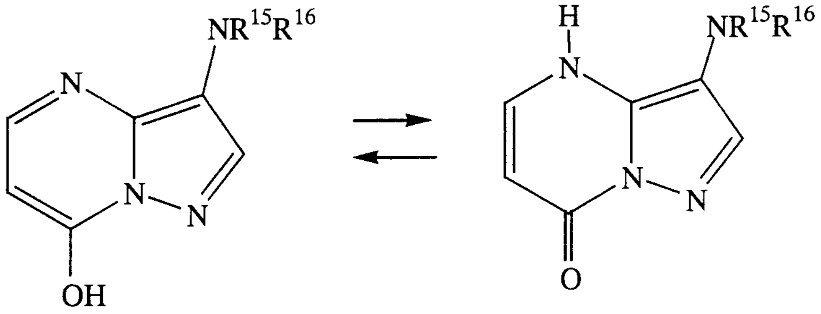
- $R^{15}$, $R^{16}$, $R^{17}$ and $R^{18}$, which are identical or differ, represent a hydrogen atom, $C_1$-$C_4$alkyl, aryl, $C_1$-$C_4$hydroxyalkyl, $C_2$-$C_4$polyhydroxyalkyl, $(C_1$-$C_4)$alkoxy$(C_1$-$C_4)$alkyl, $C_1$-$C_4$aminoalkyl (where the amine can be protected by an acetyl, ureido or sulfonyl group), $(C_1$-$C_4)$alkylamino $(C_1$-$C_4)$alkyl, di-[$(C_1$-$C_4)$alkyl] amino $C_1$-$C_4$alkyl (where the dialkyl groups can form a carbon ring or a heterocyclic ring with 5 or 6 members), hydroxy-$C_1$-$C_4$alkyl or di-[hydroxy$(C_1$-$C_4)$alkyl]-amino $C_1$-$C_4$alkyl;

- the groups X, which are identical or differ, represent a hydrogen atom, $C_1$-$C_4$alkyl, aryl, $C_1$-$C_4$hydroxyalkyl, $C_2$-$C_4$polyhydroxyalkyl, amino $C_1$-$C_4$alkyl, ($C_1$-$C_4$)alkyl($C_1$-$C_4$)aminoalkyl, di-[($C_1$-$C_4$)alkyl] amino$C_1$-$C_4$alkyl (where the dialkyl groups can form a carbon ring or a heterocyclic ring with 5 or 6 members), hydroxy ($C_1$-$C_4$)alkyl or di-[hydroxy($C_1$-$C_4$)alkyl]amino-$C_1$-$C_4$alkyl, amino, $C_1$-$C_4$alkyl or di-[($C_1$-$C_4$)alkyl]-amino, a halogen atom, a carboxylic acid group or a sulfonic acid group;
- i is 0, 1, 2 or 3;
- p is 0 or 1;
- q is 0 or 1;
- n is 0 or 1;

with the proviso that

- the sum p + q differs from 0;
- when p + q is 2, n has the value 0, and the groups $NR^{15}R^{16}$ and $NR^{17}R^{18}$ occupy the positions (2,3); (5,6); (6,7); (3,5) or (3,7);
- when p + q is 1, n has the value 1, and the group $NR^{15}R^{16}$ (or $NR^{17}R^{18}$) and the group OH occupy the positions (2,3); (5,6); (6,7); (3,5) or (3,7).

When the pyrazolo-[1,5-a]-pyrimidines of the above formula (6) are such which include a hydroxyl group in one of the positions 2, 5 or 7 in the α-position to a nitrogen atom, a tautomeric equilibrium exists which for instance can be indicated by the following reaction scheme.



Among the pyrazolo-[1,5-a]-pyrimidines of the above formula (6), the following can be mentioned in particular:

- pyrazolo-[1,5-a]-pyrimidine-3,7-diamine;

- 2,5-dimethyl pyrazolo-[1,5-a]-pyrimidine-3,7-diamine;
- pyrazolo-[1,5-a]-pyrimidine-3,5-diamine;
- 2,7-dimethyl pyrazolo-[1,5-a]-pyrimidine-3,5-diamine;
- 3-amino pyrazolo-[1,5-a]-pyrimidine-7-ol;
- 3-amino pyrazolo-[1,5-a]-pyrimidine-5-ol;
- 2-(3-amino pyrazolo-[1,5-a]-pyrimidine-7-ylamino)-ethanol;
- 2-(7-amino pyrazolo-[1,5-a]-pyrimidine-3-ylamino)-ethanol;
- 2-[(3-amino-pyrazolo[1,5-a]pyrimidine-7-yl)-(2-hydroxy-ethyl)-amino]ethanol;
- 2-[(7-amino-pyrazolo[1,5-a]pyrimidine-3-yl)-(2-hydroxy-ethyl)-amino]ethanol;
- 5,6-dimethyl pyrazolo-[1,5-a]-pyrimidine-3,7-diamine;
- 2,6-dimethyl pyrazolo-[1,5-a]-pyrimidine-3,7-diamine;
- 2,5, N 7, N 7-tetramethyl pyrazolo-[1,5-a]-pyrimidine-3,7-diamine;

and their addition salts and tautomeric forms, provided a tautomeric equilibrium exists.

The pyrazolo-[1,5-a]-pyrimidines of the above formula (6) can be prepared by way of cyclisation of an aminopyrazole according to the syntheses described in the following references:

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

The pyrazolo-[1,5-a]-pyrimidines of the above formula (6) can furthermore be produced by cyclisation from a hydrazine according to the syntheses described in the following references:

- A. McKillop, R.J. Kobilecki, Heterocycles, 6(9), 1355, 1977.

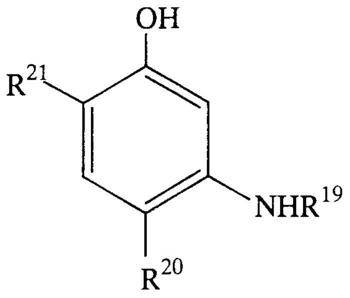
- E. Alcade, J. De Mendoza, J.M. Marcia-Marquina, C. Almera, J. Elguero, J. Heterocyclic Chem., 11(3), 423, 1974.
- K. Saito, I. Hori, M. Higarashi, H. Midorikawa, Bull. Chem. Soc. Japan, 47(2), 476, 1974.

The oxidation base or bases represent preferably between approximately 0.0005% and approximately 12% by weight of the total weight of the dye composition according to the invention, especially between approximately 0.005% and approximately 6% by weight.

The coupling agent or coupling agents suitable in the ready-to-use dye compositions according to the invention are such which are conventionally used in oxidation dye composition, viz. metaphenylene diamines, metaaminophenols, metadiphenols, heterocyclic coupling agents and their addition salts with an acid.

These coupling agents can especially be selected among 2-methyl-5-amino-phenol, 5-N-(β-hydroxyethyl)-amino-2-methyl-phenol, 3-amino-phenol, 1,3-dihydroxybenzene, 1,3-dihydroxy-2-methyl-benzene, 4-chloro-1,3-dihydroxy-benzene, 2,4-diamino-1-(β-hydroxyethyloxy)-benzene, 2-amino-4-(β-hydroxyethylamino)-1-methoxy-benzene, 1,3-diamino-benzene, 1,3-bis-(2,4-diaminophenoxy)-propane, sesamol, α-naphtol, 6-hydroxy-indole, 4-hydroxy-indole, 4-hydroxy-N-methyl-indole, 6-hydroxy-indolin, 2,6-dihydroxy-4-methyl-pyridine, 1-H-3-methyl-pyrazole-5-on, 1-phenyl-3-methyl-pyrazole-5-one, 2,6-dimethyl-pyrazolo-[1,5-b]-1,2,4-triazole, 2,6-dimethyl-[3,2-c]-1,2,4-triazole, 6-methyl-pyrazolo-[1,5-a]-benzimidazole and acid addition salts thereof.

The meta-aminophenol or meta-aminophenols applicable as coupling agents in the ready-to-use dye composition according to the invention is/are preferably selected from compounds of the following formula (7) and acid addition salts thereof:



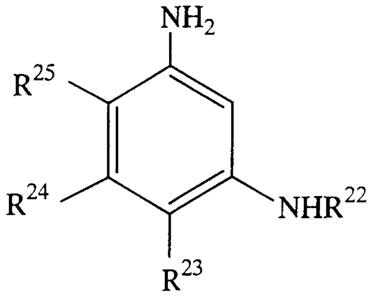
(7)

in which

- $R^{19}$ represents a hydrogen atom, $C_1$-$C_4$-alkyl, $C_1$-$C_4$monohydroxyalkyl or $C_2$-$C_4$polyhydroxyalkyl,
- $R^{20}$ represents a hydrogen atom, $C_1$-$C_4$alkyl, $C_1$-$C_4$alkoxy or a halogen atom selected from chlorine, bromine and fluorine,
- $R^{21}$ represents a hydrogen atom, $C_1$-$C_4$alkyl, $C_1$-$C_4$alkoxy, $C_1$-$C_4$mono-hydroxyalkyl, $C_2$-$C_4$polyhydroxyalkyl, $C_1$-$C_4$monohydroxyalkoxy or $C_2$-$C_4$poly-hydroxyalkoxy.

Among the meta-aminophenols of the above formula (5), the following can be mentioned in particular: meta-aminophenol, 5-amino-2-methoxy phenol, 5- amino-2-(β-hydroxyethyloxy)-phenol, 5-amino-2-methyl phenol, 5-N-(β-hydroxyethyl)amino-2-methyl phenol, 5-N-(β-hydroxyethyl)amino-4-methoxy-2-methyl phenol , 5-amino-4-methoxy-2-methyl phenol, 5-amino-4-chloro-2-methyl phenol, 5-amino-2,4-dimethoxy phenol, 5-(γ-hydroxypropylamino)-2-methyl phenol and acid addition salts thereof.

The meta-phenylenediamine or meta-phenylenediamines applicable as coupling agents in the ready-to-use dye composition according to the invention is/are preferably selected from compounds of the following formula (8) and acid addition salts thereof:



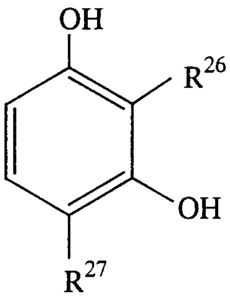
(8)

in which

- $R^{22}$ represents a hydrogen atom, $C_1$-$C_4$alkyl, $C_1$-$C_4$monohydroxyalkyl or $C_2$-$C_4$polyhydroxyalkyl;
- $R^{23}$ and $R^{24}$, which are identical or differ, each represents a hydrogen atom, $C_1$-$C_4$alkyl, $C_1$-$C_4$monohydroxyalkoxy or $C_2$-$C_4$polyhydroxyalkoxy;
- $R^{25}$ represents a hydrogen atom, $C_1$-$C_4$alkoxy, $C_1$-$C_4$aminoalkoxy, $C_1$-$C_4$mono-hydroxyalkoxy, $C_2$-$C_4$polyhydroxyalkoxy or 2,4-diaminophenoxyalkoxy.

Among the meta-phenylenediamines of the above formula (8), the following can in particular be mentioned: 2,4-diaminobenzene, 3,5-diamino-1-ethyl-2-methoxybenzene, 3,5-diamino-2-methoxy-1-methyl benzene, 2,4-diamino-1-ethoxybenzene, 1,3-bis-(2,4-diaminophenoxy) propane, bis-(2,4-diaminophenoxy)-methane, 1-(β-aminoethyloxy)-2,4-diaminobenzene, 2-amino-1-(β-hydroxy-ethyloxy)-4-methylamino-benzene, 2,4-diamino-1-ethoxy 5-methyl-benzene, 2,4-diamino-5-(β-hydroxyethyloxy)-1-methylbenzene, 2,4-diamino-1-(β,γ-dihydroxy-propyloxy) benzene, 2,4-diamino-1-(β-hydroxyethyloxy)-benzene, 2-amino-4-N-(β-hydroxyethyl)-amino-1-methoxy-benzene and acid addition salts thereof.

The meta-diphenol or meta-diphenols applicable as coupling agents in the ready-to-use dye composition according to the invention is/are preferably selected from the compounds of the following formula (9) and acid addition salts thereof:



(9)

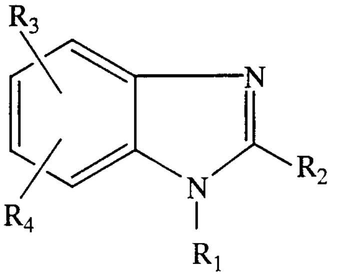
in which

- $R^{26}$ and $R^{27}$, which are identical or differ, each represents a hydrogen atom, $C_1$-$C_4$alkyl or a halogen atom selected from chlorine, bromine and fluorine.

Among the meta-diphenols of the above formula (9), the following can in particular be mentioned: 1,3-dihydroxy-benzene, 2-methyl-1,3-dihydroxy-benzene, 4-chloro-1,3-dihydroxy-benzene, 2-chloro-1,3-dihydroxybenzene, and acid addition salts thereof.

Among the heterocyclic coupling agents applicable in the ready-to-use dye composition according to the invention, derivatives of benzimidazole, derivatives of benzomorpholine, derivatives of sesamol, pyrazolo-azol derivatives, pyrrolo-azole derivatives, imidazolo-azole derivatives, pyrazolo-pyrimidine derivatives, derivatives of pyrazoline-3,5-diones, pyrrolo-[3,2-d]oxazole derivatives, pyrazolo-[3,4-d]-thiazole derivatives, thiazolo-azole S-oxide derivatives, thiazolo-azole S,S-dioxide derivatives and their addition salts with an acid can in particular be mentioned.

Among the benzimidazole derivatives applicable as heterocyclic coupling agents in the dye composition according to the invention, the compounds of the following formula (I) and their acid addition salts can in particular be mentioned:



(I)

in which:

$R_1$ represents a hydrogen atom or $C_1$-$C_4$-alkyl,

$R_2$ represents a hydrogen atom, $C_1$-$C_4$alkyl or phenyl,

$R_3$ represents a hydroxyl, amino or methoxy group,

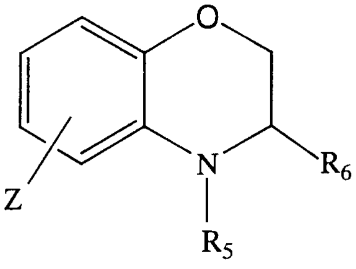
$R_4$ represents a hydrogen atom, a hydroxyl group, a methoxy group or $C_1$-$C_4$alkyl group,

with the proviso that:

- when $R_3$ is an amino group, it is in position 4,
- when $R_3$ is in position 4, $R_4$ is in position 7,
- when $R_3$ is in position 5, $R_4$ is in position 6.

Among the benzimidazole derivatives of the above formula (I), the following can in particular be mentioned: 4-hydroxy benzimidazole, 4-amino benzimidazole, 4-hydroxy-7-methyl benzimidazole, 4-hydroxy-2-methyl benzimidazole, 1-butyl-4-hydroxy benzimidazole, 4-amino-2-methyl benzimidazole, 5,6-dihydroxy benzimidazole, 5-hydroxy-6-methoxy benzimidazole, 4,7-dihydroxy benzimidazole, 4,7-dihydroxy-1-methyl benzimidazole, 4,7-dimethoxy benzimidazole, 5,6-dihydroxy-1-methyl benzimidazole, 5,6-dihydroxy-2-methyl benzimidazole, 5,6-dimethoxy benzimidazole and their addition salts with an acid.

Among the benzomorpholine derivatives applicable as heterocyclic coupling agents in the ready-to-use dye composition according to the invention, the compounds of the following formula (II) and their addition salts with an acid can in particular be mentioned:



(II)

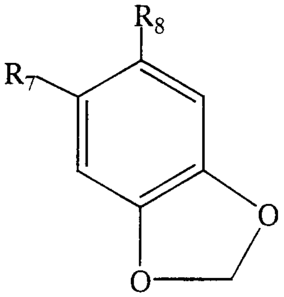
in which

$R_5$ and $R_6$, which are identical or differ, each represents a hydrogen atom or $C_1$-$C_4$-alkyl, and

Z represents a hydroxyl group or an amino group.

Among the benzomorpholine derivatives of the above formula (II) the following can in particular be mentioned: 6-hydroxy 1,4-benzomorpholine, N-methyl 6-hydroxy 1,4-benzomorpholine, 6-amino 1,4-benzomorpholine and their acid addition salts.

Among the derivatives of sesamol applicable as heterocyclic coupling agents in the ready-to-use dye composition according to the invention, the compounds of the following formula (III) and their addition salts with an acid can in particular be mentioned:


(III)

in which

- $R_7$ represents a hydroxyl group, an amino group, a $C_1$-$C_4$-alkylamino group, a $C_1$-$C_4$monohydroxyalkylamino group or a $C_2$-$C_4$polyhydroxyalkylamino group,
- $R_8$ represents a hydrogen atom, a halogen atom or a $C_1$-$_4$alkoxy group.

Among the derivatives of sesamol of the above formula (III), the following can in particular be mentioned: 2-bromo 4,5-methylenedioxy phenol, 2-methoxy 4,5-methylenedioxy aniline, 2-(β-hydroxyethyl)amino 4,5-methylenedioxy benzene and their acid addition salts.

Among the pyrazolo-azole derivatives applicable as heterocyclic coupling agents in the ready-to-use dye composition according to the invention, the compounds can in particular be mentioned which are described in the following Patents and Patent Applications: FR 2 075 583, EP-A-119 860, EP-A-285 274, EP-A-244 160, EP-A-578 248, GB 1 458 377, US 3 277 554, US 3 419 391, US 3 061 432, US 4 500 630, US 3 725 067, US 3 926 631, US 5 457 210, JP 84/99437, JP 83/42045, JP 84/162548, JP 84/171956, JP 85/33552, JP 85/43659, JP 85/172982, JP 85/190779 as well in the following publications: Chem. Ber. 32, 797, (1899), Chem. Ber. 89, 2550, (1956), J. Chem. Soc. Perkin trans I, 2047, (1977), J. Prakt. Chem., 320, 533, (1978), the subject matter of which constitute an integrated part of the present application.

As the pyrazolo-azole derivatives, the following can in particular be mentioned:

- 2-methyl pyrazolo[1,5-b]-1,2,4-triazole,
- 2-ethyl pyrazolo[1,5-b]-1,2,4-triazole,
- 2-isopropyl pyrazolo[1,5-b]-1,2,4-triazole,
- 2-phenyl pyrazolo[1,5-b]-1,2,4-triazole,

- 2,6-dimethyl pyrazolo[1,5-b]-1,2,4-triazole,
- 7-chloro-2,6-dimethylpyrazolo[1,5-b]-1,2,4-triazole,
- 3,6-dimethyl-pyrazolo[3,2-c]-1,2,4-triazole,
- 6-phenyl-3-methylthio- pyrazolo[3,2-c]-1,2,4-triazole,
- 6-amino-pyrazolo[1,5-a]benzimidazole,

and their addition salts with an acid.

Among the pyrrolo-azole derivatives applicable as heterocyclic coupling agents in the ready-to-use dye composition according to the invention, the compounds can in particular be mentioned which are described in the following Patents and Patent Applications: US 5 256 526, EP-A-557 851, EP-A-578 248, EP-A-518 238, EP-A-456 226, EP-A-488 909, EP-A-488 248 and in the following publications:

- D.R. Liljegren Ber. 1964, 3436;
- E.J. Browne, J.C.S., 1962, 5149;
- P. Magnus, J.A.C.S., 1990, 112, 2465;
- P. Magnus, J.A.C.S., 1987, 109, 2711;
- Angew. Chem. 1960, 72, 956;
- and Rec. Trav. Chim. 1961, 80, 1075, the subject matter of which constitute an integrated part of the present application.

As the pyrazolo-azole derivatives, the following can in particular be mentioned:

- 5-cyano-4-ethoxycarbonyl-8-methyl pyrrolo [1,2-b]-1,2,4-triazole,
- 5-cyano-8-methyl-4-phenyl pyrrolo [1,2-b]-1,2,4-triazole,
- 7-amido-6-ethoxycarbonyl pyrrolo [1,2-a]-benzimidazole,

and their addition salts with an acid.

Among the imidazolo-azole derivatives applicable as heterocyclic coupling agents in the ready-to-use dye composition according to the invention, the compounds can in particular be mentioned which are described in the following Patents and Patent Applications: US 5 441 863, JP 62-279 337, JP 06-236 011 and JP 07-092 632, the subject matter of which constitute an integrated part of the present application.

As the imidazolo-azole derivatives, the following can in particular be mentioned:

- 7,8-dicyano-imidazolo-[3,2-a]-imidazole,
- 7,8-dicyano-4-methyl-imidazolo-[3,2-a]-imidazole,

and their addition salts with an acid.

Among the pyrazolo-pyrimidine derivatives applicable as heterocyclic coupling agents in the ready-to-use dye composition according to the invention, the compounds can in particular be mentioned which are described in the following Patent Application: EP-A-304-001, the subject matter of which constitute an integrated part of the present application.

As the pyrazolo-pyrimidine derivatives, the following can in particular be mentioned:

- pyrazolo-[1,5-a]-pyrimidine-7-one,
- 2,5-dimethyl pyrazolo [1,5-a] pyrimidine-7-one,
- 2-methyl-6-ethoxycarbonyl pyrazolo [1,5-a] pyrimidine-7-one,
- 2-methyl-5-methoxymethyl pyrazolo [1,5-a] pyrimidine-7-one,
- 2-tert-butyl-5-trifluoromethyl pyrazolo [1,5-a] pyrimidine-7-one,
- 2,7-dimethyl pyrazolo [1,5-a] pyrimidine-5-one,

and their addition salts with an acid.

Among the pyrazoline-3,5-diones derivatives applicable as heterocyclic coupling agents in the ready-to-use dye composition according to the invention, the compounds can in particular be mentioned which are described in the following Patents and Patent Applications: JP 07-036159, JP 07-084348 and US 4 128 425, and in the following publications:

- L. WYZGOWSKA, Acta. Pol. Pharm. 1982, 39 (1-3), 83.
- E. HANNIG, Pharmazie, 1980, 35 (4), 231
- M.H. ELNAGDI, Bull. Chem. Soc. Jap., 46(6), 1830, 1973
- G. CARDILLO, Gazz. Chim. Ital. 1966, 96, (8-9), 973,

the subject matter of which constitute an integrated part of the present application.

As the derivatives of pyrazolin-3,5-diones, the following can in particular be mentioned:

- 1,2-diphenyl pyrazoline-3,5-dione,
- 1,2-diethyl pyrazoline-3,5-dione,

and their addition salts with an acid.

Among the pyrrolo-[3,2-d]-oxazole derivatives applicable as heterocyclic coupling agents in the ready-to-use dye composition according to the invention, the compounds can in particular be mentioned which are described in the Patent Application JP 07-325 375, the subject matter of which constitute an integrated part of the present application.

Among the pyrazolo-[3,4-d]-thiazole derivatives applicable as heterocyclic coupling agents in the ready-to-use dye composition according to the invention, the compounds can in particular be mentioned which are described in the Patent Application JP 07-244 361 and in J. Heterocycl. Chem. 16, 13, (1979).

Among the thiazolo-azole S-oxide derivatives and thiazolo-azole S,S-dioxide derivatives applicable as heterocyclic coupling agents in the ready-to-use dye composition according to the invention, the compounds can in particular be mentioned which are described in the following documents:

- JP 07-098 489;
- Khim. Geterotsilk. Soedin, 1967, p. 93;
- J. Prakt. Chem., 318, 1976, p. 12;
- Indian J. Heterocycl. Chem. 1995, 5(2), p. 135;
- Acta. Pol. Pharm. 1995, 52(5), 415;
- Heterocycl. Commun. 1995, 1(4), 297;
- Arch. Pharm. (Weinheim, Ger.), 1994, 327(12), 825.

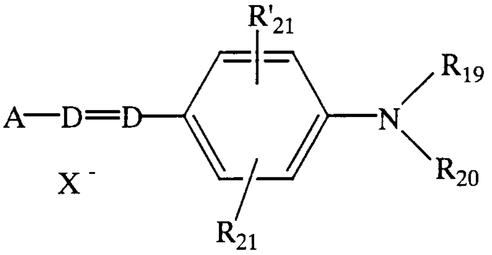
These coupling agents constitute preferably between approximately 0.0001% and approximately 10% by weight of the ready-to-use dye composition, especially between approximately 0.005% and approximately 5% by weight.

The cationic direct dye(s) applicable in the ready-to-use dye composition according to the invention is/are preferably selected among cationic amino-anthraquinone dyes, cationic mono or di-azo dyes and cationic naphtoquinone dyes.

Examples of the above are especially[8-[(p-aminophenyl)azo]-7-hydroxy-2-naphtyl]trimethylammonium chloride (also called Basic Brown 16 or Arianor Mahogany 306002 in Color Index), 3-[(4-amino-6-bromo-5,8-dihydro-1-hydroxy-8-imino-5-oxo-2-naphtalenyl)amino]-N,N,N-trimethyl-benzeneaminium chloride (also called Basic Blue 99 or Arianor Steel Blue 306004 in Color Index), 7-hydroxy-8-[(2-methoxyphenyl)azo]-N,N,N-trimethyl-2-naphtaleneaminium chloride (also called Basic Red 76 or Arianor Madder Red in Color Index), [8-[(4-amino-2-nitrophenyl)azo]-7-hydroxy-2-naphtyl]trimethylammonium chloride (also called Basic Brown 17 or Arianor Sienna Brown 306001 in Color Index) and 3-[(4,5-dihydro-3-methyl-5-oxo-1-phenyl-1H-pyrazol-4-yl)azo]-N,N,N-trimethyl-benzenaminium chloride (also called Basic Yellow 57 or Arianor Straw Yellow 306005 in Color Index).

The cationic direct dye(s) can furthermore be selected among:

a) Compounds of the formula (V):



(V)

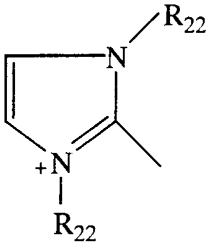
in which

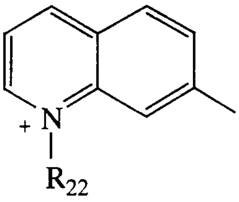
D represents a nitrogen atom or a group -CH,

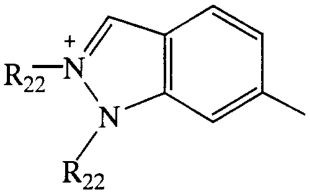
$R_{19}$ and $R_{20}$, which are identical or differ, each represents a hydrogen atom, a $C_1$-$C_4$alkyl group, which can be substituted with one of the groups -CN, -OH or $-NH_2$ or together with a carbon atom in the benzene ring form an optionally oxygen-containing or nitrogen-containing heterocyclic group, which can be substituted with one or more $C_1$-$C_4$alkyl groups; or a 4'-aminophenyl group,

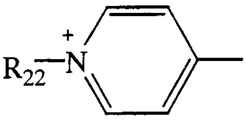
$R_{21}$ and $R'_{21}$, which are identical or differ, each represents a hydrogen atom or a halogen atom selected from chlorine, bromine, iodine and fluorine, cyano, $C_1$-$C_4$-alkoxy or acetyloxy,

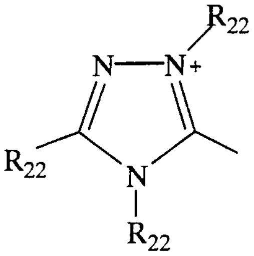
$X^-$ represents an anion, preferably selected from chloride, methylsulphate and acetate, A represents a group selected from the following structures A1-A19:

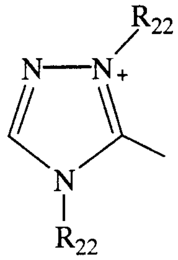

A1 ;

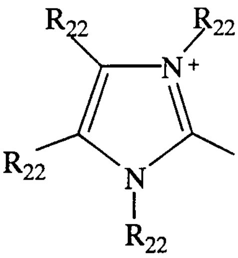

A2 ;


A3 ;


A4 ;


A5 ;


A6 ;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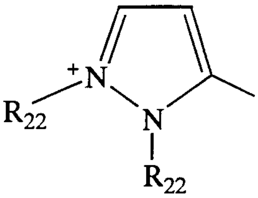
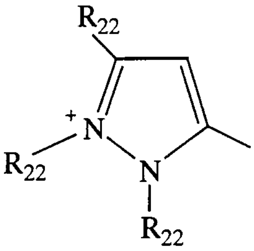

A8 ;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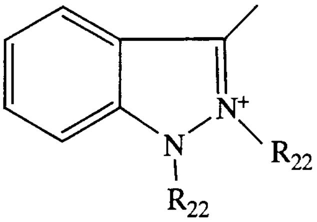
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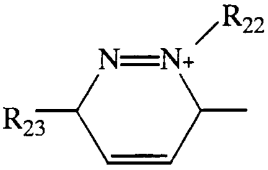
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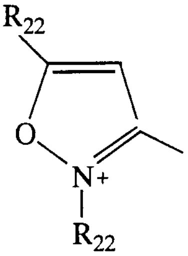
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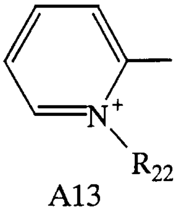
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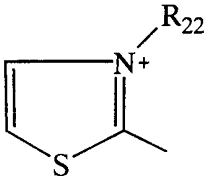
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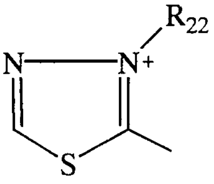
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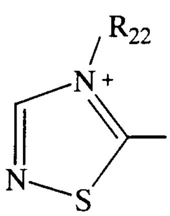
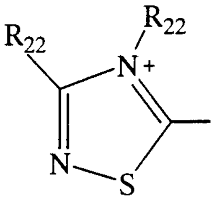


A16

;



A17

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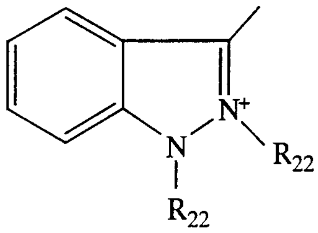
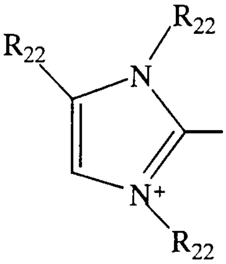


A18

and

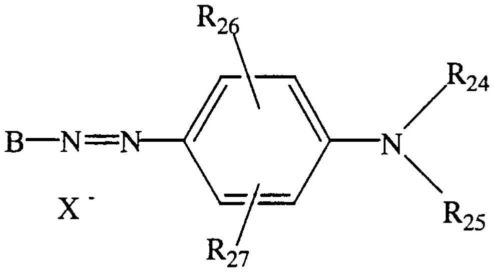


A19

;

wherein $R_{22}$ represents a $C_1$-$C_4$alkyl group, which can be substituted with a hydroxyl group, and $R_{23}$ represents a $C_1$-$C_4$alkoxy group;

b) compositions of the formula (VI):



(VI)

in which

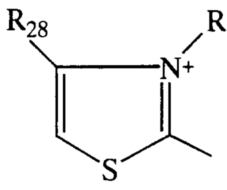
$R_{24}$ represents a hydrogen atom or a $C_1$-$C_4$alkyl group,

$R_{25}$ represents a hydrogen atom, an alkyl group, which can be substituted with a group -CN or with an amino group, or 4'-aminophenyl, or $R_{25}$ represents together with $R_{24}$ an optionally oxygen and/or nitrogen-containing heterocyclic group, which can be substituted with a $C_1$-$C_4$alkyl group,

$R_{26}$ and $R_{27}$, which are identical or differ, represent a hydrogen atom, a halogen atom such as bromine, chlorine, iodine or fluorine, $C_1$-$C_4$alkyl, $C_1$-$C_4$alkoxy or the group -CN,

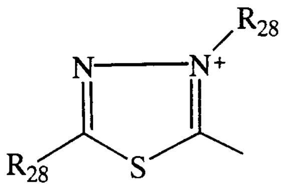
$X^-$ represents an anion, preferably selected from chloride, methylsulphate and acetate,

B represents a group selected from the following structures B1-B6:



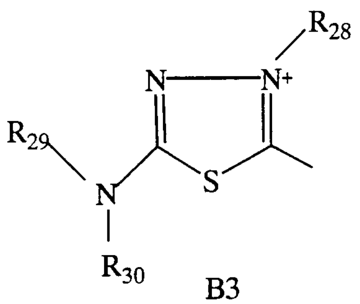
B1

;



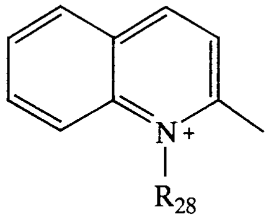
B2

;



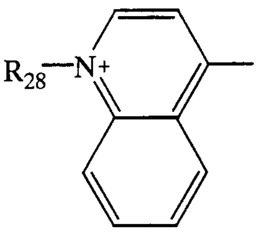
B3

;



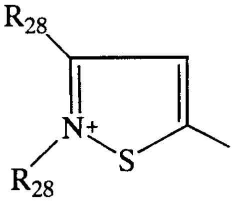
B4

;



B5

and

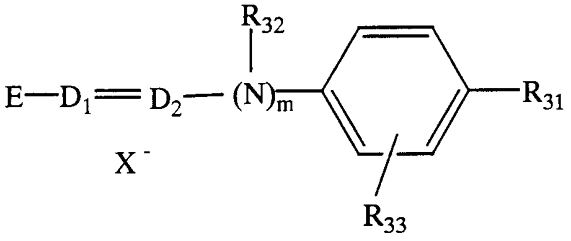


B6

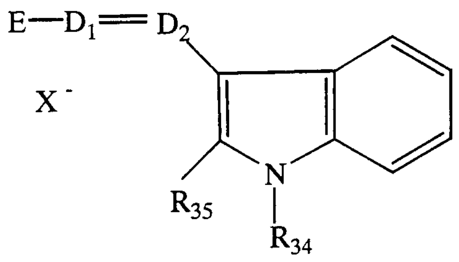
;

in which $R_{28}$ represents a $C_1$-$C_4$alkyl group, and $R_{29}$ and $R_{30}$, which are identical or differ, each represents a hydrogen atom or a $C_1$-$C_4$alkyl group;

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



(VII)



(VII')

in which

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

$R_{32}$ represents a hydrogen atom or a $C_1$-$C_4$alkyl group, or $R_{32}$ together with a carbon atom in the benzene ring forms a heterocyclic group, which optionally includes an oxygen atom and/or is substituted with one or more $C_1$-$C_4$alkyl groups,

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

$R_{34}$ and $R_{35}$, which are identical or differ, each represents a hydrogen atom or a $C_1$-$C_4$alkyl group,

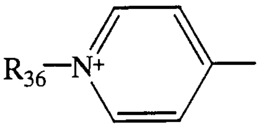
$D_1$ and $D_2$, which are identical or differ, represent a nitrogen atom or a group -CH,

m = 0 or 1,

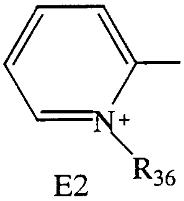
whereby it should be understood that when $R_{31}$ represents a non-substituted amino group, $D_1$ and $D_2$ represent simultaneously a group -CH, and m = 0,

$X^-$ represents an anion, preferably selected from chloride, methylsulphate and acetate,

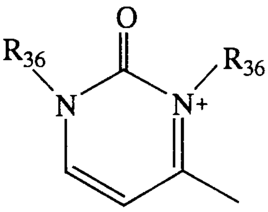
E represents a group selected from the following structures E1-E8:


E1

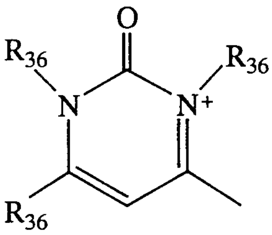
;


E2

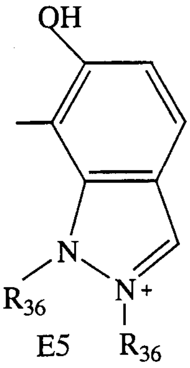
;


E3

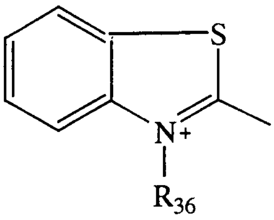
;


E4

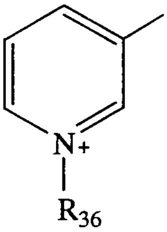
;


E5

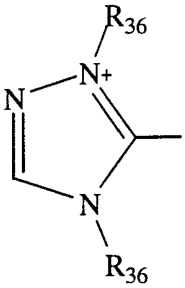
;


E6

;

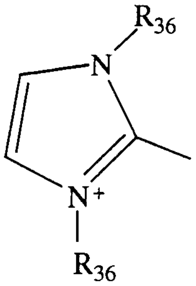

E7

and


E8

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

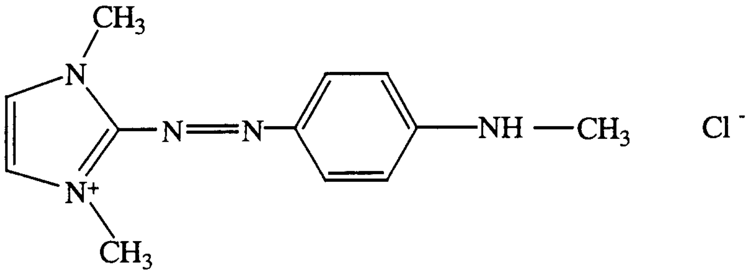
when m = 0 and $D_1$ represents a nitrogen atom, E can also represent a group with the following structure E9:

E9  ;

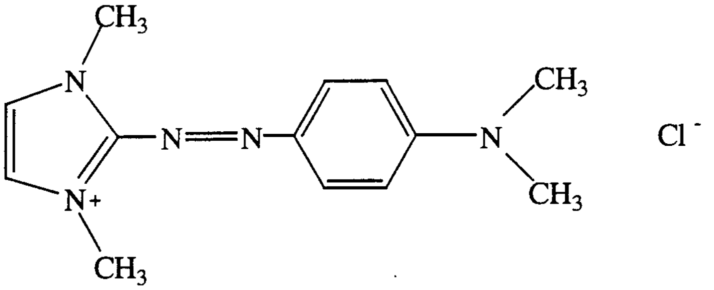
in which $R_{36}$ represents a $C_1$-$C_4$alkyl group.

The cationic direct dyes of the formulae (V), (VI), (VII) and (VII'), which are applicable in the ready-to-use dye compositions according to the invention, are compositions known per se, which are described for instance in the Patent Applications WO 95/01772, WO 95/15144 and EP-A-0 714 954.

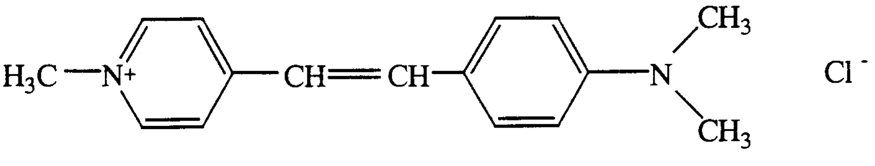
Among the cationic direct dyes of the formula (V), which are applicable in the ready-to-use dye compositions according to the invention, the compounds of the following structures (V1) to (V52) can in particular be mentioned:


(V1)

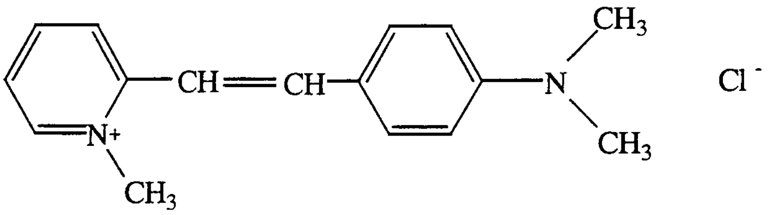
,


(V2)

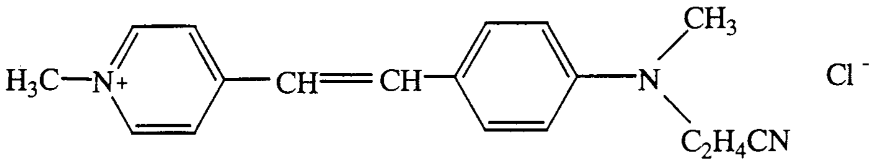
,


(V3)

,

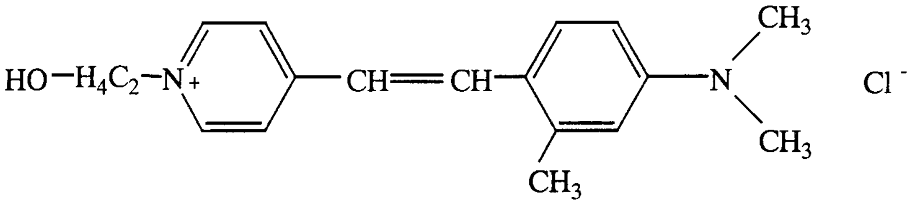

(V4)

,



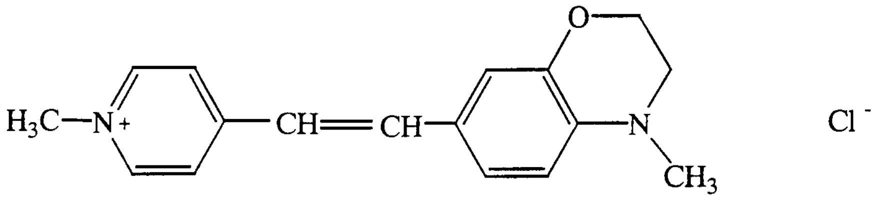
(V5)

,



(V6)

,



(V7)

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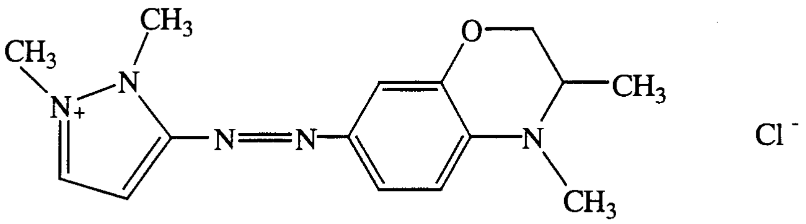
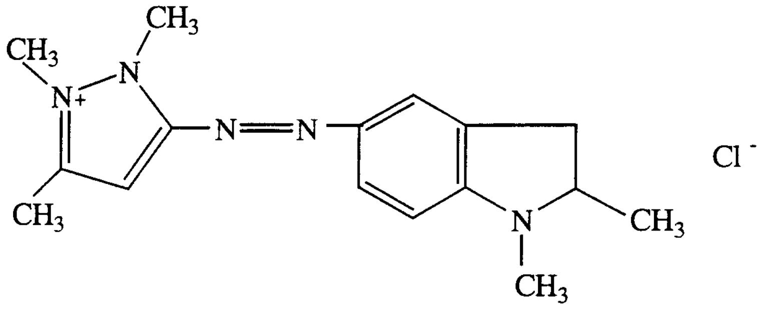


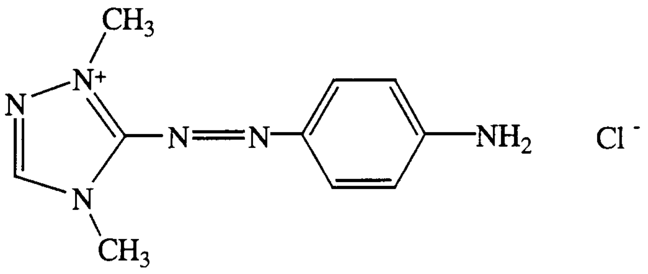
(V8)

,



(V9)

,



(V10)

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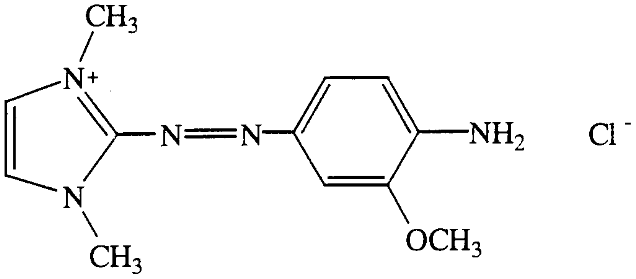

(V11)

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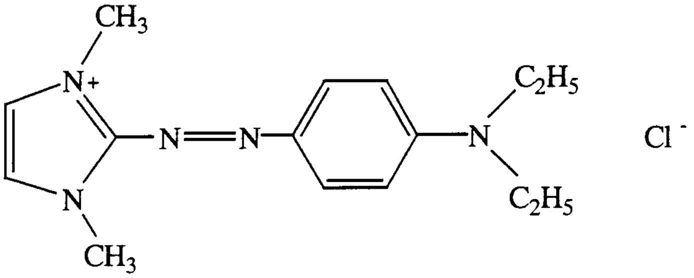

(V12)

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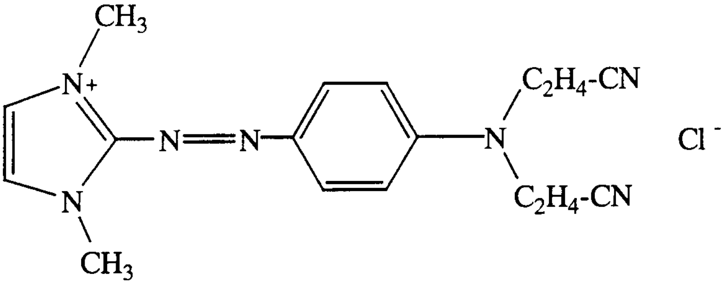

(V13)

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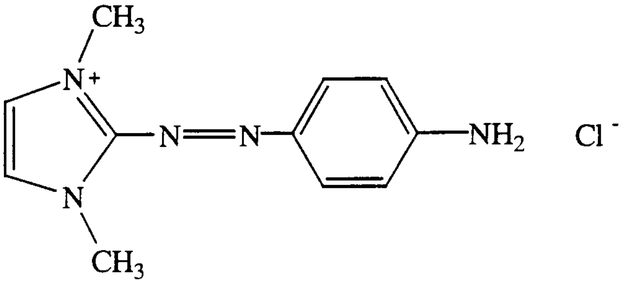

(V14)

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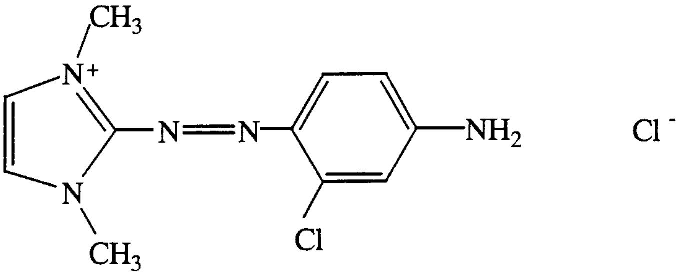

(V15)

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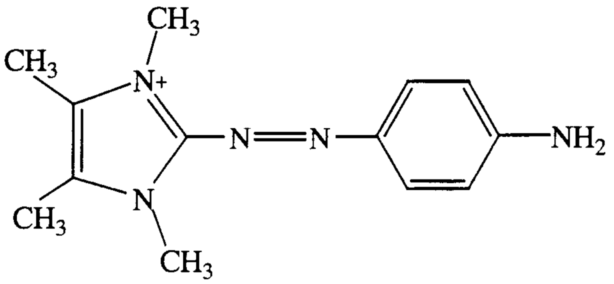
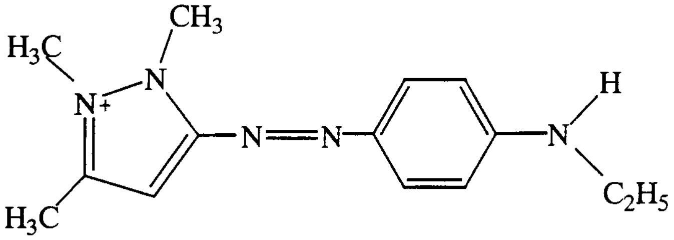


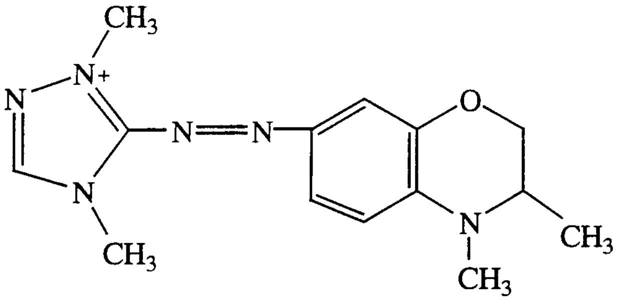
$Cl^-$ (V16)

,



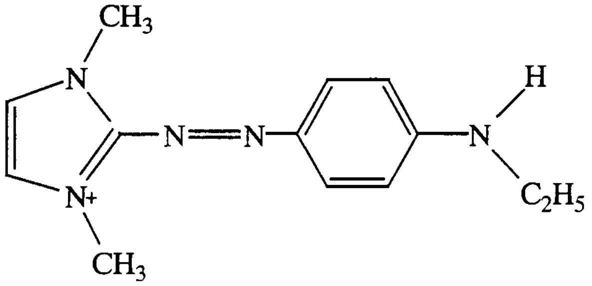
$Cl^-$ (V17)

,



$Cl^-$ (V18)

,



$Cl^-$ (V19)

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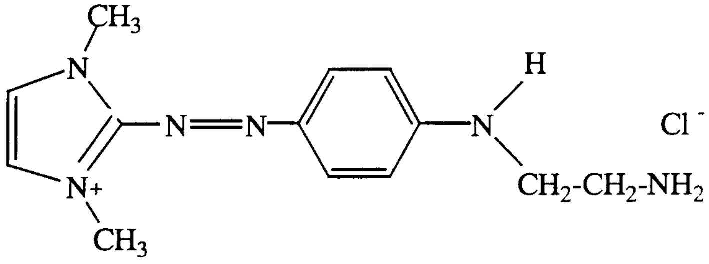

$Cl^-$ (V20)

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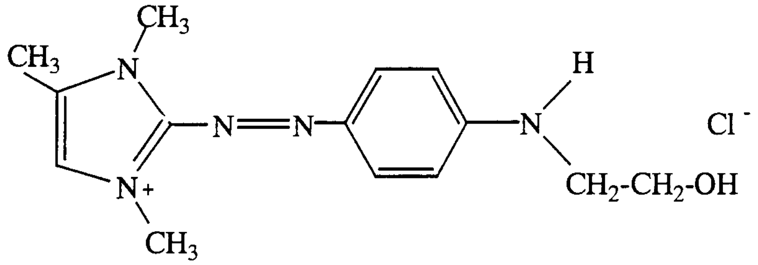

(V21)

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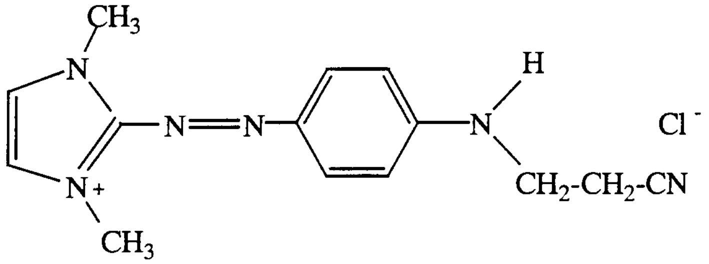

(V22)

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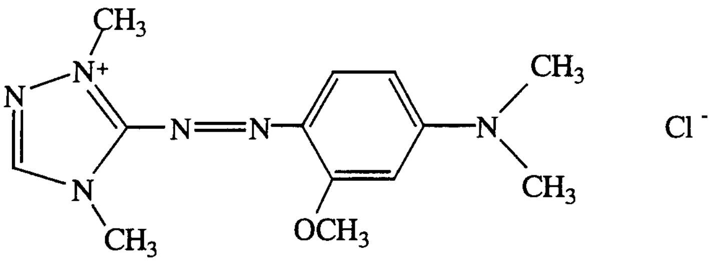

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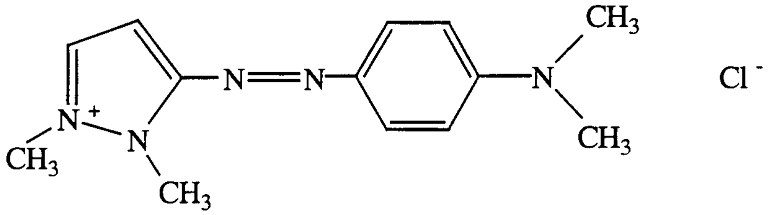

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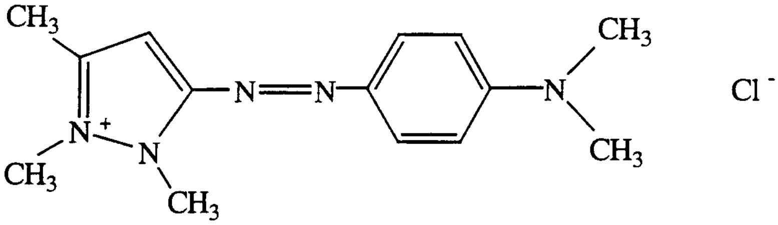

(V25)

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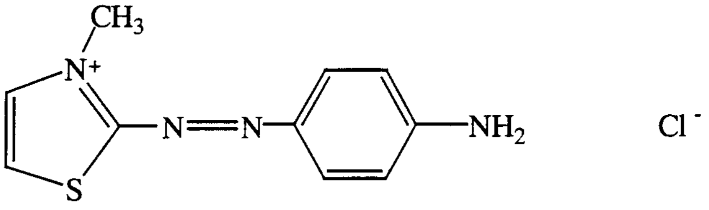

(V26)

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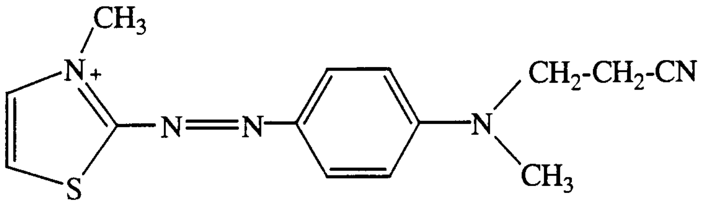
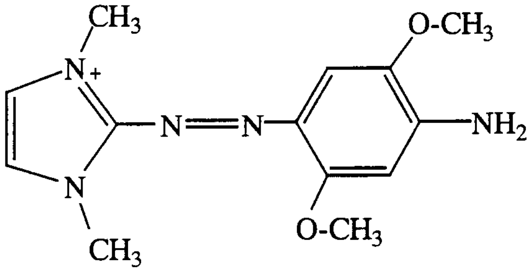


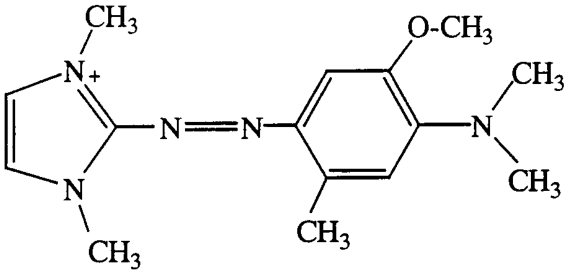
$Cl^-$ (V27)

,



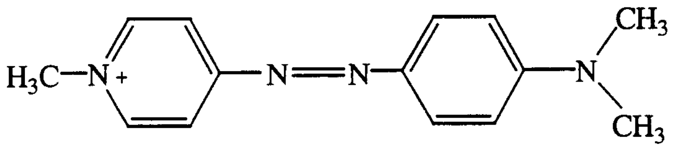
$Cl^-$ (V28)

,



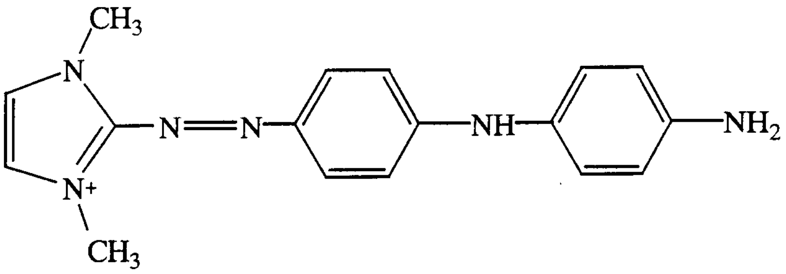
$Cl^-$ (V29)

,



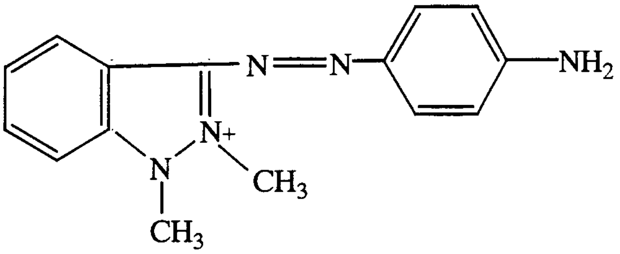
$Cl^-$ (V30)

,



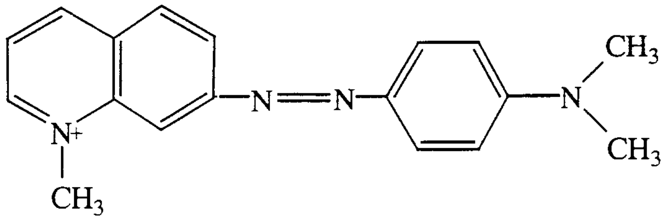
$Cl^-$ (V31)

,

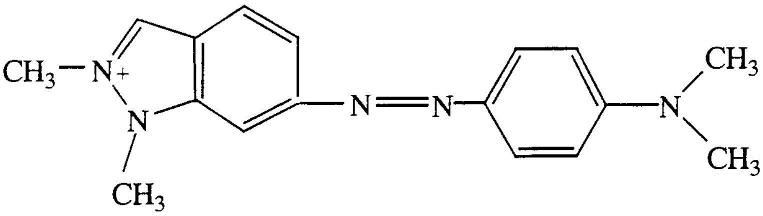


$Cl^-$ (V32)

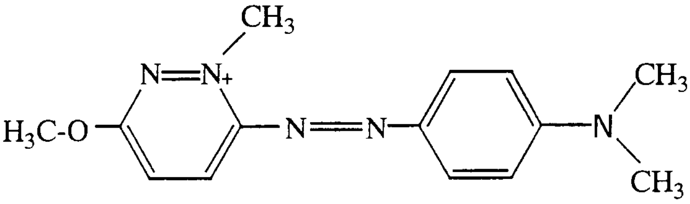
,


Cl$^-$ (V33)

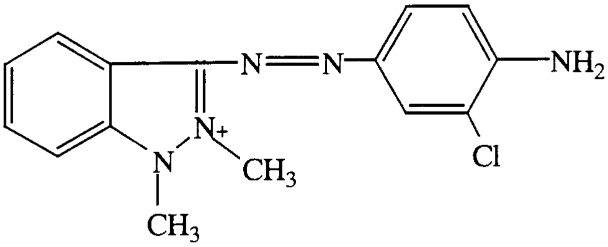
,


Cl$^-$ (V34)

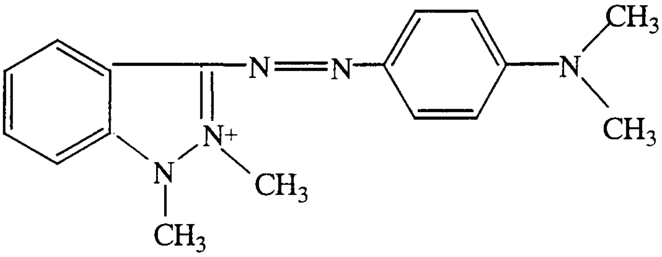
,


Cl$^-$ (V35)

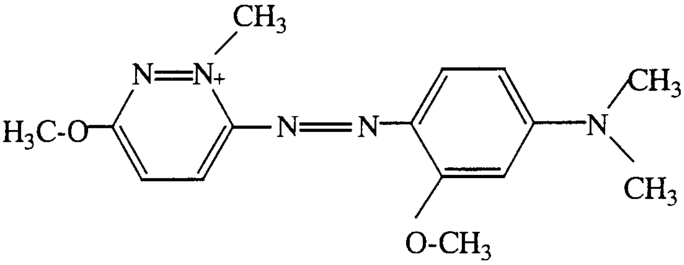
,


Cl$^-$ (V36)

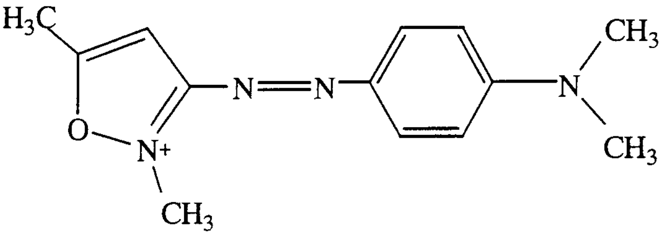
,


Cl$^-$ (V37)

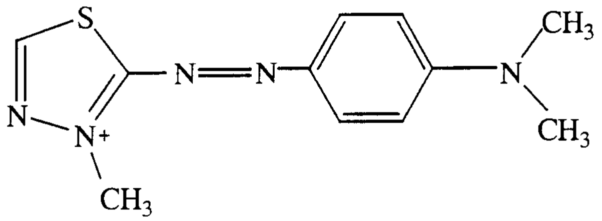
,


Cl$^-$ (V38)

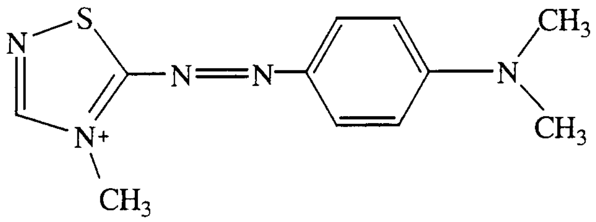
,


Cl$^-$ (V39)

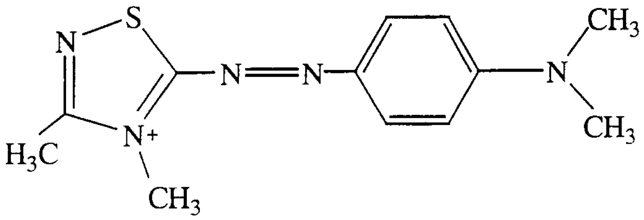
,


Cl$^-$ (V40)

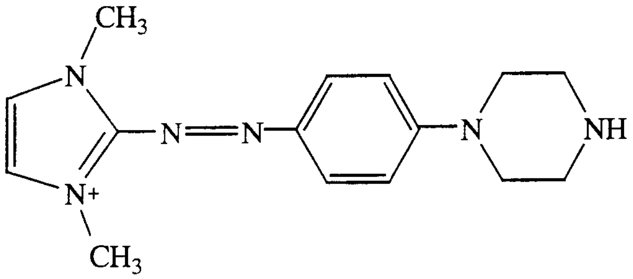
,


Cl$^-$ (V41)

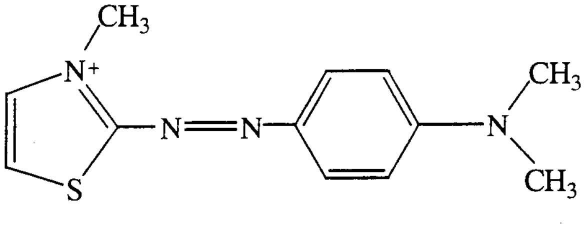
,


Cl$^-$ (V42)

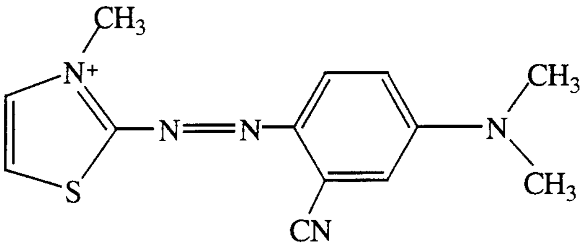
,


Cl$^-$ (V43)

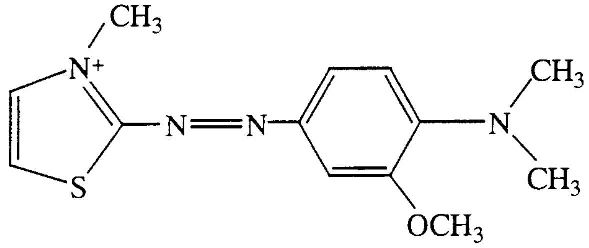
,


Cl$^-$ (V44)

,

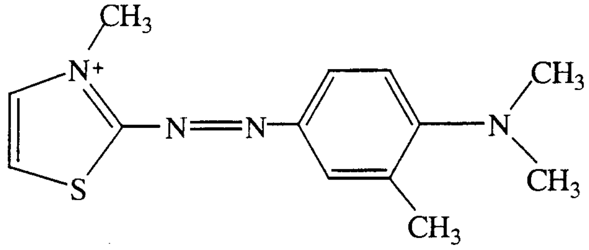

Cl$^-$ (V45)

,



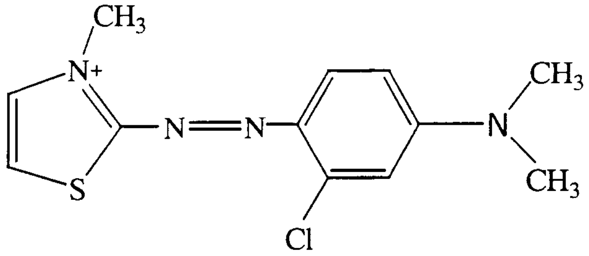
$Cl^-$ (V46)

,



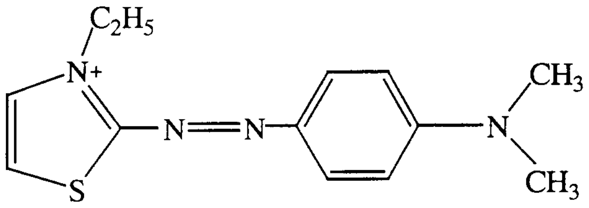
$Cl^-$ (V47)

,



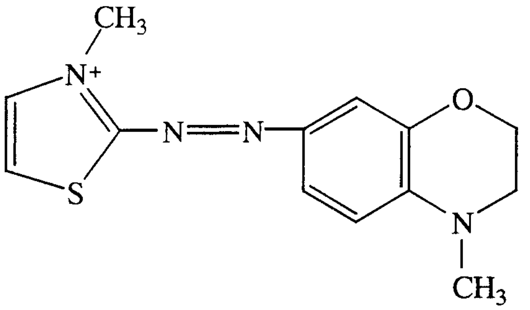
$CH_3SO_4^-$ (V48)

,



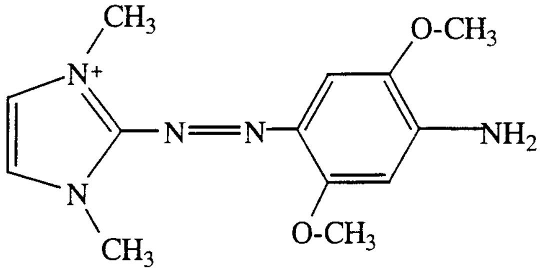
$CH_3SO_4^-$ (V49)

,



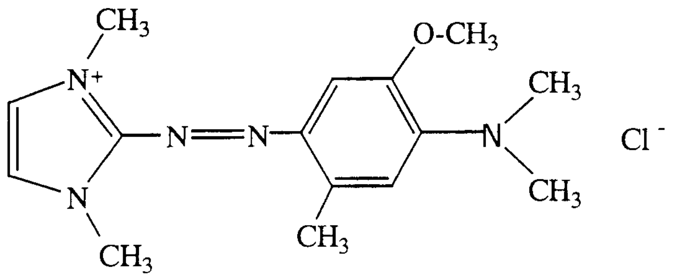
$Cl^-$ (V50)

,



$Cl^-$ (V51)

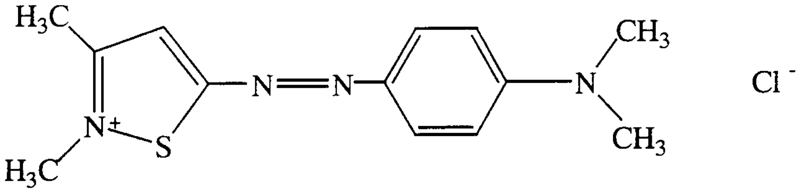
and



(V52)

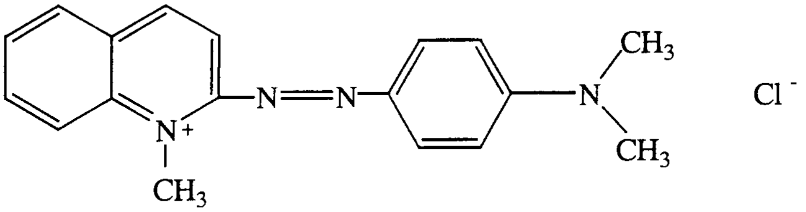
Among the above compounds with the structures (V1) to (V52), the compounds with the structures (V1), (V2), (V4), (V14) and (V31) are particularly preferred.

Among the cationic direct dyes of the formula (VI), which are applicable in the ready-to-use dye compositions according to the invention, the compounds with the following structures (VI1) to (VI12) can in particular be mentioned:



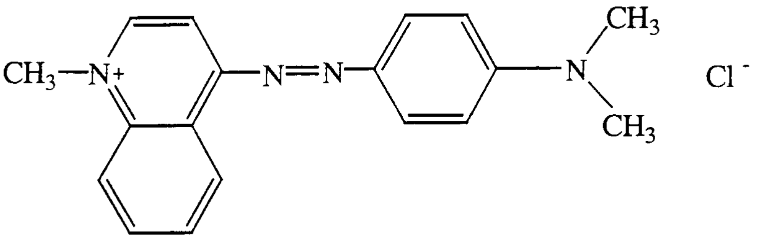
(VI1)

;



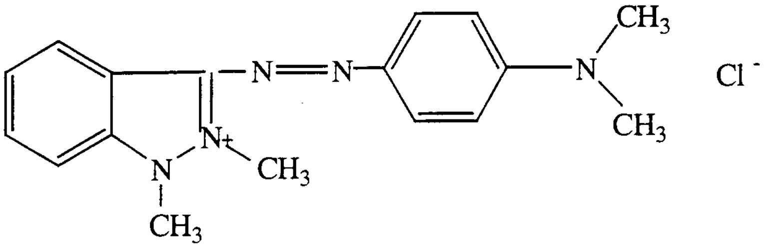
(VI2)

;



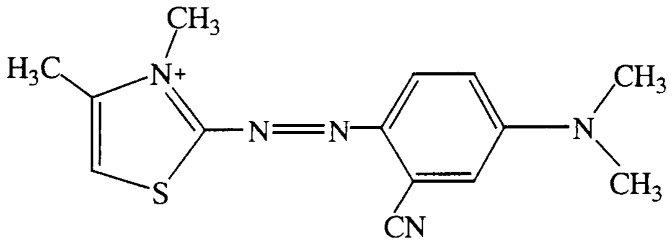
(VI3)

;



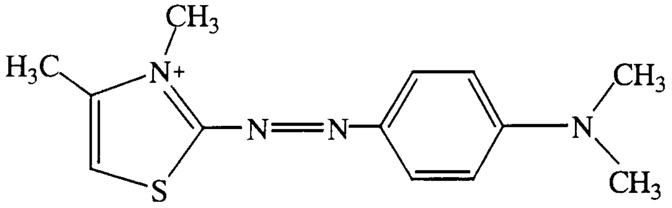
(VI4)

;



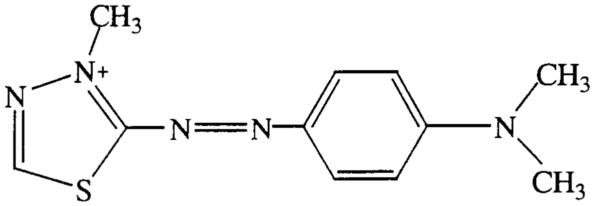
$Cl^-$ (VI5)

;



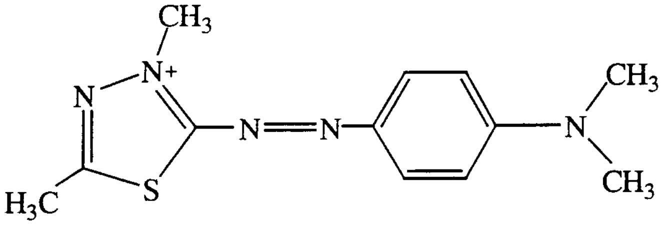
$CH_3SO_4^-$ (VI6)

;



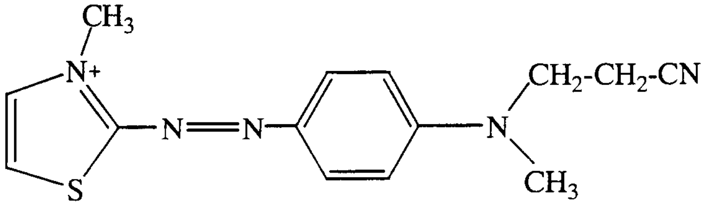
$CH_3SO_4^-$ (VI7)

;



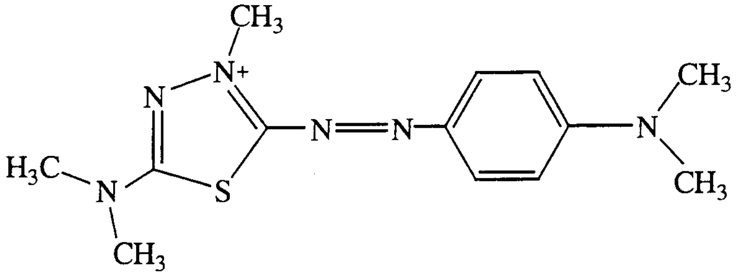
$CH_3SO_4^-$ (VI8)

;



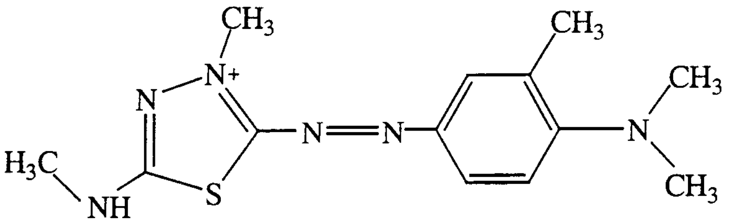
$Cl^-$ (VI9)

;



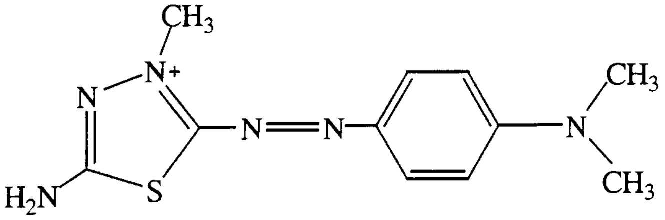
$CH_3SO_4^-$ (VI10)

;

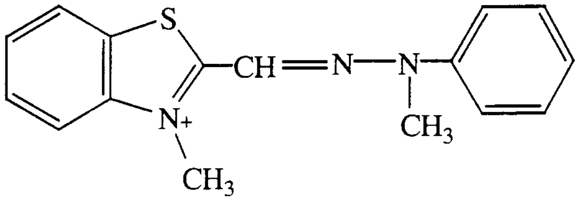


$CH_3SO_4^-$ (VI11)

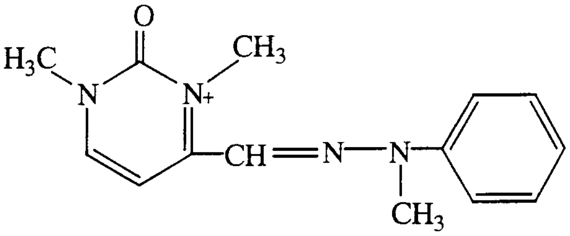
and

 $CH_3SO_4^-$ (VI12)

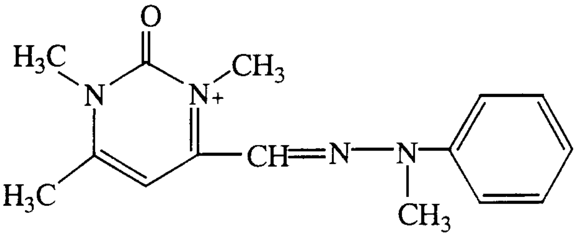
Among the cationic direct dyes of the formula (VII), which are applicable in the ready-to-use dye compositions according to the invention, the compounds with the following structures (VII1) to (VII18) can in particular be mentioned:

 $Cl^-$ (VII1)

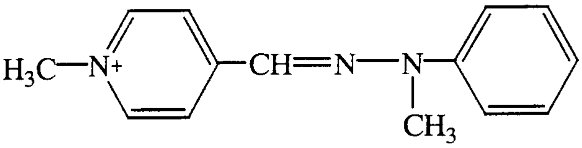
;

 $Cl^-$ (VII2)

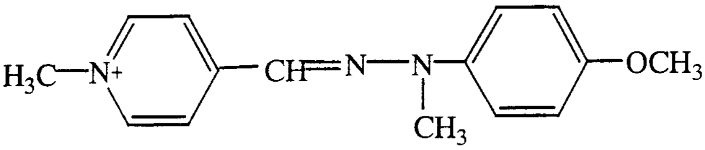
;

 $Cl^-$ (VII3)

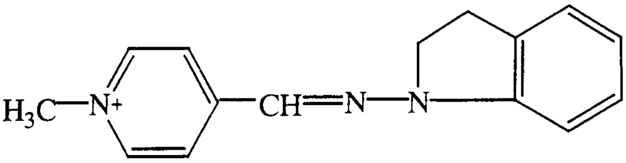
;

 $CH_3SO_4^-$ (VII4)

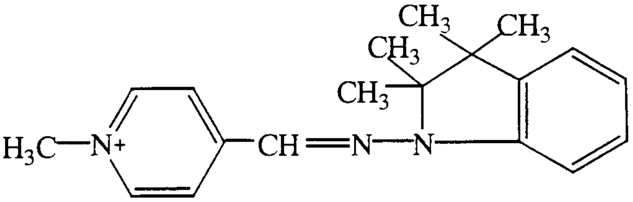
;

 $Cl^-$ (VII5)

;

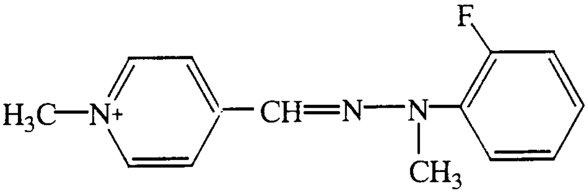
 $CH_3SO_4^-$ (VII6)

;



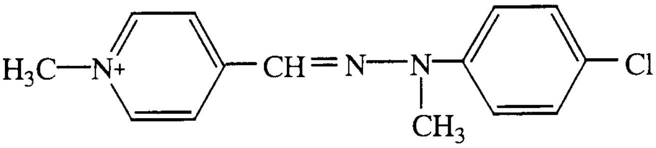
$CH_3SO_4^-$ (VII7)

;



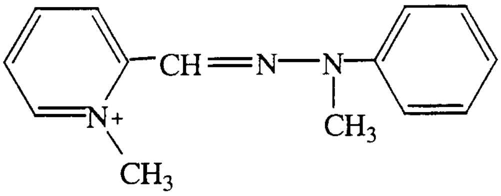
$Cl^-$ (VII8)

;



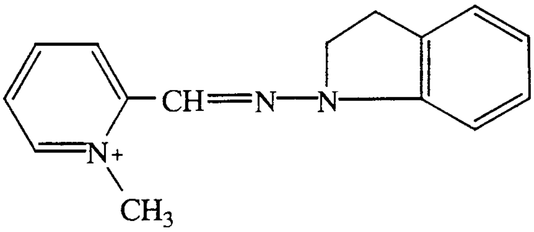
$Cl^-$ (VII9)

;



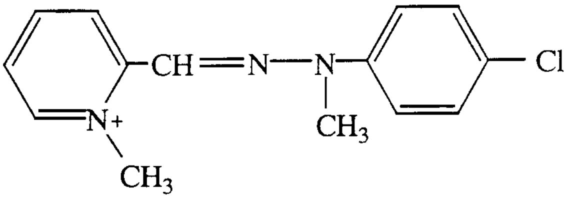
$CH_3SO_4^-$ (VII10)

;



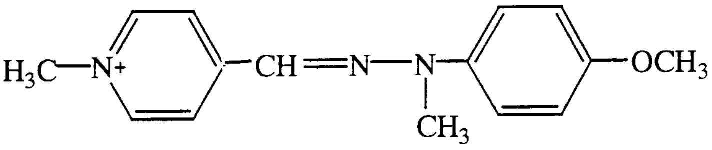
$CH_3SO_4^-$ (VII11)

;



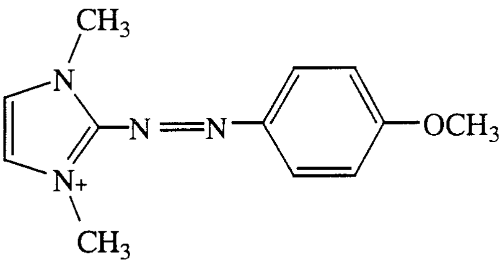
$CH_3SO_4^-$ (VII12)

;



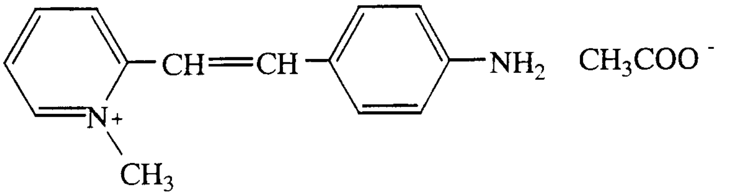
$CH_3SO_4^-$ (VII13)

;



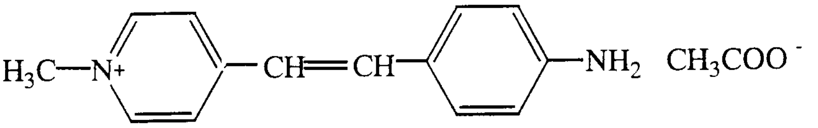
$Cl^-$ (VII14)

;



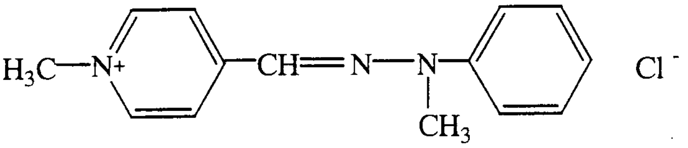
(VII15)

;



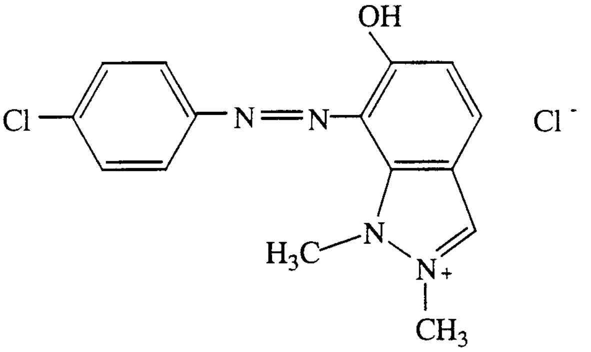
(VII16)

;



(VII17)

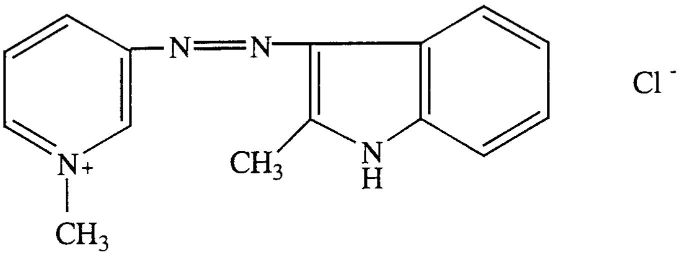
and



(VII18)

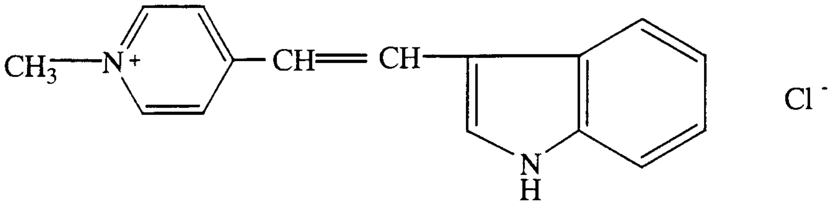
Among the above particular compositions with the structures (VII1) to (VII18), the compounds with the structures (VII4), (VII5) and (VII13) are particularly preferred.

Among the cationic direct dyes of the formula (VII'), which are applicable in the ready-to-use dye compositions according to the invention, the compounds with the following structures (VII'1) to (VII'3) can in particular be mentioned:



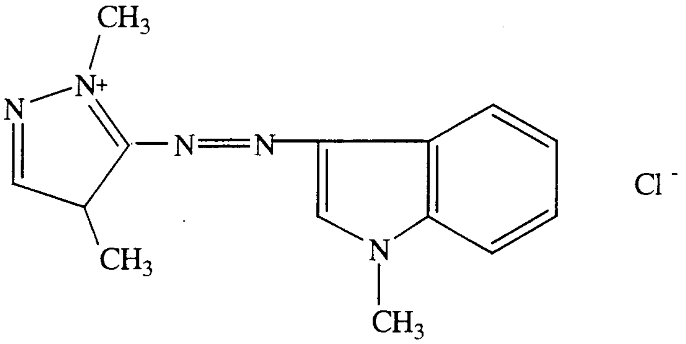
(VII'1)

;



(VII'2)

and



(VII'3)

The cationic direct dye or dyes used according to the invention represent preferably between approximately 0.001% and approximately 10% by weight of the total weight of the ready-to-use dye composition, especially between approximately 0.05% and approximately 5% by weight.

In general, the acid addition salts suitable within the scope of the dye compositions according to the invention (oxidation bases and coupling agents) are especially selected from hydrochlorides, hydrobromides, sulphates, tartrates, lactates and acetates.

As mentioned already, the oxidase used in the present invention is that which uses oxygen as a substrate and does not generate hydrogen peroxide. With regard to such an oxidase, an oxidase of a four-electron reduced type has been known and its examples are catechol oxidase, amine oxidase and laccase. Each of them may be used solely or two or more thereof may be used jointly.

Particularly preferred enzymes are laccases and related enzymes, the term "laccases and related enzymes" including enzymes comprised by the enzyme classification E.C. 1.10.3.2 (laccases) and catechol oxidase enzymes comprised by E.C. 1.10.3.1, bilirubin oxidase enzymes comprised by the enzyme classification E.C. 1.3.3.5 and mono-phenol mono-oxygenase enzymes comprised by the enzyme classification E.C. 1.14.99.1. Laccases are multi-copper containing enzymes that catalyze the oxidation of phenols and aromatic amines. Laccase-mediated oxidations result in the production of aryloxy-radical intermediates from suitable phenolic substrates; the ultimate coupling of the intermediates so produced provides a combination of dimeric, oligomeric, and polymeric reaction products.

The laccase may be derived from a microorganism, e.g. a fungus or a bacteria, or a plant. Preferably, the laccase employed is derived from a fungus. More preferably, it is derived from a strain of *Polyporus* sp., in particular a strain of *P. pinsitus* or *P. versicolor*, a strain of *Myceliophthora* sp., *e.g. M. thermophila*, a strain of *Rhizoctonia* sp., in particular a strain of *Rh. praticola* or *Rh. solani*, a strain of *Pyricularia* sp, in particular *P. oryzae*, or a strain of *Scytalidium*, such as *S. thermophilium.* The laccase may also be from a plant such as *Rhus* sp., e.g. *Rhus vernicifera*,

In specific embodiments of the invention the oxidoreductase is a laccase such as a *Polyporus* sp. laccase, especially the *Polyporus pinisitus* laccase (also called *Trametes villosa* laccase) described in WO 96/00290 (from Novo Nordisk Biotec Inc.) or a *Myceliophthora sp.* laccase, especially the *Myceliophthora thermophila* laccase described in WO 95/33836 (from Novo Nordisk Biotech Inc.).

Further, the laccase may be a *Scytalidium sp.* laccase such as the *S. thermophilium* laccase described in WO 95/33837 and WO 97/19998 (from Novo Nordisk Biotech Inc.), the contents of which is incorporated herein by reference, or a *Pyricularia* sp. laccase, such as the *Pyricularia oryzae* laccase which can be purchased from SIGMA under the trade name SIGMA No. L5510, or a *Coprinus* sp. laccase, such as a *C. cinereus laccase*, especially a *C. cinereus* IFO 30116 laccase, or a *Rhizoctonia* sp. laccase, such as a *Rh. solani* laccase, especially the neutral *Rh. solani* laccase described in WO 95/07988 (from Novo Nordisk A/S) having a pH optimum in the range of from 6.0 to 8.5.

The laccase may also be derived from a fungus such as *Collybia*, *Fomes*, *Lentinus*, *Pleurotus*, *Aspergillus*, *Neurospora*, *Podospora*, *Phlebia*, *e.g. P. radiata* (WO 92/01046), *Coriolus* sp., *e.g. C. hirsitus* (JP 2-238885), or *Botrytis*.

Bilirubin oxidase may preferably be derived from a strain of *Myrothecium* sp., such as *M. verrucaria*.

Oxidases yielding peroxide ($H_2O_2$) are typically used in combination with a peroxidase to remove or at least reduce the peroxide produced.

Suitable oxidases include glucose oxidase (E.C. 1.1.3.4), hexose oxidase (E.C. 1.1.3.5), L-amino-acid oxidase (E.C. 1.4.3.2), xylitol oxidase, galactose oxidase (E.C. 1.1.3.9), pyranose oxidase (E.C. 1.1.3.10) and alcohol oxidase (E.C. 1.1.3.13).

If an L-amino acid oxidase is used, it may be derived from a *Trichoderma* sp. such as *Trichoderma harzianum*, such as the L-amino acid oxidase described in WO 94/25574 (from Novo Nordisk A/S), or *Trichoderma viride.*

A suitable glucose oxidase may originate from *Aspergillus* sp., such as a strain of *Aspergillus niger*, or from a strain of *Cladosporium* sp. in particular *Cladosporium oxysporum.*

Hexose oxidases from the red sea-weed *Chondrus crispus* (commonly known as Irish moss)(Sullivan and Ikawa, (1973), Biochim. Biophys. Acts, 309, p. 11-22; Ikawa, (1982), Meth. in Enzymol. 89, Carbohydrate Metabolism Part D, 145-149) oxidise a broad spectrum of carbohydrates, such as D-glucose, D-galactose, maltose, cellobiose, lactose, D-glucose 6-phosphate, D-mannose, 2-deoxy-D-glucose, 2-deoxy-D-galactose, D-fructose, D-glucuronic acid, and D-xylose.

There is no particular limitation for the compounding amount of the above-mentioned oxidase in the composition of the present invention but the amount may be appropriately selected depending upon the form of the product, frequency of use, treating time, titer of the enzyme, etc. and, for example, it is preferred to compound in an amount of 0.0005-20% or, more preferably, 0.001-15% to the total composition. When the amount is too small, there is a tendency that the effect by compounding the oxidase is not sufficiently achieved while, when it is too much, there is a tendency that an increase in the effect proportional to an increase in the compounding amount is not available.

With regard to the cyclodextrin compound of the present invention, cyclodextrin and its derivatives may be used. Cyclodextrin is a non-reducing malto-oligosaccharide having a structure wherein 6-8 glucose molecules were connected in a ring form by means of α-1,4-glucoside bond. There are α-, β- and γ-compounds depending upon the numbers of the connected glucose molecules and any of them may be used. With regard to a cyclodextrin derivative, an adduct of the above cyclodextrin with propylene oxide is particularly effective and, although there is no particular limitation for the adding molar numbers thereto, 3-8 moles per molecule are preferred. Depending upon the compound included therein, each of such cyclodextrin compounds may be used solely or two or more thereof may be used jointly.

Although there is no particular limitation for the compounding amount of the cyclodextrin compound in the composition, it is preferred to compound 0.1-75% or, particularly preferably, 0.5-60% to the total composition. When the compounding amount is too small, the effect by compounding of the cyclodextrin compound may not be well achieved while, when it is too much, there is a tendency that an increase in the effect proportional to an increase in the compounding amount is not resulted.

The hair composition of the present invention may be further compounded with a solvent. There is no particular limitation for the type of the solvent but a solvent which has been used for various hair compositions of a single preparation type such as a hairdye of a single preparation type, a permanent-waving preparation of a single preparation type and a depilatory of a single preparation type may be used. Thus, its examples are pure water; alcohol such as ethanol, propanol, n-butanol, sec-butanol and isopropanol; aromatic alcohol such as benzyl alcohol, phenoxyethanol and 2-benzyloxyethanol; polyhydric alcohol such as ethylene glycol, propylene glycol, butylene glycol and glycerol; aqueous ether such as methyl cellosolve, ethyl cellosolve, butyl cellosolve, methyl carbitol and ethyl carbitol; cyclic ketone such as propylene carbonate, N-methylpyrrolidone, N-ethylpyrrolidone and Nhexylpyrrolidone; formamide derivative such as N-cyclohexyl formamide and N,N-dibutyl formamide; and acid such as glycolic acid and levulinic acid. Each of them may be used solely or two or more thereof may be used jointly.

There is no particular limitation for the compounding amount of the said solvent but the amount may be appropriately selected depending upon the type of the composition. Usually, it is appropriate to compound about 1-50% to the total composition.

Unless the effect of the present invention is not disturbed, the hair composition of the present invention may be further compounded, if necessary, with other components which have been conventionally used including pH adjusting agents such as acid and alkali; various kinds of surface-active agents; ionic or nonionic and natural, synthetic or semi-synthetic high-molecular compounds; oil such as ester oil and vegetable oil; silicone derivatives; fluorine derivatives; amino acids; various salts; dandruff removers; chelating agents; antiseptics; ultraviolet absorbers; antibacterials; antioxidants; perfumes; acidic dyes; and natural dyes. They may be compounded in their usual amount so far as the effect of the present invention is not deteriorated.

In the hair composition of the present invention, the above-mentioned components are mixed and then dissolved, dispersed, emulsified, etc. by a conventional means to prepare a hair composition of a single preparation type such as a hairdye of a single preparation type, a depilatory of a single preparation type and a permanent-waving preparation of a single preparation type. In the case of the present invention, it is particularly advantageous to prepare a hair composition of a solvent type (in a liquid form) and, as mentioned already, it can be made into any of the preparations including paste (cream), aerosol, gel, liquid, foams, etc. When the product is applied to the common usage of each of the preparations, it is possible to dye the hair, to depilate or to give permanent wave to hair easily and surely.

## Examples

The present invention will now be specifically illustrated by way of the following Examples and Comparative Examples although the present invention is not limited thereto.

[Examples 1-5 and Comparative Examples 1-3]

The components as shown in Table 1 were used, mixed by a conventional method so as to make the components homogeneous, the resulting original hairdye liquid was charged into a glass pressure bottle, clinched *in vacuo* and 2.0 kg of LPG (a propellant) were charged so as to make the ratio of the original liquid to gas 95:5 (by weight) whereupon hairdyes (hair compositions) of an aerosol type of Examples 1-5 and Comparative Examples 1-3 were prepared. Each of the hairdye compositions was evaluated for stability upon preservation and hair-dyeing property by the following methods. The result is shown in Table 1 as well.

<Test for Stability upon Preservation>

After preserved at room temperature for six months, observation was carried out by visual observation whether the aggregates and precipitates were present in the composition and evaluation was conducted according to the following criteria.

Criteria for Evaluation

OO: aggregates, precipitates, etc. were not noted at all

O : aggregates, precipitates, etc. were noted when observed carefully

Δ : aggregates, precipitates, etc. were well noted

× : aggregates, precipitates, etc. were formed to such an extent that the product is unable to be used

<Test on Dyeing Property>

About 10 g of a dried tuft of white hair of goat were shampooed and dried. Each 3 g of the compositions as shown in Table 1 were applied thereto quickly and uniformly. After allowing to stand for about 20 minutes, the dyed tuft was rinsed with warm water, shampooed and dried. After drying, a dyeing index (ΔE) was measured as an index for the dyeing property to the dyed tuft using a color difference meter (SE 2000 manufactured by Nippon Denshoku). Here, the hair-dyeing index (ΔE) was measured in such a manner that the values of L, a and b of the dyed tuft were measured by a color difference meter (SE2000 manufactured by Nippon Denshoku) and the color difference (ΔE) from the hair which was not dyed was calculated. This operation was carried out for the composition of Table 1 immediately after compounding and after allowing to stand at room temperature for six months whereby the hair-dyeing property upon preservation was grasped. Incidentally, the more the ΔE, the better the hair dyeing property.

Table 1

| | Examples | | | | | Comparative Examples | | |
|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 1 | 2 | 3 |
| (Components) | | | | | | | | |
| Toluene-2,5-diamine sulfate | 2.0 | - | 1.5 | 2.0 | 2.0 | 2.0 | 2.0 | 2.0 |
| p-Phenylenediamine | - | 1.5 | 0.5 | 1.5 | - | - | - | - |
| Resorcinol | 0.5 | 0.75 | 0.25 | - | 1.5 | 0.5 | 0.5 | 0.5 |
| Nitro-p-phenylenediamine | 1.0 | - | 0.1 | - | - | 1.0 | 1.0 | 1.0 |
| 2,6-Diaminopyridine | - | 2.0 | 0.3 | 1.0 | 0.75 | - | - | - |
| Lauric acid | 0.3 | 0.3 | 0.3 | 0.3 | 0.3 | 0.3 | 0.3 | 0.3 |
| Coconut oil fatty acid diethanolamide | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 |
| Sorbitan laurate | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| Ethanol | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 |
| Hydroxyethyl cellulose | 2.5 | 2.5 | 2.5 | 2.5 | 2.5 | 2.5 | 2.5 | 2.5 |
| Lactic acid | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 |
| β-Cyclodextrin | 1.0 | 1.0 | 1.2 | 1.0 | 1.5 | - | 1.0 | - |
| Laccase | 0.01 | 0.01 | - | 0.005 | - | - | - | 0.01 |
| Catechol oxidase | - | - | 0.01 | 0.005 | 0.02 | - | - | - |
| Monoethanolamine | ( adjusted so as to make pH 8.0 ) | | | | | | | |
| Pure water | b | b | b | b | b | b | b | b |
| Total (% by weight) | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |
| (Stability) | | | | | | | | |
| Immediately after compounding | OO | OO | OO | OO | OO | OO | OO | OO |
| After preserved* | OO | OO | OO | OO | OO | OO | OO | × |
| (Dyeing Property [ΔE]) | | | | | | | | |
| Dyed color | bbr | dbl | dbr | blk | blk | nd | nd | bbr |
| Immediately after compounding | 31.5 | 30.9 | 32.0 | 35.0 | 33.5 | 5.4 | 6.6 | 29.9 |
| After preserved* | 30.8 | 29.8 | 30.4 | 32.3 | 30.3 | 3.2 | 4.2 | 8.4 |

*: at room temperature for six months; b: balance

bbr: bright brown; dbl: dark blue; dbr: dark brown; blk: black; nd: not dyed

According to the result shown in Table 1, the hair compositions (hairdyes of a reactive type) of the present invention showed very good stability of the product and hair-dyeing property. However, in the cases where the oxidase and the cyclodextrin compound of the present invention were not compounded (Comparative Example 1) and where the oxidase of the present invention was not compounded (Comparative Example 2), the stability of the products was good but, because of no dyeing property, it was not possible to dye the hair; and, in the case where the cyclodextrin compound was not compounded (Comparative Example 3), the dyeing property immediately after preparation was good but the stability of the product was poor and, when preserved at room temperature for six months, aggregates, precipitate, etc. were produced and the dyeing property was deteriorated as well.

[Examples 6-8 and Comparative Examples 4-8]

The components shown in Table 2 were used and mixed by a conventional method so as to make them homogeneous, the resulting original liquid for permanent-waving preparation was charged in a glass pressure bottle and clinched *in vacuo* and 2.0 kg of LPG (a propellant) were charged so as to make the ratio of the original liquid to gas 95:5 (by weight) whereupon permanent-waving preparations (hair compositions) of an aerosol type of Examples 6-8 and Comparative Example 4-8 were prepared. They were evaluated for stability upon preservation by the same method as mentioned already and also for waving property by the following method. The result is shown in Table 2 as well.

<Waving Property>

A tuft of dried normal hair (about 15 cm; 10 g) was shampooed and dried. This was quickly and uniformly applied with about 5 g of each of the compositions of Table 2 and then obliquely wound on a glass rod of 3 cm in diameter and 10 cm in length so as not to overlapping the hair flow one another.

After allowing to stand for about 30 minutes, the treated hair was rinsed with warm running water, shampooed and dried. After drying, the tuft was hung and the degree of waving was evaluated according to the following evaluating criteria. This operation was carried out immediately after the compounding of the composition of Table 2 and also after preserving for six months and the effect upon preservation was grasped.

Criteria for Evaluation

OO: waved
: waved though loose
: rarely waved
: not waved

Table 2

| | Examples | | | Comparative Examples | | | | |
|---|---|---|---|---|---|---|---|---|
| | 6 | 7 | 8 | 4 | 5 | 6 | 7 | 8 |
| (Components) | | | | | | | | |
| L-Cysteine hydrochloride | 5.0 | 2.0 | - | 5.0 | 5.0 | 5.0 | 5.0 | 5.0 |
| Acetylcysteine | 3.0 | 2.0 | 4.0 | 3.0 | 3.0 | 3.0 | 3.0 | 3.0 |
| Thioglycolic acid | - | 0.05 | 0.05 | - | - | - | - | - |
| Ethanol | 20.0 | 15.0 | 20.0 | 20.0 | 20.0 | 20.0 | 20.0 | 20.0 |
| Hydroxyethyl cellulose | 1.7 | 1.7 | 1.7 | 1.7 | 1.7 | 1.7 | 1.7 | 1.7 |
| Coconut oil fatty acid sorbitan | - | 1.0 | - | - | - | - | - | - |
| Coconut oil fatty acid diethanolamide | 1.0 | - | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 |
| Lactic acid | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 |
| β-Cyclodextrin | 1.0 | 1.0 | 1.0 | - | 1.0 | - | - | - |
| Laccase | 0.001 | - | 0.001 | - | - | 0.001 | 0.0001 | 30 |
| Catechol oxidase | - | 0.001 | 0.001 | - | - | - | - | - |
| Monoethanolamine | ( adjusted so as to make pH 9.5 ) | | | | | | | |
| Pure water | b | b | b | b | b | b | b | b |
| Total (% by weight) | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |
| (Stability) | | | | | | | | |
| Immediately after compounding | OO | OO | OO | OO | OO | OO | OO | OO |
| After preserved* | OO | OO | OO | O | OO | × | Δ | OO |
| (Waving Property) | | | | | | | | |
| Immediately after compounding | OO | OO | OO | × | × | OO | O | O |
| After preserved* | OO | OO | OO | × | × | × | × | Δ |

*: at room temperature for six months; b: balance

According to the result as shown in Table 2, the hair compositions (permanent-waving preparations) of the present invention showed very good stability of the product and waving property. However, in the cases where the oxidase and the cyclodextrin compound of the present invention were not compounded (Comparative Example 4) and where the oxidase of the present invention was noted compounded (Comparative

Example 5), the stability of the products was good but, because of no oxidizing property, it was not possible to give waves; and, in the cases where the cyclodextrin compound was not compounded (Comparative Examples 6, 7 and 8), the waving property immediately after preparation was good but the stability of the product was poor and, when preserved at room temperature for six months, aggregates, precipitate, etc. were produced and the waving property was deteriorated as well.

[Example 9] Hairdye of a Single Preparation Type (Foamy)

| Compounding Components | Compounding Amount(wt%) |
|---|---|
| (Original Liquid) | |
| p-Phenylenediamine | 1.0 |
| 2,5-Diaminotoluene sulfate | 2.0 |
| m-Phenylenediamine | 0.5 |
| p-Aminophenol | 0.5 |
| 2-(2'-Hydroxyethylamino)-5-aminotoluene sulfate | 0.15 |
| Oleic acid | 0.2 |
| Oleyl alcohol | 0.2 |
| β-Cyclodextrin | 1.0 |
| Laccase | 0.01 |
| Xanthan gum | 0.5 |
| Sorbitan monolaurate | 1.0 |
| Ethanol | 10.0 |
| Glycolic acid | 0.2 |
| Pure water | balance |
| (pH adjusted to 7.5 by monoethanolamine) | |
| Total | 100 |

The original liquid was prepared by a conventional method according to the above formulation, charged in an aerosol can and clinched *in vacuo* and 2.0 kg of LPG (a propellant) were charged so as to make the ratio of the original liquid to the gas 95:5 (by weight) whereupon a hairdye of an aerosol type was prepared. LPG was used at this time as a compressed gas but any of nitrogen, carbon dioxide gas, laughing gas and Flon 11, 12 and 114 may be used either solely or jointly. With regard to a form of the aerosol, ordinary containers such as aluminum can or tin-plated can with direct-jet nozzle or piston type nozzle may be used or a double container such as a bag-in type or an EXXEL type may be used as well.

The above hairdye was preserved at room temperature for six months, its appropriate amount was applied to 1.0 g of white hair and the hair was allowed to stand for 20 minutes, washed with water and shampooed. The hair treated as such was dried using a drier whereupon the white hair was dyed in blue black color and its shade was the same as that immediately after being prepared.

[Example 10] Hairdye of a Single Preparation Type (Foamy)

| Compounding Components | Compounding Amount(wt%) |
|---|---|
| (Original Liquid) | |
| 5,6-Dihydroxyindoline hydrobromide | 1.0 |
| 5,6-Dihydroxyindole hydrochloride | 1.0 |
| N-Ethyl-5,6-dihydroxyindole hydrochloride | 0.05 |
| Linoleic acid | 0.2 |
| Oleyl alcohol | 0.2 |
| β-Cyclodextrin | 1.0 |
| Laccase | 0.01 |
| Hydroxyethyl cellulose | 0.5 |
| Sodium coconut oil fatty acid acyl-glutamate | 1.0 |
| Ethanol | 10.0 |
| Lactic acid | 0.2 |
| Pure water | balance |
| (pH adjusted to 7.5 by monoethanolamine) | |
| Total | 100 |

The original liquid was prepared by a conventional method according to the above formulation, charged in an aerosol can and clinched *in vacuo* and 2.0 kg of LPG (a propellant) were charged so as to make the ratio of the original liquid to the gas 95:5 (by weight) whereupon a hairdye of an aerosol type was prepared. This hairdye was preserved at room temperature for six months, its appropriate amount was applied to 1.0 g of white hair and the hair was allowed to stand for 20 minutes, washed with water and shampooed. The hair treated as such was dried using a drier whereupon the white hair was dyed in black color and its shade was the same as that immediately after being prepared.

[Example 11] Hairdye of a Single Preparation Type (Creamy and Foamy)

| Compounding Components | Compounding Amount(wt%) |
|---|---|
| (Original Liquid) | |
| 2,5-Diaminotoluene sulfate | 2.0 |
| m-Phenylenediamine | 0.5 |
| m-Aminophenol | 0.5 |
| Resorcinol | 0.1 |
| o-Aminocresol | 0.05 |
| Oleic acid | 0.2 |
| β-Cyclodextrin | 1.2 |
| Laccase | 0.01 |
| Xanthan gum | 0.05 |
| Stearyltrimethylammonium chloride | 0.2 |
| Cetostearyl alcohol | 0.6 |
| POE(20) Hydrogenated castor oil triisostearate | 0.2 |
| Sorbitan monostearate | 0.1 |
| Methyl paraben | 0.3 |
| Glycolic acid | 0.2 |
| Pure water | balance |
| (pH adjusted to 7.5 by monoethanolamine) | |
| Total | 100 |

The original liquid was prepared by a conventional method according to the above formulation, charged in an aerosol can and clinched *in vacuo* and 4.0 kg of LPG (a propellant) were charged so as to make the ratio of the original liquid to the gas 95:5 (by weight) whereupon a hairdye of an aerosol type was prepared. This hairdye was preserved at room temperature for six months, its appropriate amount was applied to 1.0 g of white hair and the hair was allowed to stand for 20 minutes, washed with water and shampooed. The hair treated as such was dried using a drier whereupon the white hair was dyed in dark brown color and its shade was the same as that immediately after being prepared.

[Example 12] Hairdye of a Single Preparation Type (Creamy and Foamy)

| Compounding Components | Compounding Amount(wt%) |
|---|---|
| (Original Liquid) | |
| 5,6-Dihydroxyindoline hydrobromide | 1.0 |
| 5,6-Dihydroxyindole hydrochloride | 1.0 |
| N-Methyl-5,6-dihydroxyindoline hydrobromide | 0.05 |
| Linoleic acid | 0.2 |
| β-Cyclodextrin | 1.0 |
| Laccase | 0.01 |
| Cetostearyltrimethylammonium chloride | 0.2 |
| Cetostearyl alcohol | 0.6 |
| POE(20) Hydrogenated castor oil monoisostearate | 0.2 |
| Sorbitan monostearate | 0.1 |
| Methyl paraben | 0.3 |
| Lactic acid | 0.2 |
| Pure water | balance |
| (pH adjusted to 7.5 by monoethanolamine) | |
| Total | 100 |

The original liquid was prepared by a conventional method according to the above formulation, charged in an aerosol can and clinched *in vacuo* and 4.0 kg of LPG (a propellant) were charged so as to make the ratio of the original liquid to the gas 95:5 (by weight) whereupon a hairdye of an aerosol type was prepared. This hairdye was preserved at room temperature for six months, its appropriate amount was applied to 1.0 g of white hair and the hair was allowed to stand for 20 minutes, washed with water and shampooed. The hair treated as such was dried using a drier whereupon the white hair was dyed in black color and its shade was the same as that immediately after being prepared.

[Example 13] Hairdye of a Single Preparation Type
(Cream Type)

| Compounding Components | Compounding Amount(wt%) |
|---|---|
| 5,6-Dihydroxyindoline hydrobromide | 1.0 |
| 5,6-Dihydroxyindole hydrochloride | 1.0 |
| N-Methyl-5,6-dihydroxyindoline hydrobromide | 0.05 |
| N-Methyl-5,6-dihydroxyindole hydrochloride | 0.05 |
| 2,5-Diaminotoluene sulfate | 0.01 |
| β-Cyclodextrin | 1.0 |
| Laccase | 0.01 |
| Alkyltrimethylammonium chloride | 0.5 |
| Coconut oil fatty acid acyl-L-arginine ethyl D,L-pyrrolidonecarboxylate | 0.5 |
| Cetostearyl alcohol | 2.0 |
| Oleyl alcohol | 1.0 |
| POE(40) Hydrogenated castor oil | 0.75 |
| POE(20) Stearyl alcohol | 0.75 |
| Sorbitan sesquistearate | 1.0 |
| Methyl paraben | 0.3 |
| Propylene glycol | 5.0 |
| Glycolic acid | 0.2 |
| Pure water | balance |
| (pH adjusted to 7.5 by monoethanolamine) | |
| Total | 100 |

The above components were mixed until the whole became homogeneous to prepare a hairdye of a cream type. This hairdye was preserved at room temperature for six months, its appropriate amount was applied to 1.0 g of white hair and the hair was allowed to stand for 20 minutes, washed with water and shampooed. The hair treated as such was dried using a drier whereupon the white hair was dyed in dark brown color and its shade was the same as that immediately after being prepared.

[Example 14] Hairdye of a Single Preparation Type
(Cream Type)

| Compounding Components | Compounding Amount(wt%) |
|---|---|
| 2,5-Diaminotoluene sulfate | 2.0 |
| 2,6-Diaminopyridine | 0.05 |
| N,N-Bis(β-hydroxyl)-p-phenylenediamine | 0.1 |
| 2-Amino-5-o-phenol | 0.5 |
| 2-(2'-Hydroxyethylamino)-5-aminotoluene | 0.15 |
| Linoleic acid | 0.2 |
| β-Cyclodextrin | 1.0 |
| Laccase | 0.01 |
| Stearyltrimethylammonium chloride | 0.5 |
| Behenyltrimethylammonium chloride | 0.5 |
| Cetostearyl alcohol | 2.0 |
| Oleyl alcohol | 1.0 |
| POE(40) Glycerol triisostearate | 0.75 |
| POE(20) Lauryl ether | 0.75 |
| Sorbitan monostearate | 1.0 |
| Methyl paraben | 0.3 |
| Propylene glycol | 5.0 |
| Lactic acid | 0.2 |
| Pure water | balance |
| (pH adjusted to 7.5 by monoethanolamine) | |
| Total | 100 |

The above components were mixed until the whole became homogeneous to prepare a hairdye of a cream type. This hairdye was preserved at room temperature for six months, its appropriate amount was applied to 1.0 g of white hair and the hair was allowed to stand for 20 minutes, washed with water and shampooed. The hair treated as such was dried using a drier whereupon the white hair was dyed in bright brown color and its shade was the same as that immediately after being prepared.

[Example 15] Hairdye of a Single Preparation Type (Treatment Type)

| Compounding Components | Compounding Amount(wt%) |
|---|---|
| 2,5-Diaminotoluene sulfate | 5.0 |
| 2-Amino-4-nitrophenol | 3.0 |
| 5-Amino-o-cresol | 1.0 |
| p-Aminophenol | 1.0 |
| Oleic acid | 0.5 |
| Linoleic acid | 0.5 |
| β-Cyclodextrin | 2.0 |
| Laccase | 0.05 |
| Stearyltrimethylammonium chloride | 0.5 |
| Cetyltrimethylammonium chloride | 0.5 |
| Cetostearyl alcohol | 4.0 |
| Oleyl alcohol | 1.0 |
| Ethyl oleate | 0.5 |
| Isopropyl palmitate | 0.5 |
| Liquid paraffin | 1.0 |
| Beeswax | 0.5 |
| POE(40) Hydrogenated castor oil triisostearate | 0.25 |
| POE(20) Hydrogenated castor oil triisostearate | 0.25 |
| POE(30) Stearyl ether | 0.75 |
| Sorbitan monostearate | 1.0 |
| Glycerol monostearate | 0.5 |
| Methyl paraben | 0.3 |
| Propylene glycol | 5.0 |
| Glycolic acid | 0.2 |
| Pure water | balance |
| (pH adjusted to 7.5 by monoethanolamine) | |
| Total | 100 |

The above components were mixed until the whole became homogeneous to prepare a hairdye of a treatment type. This hairdye was preserved at room temperature for six months, its appropriate amount was applied to 1.0 g of white hair and the hair was allowed to stand for 20 minutes, washed with water and shampooed. The hair treated as such was dried using a drier whereupon the white hair was dyed in reddish brown color and its shade was the same as that immediately after being prepared. Moreover, the tuft treated with this hairdye showed a good touch and showed an excellent treatment effect as well.

[Example 16] Hairdye of a Single Preparation Type
(Treatment Type)

| Compounding Components | Compounding Amount(wt%) |
|---|---|
| 5,6-Dihydroxyindoline hydrobromide | 1.0 |
| 5,6-Dihydroxyindole hydrochloride | 1.0 |
| N-Methyl-5,6-dihydroxyindoline hydrobromide | 0.5 |
| N-Methyl-5,6-dihydroxyindole hydrochloride | 0.5 |
| 5-Aminoindole hydrochloride | 0.25 |
| 2,3-Dimethyl-5,6-dihydroxyindoline hydrobromide | 0.25 |
| Oleic acid | 0.5 |
| Linoleic acid | 0.5 |
| β-Cyclodextrin | 2.0 |
| Laccase | 0.05 |
| Stearyltrimethylammonium chloride | 0.5 |
| Cetyltrimethylammonium chloride | 0.5 |
| Cetostearyl alcohol | 4.0 |
| Oleyl alcohol | 1.0 |
| Ethyl oleate | 0.5 |
| Isopropyl palmitate | 0.5 |
| Liquid paraffin | 1.0 |
| Beeswax | 0.5 |
| POE(40) Hydrogenated castor oil triisostearate | |

| | |
|---|---|
| | 0.25 |
| POE(20) Hydrogenated castor oil triisostearate | 0.25 |
| POE(30) Stearyl ether | 0.75 |
| Sorbitan monostearate | 1.0 |
| Glycerol monostearate | 0.5 |
| Methyl paraben | 0.3 |
| Propylene glycol | 5.0 |
| Lactic acid | 0.2 |
| Pure water | balance |
| (pH adjusted to 7.5 by monoethanolamine) | |
| Total | 100 |

The above components were mixed until the whole became homogeneous to prepare a hairdye of a treatment type. This hairdye was preserved at room temperature for six months, its appropriate amount was applied to 1.0 g of white hair and the hair was allowed to stand for 20 minutes, washed with water and shampooed. The hair treated as such was dried using a drier whereupon the white hair was dyed in dark gray black brown color and its shade was the same as that immediately after being prepared. Moreover, the tuft treated with this hairdye showed a good touch and showed an excellent treatment effect as well.

[Example 17] Hairdye of a Single Preparation Type (Gel Type)

| Compounding Components | Compounding Amount(wt%) |
|---|---|
| p-Phenylenediamine | 1.0 |
| 2,5-Diaminotoluene sulfate | 2.0 |
| m-Phenylenediamine | 0.5 |
| p-Aminophenol | 0.5 |
| 2-(2'-Hydroxyethylamino)-5-aminotoluene sulfate | 0.15 |
| Oleic acid | 0.2 |
| β-Cyclodextrin | 1.0 |
| Laccase | 0.01 |
| Xanthan gum | 0.5 |
| Hydroxyethyl cellulose | 1.0 |

| | |
|---|---|
| POE(40) Lauryl ether | 1.0 |
| POE(30) Hydrogenated castor oil | 1.0 |
| Ethanol | 10.0 |
| Glycolic acid | 0.2 |
| Pure water | balance |
| (pH adjusted to 7.5 by monoethanolamine) | |
| Total | 100 |

The above components were mixed by a conventional method to prepare a hairdye of a gel type. This hairdye was preserved at room temperature for six months, its appropriate amount was applied to 1.0 g of white hair and the hair was allowed to stand for 20 minutes, washed with water and shampooed. The hair treated as such was dried using a drier whereupon the white hair was dyed in blue black color and its shade was the same as that immediately after being prepared.

[Example 18] Hairdye of a Single Preparation Type (Gel Type)

| Compounding Components | Compounding Amount(wt%) |
|---|---|
| 5,6-Dihydroxyindoline hydrobromide | 1.0 |
| 5,6-Dihydroxyindole hydrochloride | 1.0 |
| N-Ethyl-5,6-dihydroxyindole hydrochloride | 0.05 |
| Oleic acid | 0.2 |
| β-Cyclodextrin | 1.0 |
| Laccase | 0.01 |
| Xanthan gum | 0.5 |
| Hydroxyethyl cellulose | 1.0 |
| POE(40) Lauryl ether | 1.0 |
| POE(30) Hydrogenated castor oil | 1.0 |
| Ethanol | 10.0 |
| Glycolic acid | 0.2 |
| Pure water | balance |
| (pH adjusted to 7.5 by monoethanolamine) | |
| Total | 100 |

The above components were mixed by a conventional method to prepare a hairdye of a gel type. This hairdye was preserved at room temperature for six months, its appropriate amount was applied to 1.0 g of white hair and the hair was allowed to stand for 20 minutes, washed with water and shampooed. The hair treated as such was dried using a drier whereupon the white hair was dyed in blue black color and its shade was the same as that immediately after being prepared.

[Example 19] Permanent-Waving Preparation of a Single Preparation Type (Foamy)

| Compounding Components | Compounding Amount(wt%) |
|---|---|
| (Original Liquid) | |
| L-Cysteine hydrochloride | 5.0 |
| Acetylcysteine | 2.0 |
| β-Cyclodextrin | 0.1 |
| Laccase | 0.001 |
| Hydroxyethyl cellulose | 0.5 |
| Sodium coconut oil fatty acid acyl-glutamate | 1.0 |
| Ethanol | 10.0 |
| Lactic acid | 0.2 |
| Pure water | balance |
| (pH adjusted to 9.5 by monoethanolamine) | |
| Total | 100 |

The original liquid was prepared by a conventional method according to the above formulation to prepare an original liquid for a permanent-waving preparation. The original liquid was charged in an aerosol can and clinched *in vacuo* and 2.0 kg of LPG (a propellant) were charged so as to make the ratio of the original liquid to the gas 95:5 (by weight) whereupon a permanent-waving preparation of an aerosol type of a single preparation type was prepared. This permanent-waving preparation of a single preparation type was preserved at room temperature for six months, its appropriate amount was applied to 1.0 g of normal hair and the hair was wound on a curler, allowed to stand for 30 minutes, washed with water and shampooed. The hair treated as such was in a waved state and the waves became further fixed as the time went by. Such an action was the same as that immediately after being prepared. Incidentally, when thioglycolic acid was used as a reducing agent in the above formulation, a reducing force became strong whereupon a depilatory was prepared.

[Example 20] Depilatory of a Single Preparation Type (Foamy)

| Compounding Components | Compounding Amount(wt%) |
|---|---|
| (Original Liquid) | |
| Thioglycolic acid | 5.0 |
| L-Cysteine hydrochloride | 3.0 |
| β-Cyclodextrin | 0.2 |
| Laccase | 0.002 |
| Hydroxyethyl cellulose | 0.5 |
| Sodium coconut oil fatty acid acyl-glutamate | 1.0 |
| Ethanol | 5.0 |
| Lactic acid | 0.2 |
| Pure water | balance |
| (pH adjusted to 9.5 by monoethanolamine) | |
| Total | 100 |

The original liquid was prepared by a conventional method according to the above formulation to prepare an original liquid for a depilatory. The original liquid was charged in an aerosol can and clinched *in vacuo* and 2.0 kg of LPG (a propellant) were charged so as to make the ratio of the original liquid to the gas 95:5 (by weight) whereupon a depilatory of an aerosol type of a single preparation type was prepared. This depilatory of a single preparation type was subjected to evaluation for a depilatory force by ten female panelists using a product immediately after manufacture and that preserved at room temperature for six months whereupon all panelists evaluated that this depilatory showed an excellent depilatory force for repeated use for two to three times and that such an action was unchanged before and after the preservation. Thus, it was ascertained that the said depilatory was excellent.

[Examples 21-25 and Comparative Examples 9-11]

The components as shown in Table 3 were used, mixed by a conventional method so as to make the components homogeneous, the resulting original hairdye liquid was charged into a glass pressure bottle, clinched *in vacuo* and 2.0 kg of LPG (a propellant) were charged so as to make the ratio of the original liquid to gas 95:5 (by weight) whereupon hairdyes (hair compositions) of an aerosol type of Examples 21-25 and Comparative Examples 9-11 were prepared. Each of the hairdye compositions was evaluated for stability upon preservation and hair-dyeing property by the same methods as mentioned already. The result is shown in Table 3 as well.

Table 3

| | Examples | | | | | Comparative Examples | | |
|---|---|---|---|---|---|---|---|---|
| | 21 | 22 | 23 | 24 | 25 | 9 | 10 | 11 |
| (Components) | | | | | | | | |
| Toluene-2,5-diamine sulfate | - | 2.0 | 2.0 | 2.0 | 1.5 | 2.0 | 2.0 | 2.0 |
| p-Phenylenediamine | 1.5 | - | 0.15 | 1.0 | - | 1.0 | 1.0 | 1.0 |
| Resorcinol | - | - | - | 0.1 | - | 0.1 | 0.1 | 0.1 |
| m-Aminophenol | - | 0.08 | - | - | - | - | - | - |
| p-Aminophenol | 0.1 | 0.1 | 0.1 | - | - | - | - | - |
| m-Phenylenediamine hydrochloride | 0.15 | - | - | 0.05 | 0.75 | 0.05 | 0.05 | 0.05 |
| Coconut oil fatty acid diethanolamide | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 |
| Sorbitan palmitate | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| Ethanol | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 |
| Hydroxyethyl cellulose | 2.5 | 2.5 | 2.5 | 2.5 | 2.5 | 2.5 | 2.5 | 2.5 |
| Glycolic acid | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 |
| Hydroxypropylβ-cyclodextrin | 1.0 | 1.0 | 1.2 | 1.0 | 1.5 | - | 1.0 | - |
| Laccase | 0.01 | 0.01 | 0.02 | 0.02 | 0.01 | - | - | 0.02 |
| Monoethanolamine | ( | adjusted | so | as | to | make | pH | 8.0 ) |
| Pure water | b | b | b | b | b | b | b | b |
| Total (% by weight) | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |
| (Stability) | | | | | | | | |
| Immediately after compounding | OO | OO | OO | OO | OO | OO | OO | OO |
| After preserved* | OO | OO | OO | OO | OO | OO | OO | × |
| (Dyeing Property [$\Delta E$]) | | | | | | | | |
| Dyed color | gbl | dbr | blk | blk | dbl | nd | nd | lbr |
| Immediately after compounding | 30.6 | 30.4 | 33.4 | 35.1 | 30.6 | 3.3 | 4.0 | 33.9 |
| After preserved* | 29.8 | 29.1 | 31.7 | 33.2 | 29.3 | 1.5 | 2.3 | 11.2 |

*: at room temperature for six months; b: balance

gbl: grayish black; dbr: dark brown; blk: black; dbl: dark blue; nd: not dyed; lbr: light brown

According to the result shown in Table 3, the hairdye which is the hair composition of the present invention shows very good stability of the product and hair-dyeing property. However, in the cases where hydroxypropyl-β-cyclodextrin and laccase were not used together (Comparative Examples 9-11), they were inferior in stability of the products and in dyeing property.

[Example 26] Hairdye in Gel Type

| Compounding Components | Compounding Amount(wt%) |
|---|---|
| p-Phenylenediamine | 1 |
| p-Aminophenol | 0.1 |
| m-Aminophenol | 0.2 |
| Hydroxypropyl-β-cyclodextrin | 1.0 |
| Laccase | 0.01 |
| Xanthan gum | 0.5 |
| Glycolic acid | 0.2 |
| Pure water | balance |
| Total | 100.0% |

(pH adjusted to 7.5 by monoethanolamine)

The above components were mixed by a conventional method to prepare a hairdye of a gel type. This hairdye was preserved at room temperature for six months, its appropriate amount was applied to 1.0 g of white hair and the hair was allowed to stand for 20 minutes, washed with water and shampooed. The hair treated as such was dried using a drier whereupon the white hair was dyed in blue black color and its shade was the same as that immediately after being prepared.

[Example 27] Hairdye of a Cream Type

| Compounding Components | Compounding Amount(wt%) |
|---|---|
| p-Phenylenediamine | 0.5 |
| Toluene-2,5-diamine sulfate | 1 |
| Hydroxypropyl-β-cyclodextrin | 1.5 |
| Laccase | 0.05 |
| Decaglyceryl monostearate | 3 |

| | |
|---|---|
| Cetostearyl alcohol | 0.5 |
| Stearic acid | 0.8 |
| Xanthan gum | 1 |
| Carboxymethyl cellulose | 1 |
| Sodium hydroxide | q.s. |
| Pure water | balance |
| Total | 100.0% |

(pH adjusted to 7.5 by sodium hydroxide)

The above components were mixed by a conventional method until the whole became homogeneous to prepare a hairdye of a cream type. This hairdye was preserved at room temperature for six months, its appropriate amount was applied to 1.0 g of white hair and the hair was allowed to stand for 20 minutes, washed with water and shampooed. The hair treated as such was dried using a drier whereupon the white hair was dyed in dark brown color and its shade was the same as that immediately after being prepared.

[Example 28] Hairdye of a Treatment Type

| Compounding Components | Compounding Amount(wt%) |
|---|---|
| p-Phenylenediamine | 2 |
| Toluene-2,5-diamine sulfate | 1 |
| m-Phenylenediamine hydrochloride | 0.1 |
| m-Aminophenol | 0.8 |
| Hydroxypropyl-β-cyclodextrin | 2.5 |
| Laccase | 0.3 |
| POE(10) Cetyl ether | 8 |
| Stearyl alcohol | 2.5 |
| Oleyl alcohol | 5 |
| Behenyl alcohol | 2 |
| Cetyl alcohol | 2 |
| Stearyltrimethylammonium chloride | 1 |
| Glycerol | 2 |
| Triethanolamine | q.s. |
| Pure water | balance |
| Total | 100.0% |

(pH adjusted to 7.5 by triethanolamine)

The above components were mixed by a conventional method until the whole became homogeneous to prepare a hairdye of a treatment type. This hairdye was preserved at room temperature for six months, its appropriate amount was applied to 1.0 g of white hair and the hair was allowed to stand for 20 minutes, washed with water and shampooed. The hair treated as such was dried using a drier whereupon the white hair was dyed in black color and its shade was the same as that immediately after being prepared. Further, the tuft which was treated with this hairdye showed a good touch and a treatment effect was excellent as well.

[Example 29] Hairdye of Aerosol Type

| Compounding Components | Compounding Amount(wt%) |
|---|---|
| p-Phenylenediamine | 2 |
| Toluene-2,5-diamine sulfate | 1 |
| m-Phenylenediamine hydrochloride | 0.1 |
| m-Aminophenol | 0.8 |
| Hydroxypropyl-β-cyclodextrin | 1.2 |
| Laccase | 0.001 |
| Amisoft (manufactured by Ajinomoto) | 1 |
| Glycerol | 2 |
| Triethanolamine | q.s. |
| Pure water | balance |
| Total | 100.0% |

(pH adjusted to 7.5 by triethanolamine)

The original liquid was prepared by a conventional method according to the above formulation, charged in an aerosol can and clinched *in vacuo* and 2.0 kg of LPG (a propellant) were charged so as to make the ratio of the original liquid to the gas 95:5 (by weight) whereupon a hairdye of an aerosol type was prepared. LPG was used at this time as a compressed gas but any of nitrogen, carbon dioxide gas, laughing gas and Flon 11, 12 and 114 may be used either solely or jointly. With regard to a form of the aerosol, ordinary containers such as aluminum can or tin-plated can with direct-jet nozzle or piston type nozzle may be used or a double container such as a bag-in type or an EXXEL type may be used as well.

The above hairdye was preserved at room temperature for six months, its appropriate amount was applied to 1.0 g of white hair and the hair was allowed to stand for 20 minutes, washed with water and shampooed. The hair treated as such was dried using a drier whereupon the white hair was dyed in dark brown color and its shade was the same as that immediately after being prepared.

In accordance with the hair composition of the present invention, it is now possible to give a hair composition which is not a mixed type where the first preparation and the second preparation are mixed but a cyclodextrin compound is compounded with a hair composition in a single preparation type where such a mixing operation is not necessary and the usability for consumers is very high whereby generation of aggregates, precipitates, etc. in the product can be prevented, stability of the product becomes very good and the function and merit by the reaction of a substance to be oxidized with oxidase are fully achieved in any of the forms of aerosol, cream, gel, liquid, etc.

# CLAIM

1. A hair composition which is characterized in that a substance to be oxidized, an oxidase which utilizes oxygen as a substrate and does not generate hydrogen peroxide, and a cyclodextrin compound are compounded in the said composition.