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(54) **Title**: COMPOSITION COMPRISING A NATURAL DYE AND/OR A CATIONIC AND/OR NONIONIC DIRECT DYE, AND/OR A DYE PRECURSOR, AN INSOLUBLE SILICATE AND A MONO- OR POLYGLYCOSIDE

(57) **Abstract**: The present invention relates to a dye composition comprising at least one water-insoluble silicate, at least one coloured or colouring species chosen from oxidation dye precursors, natural dyes, cationic direct dyes and nonionic direct dyes, and at least one mono- or polyglycoside. The invention also relates to a dyeing process using this composition.

COMPOSITION COMPRISING A NATURAL DYE AND/OR A CATIONIC AND/OR NONIONIC DIRECT DYE, AND/OR A DYE PRECURSOR, AN INSOLUBLE SILICATE AND A MONO- OR POLYGLYCOSIDE

The present invention relates to a composition for dyeing human keratin fibres, especially the hair. The invention also relates to a dyeing process using this composition, and to a multi-compartment device containing it.

Two major methods for dyeing human keratin fibres, and in particular the hair, are known.

One of these methods is oxidation dyeing or permanent dyeing. This dyeing method uses one or more oxidation dyes and usually one or more oxidation bases optionally combined with one or more couplers.

In general, oxidation bases are chosen from ortho- or para-phenylenediamines, ortho- or para-aminophenols and heterocyclic compounds. These oxidation bases are colourless or weakly coloured compounds which, when combined with oxidizing products, can give access to coloured species.

The shades obtained with these oxidation bases are often varied by combining them with one or more couplers, these couplers being chosen especially from aromatic meta-diamines, meta-aminophenols, meta-diphenols and certain heterocyclic compounds, such as indole compounds.

The variety of molecules used as oxidation bases and couplers allows a wide range of colours to be obtained. This type of dyeing also makes it possible to obtain permanent colorations, but the use of oxidizing agents may lead to degradation of the keratin fibres.

Oxidation dyeing must moreover satisfy a certain number of requirements. Thus, it must be free of toxicological drawbacks, it must enable shades to be obtained in the desired intensity and it must show the resistance to external attacking factors such as light, bad weather, washing, permanent waving, or aspiration and rubbing.

The dye compositions must also be able to cover grey hair and, finally, they must be as unselective as possible, i.e. they must produce the smallest possible colour differences along the same keratin fibre, which generally comprises areas that are differently sensitized (i.e. damaged) from its end to its root.

The second dyeing method, known as direct dyeing or semi-permanent dyeing, comprises the application of direct dyes, which are molecules with affinity for the fibres and which colour even in the absence of an oxidizing agent added to the compositions containing them. Given the nature of the molecules used, they tend rather to remain on the surface of the fibre and penetrate relatively little into the fibre, when compared with the small molecules of oxidation dye precursors.

The direct dyes generally used are chosen from nitrobenzene, anthraquinone, nitropyridine, azo, methine, azomethine, xanthene, acridine, azine and triarylmethane

direct dyes. The chemical species used may be nonionic, anionic (acidic dyes) or cationic (basic dyes). Direct dyes may also be natural dyes.

Compositions containing one or more direct dyes are applied to keratin fibres for a time necessary to obtain the desired coloration, and are then rinsed out.

However, the colorations resulting therefrom are particularly chromatic colorations but are, however, only temporary or semi-permanent since their desorption from the surface and/or the core of the fibre are responsible for their lack of dyeing power and their poor fastness with respect to washing.

It is common practice to use dye compositions containing thickeners, in order to keep the dye composition on the hair during the time of reaction/penetration of the dyes into the keratin fibre and to limit the risks of running onto the face. However, the choice of these thickeners remains problematic insofar as they must not reduce the dyeing properties of the composition. In particular, the addition of thickeners must not reduce the intensity or chromaticity of the colorations obtained on the hair. Moreover, the addition of these thickeners especially in the presence of certain organic solvents occasionally leads to a reduction of the stability of the dye compositions.

One of the aims of the present invention is to obtain a composition for dyeing the hair, which is stable over time and which remains on the hair during application, without running, while at the same time conserving the dyeing properties obtained on the hair, in particular conserving powerful, chromatic and uniform colorations between the end and the root of the same fibre and from one fibre to another.

This aim is achieved by the present invention, one subject of which is a dye composition comprising at least one water-insoluble silicate of the smectite type, at least one coloured or colouring species chosen from oxidation dye precursors, natural dyes, cationic direct dyes and nonionic direct dyes, and at least one mono- or polyglycoside.

The invention also relates to a process for dyeing human keratin fibres that consists in applying to the fibres the composition of the invention, optionally in the presence of an oxidizing agent.

Thus, the invention makes it possible to obtain thickened compositions that are stable over time without degradation of the dyeing properties and that stay in place after being applied to the hair. Moreover, the composition of the invention substantially limits the problems of staining with dyes of the scalp and the tools used for the dyeing of the hair.

In the context of the invention, the term "insoluble silicate" means a silicate which has a solubility in water of less than 0.5% preferably less than 0.1% weight at 25°C.

In the description, the term "at least one" is equivalent to "one or more".

The insoluble silicates that are useful in the composition of the invention are silica derivatives. The silicates may be natural or chemically modified (or synthetic).

Silicates correspond to optionally hydrated silica in which some of the silicon atoms are replaced with metal cations such as Al^{3+}, B^{3+}, Fe^{3+}, Ga^{3+}, Be^{2+}, Zn^{2+}, Mg^{2+}, Co^{3+}, Ni^{3+}, Na^{+}, Li^{+}, Ca^{2+}, Cu^{2+}.

More particularly, the silicates of the smectite family that may be used may be chosen from montmorillonites, hectorites, bentonites, beidellites and saponites.

These clays may be of natural or synthetic origin. Clays that are cosmetically compatible and acceptable with keratin materials are preferably used.

The silicate may be chosen from montmorillonite, bentonite, hectorite, attapulgite and sepiolite, and mixtures thereof.

Mention may thus be made of the compounds sold by the company Laporte under the name Laponite XLG and Laponite XLS.

According to one particular embodiment, the silicate(s) are chosen from laponite, montmorillonite, hectorites or bentonite, preferably laponite and montmorillonite, or bentonite.

The silicates may be modified with a compound chosen from quaternary amines, tertiary amines, amine acetates, imidazolines, amine soaps, fatty sulfates, alkylarylsulfonates and amine oxides, and mixtures thereof.

As silicates that may be suitable for use, mention may be made of quaternium-18 bentonites such as those sold under the names Bentone 3, Bentone 38 and Bentone 38V by the company Rheox, Tixogel VP by the company United Catalyst, Claytone 34, Claytone 40 and Claytone XL by the company Southern Clay; stearalkonium bentonites such as those sold under the names Bentone 27 by the company Rheox, Tixogel LG by the company United Catalyst and Claytone AF and Claytone APA by the company Southern Clay; quaternium-18/benzalkonium bentonites such as those sold under the names Claytone HT and Claytone PS by the company Southern Clay; quaternium-18 hectorites such as those sold under the names Bentone Gel DOA, Bentone Gel ECO5, Bentone Gel EUG, Bentone Gel IPP, Bentone Gel ISD, Bentone Gel SS71, Bentone Gel VS8 and Bentone Gel VS38 by the company Rheox, and Simagel M and Simagel SI 345 by the company Biophil. According to one particular embodiment, the silicates are unmodified.

The amount of insoluble silicates may vary widely, for example between 0.1% and 20% relative to the weight of the composition, preferably from 0.2% to 15% by weight and better still from 0.5% to 10% relative to the weight of the composition.

The term "cationic direct dye" means a dye which has in its structure one or more permanent cationic charges (quaternized nitrogen atom).

The term "natural dye" means any dye or dye precursor that is at least naturally occurring and that is produced either by extraction (and possible purification) from a plant matrix, or via chemical synthesis. In contrast, the term "direct dyes" means synthetic dyes that are not naturally occurring.

Examples of suitable direct dyes that may be mentioned include the following direct dyes: azo dyes; methine dyes; carbonyl dyes; azine dyes; nitro(hetero)aryl dyes; tri(hetero)arylmethane dyes; alone or as mixtures.

More particularly, the azo dyes comprise an -N=N- function in which the two nitrogen atoms are not simultaneously engaged in a ring. However, it is not excluded for one of the two nitrogen atoms of the sequence -N=N- to be engaged in a ring.

The dyes of the methine family are more particularly compounds comprising at least one sequence selected from >C=C< and -N=C< in which the two atoms are not simultaneously engaged in a ring. However, it is pointed out that one of the nitrogen or carbon atoms of the sequences may be engaged in a ring. More particularly, the dyes of this family are derived from compounds of true methine type (comprising one or more above-mentioned sequences -C=C-); of azomethine type (comprising at least one, or more, sequences -C=N-) with, for example, azacarbocyanins and their isomers, diazacarbocyanins and their isomers, and tetraazacarbocyanins; of mono- and diarylmethane type; of indoamine (or diphenylamine) type; of indophenol type; or of indoaniline type.

As regards the dyes of the carbonyl family, examples that may be mentioned include dyes chosen from acridone, benzoquinone, anthraquinone, naphthoquinone, benzanthrone, anthranthrone, pyranthrone, pyrazolanthrone, pyrimidinoanthrone, flavanthrone, idanthrone, flavone, (iso)violanthrone, isoindolinone, benzimidazolone, isoquinolinone, anthrapyridone, pyrazoloquinazolone, perinone, quinacridone, quinophthalone, indigoid, thioindigo, naphthalimide, anthrapyrimidine, diketopyrrolopyrrole and coumarin.

As regards the dyes of the azine family, mention may be made especially of azine, xanthene, thioxanthene, fluorindine, acridine, (di)oxazine, (di)thiazine and pyronin dyes.

The nitro (hetero)aromatic dyes are more particularly nitrobenzene or nitropyridine direct dyes.

As regards the dyes of porphyrin or phthalocyanin type, it is possible to use cationic or non-cationic compounds, optionally comprising one or more metals or metal ions, for instance alkali metals, alkaline-earth metals, zinc and silicon.

Examples of particularly suitable direct dyes that may be mentioned include nitrobenzene dyes; azo direct dyes; methine direct dyes; azomethine direct dyes, with, more particularly, diazacarbocyanins and isomers thereof and tetraazacarbocyanins (tetraazapentamethines); quinone direct dyes, and in particular anthraquinone, naphthoquinone or benzoquinone dyes; azine direct dyes; xanthene direct dyes; triarylmethane direct dyes; indoamine direct dyes; indigoid direct dyes; phthalocyanine and porphyrin direct dyes; alone or in mixtures.

The direct dyes are preferably selected from nitrobenzene dyes; azo dyes; azomethine dyes, with the diazacarbocyanins and their isomers, the

tetraazacarbocyanins (tetraazapentamethines); anthraquinone direct dyes; triarylmethane direct dyes; alone or as mixtures.

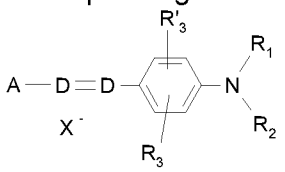
More preferably still, these direct dyes are selected from nitro dyes of the benzene series; azo direct dyes; azomethine direct dyes, with diazacarbocyanins and their isomers, tetraazacarbocyanins (tetraazapentamethines); anthraquinone dyes, alone or as a mixture.

Among the nitrobenzene direct dyes that may be used according to the invention, mention may be made in a non-limiting manner of the following compounds:

-1,4-diamino-2-nitrobenzene
-1-amino-2-nitro-4-β-hydroxyethylaminobenzene
-1-amino-2-nitro-4-bis(β-hydroxyethyl)aminobenzene
-1,4-bis(β-hydroxyethylamino)-2-nitrobenzene
-1-β-hydroxyethylamino-2-nitro-4-bis(β-hydroxyethylamino)benzene
-1-β-hydroxyethylamino-2-nitro-4-aminobenzene
-1-β-hydroxyethylamino-2-nitro-4-(ethyl)(β-hydroxyethyl)aminobenzene
-1-amino-3-methyl-4-β-hydroxyethylamino-6-nitrobenzene
-1-amino-2-nitro-4-β-hydroxyethylamino-5-chlorobenzene
-1,2-diamino-4-nitrobenzene
-1-amino-2-β-hydroxyethylamino-5-nitrobenzene
-1,2-bis(β-hydroxyethylamino)-4-nitrobenzene
-1-amino-2-tris(hydroxymethyl)methylamino-5-nitrobenzene
-1-hydroxy-2-amino-5-nitrobenzene
-1-hydroxy-2-amino-4-nitrobenzene
-1-hydroxy-3-nitro-4-aminobenzene
-1-hydroxy-2-amino-4,6-dinitrobenzene
-1- -hydroxyethyloxy-2-β-hydroxyethylamino-5-nitrobenzene
-1-methoxy-2-β-hydroxyethylamino-5-nitrobenzene
-1-β-hydroxyethyloxy-3-methylamino-4-nitrobenzene
-1-β,γ-dihydroxypropyloxy-3-methylamino-4-nitrobenzene
-1-β-hydroxyethylamino-4-β,γ-dihydroxypropyloxy-2-nitrobenzene
-1-βγ-dihydroxypropylamino-4-trifluoromethyl-2-nitrobenzene
-1-β-hydroxyethylamino-4-trifluoromethyl-2-nitrobenzene
-1-β-hydroxyethylamino-3-methyl-2-nitrobenzene
-1-β-aminoethylamino-5-methoxy-2-nitrobenzene
-1-hydroxy-2-chloro-6-ethylamino-4-nitrobenzene
-1-hydroxy-2-chloro-6-amino-4-nitrobenzene
-1-hydroxy-6-bis(β-hydroxyethyl)amino-3-nitrobenzene
-1-β-hydroxyethylamino-2-nitrobenzene
-1-hydroxy-4β-hydroxyethylamino-3-nitrobenzene.

Among the azo, azomethine, and methine direct dyes that may be used according to the invention, mention may be made of the cationic dyes described in patent applications WO 95/15144, WO 95/01772 and EP 714 954; FR 2 189 006, FR 2 285 851, FR 2 140 205, EP 1 378 544 and EP 1 674 073.

Thus, mention may be made especially of the cationic direct dyes corresponding to the following formulae:



in which:

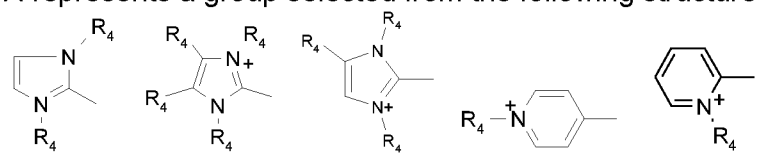
D represents a nitrogen atom or the -CH group,

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

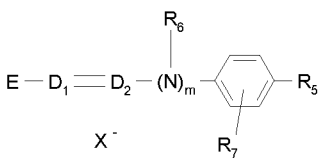
R_3 and R'_3, which may be identical or different, represent a hydrogen atom or a halogen atom chosen from chlorine, bromine, iodine and fluorine, or a cyano, C_1-C_4 alkyl, C_1-C_4 alkoxy or acetyloxy radical,

X^- represents an anion preferably selected from chloride, methyl sulfate and acetate,

A represents a group selected from the following structures:



in which R_4 represents a C_1-C_4 alkyl radical which may be substituted with a hydroxyl radical;



in which:

R_5 represents a hydrogen atom, a C_1-C_4 alkoxy radical or a halogen atom such as bromine, chlorine, iodine or fluorine,

R_6 represents a hydrogen atom or a C_1-C_4 alkyl radical or forms, with a carbon atom of the benzene ring, a heterocycle which optionally contains oxygen and/or is substituted with one or more C_1-C_4 alkyl groups,

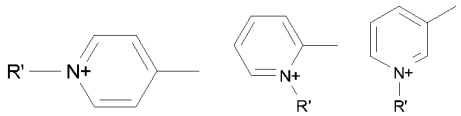
R_7 represents a hydrogen or halogen atom such as bromine, chlorine, iodine or fluorine;

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

m = 0 or 1,

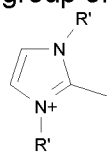
X^- represents a cosmetically acceptable anion which is preferably selected from chloride, methyl sulfate and acetate,

E represents a group selected from the following structures:



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

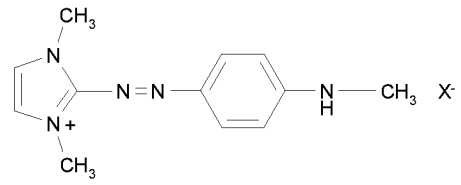
when m = 0 and when D_1 represents a nitrogen atom, E may then also denote a group of the following structure:



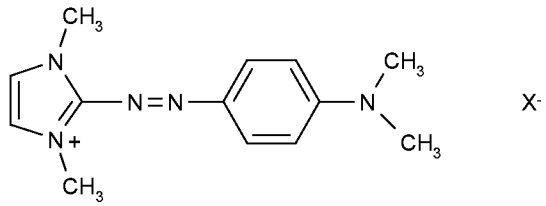
;

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

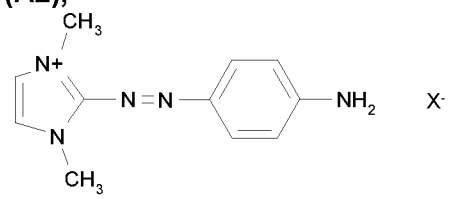
Among the above-mentioned compounds, use is made most particularly of the following compounds:



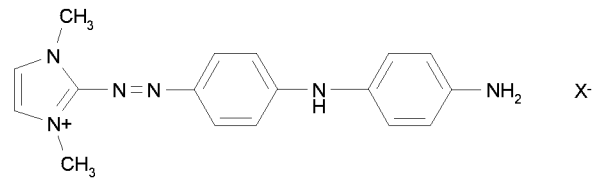
(A1)



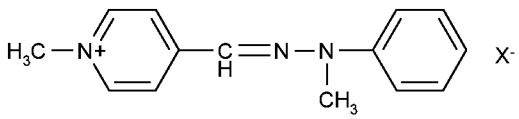
(A2),



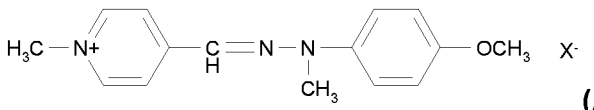
(A3)



(A4)°



(A5)



(A6)

As other dyes that may be used according to the invention, mention may be made, among the azo direct dyes, of the following dyes, which are described in the Colour Index International, 3rd edition:

-Disperse Red 17
-Disperse Red 13
-Basic Red 22
-Basic Red 76
-Basic Yellow 57
-Basic Brown 16
-Basic Brown 17
-Disperse Green 9
-Disperse Black 9
-Solvent Black 3
-Disperse Blue 148
-Disperse Violet 63
-Solvent Orange 7

Mention may also be made of 1-(4'-aminodiphenylazo)-2-methyl-4-bis(β-hydroxyethyl)aminobenzene (INCI name: HC Yellow 7).

Among the quinone direct dyes that may be mentioned are the following dyes:

-Disperse Red 15
-Solvent Violet 13
-Solvent Blue 14
-Disperse Violet 1
-Disperse Violet 4
-Disperse Blue 1
-Disperse Violet 8
-Disperse Blue 3
-Disperse Red 11
-Disperse Blue 7
-Disperse Blue 14
-Basic Blue 22
-Disperse Violet 15
-Disperse Blue 377
-Disperse Blue 60
-Basic Blue 99

and also the following compounds:

-1-N-methylmorpholiniumpropylamino-4-hydroxyanthraquinone
-1-aminopropylamino-4-methylaminoanthraquinone
-1-aminopropylaminoanthraquinone
-5-β-hydroxyethyl-1,4-diaminoanthraquinone
-2-aminoethylaminoanthraquinone

1,4-bis(β,γ-dihydroxypropylamino)anthraquinone

Mention may also be made of coumarin and Disperse Yellow 82.

Among the azine dyes that may be mentioned are the following compounds:

-Basic Blue 17

-Basic Red 2

-Solvent Orange 15

Among the triarylmethane dyes that may be used according to the invention, mention may be made of the following compounds:

-Basic Green 1

-Basic Violet 3

-Basic Violet 14

-Basic Blue 7

-Basic Blue 26

Among the indoamine dyes that can be used according to the invention, mention may be made of the following compounds:

-2-β-hydroxyethylamino-5-[bis(β-4'-hydroxyethyl)amino]anilino-1,4-benzoquinone

-2-β-hydroxyethylamino-5-(2'-methoxy-4'-amino)-anilino-1,4-benzoquinone

-3-N-(2'-chloro-4'-hydroxy)phenylacetylamino-6-methoxy-1,4-benzoquinone imine

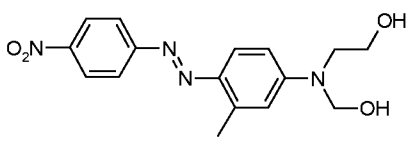
-3-N-(3'-chloro-4'-methylamino)phenylureido-6-methyl-1,4-benzoquinone imine

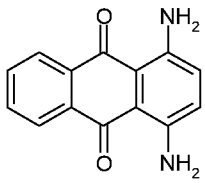
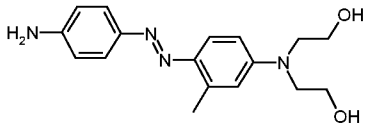
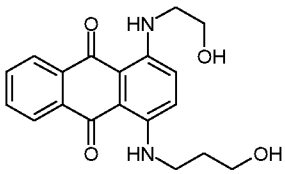
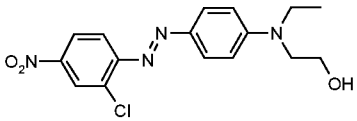
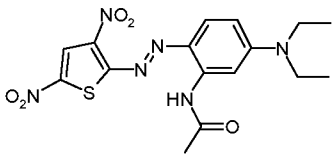
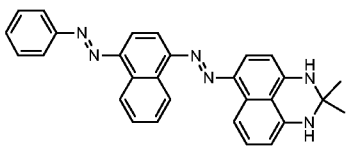
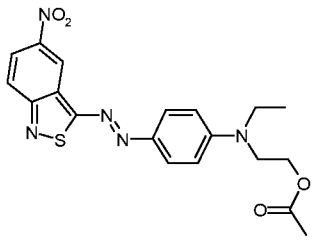
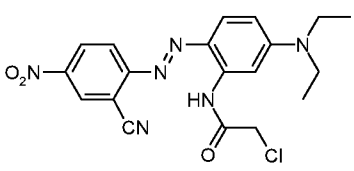
-3-[4'-N-(ethyl,carbamylmethyl)amino]phenylureido-6-methyl-1,4-benzoquinone imine

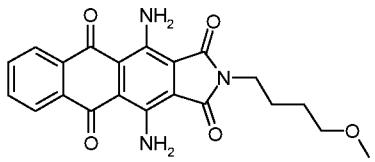
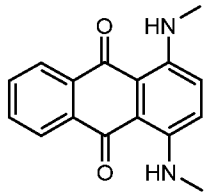
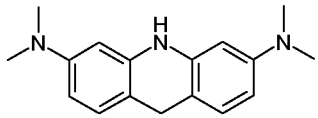
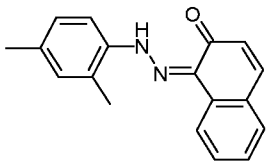
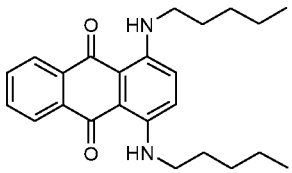
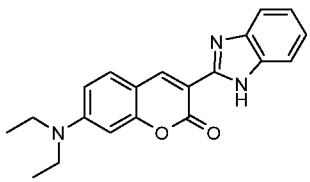
For the nonionic dyes, compounds with a logP of greater than or equal to 2 are most particularly preferred.

As regards the direct dyes with a logP of greater than or equal to 2, it is recalled that the logP value conventionally represents the partition coefficient of the dye between octanol and water. The logP may be calculated according to the method described in the article by Meylan and Howard "*Atom/fragment contribution method for estimating octanol-water partition coefficient*", J. Pharm. Sci. 84: 83-92, 1995. This value may also be calculated by means of numerous software packages available on the market, which determine the logP as a function of the structure of a molecule. An example that may be mentioned is the Epiwin software from the United States Environmental Agency.

Preferably, the direct dye(s) with a logP of greater than 2 are chosen from

Dye	Chemical structure	logP
Disperse Red 17		3.69

Disperse Violet 1		3.0
HC Yellow 7		2.38
Disperse Blue 377		3.21
Disperse Red 13		5.22
Disperse Green 9		4.23
Solvent Black 3		7.50
Disperse Blue 148		4.81
Disperse Violet 63		5.30

Disperse Blue 60		3.38
Disperse Blue 14		4.25
Solvent Orange 15		3.90
Solvent Orange 7		4.40
Solvent Blue 14		8.18
Disperse Yellow 82		3.68

Even more preferentially, the direct dyes of the invention are chosen from cationic dyes of the following types: azos; methines; azomethines with diazacarbocyanins and isomers thereof, and tetraazacarbocyanins (tetraazapentamethines); anthraquinones; alone or as a mixture, and in particular the dyes (A1) to (A6) mentioned previously, and also nonionic dyes with a logP of greater than or equal to 2.

According to one particular embodiment, the direct dye as base (s) are chosen from nonionic dyes and in particular dyes with a logP of greater than 2.

In the context of the invention, the term "natural dye" means any dye that is at least naturally occurring and that is produced either by extraction (and possible purification) from a plant matrix, or via chemical synthesis.

The natural dye(s) are chosen, for example, from lawsone, juglone, alizarin, purpurin, carminic acid, kermesic acid, laccaic acid, purpurogallin, anthragallol protocatechaldehyde, indigo, isatin, curcumin, spinulosin, chlorophylls, chlorophyllines, orceins, hematin, hematoxylin, brazilin, brazileine, santaline, santarubin, carthamine, flavonoids (with, for example, morin, apigenidin and quercetin), anthocyans (such as apigeninidin) and carotenoids, or mixtures thereof.

It is also possible to use extracts or decoctions containing these natural dyes are especially extracts obtained, for example, from henna, pernambuco wood, logwood wood, sandalwood, cudbear wood, curcuma wood, madder wood, true indigo wood,sorghum, cochineal, carrot, annatto,murex, Brazil wood and safflower.

Preferably, the natural dye(s) are chosen from lawsone, juglone, alizarin, purpurin, carminic acid, kermesic acid, laccaic acid, protocatechaldehyde, indigo, isatin, curcumin, spinulosin, apigenidin, chlorophylline, sorghum extracts, orceins, cochineal carmine, hematin, hematoxylin, brazilin, brazileine, extracts of logwood wood, cudbear wood and Brazil wood, and mixtures thereof.

The direct dyes that are useful for the invention are generally present in contents ranging from 0.001% to 20% by weight, preferably from 0.005% to 8% by weight and better still from 0.01% to 5% by weight, relative to the total weight of the composition.

The oxidation dyes that are useful in the composition of the invention are generally chosen from oxidation bases and couplers.

Examples of oxidation bases that may be mentioned include para-phenylenediamines, bis(phenyl)alkylenediamines, para-aminophenols, ortho-aminophenols and heterocyclic bases, and the addition salts thereof.

Among the para-phenylenediamines that may be mentioned, for example, are para-phenylenediamine, para-toluenediamine, 2-chloro-para-phenylenediamine, 2,3-dimethyl-para-phenylenediamine, 2,6-dimethyl-para-phenylenediamine, 2,6-diethyl-para-phenylenediamine, 2,5-dimethyl-para-phenylenediamine, N,N-dimethyl-para-phenylenediamine, N,N-diethyl-para-phenylenediamine, N,N-dipropyl-para-phenylenediamine, 4-amino-N,N-diethyl-3-methylaniline, N,N-bis(β-hydroxyethyl)-para-phenylenediamine, 4-N,N-bis(β-hydroxyethyl)amino-2-methylaniline, 4-N,N-bis(β-hydroxyethyl)amino-2-chloroaniline, 2-β-hydroxyethyl-para-phenylenediamine, 2-fluoro-para-phenylenediamine, 2-isopropyl-para-phenylenediamine, N-(β-hydroxypropyl)-para-phenylenediamine, 2-hydroxymethyl-para-phenylenediamine, N,N-dimethyl-3-methyl-para-phenylenediamine, N,N-(ethyl-β-hydroxyethyl)-para-phenylenediamine, N-(β,γ-dihydroxypropyl)-para-phenylenediamine, N-(4'-aminophenyl)-para-phenylenediamine, N-phenyl-para-phenylenediamine, 2-β-hydroxyethyloxy-para-phenylenediamine, 2-β-acetylaminoethyloxy-para-phenylenediamine, N-(β-methoxyethyl)-para-phenylenediamine, 4-aminophenylpyrrolidine, 2-thienyl-para-phenylenediamine, 2-β-hydroxyethylamino-5-

aminotoluene and 3-hydroxy-1-(4'-aminophenyl)pyrrolidine, and the addition salts thereof with an acid.

Among the para-phenylenediamines mentioned above, para-phenylenediamine, para-toluenediamine, 2-isopropyl-para-phenylenediamine, 2-β-hydroxyethyl-para-phenylenediamine, 2-β-hydroxyethyloxy-para-phenylenediamine, 2,6-dimethyl-para-phenylenediamine, 2,6-diethyl-para-phenylenediamine, 2,3-dimethyl-para-phenylenediamine, N,N-bis(β-hydroxyethyl)-para-phenylenediamine, 2-chloro-para-phenylenediamine and 2-β-acetylaminoethyloxy-para-phenylenediamine, and the addition salts thereof with an acid, are particularly preferred.

Among the bis(phenyl)alkylenediamines that may be mentioned, for example, are N,N'-bis(β-hydroxyethyl)-N,N'-bis(4'-aminophenyl)-1,3-diaminopropanol, N,N'-bis(β-hydroxyethyl)-N,N'-bis(4'-aminophenyl)ethylenediamine, N,N'-bis(4-aminophenyl)tetramethylenediamine, N,N'-bis(β-hydroxyethyl)-N,N'-bis(4-aminophenyl)tetramethylenediamine, N,N'-bis(4-methylaminophenyl)tetramethylenediamine, N,N'-bis(ethyl)-N,N'-bis(4'-amino-3'-methylphenyl)ethylenediamine and 1,8-bis(2,5-diaminophenoxy)-3,6-dioxaoctane, and the addition salts thereof.

Among the para-aminophenols that may be mentioned, for example, are para-aminophenol, 4-amino-3-methylphenol, 4-amino-3-fluorophenol, 4-amino-3-chlorophenol, 4-amino-3-hydroxymethylphenol, 4-amino-2-methylphenol, 4-amino-2-hydroxymethylphenol, 4-amino-2-methoxymethylphenol, 4-amino-2-aminomethylphenol, 4-amino-2-(β-hydroxyethylaminomethyl)phenol and 4-amino-2-fluorophenol, and the addition salts thereof with an acid.

Among the ortho-aminophenols that may be mentioned, for example, are 2-aminophenol, 2-amino-5-methylphenol, 2-amino-6-methylphenol and 5-acetamido-2-aminophenol, and the addition salts thereof.

Among the heterocyclic bases that may be mentioned, for example, are pyridine derivatives, pyrimidine derivatives and pyrazole derivatives.

Among the pyridine derivatives that may be mentioned are the compounds described, for example, in patents GB 1 026 978 and GB 1 153 196, for instance 2,5-diaminopyridine, 2-(4-methoxyphenyl)amino-3-aminopyridine and 3,4-diaminopyridine, and the addition salts thereof.

Other pyridine oxidation bases that are useful in the present invention are the 3-aminopyrazolo[1,5-a]pyridine oxidation bases or the addition salts thereof described, for example, in patent application FR 2 801 308. Examples that may be mentioned include pyrazolo[1,5-a]pyrid-3-ylamine, 2-acetylaminopyrazolo[1,5-a]pyrid-3-ylamine, 2-morpholin-4-ylpyrazolo[1,5-a]pyrid-3-ylamine, 3-aminopyrazolo[1,5-a]pyridine-2-carboxylic acid, 2-methoxypyrazolo[1,5-a]pyrid-3-ylamine, (3-aminopyrazolo[1,5-a]pyrid-7-yl)methanol, 2-(3-aminopyrazolo[1,5-a]pyrid-5-yl)ethanol, 2-(3-aminopyrazolo[1,5-a]pyrid-7-yl)ethanol, (3-aminopyrazolo[1,5-a]pyrid-2-yl)methanol, 3,6-diaminopyrazolo[1,5-a]pyridine, 3,4-diaminopyrazolo[1,5-a]pyridine, pyrazolo[1,5-

a]pyridine-3,7-diamine, 7-morpholin-4-ylpyrazolo[1,5-a]pyrid-3-ylamine, pyrazolo[1,5-a]pyridine-3,5-diamine, 5-morpholin-4-ylpyrazolo[1,5-a]pyrid-3-ylamine, 2-[(3-aminopyrazolo[1,5-a]pyrid-5-yl)(2-hydroxyethyl)amino]ethanol, 2-[(3-aminopyrazolo[1,5-a]pyrid-7-yl)(2-hydroxyethyl)amino]ethanol, 3-aminopyrazolo[1,5-a]pyridin-5-ol, 3-aminopyrazolo[1,5-a]pyridin-4-ol, 3-aminopyrazolo[1,5-a]pyridin-6-ol and 3-aminopyrazolo[1,5-a]pyridin-7-ol, and the addition salts thereof.

Among the pyrimidine derivatives that may be mentioned are the compounds described, for example, in the patents DE 2359399; JP 88-169571; JP 05-63124; EP 0770375 or patent application WO 96/15765, such as 2,4,5,6-tetraaminopyrimidine, 4-hydroxy-2,5,6-triaminopyrimidine, 2-hydroxy-4,5,6-triaminopyrimidine, 2,4-dihydroxy-5,6-diaminopyrimidine, 2,5,6-triaminopyrimidine and their addition salts and their tautomeric forms, when a tautomeric equilibrium exists.

Among the pyrazole derivatives that may be mentioned are the compounds described in the patents DE 3843892, DE 4133957 and patent applications WO 94/08969, WO 94/08970, FR-A-2 733 749 and DE 195 43 988, such as 4,5-diamino-1-methylpyrazole, 4,5-diamino-1-(β-hydroxyethyl)pyrazole, 3,4-diaminopyrazole, 4,5-diamino-1-(4'-chlorobenzyl)pyrazole, 4,5-diamino-1,3-dimethylpyrazole, 4,5-diamino-3-methyl-1-phenylpyrazole, 4,5-diamino-1-methyl-3-phenylpyrazole, 4-amino-1,3-dimethyl-5-hydrazinopyrazole, 1-benzyl-4,5-diamino-3-methylpyrazole, 4,5-diamino-3-*tert*-butyl-1-methylpyrazole, 4,5-diamino-1-*tert*-butyl-3-methylpyrazole, 4,5-diamino-1-(β-hydroxyethyl)-3-methylpyrazole, 4,5-diamino-1-ethyl-3-methylpyrazole, 4,5-diamino-1-ethyl-3-(4'-methoxyphenyl)pyrazole, 4,5-diamino-1-ethyl-3-hydroxymethylpyrazole, 4,5-diamino-3-hydroxymethyl-1-methylpyrazole, 4,5-diamino-3-hydroxymethyl-1-isopropylpyrazole, 4,5-diamino-3-methyl-1-isopropylpyrazole, 4-amino-5-(2'-aminoethyl)amino-1,3-dimethylpyrazole, 3,4,5-triaminopyrazole, 1-methyl-3,4,5-triaminopyrazole, 3,5-diamino-1-methyl-4-methylaminopyrazole, 3,5-diamino-4-(β-hydroxyethyl)amino-1-methylpyrazole, and the addition salts thereof. 4,5-Diamino-1-(β-methoxyethyl)pyrazole may also be used. A 4,5-diaminopyrazole will preferably be used, and even more preferentially 4,5-diamino-1-(β-hydroxyethyl)pyrazole and/or a salt thereof.

Pyrazole derivatives that may also be mentioned include diamino-N,N-dihydropyrazolopyrazolones and especially those described in patent application FR-A-2 886 136, such as the following compounds and the addition salts thereof: 2,3-diamino-6,7-dihydro-1H,5H-pyrazolo[1,2-a]pyrazol-1-one, 2-amino-3-ethylamino-6,7-dihydro-1H,5H-pyrazolo[1,2-a]pyrazol-1-one, 2-amino-3-isopropylamino-6,7-dihydro-1H,5H-pyrazolo[1,2-a]pyrazol-1-one, 2-amino-3-(pyrrolidin-1-yl)-6,7-dihydro-1H,5H-pyrazolo[1,2-a]pyrazol-1-one, 4,5-diamino-1,2-dimethyl-1,2-dihydropyrazol-3-one, 4,5-diamino-1,2-diethyl-1,2-dihydropyrazol-3-one, 4,5-diamino-1,2-di-(2-hydroxyethyl)-1,2-dihydropyrazol-3-one, 2-amino-3-(2-hydroxyethyl)amino-6,7-dihydro-1H,5H-pyrazolo[1,2-a]pyrazol-1-one, 2-amino-3-dimethylamino-6,7-dihydro-1H,5H-pyrazolo[1,2-a]pyrazol-1-one, 2,3-diamino-5,6,7,8-tetrahydro-1H,6H-

pyridazino[1,2-a]pyrazol-1-one, 4-amino-1,2-diethyl-5-(pyrrolidin-1-yl)-1,2-dihydropyrazol-3-one, 4-amino-5-(3-dimethylaminopyrrolidin-1-yl)-1,2-diethyl-1,2-dihydropyrazol-3-one, 2,3-diamino-6-hydroxy-6,7-dihydro-1H,5H-pyrazolo[1,2-a]pyrazol-1-one. 2,3-Diamino-6,7-dihydro-1H,5H-pyrazolo[1,2-a]pyrazol-1-one and/or a salt thereof will preferably be used.

4,5-Diamino-1-(β-hydroxyethyl)pyrazole and/or 2,3-diamino-6,7-dihydro-1H,5H-pyrazolo[1,2-a]pyrazol-1-one and/or a salt thereof will preferentially be used as heterocyclic bases.

Among these couplers, mention may be made especially of meta-phenylenediamines, meta-aminophenols, meta-diphenols, naphthalene-based couplers and heterocyclic couplers, and also the addition salts thereof.

Mention may be made, for example, of 1,3-dihydroxybenzene, 1,3-dihydroxy-2-methylbenzene, 4-chloro-1,3-dihydroxybenzene, 2,4-diamino-1-(β-hydroxyethyloxy)benzene, 2-amino-4-(β-hydroxyethylamino)-1-methoxybenzene, 1,3-diaminobenzene, 1,3-bis(2,4-diaminophenoxy)propane, 3-ureidoaniline, 3-ureido-1-dimethylaminobenzene, sesamol, 1-β-hydroxyethylamino-3,4-methylenedioxybenzene, α-naphthol, 2-methyl-1-naphthol, 6-hydroxyindole, 4-hydroxyindole, 4-hydroxy-N-methylindole, 2-amino-3-hydroxypyridine, 6-hydroxybenzomorpholine, 3,5-diamino-2,6-dimethoxypyridine, 1-N-(β-hydroxyethyl)amino-3,4-methylenedioxybenzene, 2,6-bis(β-hydroxyethylamino)toluene, 6-hydroxyindoline, 2,6-dihydroxy-4-methylpyridine, 1-H-3-methylpyrazol-5-one, 1-phenyl-3-methylpyrazol-5-one, 2,6-dimethylpyrazolo[1,5-b]-1,2,4-triazole, 2,6-dimethyl[3,2-c]-1,2,4-triazole and 6-methylpyrazolo[1,5-a]benzimidazole, the addition salts thereof with an acid, and mixtures thereof.

In general, the addition salts of the oxidation bases and couplers that may be used in the context of the invention are especially selected from the addition salts with an acid such as the hydrochlorides, hydrobromides, sulfates, citrates, succinates, tartrates, lactates, tosylates, benzenesulfonates, phosphates and acetates.

According to one embodiment, the composition comprises at least one oxidation base and optionally a coupler.

The oxidation base(s) each advantageously represent from 0.0001% to 10% by weight relative to the total weight of the composition, and preferably from 0.005% to 5% by weight relative to the total weight of the composition.

The content of coupler(s), if it is (they are) present, each advantageously represent from 0.0001% to 10% by weight relative to the total weight of the composition, and preferably from 0.005% to 5% by weight relative to the total weight of the composition.

The mono- or polyglycosides that are useful in the composition of the invention are molecules obtained from the condensation of one or more saccharides and of non-carbohydrate molecules.

The mono- or polyglycosides that may be used in the invention are well known and may be represented more particularly by the following general formula:

$$R_1O\text{-}(R_2O)_t\,(G)_v \qquad (I)$$

in which:

- R_1 represents a linear or branched alkyl and/or alkenyl group, comprising from about 8 to 24 carbon atoms, or an alkylphenyl group whose linear or branched alkyl group comprises from 8 to 24 carbon atoms,
- R_2 represents an alkylene group comprising from about 2 to 4 carbon atoms,
- G represents a sugar unit comprising from 5 to 6 carbon atoms,
- t denotes a value ranging from 0 to 10 and preferably 0 to 4, and
- v denotes an integer ranging from 1 to 15.

Mono- or polyglycosides that are preferred in the present invention are (C_{8-18})alkyl mono- or polyglycosides and are compounds of formula (I) in which:

- R_1 more particularly denotes a saturated or unsaturated, linear or branched alkyl group comprising from 8 to 18 carbon atoms,
- t denotes a value ranging from 0 to 3 and even more particularly is equal to 0,
- G may denote glucose, fructose or galactose, preferably glucose.

The degree of polymerization, i.e. the value of v in formula (I), may range from 1 to 15 and preferably from 1 to 4. The average degree of polymerization is more particularly between 1 and 2 and even more preferentially from 1.1 to 1.5.

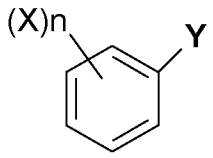
The glycoside bonds between the sugar units are of 1-6 or 1-4 type and preferably of 1-4 type.

Examples of compounds of formula (I) are especially caprylylglucoside, decylglucoside or caprylglucoside, laurylglucoside, cetearylglucoside and cocoglucoside, and mixtures thereof. These preferred compounds of formula (I) are especially represented by the products sold by the company Cognis under the names Plantaren® (600 CS/U, 1200 and 2000) or Plantacare® (818, 1200 and 2000). It is also possible to use the products sold by the company SEPPIC under the names Triton CG 110 or Oramix CG 110 and Triton CG 312 or Oramix® NS 10, the products sold by the company BASF under the name Lutensol GD 70 or those sold by the company Chem Y under the name AG10 LK.

It is also possible to use, for example, the C8/C16 alkyl 1,4-polyglucoside as an aqueous 53% solution sold by Cognis under the reference Plantacare® 818 UP.

The mono- or polyglycoside(s) may be used in an amount ranging from 0.1% to 20% by weight, preferably from 0.2% to 10% by weight and better still from 0.2% to 5% by weight, relative to the total weight of the composition.

According to one particular embodiment, the composition according to the invention comprises at least one compound of formula (II):



in which Y represents a C_1-C_4 hydroxyalkyl group or a C_1-C_4 hydroxyalkyloxy radical, n denotes an integer ranging from 0 to 5, and X, which may be identical or different, represent a C_1-C_4 alkyl radical or a halogen. Preferably, n is equal to 0. According to one particular embodiment, Y represents a hydroxymethyl, hydroxyethyl or hydroxyethyloxy radical.

Examples of compounds of formula (II) that may be mentioned include benzyl alcohol, phenylethanol and phenoxyethanol. According to one particular embodiment, the compound of formula (II) is benzyl alcohol.

According to one particular embodiment, the amount of compounds of formula (II) ranges between 0.1% and 10% and preferably from 0.1% to 5% by weight relative to the weight of the composition.

The composition of the invention may also comprise at least one C_2-C_6 hydroxylated aliphatic solvent. The term "aliphatic" refers to a compound not containing an aromatic nucleus. The solvents of this type may be monoalcohols or polyalcohols that are liquid at room temperature (25°C) and at atmospheric pressure (10^5Pa). Preferably, these solvents are non-ethereal solvents. According to one particular embodiment, these solvents are chosen from ethanol, glycerol, propylene glycol, dipropylene glycol and hexylene glycol. Preferably, the C_2-C_6 hydroxylated aliphatic solvent is ethanol or hexylene glycol, and better still ethanol.

When it is present, the amount of hydroxylated aliphatic solvent generally ranges from 0.5% to 20%, preferably from 1% to 15% and better still from 2% to 10% by weight relative to the weight of the composition.

According to one particular embodiment, the composition comprises at least one compound of formula (II) and at least one C_2-C_6 hydroxylated aliphatic solvent.

The composition according to the invention generally comprises water or a mixture of water and optionally one or more solvents other than the compounds of formula (II) and the C_2-C_6 hydroxylated aliphatic solvents, such as polyol ethers, for instance dipropylene glycol monomethyl ether.

These additional solvents are generally present in proportions that may be between 1% and 40% by weight approximately and even more preferentially between 3% and 30% by weight approximately relative to the total weight of the dye composition.

When the composition of the invention comprises natural dyes, they may be combined with metal salts such as salts of elements from columns 6 to 13 of the periodic Table of the Elements and in particular zinc, manganese, aluminium and iron salts, preferably zinc salts. These metal salts may be introduced into the composition

according to the invention or may be used as a pre- or post-treatment. The amount of metal salts ranges from 0.001% to 20%, preferably from 0.01% to 10% and better still from 0.1% to 5% by weight relative to the total weight of the composition. The preferred salts are the chlorides, glycinates and gluconates.

The dye composition in accordance with the invention may also contain various adjuvants conventionally used in hair dye compositions, such as anionic, cationic, nonionic, amphoteric or zwitterionic surfactants or mixtures thereof, anionic, cationic, nonionic, amphoteric or zwitterionic polymers other than the mono- or polyglycosides of the invention, or mixtures thereof, mineral thickeners other than the silicates described previously or organic thickeners, and in particular anionic, cationic, nonionic and amphoteric polymeric associative thickeners, antioxidants, penetrants, sequestrants, fragrances, buffers, dispersants, conditioning agents, for instance volatile or non-volatile, modified or unmodified silicones, film-forming agents, ceramides, preserving agents and opacifiers.

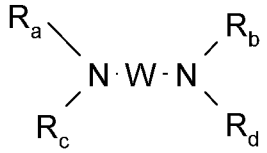
The above adjuvants are generally present in an amount, for each of them, of between 0.01% and 20% by weight relative to the weight of the composition.

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

The pH of the dye composition in accordance with the invention is generally between 2 and 14 approximately. According to one particular embodiment, the pH is between 2.5 and 10 approximately. It may be adjusted to the desired value by means of acidifying or basifying agents usually used in the dyeing of keratin fibres, or alternatively using standard buffer systems.

Among the acidifying agents that may be mentioned, for example, are mineral or organic acids, for instance hydrochloric acid, orthophosphoric acid or sulfuric acid, carboxylic acids, for instance acetic acid, tartaric acid, citric acid and lactic acid, and sulfonic acids.

Among the basifying agents, examples that may be mentioned include aqueous ammonia, alkali metal carbonates, alkanolamines, such as monoethanolamine, diethanolamine and triethanolamine and derivatives thereof, sodium hydroxide, potassium hydroxide and the compounds of the following formula:



in which W is a propylene residue optionally substituted with a hydroxyl group or a C_1-C_4 alkyl radical; R_a, R_b, R_c and R_d, which may be identical or different, represent a hydrogen atom or a C_1-C_4 alkyl or C_1-C_4 hydroxyalkyl radical.

Advantageously, the composition according to the invention has a content of basifying agent(s) ranging from 0.01% to 30% by weight and preferably from 0.1% to 20% by weight relative to the weight of the said composition.

The composition according to the invention may comprise one or more oxidizing agents. Conventionally, the oxidizing agent is added to the composition at the time of use.

More particularly, the oxidizing agent(s) are chosen from hydrogen peroxide, urea peroxide, alkali metal bromates or ferricyanides, peroxygenated salts, for instance alkali metal or alkaline-earth metal persulfates, perborates and percarbonates, and also peracids and precursors thereof.

The content of oxidizing agent(s) more particularly represents from 0.1% to 20% by weight and preferably from 0.5% to 10% by weight relative to the weight of the composition.

Preferably, the oxidizing agent is hydrogen peroxide in aqueous solution, the concentration of which ranges, more particularly, from 0.1% to 50% by weight, more particularly between 0.5% and 20% by weight and even more preferentially between 1% and 15% by weight relative to the weight of the oxidizing composition.

The dyeing process according to the invention thus consists in applying a composition comprising at least one cationic and/or nonionic direct dye, at least one water-insoluble silicate and at least one mono- or polyglycoside to wet or dry human keratin fibres.

According to one particular embodiment, the applied composition comprises one or more oxidizing agents.

The composition is then left in place for a time usually ranging from one minute to one hour and preferably from 5 minutes to 30 minutes.

The temperature during the process is conventionally between room temperature (between 15 and 25°C) and 80°C and preferably between room temperature and 60°C.

After the treatment, the human keratin fibres are optionally rinsed with water, optionally washed with a shampoo and then rinsed with water, before being dried or left to dry.

Example 1:

The following dye compositions are prepared from the ingredients in the proportions indicated as grams of active material:

	A	B
Bentonite [b]	**3.8 g**	**6 g**
Cocoglucoside [a]	**15g**	**2g**
Haematin (Ichimaru Pharcos)	**4g**	**4g**
Fragrance	**qs**	**qs**
Water	**qs 100g**	**qs 100g**
pH agent	**pH = 9**	**pH = 9**

[a] Alkyl (C8/C16) polyglucoside (1.4) as an aqueous solution, sold under the name Plantacare 818 UP by Cognis
[b]Bentone MA sold by Elementis

Locks of natural hair containing 90% white hairs are treated for 30 minutes at 40°C with the dye compositions A and B. They are then rinsed, shampooed and dried.

Mahogany-coloured locks are obtained with shade A and violet-coloured locks are obtained with shade B. The colorations are powerful, as confirmed by the colorimetric measurements taken in the L*a*b* system, with a Minolta CM2600D® spectrophotometer.

In this system, L* represents the intensity: the lower the value of L*, the more intense the colorations obtained. The chromaticity is measured by the values a* and b*, a* representing the red/green axis and b* the yellow/blue axis.
Determination of the colour uptake

The coloration obtained is evaluated by the measurement of

ΔE, which is the variation in colour before and after applying the coloration, using the formula:

$$\Delta E = \sqrt{(L^* - L_o^*)^2 + (a^* - a_o^*)^2 + (b^* - b_o^*)^2}$$

in which L* represents the intensity and a* and b* represent the chromaticity of the dyed hair, and L_0* represents the intensity and a_0* and b_0* represent the chromaticity of the hair before dyeing. The colour is proportionately more intense the larger the value of ΔE.

Composition	L*	a*	b*	Uptake (DE)
no applied coloration	62.49	0.48	15.09	-
coloration after application of composition A	31.56	10.91	4.12	34.43
coloration after application of composition B	31.62	10.31	-0.57	38.36

These colorations are very fast with respect to shampoo and to UV.
It is moreover noted that the tools used for dyeing the locks (brushes and bowls) are not stained with the dyeing mixtures prepared.

Example 2:

The following dye compositions are prepared from the ingredients in the proportions indicated as grams of active material:

	C	D
Bentonite [b]	6 g	6 g
Benzyl alcohol	5g	1g
Ethanol	15g	-
Cocoglucoside [a]	2g	2g
Haematin (Ichimaru Pharcos)	4g	4g
Fragrance	qs	qs
pH agent	pH = 7	pH = 7
Water	qs 100g	qs 100g

[a]Alkyl (C8/C16) polyglucoside (1.4) as an aqueous solution, sold under the name Plantacare 818 UP by Cognis
[b]Bentone MA sold by Elementis

Locks of natural hair containing 90% white hairs are treated for 30 minutes at 40°C with the dye compositions C and D. They are then rinsed, shampooed and dried.

Brown/mahogany-coloured colorations are obtained on the locks.
The colorations are powerful, as confirmed by the colorimetric measurements taken in the L*a*b* system with the CM2600D spectrocolorimeter.

	L*	a*	b*	Uptake (DE)
no applied coloration	64.82	0.61	16	-
coloration after application of composition C	27.82	14.11	8.3	40.13
coloration after application of composition D	28.57	14.06	9.27	39.25

These colorations are very fast with respect to shampoo and to UV.
Formulations C and D are moreover stable for 1 month at 45°C.

It is moreover noted that the tools used for dyeing the locks (brushes and bowls) are not stained with the dyeing mixtures prepared.

Example 3

The following dye compositions are prepared from the ingredients in the proportions indicated as grams of active material or in moles for the dyes:

	3A	**3B**	**3C**
para-Phenylenediamine	0.002mol	0.002mol	0.002mol
2,4-Diaminophenoxyethanol dihydrochloride	0.002mol	0.002mol	0.002mol
Bentonite [b]	6 g	6 g	6 g
Cocoglucoside [a]	2g	2g	2g
Benzyl alcohol	5g	1g	-
Ethanol	15g	-	15g
Fragrance	qs	qs	qs
pH agent	qs pH = 10	qs pH = 10	qs pH = 10
Water	qs 100g	qs 100g	qs 100g

[a] Alkyl (C8/C16) polyglucoside (1.4) as an aqueous solution, sold under the name Plantacare 818 UP by Cognis
[b]Bentone MA sold by Elementis

Each of the compositions 3A to 3C is mixed weight for weight with 20-volumes aqueous hydrogen peroxide solution at pH 2.2.
Each of the mixtures is then applied to locks of natural and permanent-waved hair containing 90% white hairs, for 30 minutes at room temperature. The locks are then wrung dry, shampooed, rinsed and dried.

Powerful, fast and sparingly selective blue colorations are obtained on the locks. It is moreover noted that the tools used for dyeing the locks (brushes and bowls) are not stained with the dyeing mixtures prepared.

Example 4:

The following dye compositions are prepared from the ingredients in the proportions indicated as grams of active material or in moles for the dyes:

	4D	4E	4F
para-Phenylenediamine	0.002 mol	0.002 mol	-
para-Aminophenol	-	-	0.002 mol
2-Methyl-5-aminophenol	0.002mol	-	0.002 mol
2,4-Diaminophenoxyethanol dihydrochloride	-	0.002mol	-
Bentonite [b]	6 g	6 g	6 g
Cocoglucoside [a]	2g	2g	2g
Benzyl alcohol	1g	1g	1g
Fragrance	qs	qs	qs
pH agent	qs pH = 10	qs pH = 10	qs pH = 10
Water	qs 100g	qs 100g	qs 100g

[a] Alkyl (C8/C16) polyglucoside (1.4) as an aqueous solution, sold under the name Plantacare 818 UP by Cognis
[b]Bentone MA sold by Elementis

Each of the compositions 4D to 4F is mixed weight for weight with 20-volumes aqueous hydrogen peroxide solution at pH 2.2.
Each of the mixtures is then applied to locks of natural and permanent-waved hair containing 90% white hairs, for 30 minutes at room temperature. The locks are then wrung dry, shampooed, rinsed and dried.

Powerful, fast and sparingly selective violet-red colorations (composition 4D) blue colorations (composition 4E) and coppery colorations (composition 4F) are obtained on the locks using compositions 4D, 4E and 4F, respectively.

It is moreover noted that the tools used for dyeing the locks (brushes and bowls) are not stained with the dyeing mixtures prepared.

CLAIMS

1. Dye composition comprising at least one water-insoluble silicate of the smectite type, at least one coloured or colouring species chosen from oxidation dye precursors, natural dyes, cationic direct dyes and nonionic direct dyes, and at least one mono- or polyglycoside.

2. Composition according to Claim 1, in which the insoluble silicate(s) are chosen from montmorillonites, hectorites, bentonites, beidellites and saponites, preferably laponite, montmorillonite or bentonite.

3. Composition according to Claim 1, in which the amount of insoluble silicate ranges between 0.1% and 20% relative to the weight of the composition, preferably from 0.2% to 15% by weight and better still from 0.5% to 10% relative to the weight of the composition.

4. Composition according to any one of the preceding claims, in which the cationic direct dye(s) are chosen from direct dyes of the following types: azo dyes, methine dyes; azomethine dyes with diazacarbocyanins and their isomers, and tetraazacarbocyanins (tetraazapentamethines); anthraquinone dyes; alone or as a mixture.

5. Composition according to any one of the preceding claims, in which the nonionic direct dye(s) are chosen from dyes with a logP of greater than or equal to 2.

6. Composition according to any one of the preceding claims, in which the natural dye(s) are chosen from lawsone, juglone, alizarin, purpurin, carminic acid, kermesic acid, laccaic acid, protocatechaldehyde, indigo, isatin, curcumin, spinulosin, apigenidin, chlorophylline, sorghum extracts, orceins, cochineal carmine, hematin, hematoxylin, brazilin, brazileine, extracts of logwood wood, cudbear wood and Brazil wood, and mixtures thereof.

7. Composition according to the preceding claim, characterized in that it comprises as oxidation dyes one or more oxidation bases chosen from para-phenylenediamines, bis(phenyl)alkylenediamines, para-aminophenols, ortho-aminophenols and heterocyclic bases, and the addition salts thereof, and optionally one or more couplers chosen from meta-phenylenediamines, meta-aminophenols, meta-diphenols, naphthalene-based couplers and heterocyclic couplers, and also the addition salts thereof.

8. Composition according to any one of the preceding claims, in which the mono- or polyglycoside corresponds to formula (I)

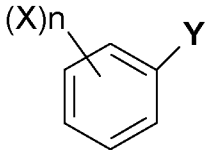
$$R_1O\text{-}(R_2O)_t\,(G)_v \quad (I)$$

in which:

- R_1 represents a linear or branched alkyl and/or alkenyl group, comprising from about 8 to 24 carbon atoms, or an alkylphenyl group whose linear or branched alkyl group comprises from 8 to 24 carbon atoms,
- R_2 represents an alkylene group comprising from about 2 to 4 carbon atoms,
- G represents a sugar unit comprising from 5 to 6 carbon atoms,
- t denotes a value ranging from 0 to 10, and
- v denotes a value ranging from 1 to 15.

9. Composition according to any one of the preceding claims, in which the mono- or polyglycoside is chosen from caprylylglucoside, decylglucoside, laurylglucoside, cetearylglucoside and cocoglucoside, and mixtures thereof.

10. Composition according to any one of the preceding claims, comprising at least one compound of formula (II):



in which Y represents a C_1-C_4 hydroxyalkyl group or a C_1-C_4 hydroxyalkyloxy radical, n denotes an integer ranging from 0 to 5, and X, which may be identical or different, represent a C_1-C_4 alkyl radical or a halogen.

11. Composition according to any one of the preceding claims, in which the compound(s) of formula (II) are chosen from benzyl alcohol, phenylethanol and phenoxyethanol, preferably benzyl alcohol.

12. Composition according to any one of the preceding claims, comprising at least one C_2-C_6 hydroxylated aliphatic solvent, preferably chosen from ethanol, glycerol, propylene glycol, dipropylene glycol and hexylene glycol, preferably ethanol and/or hexylene glycol.

13. Composition according to any one of the preceding claims, comprising at least one oxidizing agent.

14. Hair dyeing process, characterized in that the composition according to any one of Claims 1 to 11 is applied to the hair.