Abstract:
The present invention relates to an agent for dyeing and/or bleaching keratin fibres, comprising: - a water-in-oil inverse emulsion (A) comprising: -30% to 70% by weight, relative to the weight of the inverse emulsion (A), of one or more oils not containing any carboxylic acid functions, -water, -one or more surfactants with an HLB value of greater than or equal to 8, -one or more basifying agents, -an oil-in-water direct emulsion (B) comprising: -water, -one or more oils not containing any carboxylic acid functions, -one or more oxidizing agents, the total amount of the said oils contained in the mixture of the emulsions (A) and (B) representing at least 20% by weight relative to the total weight of the said mixture. The present invention also relates to a process for dyeing and/or bleaching keratin fibres using such an agent, and also to a kit containing it.
Agent in two or more parts, in emulsion form, for dyeing and/or bleaching keratin fibres

The present invention relates to an agent in two or more parts, for dyeing and/or bleaching keratin fibres, in particular human keratin fibres such as the hair.

A subject of the present invention is also a process for dyeing and/or bleaching keratin fibres, using the agent according to the invention.

Finally, the present invention relates to a multi-compartment device, containing the dyeing and/or bleaching agent according to the invention, and to the use of the agent for dyeing and/or bleaching keratin fibres.

Many people have for a long time sought to modify the colour of their hair, especially to bleach it or, on the contrary, to dye it in order, for example, to mask their grey hair.

Essentially two types of dyeing have been developed for dyeing keratin fibres.

The first type of dyeing is "permanent" or oxidation dyeing, which uses dye compositions containing oxidation dye precursors, generally known as oxidation bases. These oxidation bases are colourless or weakly coloured compounds, which, when combined with oxidizing products, can give rise to coloured compounds via a process of oxidative condensation.

It is also known that the shades obtained with these oxidation bases can be varied by combining them with couplers or coloration modifiers. The variety of molecules used as oxidation bases and couplers allows a wide range of colours to be obtained.

The second type of dyeing is "semi-permanent" dyeing or direct dyeing, which consists in applying to keratin fibres direct dyes, which are coloured and colouring molecules that have affinity for the said fibres, in leaving them on for a time, and then in rinsing them off.

In order to perform these colorations, the direct dyes generally used are chosen from nitrobenzene, anthraquinone, nitropyridine, azo, xanthene, acridine, azine and triarylmethane direct dyes.
This type of process does not require the use of an oxidizing agent to develop the coloration. However, it is possible to use such an agent in order to obtain a lightening effect with the coloration. This is then referred to as direct or semi-permanent dyeing under lightening conditions.

Permanent or semi-permanent dyeing processes under lightening conditions thus consist in using, with the dye composition, an aqueous composition comprising at least one oxidizing agent, under alkaline pH conditions in the vast majority of cases.

The role of this oxidizing agent is to degrade the melanin of the hair, which, depending on the nature of the oxidizing agent present, leads to more or less pronounced lightening of the fibres. Thus, for relatively mild lightening, the oxidizing agent is generally hydrogen peroxide. When greater lightening is desired, peroxygenated salts, for instance persulfates, are usually used in the presence of hydrogen peroxide.

In order to improve the performance qualities of processes for dyeing and/or bleaching human keratin fibres, and to limit the drawbacks associated with the use of alkaline agents and oxidizing agents, it has been proposed to use in dye compositions a substantial amount of one or more fatty substances.

However, the incorporation into these compositions of a sufficient amount of fatty substance proves problematic, all the more so when the dye composition is formulated in the form of a standard emulsion of oil-in-water type. The reason for this is that these formulations are thermodynamically unstable, and their viscosity changes over time, all the more so if the amount of fatty substance is large.

The Applicant has now discovered that the use of an alkaline composition in the form of a water-in-oil inverse emulsion, in the presence of certain surfactants, makes it possible to incorporate a large amount of oily compounds into compositions applied to fibres, while at the same time maintaining the stability of these compositions. Furthermore, it has been observed that the optional addition of an oil thickener to the system can stabilize the said system in the form of an inverse emulsion. The formulation of the dye composition as an
inverse emulsion allows the generally water-soluble dyes, which are thus present in the droplets of the aqueous phase, to be better protected. As a result, the said dyes do not undergo any oxidation with atmospheric oxygen. This formulation thus leads to the production of stronger and more chromatic colorations.

One subject of the invention is thus an agent for dyeing and/or bleaching keratin fibres, comprising:
- a water-in-oil inverse emulsion (A) comprising:
  - 30% to 70% by weight, relative to the weight of the emulsion (A), of one or more oils not containing any carboxylic acid functions,
  - water,
  - one or more surfactants with an HLB value of greater than or equal to 8,
  - one or more basifying agents,
- an oil-in-water direct emulsion (B) comprising:
  - water,
  - one or more oils not containing any carboxylic acid functions,
  - one or more oxidizing agents,
the total amount of the said oils contained in the mixture of the inverse emulsion (A) and of the direct emulsion (B) representing at least 20% by weight relative to the total weight of the said mixture.

When the agent according to the invention is intended for dyeing keratin fibres, the inverse emulsion (A) also comprises one or more oxidation dyes and/or one or more direct dyes.

Conversely, when the agent according to the invention is intended solely for bleaching keratin fibres, the emulsions (A) and (B) do not comprise any direct dyes or any oxidation dyes (bases and couplers), or else, if they are present, their total content does not exceed 0.005% by weight relative to the weight of each composition. Specifically, at such a content, only the composition would be dyed, i.e. no colouring effect would be observed on the keratin fibres.

The dyeing and/or bleaching agent according to the present invention does not change or changes little over time during the mixing of the inverse emulsion (A) and the direct emulsion (B), or during the sequential application of these two emulsions to the keratin
fibres. It thus shows very good efficacy, especially in terms of the quality and homogeneity of the dyeing and/or bleaching.

In addition, when it is intended for dyeing, the agent according to the invention is particularly efficient as regards the dyeing power obtained, and also as regards the power of the chromaticity and the selectivity of dyeing of the same fibre, or between differently sensitized fibres.

When it is intended for bleaching, the agent according to the invention shows lightening performance qualities equivalent to or even greater than those obtained with the existing compositions, especially with those based on ammonium hydroxide.

The agent according to the invention also has the advantage of limiting the evolution of aggressive odour during its preparation or its application to the fibres.

Other characteristics and advantages of the invention will emerge more clearly on reading the description and the examples that follow.

In the text hereinbelow, and unless otherwise indicated, the limits of a range of values are included in that range.

The human keratin fibres treated via the process according to the invention are preferably hair.

For the purposes of the present invention, the term "emulsion" means true emulsions, which are to be distinguished from microemulsions, which are thermodynamically stable systems, unlike true emulsions.

The size of the droplets of the dispersed phase of the emulsions of the invention is preferably between 10 nm and 100 μm and preferably between 200 nm and 50 μm.

This is the mean diameter D(3.2), which may be measured especially using a laser granulometer.

The inverse emulsion (A) and the direct emulsion (B) may be prepared via standard emulsion preparation processes that are well known to those skilled in the art.

The inverse emulsion (A) is in the form of a water-in-oil emulsion, i.e. the aqueous phase is dispersed in a fatty phase.
Preferably, the inverse emulsion (A) comprises from 40% to 70% and better still from 45% to 65%, relative to the weight of the inverse emulsion (A), of one or more oils not containing any carboxylic acid functions.

In one variant, the amount of water ranges from 5% to 70% and better still from 10% to 50% of the total weight of the emulsion (A).

In another variant, the aqueous phase comprising water and optionally compounds that are water-soluble at room temperature and at atmospheric pressure may range from 10% to 70% and better still from 15% to 50% of the total weight of the emulsion (A).

According to the present invention, the inverse emulsion (A) comprises one or more basifying agents.

The basifying agent may in particular be a mineral or organic base.

Preferably, the basifying agent is chosen from aqueous ammonia, alkali metal carbonates, alkanolamines and derivatives thereof, sodium hydroxide, potassium hydroxide and the compounds of formula (I) below:

\[
\begin{array}{c}
\text{Rx} \\
\text{N} \cdot \text{W} \cdot \text{N} \\
\text{Ry} \\
\text{Rz} \\
\text{Rt}
\end{array}
\]

in which W is a Ci-C6 alkylene residue optionally substituted with a hydroxyl group or a Ci-C6 alkyl radical; Rx, Ry, Rz and Rt, which may be identical or different, represent a hydrogen atom or a Ci-C6 alkyl, Ci-C6 hydroxyalkyl or Ci-C6 aminoalkyl radical.

Examples of such compounds of formula (I) that may be mentioned include 1,3-diaminopropane, 1,3-diamino-2-propanol, spermine and spermidine.

The basifying agents that are particularly preferred are alkanolamines, and in particular monoethanolamine, diethanolamine and triethanolamine.

In one preferred variant of the invention, the basifying agent is monoethanolamine.

According to one particular embodiment, the inverse emulsion (A) contains as basifying agent at least one organic amine and preferably at least one alkanolamine. When the emulsion contains
several basifying agents, including an alkanolamine and aqueous ammonia or a salt thereof, the organic amine(s) are preferably in weight majority relative to the amount of ammonia.

According to one particular embodiment of the present invention, the inverse emulsion (A) does not contain any aqueous ammonia.

According to one embodiment of the present invention, when the inverse emulsion (A) contains aqueous ammonia, it also contains one or more alkanolamines, and the weight amount of alkanolamine(s) in the inverse emulsion (A) is greater than the weight amount of ammonia in this same emulsion.

Generally, the inverse emulsion (A) has a content of basifying agent(s) ranging from 0.1% to 40% by weight and preferably from 0.5% to 20% by weight relative to the weight of this emulsion.

Preferably, the inverse emulsion (A) and/or the aqueous phase of the inverse emulsion (A) has a pH greater than or equal to 8 and more preferentially a pH ranging from 8.5 to 11.5.

This pH may also be adjusted to the desired value by using, in addition to the basifying agent, one or more acidifying agents.

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

The inverse emulsion (A) according to the present invention also comprises one or more surfactants with an HLB of greater than or equal to 8.

The term HLB is well known to those skilled in the art, and denotes the hydrophilic-lipophilic balance of a surfactant.

The HLB or hydrophilic-lipophilic balance of the surfactant(s) used according to the invention is the HLB according to Griffin, defined in the publication J. Soc. Cosm. Chem. 1954 (volume 5), pages 249-256.

Non-limiting examples of surfactants with an HLB of greater than or equal to 8 are especially given in the publication entitled McCutcheon’s Emulsifiers & Detergents, 1998 International Edition, MC Publishing Company, in the chapter entitled "HLB Index".
The surfactant(s) that may be used in the inverse emulsion (A) are preferably chosen from nonionic surfactants and anionic surfactants, and preferably from nonionic surfactants.

The anionic surfactants are more especially chosen from the salts, in particular alkali metal salts, especially sodium salts, ammonium salts, amine salts, amino alcohol salts or alkaline-earth metal salts such as magnesium salts, of the following compounds:

- alkyl sulfates, alkyl ether sulfates, alkylamido ether sulfates, alkylaryl polyether sulfates, monoglyceride sulfates;
- alkylsulfonates, alkylamidesulfonates, alkylarylsulfonates, a-olefin sulfonates, paraffin sulfonates;
- alkyl phosphates, alkyl ether phosphates;
- alkylsulfosuccinates, alkyl ether sulfosuccinates, alkylamidesulfosuccinates; alkylsulfosuccinamates;
- alkylsulfoacetates;
- acylsarcosinates; acylisethionates and N-acyltaurates;
- salts of fatty acids such as oleic acid, ricinoleic acid, palmitic acid or stearic acid, coconut oil acid or hydrogenated coconut oil acid;
- alkyl-D-galactoside uronic acid salts;
- acyllactylates;
- salts of polyoxyalkylenated alkyl ether carboxylic acids, of polyoxyalkylenated alkylaryl ether carboxylic acids or of polyoxyalkylenated alkylamido ether carboxylic acids, in particular those containing from 2 to 50 ethylene oxide groups;
- and mixtures thereof.

It should be noted that the alkyl or acyl radical of these various compounds advantageously contains from 6 to 24 carbon atoms and preferably from 8 to 24 carbon atoms, and the aryl radical preferably denotes a phenyl or benzyl group.

The nonionic surfactants are preferably chosen from oxyalkylenated or glycerolated surfactants, preferably oxyalkylenated surfactants.

According to the invention, the term "oxyalkylenated nonionic surfactants" means nonionic surfactants that bear in their molecule one
or more groups chosen from the following groups: \(-\text{CH}_2\text{CH}_2\text{-O-},\) 
\(-\text{CH}_2\text{CH}_2\text{CH}_2\text{-O-},\) 
\(-\text{CH}_2\text{-CH(CH}_3\text{-O-},\) or mixtures thereof.

The oxyalkylenated nonionic surfactants with an HLB of greater than or equal to 8 may belong, in a non-limiting manner, to the following families:

- oxyethylenated alkylphenols,
- OE/OP condensates,
- oxyethylenated plant oils,
- oxyethylenated fatty alcohols,
- fatty acid esters of polyethylene glycols,
- polyoxyethylenated fatty acid esters of sorbitol.

Commercial compounds that may be mentioned include:

- Intrasol FA28/50/4 (HLB=8.1) (Stockhausen)
- Serdox NOG 200 S (HLB=8.5) (Servo)
- Berol 26 (HLB=8.9) (Berol Nobel)
- Genapol O-050 (HLB=9) (Hoechst)
- Prox-Onic LA-1/04 (HLB=9.2) (Protex)
- Eumulgin 0 5 (HLB=9.5) (Henkel)
- Etocas 20 (HLB=9.6) (Croda)
- Antarox CO 520 (HLB=10) (Rhone-Poulenc)
- Imbentin POA/060 (HLB=10) (Kolb)
- TO-55-EL (HLB=10) (Hefti)
- Atlas G-1086 (HLB=10.2) (ICI)
- Atlox 4878B (HLB=10.5) (ICI)
- Berol 059 (HLB=10.5) (Berol Nobel)
- Kessco PEG 600 Dilaurate (HLB=10.5) (Akzo)
- Mergital LT6 (HLB=10.6) (Henko)
- Polychol 10 (HLB=10.7) (Croda)
- Prox-Onic HR-025 (HLB=10.8) (Protex)
- Tebenal NP6 (HLB=10.9) (Bohme)
- Cremophor A6 (HLB=11) (BASF)
- Genapol O-080 (HLB=11) (Hoechst)
- Genapol T-080 (HLB=11) (Hoechst)
- Kotilen-0/3 (HLB=11) (Kolb)
- Lutensol AP 7 (HLB=11) (BASF)
- Tween 85 (HLB=11) (ICI)
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Imbentin AG/1 68/ 150 (HLB=14.5) (Kolb)
Prox-Onic LA- 1/0 12 (HLB= 14.5) (Protex)
Etocas 60 (HLB=1 4.7) (Croda)
Radiasurf 7157 (HLB=1 4.9) (Oleofina)
Genapol T-180 (HLB=15) (Hoechst)
Montanox 80 (HLB=15) (SEPPIC)
Serdox NJAD 20 (HLB=15) (Servo)
Tagat R60 (HLB= 15) (Goldschmidt)
Berol 278 (HLB=1 5.2) (Berol Nobel)
Brij 78 (HLB=1 5.3) (ICI)
Simulsol 98 (HLB=1 5.3) (SEPPIC)
Montanox 40 (HLB 15.6) (SEPPIC)
Brij 58 (HLB=1 5.7) (ICI)
Aqualose L75 (HLB= 16) (Westbrook Lanolin)
Atlas G-147 1 (HLB=16) (ICI)
Berol 281 (HLB=16) (Berol Nobel)
Berol 292 (HLB=16) (Berol Nobel)
Nafolox 20-22 30OE (HLB=16) (Condea)
Genapol C-200 (HLB=16) (Hoechst)
Myrj 51 (HLB= 16) (ICI)
Simulsol PS 20 (HLB=16) (SEPPIC)
Tergitol 15 S 20 (HLB 16.3) (Union Carbide)
Synperononic PE P75 (HLB=1 6.5) (ICI)
Montanox 20 (HLB=1 6.7) (SEPPIC)
Myrj 52 (HLB=16.9) (ICI)
Simulsol 3030 NP (HLB=1 7) (SEPPIC)
Imbentin AG/1 68 / 400 (HLB=1 7.5) (Kolb)
Rhodia Surf NP40 (HLB=1 7.7) (Rhone-Poulenc)
Incropol CS-50 (HLB=1 7.9) (Croda)
Servirox OEG 90/50 (HLB=18) (Servo)
Prox-Onic HR-0200 (HLB=18.1) (Protex)
Berol 243 (HLB=1 8.2) (Berol Nobel)
Imbentin N/600 (HLB=1 8.5) (Kolb)
Antarox CO 980 (HLB=1 8.7) (Rhone-Poulenc)
Antarox CO 987 (HLB=1 8.7) (Rhone-Poulenc)
Berol 08 (HLB = 18.7) (Berol Nobel)
Brij 700 (HLB = 18.8) (ICI)
Prox-Onic NP-0100 (HLB = 19) (Protex)
Rs-55-100 (HLB = 19) (Hefti)
Imbentin AG/168S/950 (HLB = 20) (Kolb)
Synperonic PE F87 (HLB = 24) (ICI)
Alkasurf BA-PE80 (HLB = 26.1) (Rhone-Poulenc)
Synperonic PE F38 (HLB = 30.5) (ICI)

Among the latter products, oxyethyleneated fatty alcohols with an HLB of greater than or equal to 8 are preferred.

The concentration of these surfactants with an HLB of greater than or equal to 8 is preferably between 1% and 20%, more preferentially from 1% to 15% and better still from 2% to 10% by weight relative to the total weight of the inverse emulsion (A).

The inverse emulsion (A) according to the invention comprises one or more oils not containing any carboxylic acid functions contained in the continuous phase of the inverse emulsion, and the direct emulsion (B) according to the invention comprises one or more oils not containing any carboxylic acid functions contained in the dispersed phase of the direct emulsion.

The term "oil" means an organic compound that is insoluble in water at ordinary temperature (25°C) and at atmospheric pressure (760 mmHg; i.e. 1013.105 Pa) (water solubility of less than 5% by weight, preferably 1% and even more preferentially 0.1%). These compounds have in their structure at least one hydrocarbon-based chain comprising at least six carbon atoms or a sequence of at least two siloxane groups. In addition, oils are soluble in organic solvents under the same temperature and pressure conditions, for instance chloroform, ethanol or benzene. Furthermore, oils are liquid at ordinary temperature (25°C) and at atmospheric pressure (760 mmHg; i.e. 1013.105 Pa).

The term "oil not containing any carboxylic acid functions" means an oil containing no -COOH groups and no -COO- groups.

According to one preferred mode of the invention, the oil(s) not containing any carboxylic acid functions, used in the emulsion (A) and in the emulsion (B), which may be identical or different, may be
chosen especially from hydrocarbons, non-silicone oils of animal, plant, mineral or synthetic origin, fatty alcohols, fatty acid esters and/or fatty alcohol esters, and silicones, and mixtures thereof.

It is pointed out that, for the purposes of the present invention, the fatty alcohols more particularly contain one or more linear or branched, saturated or unsaturated hydrocarbon-based groups, comprising 6 to 30 carbon atoms, which are optionally substituted, in particular with one or more (in particular 1 to 4) hydroxyl groups. If they are unsaturated, these compounds may comprise one to three conjugated or unconjugated carbon-carbon double bonds.

More particularly, the liquid hydrocarbons are chosen from:
- linear or branched, optionally cyclic, C₆-C₁₆ lower alkanes. Examples that may be mentioned include hexane, undecane, dodecane, tridecane, and isoparaffins, for instance isohexadecane, isododecane and isodecane,
- linear or branched hydrocarbons of mineral, animal or synthetic origin, containing more than 16 carbon atoms, such as liquid paraffins, petroleum jelly, liquid petroleum jelly, polydecenes and hydrogenated polyisobutenes such as Parleam®, and squalane.

In one preferred variant, the liquid hydrocarbon(s) are chosen from liquid paraffins and liquid petroleum jelly.

Preferably, the silicone is chosen from liquid polydialkylsiloxanes, especially liquid polydimethylsiloxanes (PDMS) and liquid polyorganosiloxanes comprising at least one aryl group.

These silicones may also be organomodified. The organomodified silicones that may be used in accordance with the invention are liquid silicones as defined previously, comprising in their structure one or more organofunctional groups attached via a hydrocarbon-based group.

Organopolysiloxanes are defined in greater detail in Walter Noll's *Chemistry and Technology of Silicones* (1968), Academic Press. They may be volatile or non-volatile.

When they are volatile, the silicones are more particularly chosen from those having a boiling point of between 60°C and 260°C, and even more particularly from cyclic polydialkylsiloxanes containing from 3 to 7 and preferably 4 to 5 silicon atoms. These are,
for example, octamethylcyclotetrasiloxane sold in particular under the name Volatile Silicone® 7207 by Union Carbide or Silbione® 70045 V2 by Rhodia, decamethylcyclopentasiloxane sold under the name Volatile Silicone® 7158 by Union Carbide, Silbione® 70045 V5 by Rhodia, and dodecamethylcyclopentasiloxane sold under the name Silsoft 1217 by Momentive Performance Materials, and mixtures thereof.

Mention may also be made of cyclocopolymers of the dimethylsiloxane/methylalkylsiloxane type, such as Volatile Silicone® FZ 3109 sold by the company Union Carbide, of formula:

\[
\begin{array}{c}
\text{CH}_3 \\
D'\rightarrow D' \\
| \\
\text{Si} \rightarrow \text{O} \\
| \\
\text{CH}_3
\end{array}
\]

with \( D' \): \( \text{Si} \rightarrow \text{O} \) with \( D' \):

\[
\begin{array}{c}
\text{CH}_3 \\
D'' \\
| \\
\text{Si} \rightarrow \text{O} \\
| \\
\text{C}_9\text{H}_{17}
\end{array}
\]

Mention may also be made of mixtures of cyclic polydialkylsiloxanes with organosilicon compounds, such as the mixture of octamethylcyclotetrasiloxane and tetrtrimethylsilylpentamerythritol (50/50) and the mixture of octamethylcyclotetrasiloxane and oxy-1,1'-bis(2,2',2'',3,3''-hexatri(trimethylsilyloxy)neopentane; linear volatile polydialkylsiloxanes containing 2 to 9 silicon atoms and having a viscosity of less than or equal to 5x10^{-6} \text{ m}^2/\text{s} at 25\degree \text{C}. An example is decamethyltetrasiloxane sold in particular under the name SH 200 by the company Toray Silicone. Silicones belonging to this category are also described in the article published in Cosmetics and Toiletries, Vol. 91, Jan. 76, pp. 27-32, Todd & Byers: Volatile Silicone Fluids for Cosmetics. The viscosity of the silicones is measured, for example, at 25\degree \text{C} according to ASTM standard 445 Appendix C.

Non-volatile polydialkylsiloxanes may also be used. These silicones are more particularly chosen from polydialkylsiloxanes, among which mention may be made mainly of polydimethylsiloxanes containing trimethylsilyl end groups.

Among these polydialkylsiloxanes, mention may be made, in a nonlimiting manner, of the following commercial products:
- the Silbione® oils of the 47 and 70 047 series or the Mirasil® oils sold by Rhodia, for instance the oil 70 047 V 500 000;
- the oils of the Mirasil® series sold by the company Rhodia;
- the oils of the 200 series from the company Dow Corning, such as DC200 with a viscosity of 60 000 mm²/s;
- the Viscasil® oils from General Electric and certain oils of the SF series (SF 96, SF 18) from General Electric.

Mention may also be made of polydimethylsiloxanes containing dimethylsilanol end groups known under the name Dimethiconol (CTFA), such as the oils of the 48 series from the company Rhodia.

Among the silicones containing aryl groups are polydiarylsiloxanes, especially polydiphenylsiloxanes and polyalkylarylsiloxanes. Examples that may be mentioned include the products sold under the following names:

- the Silbione® oils of the 70 641 series from Rhodia;
- the oils of the Rhodorsil® 70 633 and 763 series from Rhodia;
- the oil Dow Corning 556 Cosmetic Grade Fluid from Dow Corning;
- the silicones of the PK series from Bayer, such as the product PK20;
- certain oils of the SF series from General Electric, such as SF 1023, SF 1154, SF 1250 and SF 1265.

The liquid fatty esters are preferably liquid esters of saturated or unsaturated, linear or branched C₁₋₂₆ aliphatic mono- or polyacids and of saturated or unsaturated, linear or branched C₁₋₂₆ mono- or polyalcohols, the total number of carbon atoms in the esters being greater than or equal to 10.

Preferably, for the esters of monoalcohols, at least one from among the alcohol and the acid from which the esters of the invention are derived is branched.

Among the monoesters of monoacids and of monoalcohols, mention may be made of ethyl palmitate, isopropyl palmitate, alkyl myristates such as isopropyl myristate or ethyl myristate, isocetyl stearate, 2-ethylhexyl isononanoate, isodecyl neopentanoate and isostearyl neopentanoate.
Esters of C₄-C₂₂ dicarboxylic or tricarboxylic acids and of C₁-
C₂₂ alcohols and esters of mono-, di- or tricarboxylic acids and of C₄-
C₂₆ di-, tri-, tetra- or pentahydroxy alcohols may also be used.

The following may especially be mentioned: diethyl sebacate;
diisopropyl sebacate; bis(2-ethylhexyl) sebacate; diisopropyl adipate;
di-n-propyl adipate; dioctyl adipate; bis(2-ethylhexyl) adipate;
diisostearyl adipate; bis(2-ethylhexyl) maleate; triisopropyl citrate;
triisocetyl citrate; triisostearyl citrate; glyceryl trilactate; glyceryl
trioctanoate; trioctyldodecyl citrate; trioleyl citrate; neopentyl glycol
diheptanoate; diethylene glycol diisononanoate.

The emulsion (A) or (B) may also comprise, as liquid fatty
ester, C₆-C₃₀ and preferably C₁₂-C₂₂ fatty acid esters and diesters
of sugars. It is recalled that the term "sugar" means oxygenous
hydrocarbon-based compounds that contain several alcohol functions,
with or without aldehyde or ketone functions, and that comprise at
least 4 carbon atoms. These sugars may be monosaccharides,
oligosaccharides or polysaccharides.

Examples of suitable sugars that may be mentioned include
sucrose (or saccharose), glucose, galactose, ribose, fucose, maltose,
fructose, mannose, arabinose, xylose and lactose, and derivatives
thereof, especially alkyl derivatives, such as methyl derivatives, for
instance methylglucose.

The sugar esters of fatty acids may be chosen especially from
the group comprising the esters or mixtures of esters of sugars
described previously and of linear or branched, saturated or
unsaturated C₆-C₃₀ and preferably C₁₂-C₂₂ fatty acids. If they are
unsaturated, these compounds may comprise one to three conjugated or
non-conjugated carbon-carbon double bonds.

The esters according to this variant may also be chosen from
mono-, di-, tri-, tetraesters and polyesters, and mixtures thereof.

These esters may be chosen, for example, from oleates,
laurates, palmitates, myristates, behenates, cocoates, stearates,
linoleates, linolenates, caprates and arachidonates, or mixtures thereof
such as, especially, oleo-palmitate, oleo-stearate and palmito-stearate
mixed esters.
Monoesters and diesters and especially sucrose, glucose or methylglucose mono- or dioleates, stearates, behenates, oleopalmitates, linoleates, linolenates and oleostearates are more particularly used.

An example that may be mentioned is the product sold under the name Glucate® DO by the company Amerchol, which is a methylglucose dioleate.

Finally, natural or synthetic esters of mono-, di- or triacids with glycerol may also be used.

Among these, mention may be made of plant oils.

As oils of plant origin or synthetic triglycerides that may be used in the emulsions that are useful for the agent according to the invention, as liquid fatty esters, examples that may be mentioned include triglyceride oils of plant or synthetic origin, such as liquid fatty acid triglycerides containing from 6 to 30 carbon atoms, for instance heptanoic or octanoic acid triglycerides, or alternatively, for example, sunflower oil, corn oil, soybean oil, marrow oil, grapeseed oil, sesame seed oil, hazelnut oil, apricot oil, macadamia oil, arara oil, castor oil, avocado oil, caprylic/capric acid triglycerides, for instance those sold by the company Stearineries Dubois or those sold under the names Miglyol® 810, 812 and 818 by the company Dynamit Nobel, jojoba oil and shea butter oil.

Liquid fatty esters derived from monoalcohols will preferably be used as esters according to the invention. Isopropyl myristate and isopropyl palmitate are particularly preferred.

Preferably, the liquid unsaturated fatty alcohols of the invention comprise from 8 to 30 carbon atoms.

The liquid fatty alcohols may be unsaturated.

These liquid unsaturated fatty alcohols contain in their structure at least one double or triple bond. Preferably, the fatty alcohols of the invention bear in their structure one or more double bonds. When several double bonds are present, there are preferably 2 or 3 of them, and they may be conjugated or unconjugated.

These fatty alcohols may be linear or branched.

They may optionally comprise in their structure at least one aromatic or non-aromatic ring. They are preferably acyclic.
More particularly, the liquid unsaturated fatty alcohols are chosen from oleyl alcohol, linolenyl alcohol, linolenyl alcohol and undecylenyl alcohol.

Oleyl alcohol is most particularly preferred.

The liquid fatty alcohols may also be branched saturated fatty alcohols. More particularly, the liquid branched saturated fatty alcohols of the invention are chosen from isostearyl alcohol and octyldodecanol.

Preferably, the oil(s) not containing any carboxylic acid functions, present in the emulsions (A) and (B), do not comprise any oxyalkylene units or any glycerol units.

Preferably, the oil(s) not containing any carboxylic acid functions, present in the emulsions (A) and (B), are non-silicone.

According to one preferred embodiment, the oil(s) not containing any carboxylic acid functions, present in the emulsions (A) and (B), are chosen from hydrocarbons, non-silicone oils of animal, plant, mineral or synthetic origin, fatty alcohols, fatty acid esters and/or fatty alcohol esters, and silicones, and mixtures thereof; preferably from liquid petroleum jelly, polydecenes, liquid esters of fatty acids and/or of fatty alcohols, and liquid fatty alcohols, and mixtures thereof; and more preferably from liquid petroleum jelly, polydecenes and liquid fatty alcohols, and mixtures thereof.

Even more preferentially, the oil not containing any carboxylic acid functions is liquid petroleum jelly.

The inverse emulsion (A) according to the present invention preferably comprises one or more oil-thickening agents.

The thickener may be chosen from polymeric thickeners, non-polymeric agents, mineral thickeners and organic thickeners, and mixtures thereof.

The term "thickener" means a compound that modifies the rheology of the medium into which it is incorporated.

The oily-medium thickener may be chosen from:
- organophilic clays;
- hydrophobic fumed silicas;
- alkyl guar gums (with a C1-C6 alkyl group), such as those described in EP-A-708 114;
- oil-gelling polymers, for instance triblock polymers or star polymers resulting from the polymerization or copolymerization of at least one monomer containing an ethylenic group, for instance the polymers sold under the name Kraton;

- polymers with a weight-average molecular mass of less than 100 000, comprising a) a polymer backbone containing hydrocarbon-based repeating units containing at least one heteroatom, and optionally b) at least one pendant fatty chain and/or at least one terminal fatty chain, which are optionally functionalized, containing from 6 to 120 carbon atoms and being linked to these hydrocarbon-based units, as described in patent applications WO-A-02/056847 and WO-A-02/47619, the content of which is incorporated by way of reference; in particular, polyamide resins (especially comprising alkyl groups containing from 12 to 22 carbon atoms) such as those described in US-A-5 783 657, the content of which is incorporated by way of reference;

- the silicone-based polyamide resins as described in patent application EP-A-1 266 647 and in the French patent application filed under the number 0 216 039, the content of which is incorporated by way of reference.

Such thickeners are especially described in patent application EP-A-1 400 234, the content of which is incorporated by way of reference.

The thickener may be an organic gelling agent, i.e. an agent comprising at least one organic compound. The organogelling agents may be chosen from those described in patent application WO-A-03/105 788, the content of which is incorporated by way of reference.

More precisely, the polymeric thickener present in the emulsion that is useful for the agent according to the invention is an amorphous polymer formed by polymerization of an olefin. The olefin may especially be an elastomeric ethylenically unsaturated monomer.

Examples of olefins that may be mentioned include ethylenic carbide monomers especially containing one or two ethylenic unsaturations, containing from 2 to 5 carbon atoms, such as ethylene, propylene, butadiene or isoprene.
The polymeric thickener is capable of thickening or gelling the composition. The term "amorphous polymer" means a polymer that does not have a crystalline form. The polymeric thickener may also be film-forming.

The polymeric thickener may especially be a diblock, triblock, multiblock, radial or star copolymer, or mixtures thereof.


Advantageously, the polymeric thickener is an amorphous block copolymer of styrene and of olefin.

The polymeric thickener is preferably hydrogenated to reduce the residual ethylenic unsaturations after polymerization of the monomers.

In particular, the polymeric thickener is an optionally hydrogenated copolymer, containing styrene blocks and ethylene/C₃-C₄ alkylene blocks.

Diblock copolymers, preferably hydrogenated, that may be mentioned include styrene-ethylene/propylene copolymers and styrene-ethylene/butadiene copolymers. The diblock polymers are especially sold under the name Kraton® G1701E by the company Kraton Polymers.

Triblock copolymers, which are preferably hydrogenated, that may be mentioned include styrene-ethylene/propylene-styrene copolymers, styrene-ethylene/butadiene-styrene copolymers, styrene-isoprene-styrene copolymers and styrene-butadiene-styrene copolymers. Triblock polymers are especially sold under the names Kraton® G1650, Kraton® G1652, Kraton® D1101, Kraton® D1102 and Kraton® D1160 by the company Kraton Polymers.

A mixture of hydrogenated styrene-butadiene/ethylene-styrene triblock copolymer and of hydrogenated ethylene-propylene-styrene star polymer may also be used, such a mixture especially being in isododecane. Such mixtures are sold, for example, by the company Penreco under the trade names Versagel® M5960 and Versagel® M5670.
A diblock copolymer such as those described above, in particular a styrene-ethylene/propylene diblock copolymer, is advantageously used as polymeric thickener.

More precisely, organophilic clays are clays modified with chemical compounds that make the clay able to swell.

Clays are products that are already well known per se, which are described, for example, in the publication *Mineralogie des argiles* [Mineralogy of clays], S. Caillere, S. Henin, M. Rautureau, 2nd Edition 1982, Masson, the teaching of which is included herein by way of reference.

Clays are silicates containing a cation that may be chosen from calcium, magnesium, aluminium, sodium, potassium and lithium cations, and mixtures thereof.

Examples of such products that may be mentioned include clays of the smectite family such as montmorillonites, hectorites, bentonites, beidellites and saponites, and also of the vermiculite, stevensite and chlorite families.

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

The organophilic clay may be chosen from optionally modified montmorillonite, bentonite, hectorite, attapulgite and sepiolite, and mixtures thereof. The clay is preferably a bentonite or a hectorite.

These clays may be modified with a chemical compound chosen from quaternary amines, tertiary amines, amine acetates, imidazolines, amine soaps, fatty sulfates, alkyl aryl sulfonates and amine oxides, and mixtures thereof.

Organophilic clays that may be mentioned include 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.

Fumed silicas may be obtained by high-temperature hydrolysis of a volatile silicon compound in an oxhydric flame, producing a finely divided silica. This process makes it possible especially to obtain hydrophilic silicas having a large number of silanol groups at their surface. Such hydrophilic silicas are sold, for example, under the names Aerosil 130®, Aerosil 200®, Aerosil 255®, Aerosil 300® and Aerosil 380® by the company Degussa, and Cab-O-Sil HS-5®, Cab-O-Sil EH-5®, Cab-O-Sil LM-130®, Cab-O-Sil MS-55® and Cab-O-Sil M-5® by the company Cabot.

It is possible to chemically modify the surface of the said silica, via a chemical reaction generating a reduction in the number of silanol groups. It is especially possible to substitute silanol groups with hydrophobic groups: a hydrophobic silica is then obtained.

The hydrophobic groups may be:

- trimethylsiloxyl groups, which are obtained especially by treating fumed silica in the presence of hexamethyldisilazane. Silicas thus treated are known as "silica silylate" according to the CTFA (6th Edition, 1995). They are sold, for example, under the references Aerosil R812® by the company Degussa and Cab-O-Sil TS-530® by the company Cabot.

- dimethylsilyloxyl or polydimethylsiloxane groups, which are obtained especially by treating fumed silica in the presence of polydimethylsiloxane or dimethyldichlorosilane. Silicas thus treated are known as "silica dimethyl silylate" according to the CTFA (6th Edition, 1995). They are sold, for example, under the references Aerosil R972® and Aerosil R974® by the company Degussa and Cab-O-Sil TS-6 10® and Cab-O-Sil TS-720® by the company Cabot.

The fumed silica preferably has a particle size that may be nanometric to micrometric, for example ranging from about 5 to 200 nm.

An organomodified bentonite or hectorite is preferably used as mineral thickener.

More particularly, the thickener used is a distearyldimethylammonium-modified hectorite.
Preferably, the mineral thickeners are combined with carbonates, for instance propylene carbonate.

The thickener is preferably present in the inverse emulsion (A) in a total content ranging from 0.1% to 10% by weight, preferably ranging from 0.5% to 7% by weight and more preferentially ranging from 1% to 5% by weight relative to the total weight of the emulsion.

The direct emulsion (B) is in the form of an oil-in-water emulsion, i.e. with a fatty phase dispersed in an aqueous phase.

The direct emulsion (B) preferably comprises 5% to 50% and more preferentially 10% to 30% by weight, relative to the total weight of the direct emulsion (B), of one or more oils not containing any carboxylic acid functions as described previously.

According to the present invention, the direct emulsion (B) comprises one or more oxidizing agents.

This oxidizing agent may be chosen from the oxidizing agents conventionally used for the bleaching and oxidation dyeing of keratin fibres, and among which mention may be made of hydrogen peroxide, urea peroxide, alkali metal bromates or ferricyanides, and peroxygenated salts, for instance persulfates, perborates and percarbonates of alkali metals or alkaline-earth metals such as sodium, potassium or magnesium. One or more redox enzymes such as laccases, peroxidases and 2-electron oxidoreductases (such as uricase), optionally in the presence of the respective donor or cofactor thereof, may also be used as oxidizing agent.

The use of hydrogen peroxide is particularly preferred. It may be advantageously used as an aqueous solution (aqueous hydrogen peroxide solution) whose concentration may vary more particularly from 0.1% to 50% by weight, even more preferentially from 0.5% to 20% by weight and better still from 1% to 15% by weight relative to the total weight of the direct emulsion (B).

Depending on the desired degree of bleaching, the oxidizing agent may also comprise one or more compounds preferably chosen from peroxygenated salts.

Preferably, the pH of the aqueous phase of the direct emulsion (B) is less than 7. This pH may be adjusted to the desired value by
using one or more acidifying agents, which may be chosen especially from those described previously.

The mixture of emulsions (A) and (B) contains an amount of oil(s) not containing any carboxylic acid functions of at least 20% by weight and preferably between 20.5% and 75% by weight relative to the total weight of the said mixture.

Preferably, the mixture of emulsions (A) and (B) contains an amount of oil(s) not containing any carboxylic acid functions of at least 25% by weight, more particularly between 25.5% and 75% by weight, even more preferentially of at least 30% by weight and more particularly between 30.5% and 75% by weight, relative to the total weight of the said mixture.

The emulsions (A) and/or (B) according to the invention may also contain one or more additional fatty substances other than oils not containing any carboxylic acid functions defined previously, in particular such as solid fatty alcohols such as cetyl alcohol, stearyl alcohol or mixtures thereof. These additional fatty substances are free of carboxylic acid functions.

Advantageously, the inverse emulsion (A) is in the form of a gel or a cream.

Advantageously, the direct emulsion (B) is in the form of a solution, an emulsion or a gel.

According to a first embodiment of the invention, the inverse emulsion (A) also comprises one or more oxidation dyes.

In this case, the agent according to the invention is advantageously used for the oxidation dyeing of keratin fibres.

The oxidation dyes that may be used in the present invention are generally chosen from oxidation bases, optionally combined with one or more couplers.

The oxidation bases may be chosen especially from para-phenylene diamines, bis (phenyl) alkyene diamines, 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-tolynediamine, 2-chloro-para-phenylenediamine, 2,3-dimethyl-para-phenylenediamine, 2,6-

Among the para-phenylenediamines mentioned above, para-phenylenediamine, para-tolylene diamine, 2-isopropyl-par a-phenylen e diamine, 2-P-hydroxyethyl-para-phenylenediamine, 2-P-hydroxyethoxy-par a-phenylene diamine, 2,6-dimethyl-par a-phenylene-diamine, 2,6-diethyl-para-phenylenediamine, 2,3-dimethyl-para-phenylene diamine, N,N-bis (β-hydroxy ethyl) -par a-phenylene diamine, 2-chloro-para-phenylenediamine and 2-P-acetylaminooxyethoxy-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 (P-hydroxyethyl)-N,N'-bis(4'-aminophenyl)- 1,3-diaminopropanol, N,N'-bis (P-hydroxyethyl)-N,N'-bis (4'-amino phenyl) ethylene diamine, N,N'-bis(4-aminophenyl)tetramethylene diamine, N,N'-bis (β-hydroxy ethyl) -N,N'-bis(4- aminophenyl)tetramethylene diamine, N,N'-bis(4-methylaminophenyl)tetramethylene diamine, N,N'-bis(ethyl)-N,N'-bis(4'-amino-3 '-methylphenyl)-ethylene diamine 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-(P-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 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-acetylamino pyrazolo[1,5-a]pyrid-3-ylamine, 2-morpholin-4-yl pyrazolo[1,5-a]pyrid-3-ylamine, 3-aminopyrazolo[1,5-a]pyridine-2-carboxylic acid, 2-methoxy pyrazolo[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, (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-yl pyrazolo[1,5-a]pyrid-3-ylamine, pyrazolo[1,5-a]pyridine-3,5-diamine, 5-morpholin-4-yl pyrazolo[1,5-a]pyrid-3-ylamine, 2-[(3-aminopyrazolo[1,5-a]pyrid-5-yl)(2-hydroxy ethyl)amino]ethanol, 2-[(3-aminopyrazolo[1,5-a]pyrid-7-yl)(2-hydroxy ethyl)amino]ethanol, 3-aminopyrazolo[1,5-a]pyridin-3-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 patents DE 2 359 399; JP 88-169 571; JP 05-63 124; EP 0 770 375 or patent application WO 96/1 5765, for instance 2,4,5,6-tetraaminopyrimidine, 4-hydroxy-2,5,6-triaminopyrimidine, 2-hydroxy-4,5,6-triaminopyrimidine, 2,4-dihydroxy-5,6-diaminopyrimidine and 2,5,6-triaminopyrimidine, and the addition salts thereof, and the tautomeric forms thereof, when a tautomeric equilibrium exists.

Among the pyrazole derivatives that may be mentioned are the compounds described in patents DE 3 843 892 and DE 4 133 957, and patent applications WO 94/08969, WO 94/08970, FR-A-2 733 749 and DE 195 43 988, for instance 4,5-diamino-1-methylpyrazole, 4,5-diamino-1-(P-hydroxyethyl)pyrazole, 3,4-diaminopyrazole, 4,5-diamino-1-(4'-chlorobenzyl)pyrazole, 4,5-diamino-3-methyl-1-phenylpyrazole, 4,5-diamino-1-methyl-3-phenylpyrazole, 4-amino-1,3-dimethyl-5-hydrazinopyrazole, 1-benzy1-4,5-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-ethy1-3-methylpyrazole, 4,5-diamino-1-ethy1-3-(4'-methoxyphenyl)pyrazole, 4,5-diamino-1-ethy1-3-hydroxyxmethylpyrazole, 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-1,3,4,5-triamino pyrazole, 3,5-diamino-1-methylaminopyrazole and 3,5-diamino-4-(P-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-(P-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-
lH,5H-pyrazolo[ 1,2-a]pyrazol- 1-one, 2-amino-3-ethylamino-6,7-
dihydro- lH,5H-pyrazolo[ 1,2-a]pyrazol- 1-one, 2-amino-3-isopropyl-
amino-6,7-dihydro- lH,5H-pyrazolo[ 1,2-a]pyrazol- 1-one, 2-amino-3-
(pyrrolidin- 1-yl)-6,7-dihydro- lH,5H-pyrazolo[ 1,2-a]pyrazol- 1-one, 4,5-diamino- 1,2-dimethyl- 1,2-dihydropyrazo 1-3-one, 4,5-diamino- 1,2-
diethyl- 1,2-dihydropyrazol-3-one, 4,5-diamino- 1,2-di-(2-
hydroxy ethyl)- 1,2-dihydropyrazo 1-3-one, 2-amino-3-(2-
hydroxyethyl)amino-6,7-dihydro- lH,5H-pyrazolo[ 1,2-a]pyrazol- 1-one, 2-amino-3-dimethylamino-6,7-dihydro-
lH,5H-pyrazolo[ 1,2-a]pyrazol- 1-one, 2,3-diamino-5,6,7,8-tetrahydro-
lH,6H-pyridazo[ 1,2-a]pyrazol- 1-one, 4-amino- 1,2-diethyl-5-(pyrrolidin- 1-yl)- 1,2-
dihydropyrazo 1-3-one, 4-amino-5-(3-dimethylaminopyrrolidin- 1-yl)-
1,2-diethyl- 1,2-dihydropyrazo 1-3-one and 2,3-diamino-6-hydroxy-6,7-
dihydro- lH,5H-pyrazolo[ 1,2-a]pyrazol- 1-one.

2,3-Diamino-6,7-dihydro- lH,5H-pyrazolo[ 1,2-a]pyrazol- 1-one
and/or a salt thereof will preferably be used.

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

The couplers that may be used in the present invention may be
chosen from those conventionally used for the dyeing of keratin fibres.
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-(P-hydroxyethyl)benzene, 2-amino-4 - (β-
dihydroxyethy lamino)- 1-methoxybenzene, 1,3-diaminobenzene, 1,3-
bis(2,4-diaminophenoxy)propane, 3-ureidoaniline, 3-ureido- 1-
dimethylaminobenzene, sesamol, 1-P-hydroxyethylamino-3,4-
methylenedioxypyrindine, cc-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-hydroxy ethyl) amino -3, 4-methylenedioxy-
benzene, 2,6-bis (P-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 chosen from the addition salts with an acid such as the hydrochlorides, hydrobromides, sulfates, citrates, succinates, tartrates, lactates, tosylates, benzenesulfonates, phosphates and acetates.

The oxidation base(s) may each advantageously represent an amount greater than 0.005% to 10% by weight relative to the total weight of the inverse emulsion (A), and preferably an amount greater than 0.005% to 5% by weight relative to the total weight of this emulsion.

The coupler(s), if they are present, may each advantageously represent an amount greater than 0.005% to 10% by weight relative to the total weight of the inverse emulsion (A), and preferably an amount greater than 0.005% to 5% by weight relative to the total weight of this emulsion.

According to a second embodiment of the invention, the inverse emulsion (A) comprises one or more direct dyes.

According to one embodiment, the inverse emulsion (A) may comprise one or more oxidation dyes and, as additional dye, one or more direct dyes.

According to another embodiment, the inverse emulsion (A) does not comprise any oxidation dyes, and the agent according to the invention is then advantageously used for the lightening direct dyeing of keratin fibres.

The direct dyes that may be used in the inverse emulsion (A) are more particularly chosen from ionic and nonionic species, preferably cationic or nonionic species.

As examples of direct dyes that are suitable for use, mention may be made of azo; methine; carbonyl; azine; nitro (hetero)aryl;
tri(hetero)arylmethane; porphyrin; phthalocyanin direct dyes; and natural direct dyes, alone or as mixtures.

More particularly, the azo dyes comprise an -N=N- function, the two nitrogen atoms of which 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 chosen from >C=C< and -N=C-, the two atoms of which 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 the type such as methines, azomethines, mono- and diarylmethanes, indoamines (or diphenylamines), indophenols, indoanilines, carbocyanins, azacarbocyanins and isomers thereof, diazacarbocyanins and isomers thereof, tetraazacarbocyanins and hemicyanins.

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, quinacidone, quinophthalone, indigoid, thioindigo, naphthalimide, anthrapyrimidine, diketopyrrolopyrrole and coumarin.

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

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; azomethine
direct dyes; methine direct dyes; azacarbocyanin direct dyes, for instance tetraazacarbocyanins (tetraazapentamethines); quinone and in particular anthraquinone, naphthoquinone or benzoquinone direct dyes; azine; xanthene; triarylmethane; indoamine; indigoid; phthalocyanin direct dyes, porphyrins and natural direct dyes, alone or as mixtures.

These dyes may be monochromophoric dyes (i.e. comprising only one dye) or polychromophoric, preferably di- or trichromophoric; the chromophores possibly being identical or different, and from the same chemical family or otherwise. It should be noted that a polychromophoric dye comprises several radicals each derived from a molecule that absorbs in the visible region between 400 and 800 nm. Furthermore, this absorbance of the dye does not require any prior oxidation thereof, or combination with any other chemical species.

In the case of polychromophoric dyes, the chromophores are connected together by means of at least one linker, which may be cationic or non-cationic.

Preferably, the linker is a linear, branched or cyclic C1-C20 alkyl chain, optionally interrupted with at least one heteroatom (such as nitrogen or oxygen) and/or with at least one group comprising such an atom (CO, SO₂), optionally interrupted with at least one heterocycle that may or may not be fused to a phenyl nucleus and comprising at least one quaternized nitrogen atom engaged in said ring and optionally at least one other heteroatom (such as oxygen, nitrogen or sulfur), optionally interrupted with at least one substituted or unsubstituted phenyl or naphthyl group, optionally at least one quaternary ammonium group substituted with two optionally substituted C1-C15 alkyl groups; the linker not comprising any nitro, nitroso or peroxy groups.

If the heterocycles or aromatic nuclei are substituted, they are substituted, for example, with one or more Ci-Cs alkyl radicals optionally substituted with a hydroxyl, C1-C2 alkoxy, C2-C4 hydroxyalkoxy, acetylamino, or amino group substituted with one or two C1-C4 alkyl radicals, optionally bearing at least one hydroxyl group, or the two radicals possibly forming, with the nitrogen atom to which they are attached, a 5- or 6-membered heterocycle optionally comprising another heteroatom identical to or different than nitrogen;
a halogen atom; a hydroxyl group; a C₁-C₂ alkoxy radical; a C₂-C₄ hydroxyalkoxy radical; an amino radical; an amino radical substituted with one or two identical or different C₁-C₄ alkyl radicals optionally bearing at least one hydroxyl group.

Among the benzenic direct dyes that may be used according to the invention, mention may be made in a nonlimiting manner of the following compounds:

- 1,4-diamino-2-nitrobenzene,
- 1-amino-2-nitro-4-P-hydroxyethylaminobenzene
- 1-amino-2-nitro-4-bis(β-hydroxy ethyl)aminobenzene
- 1,4-bis(P-hydroxyethylamino)-2-nitrobenzene
- 1-P-hydroxyethylamino-2-nitro-4-bis(P-hydroxyethylamino)benzene
- 1-P-hydroxyethylamino-2-nitro-4-aminobenzene
- 1-P-hydroxyethylamino-2-nitro-4-(ethyl)(P-hydroxyethylamino)benzene
- 1-amino-3-methyl-4-P-hydroxyethylamino-6-nitrobenzene
- 1-amino-2-nitro-4-P-hydroxyethylaminobenzene
- 1,2-diamino-4-nitrobenzene
- 1-amino-2-β-hydroxyethylaminobenzene-5-nitrobenzene
- 1,2-bis(P-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-amino benzene
- 1-hydroxy-2-amino-4,6-dinitrobenzene
- 1-P-hydroxyethoxy-2-P-hydroxyethylaminobenzene-5-nitrobenzene
- 1-methoxy-2-P-hydroxyethylaminobenzene-5-nitrobenzene
- 1-P-hydroxyethoxy-3-methylamino-4-nitrobenzene
- 1-P,y-dihydroxypropyloxy-3-methylamino-4-nitrobenzene
- 1-P-hydroxyethylamino-4-P,y-dihydroxypropyloxy-2-nitrobenzene
- 1-P,y-dihydroxypropyloxy-4-trifluoromethyl-2-nitrobenzene
- 1-P-hydroxyethylamino-4-trifluoromethyl-2-nitrobenzene
- 1-P-hydroxyethylamino-3-methyl-2-nitrobenzene
Among the azo, azomethine, methine and tetraazapentamethine direct dyes that may be used according to the invention, mention may be made of the cationic dyes described in patent applications WO 95/1 5144, WO 95/0 1772 and EP 7 14 954; FR 2 189 006, FR 2 285 85 1, FR 2 140 205, EP 1 378 544 and EP 1 674 073.

Thus, mention may be made most especially of the following dyes of formulae (I) to (IV), and preferably the compounds of formulae (I) and (III) below:

- 1-P-aminoethylamino-5-methoxy-2-nitrobenzene
- 1-hydroxy-2-chloro-6-ethylamino-4-nitrobenzene
- 1-hydroxy-2-chloro-6-amino-4-nitrobenzene
- 1-hydroxyethylamino-2-nitrobenzene
- 1-hydroxyethylamino-3-nitrobenzene
- 1-P-hydroxyethylamino-2-nitrobenzene
- 1-hydroxy-4-P-hydroxyethylamino-3-nitrobenzene.

Among the azo, azomethine, methine and tetraazapentamethine direct dyes that may be used according to the invention, mention may be made of the cationic dyes described in patent applications WO 95/1 5144, WO 95/0 1772 and EP 7 14 954; FR 2 189 006, FR 2 285 85 1, FR 2 140 205, EP 1 378 544 and EP 1 674 073.

Thus, mention may be made most especially of the following dyes of formulae (I) to (IV), and preferably the compounds of formulae (I) and (III) below:

\[
\begin{align*}
A & \quad D \quad D \\
N & \quad R_1 \\
X^- & \quad R_2 \\
R_3 \quad R_3' 
\end{align*}
\]

in which:
- D represents a nitrogen atom or a -CH group,
- \(R_1\) and \(R_2\), which may be identical or different, represent a hydrogen atom; a \(C_1\)-\(C_4\) alkyl radical which may be substituted with a -CN, -OH or -\(\text{NH}_2\) radical, or form, with a carbon atom of the benzene ring, a heterocycle optionally containing oxygen or nitrogen, 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 chosen from chloride, methyl sulfate and acetate,
- \(A\) represents a group chosen from structures \(A_1\) to \(A_{18}\), preferably \(A_1, A_4, A_7, A_{13}\) and \(A_{18}\), below:
in which $R_4$ represents a $C_4$ alkyl radical which may be substituted with a hydroxyl radical and $R_5$ represents a $C_4$ alkoxy radical;
in which:

\( R \) represents a hydrogen atom or a C1\-C4 alkyl radical,

\( R \) represents a hydrogen atom, an alkyl radical which may be substituted with a \(-\text{CN}\) radical or with an amino group, a 4\'-aminophenyl radical, or forms with \( R_6 \) a heterocycle optionally containing oxygen and/or nitrogen, which may be substituted with a C1\-C4 alkyl radical,

\( R_8 \) and \( R_9 \), which may be identical or different, represent a hydrogen atom, a halogen atom such as bromine, chlorine, iodine or fluorine, a C1\-C4 alkyl or C1\-C4 alkoxy radical, or a \(-\text{CN}\) radical,

\( X^- \) represents an anion preferably chosen from chloride, methyl sulfate and acetate,

\( B \) represents a group chosen from structures B1 to B6 below:

\[
\begin{align*}
\text{B1} & : \quad \text{N}^+ \quad \text{S}^- \quad \text{R}_{10} \\
\text{B2} & : \quad \text{N}^+ \quad \text{S}^- \quad \text{R}_{10} \\
\text{B3} & : \quad \text{N}^+ \quad \text{S}^- \quad \text{R}_{10} \\
\text{B4} & : \quad \text{N}^+ \quad \text{S}^- \quad \text{R}_{10} \\
\text{B5} & : \quad \text{N}^+ \quad \text{S}^- \quad \text{R}_{10} \\
\text{B6} & : \quad \text{N}^+ \quad \text{S}^- \quad \text{R}_{10}
\end{align*}
\]

in which \( R_{10} \) represents a C1\-C4 alkyl radical, \( R_{11} \) and \( R_{12} \), which may be identical or different, represent a hydrogen atom or a C1\-C4 alkyl radical;
in which:

$R_{i3}$ represents a hydrogen atom, a C1-C4 alkoxy radical, a halogen atom such as bromine, chlorine, iodine or fluorine, or an amino radical,

$R_{i4}$ represents a hydrogen atom, a C1-C4 alkyl radical or forms, with a carbon atom of the benzene ring, a heterocycle optionally containing oxygen and/or substituted with one or more C1-C4 alkyl groups,

$R_{i5}$ represents a hydrogen atom or a halogen atom such as bromine, chlorine, iodine or fluorine,

$R_{i6}$ and $R_{i7}$, which may be identical or different, represent a hydrogen atom or a C1-C4 alkyl radical,

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

$m = 0 \text{ or } 1$, preferably 1,

it being understood that when $R_{i3}$ represents an unsubstituted amino group, then $D_1$ and $D_2$ simultaneously represent a -CH group and $m = 0$,

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

$E$ represents a group chosen from structures $E_1$ to $E_8$, in particular $E_1$, $E_2$ and $E_7$, below:

![Diagram]

$E_1$  $E_2$
in which \( R' \) represents a \( C_1-C_4 \) alkyl radical; when \( m = 0 \) and \( D_i \) represents a nitrogen atom, then \( E \) may also denote a group of structure \( E_9 \) below:

\[
\begin{align*}
E_9 & \quad \text{in which } R' \text{ represents a } C_1-C_4 \text{ alkyl radical.}
\end{align*}
\]

\[
G \quad N \quad N \quad J \quad \text{(IV)}
\]

in which:

- the symbol \( G \) represents a group chosen from the structures \( G_i \) to \( G_3 \) below:

\[
\begin{align*}
G_i & \quad \text{in which structures } G_i \text{ to } G_3: \\
R_{i_8} & \text{ denotes a } C_1-C_4 \text{ alkyl radical, a phenyl radical which may be substituted with a } C_1-C_4 \text{ alkyl radical, or a halogen atom chosen from chlorine, bromine, iodine and fluorine;} \\
R_{i_9} & \text{ denotes a } C_1-C_4 \text{ alkyl radical or a phenyl radical;}
\end{align*}
\]

\[
\begin{align*}
N & \quad N \quad J
\end{align*}
\]
R20 and R21, which may be identical or different, represent a C1-C4 alkyl radical, a phenyl radical, or form together in Gi a benzene ring substituted with one or more C1-C4 alkyl, C1-C4 alkoxy or N02 radicals, or form together in G2 a benzene ring optionally substituted with one or more C1-C4 alkyl, C1-C4 alkoxy or N02 radicals;

R20 may also denote a hydrogen atom;

Z represents an oxygen or sulfur atom or a group -NR1 9;

M represents a group -CH, -CR (R denoting C1-C4 alkyl) or -NR22(X-)r;

K represents a group -CH, -CR (R denoting C1-C4 alkyl) or -NR22(X-)r;

P represents a group -CH, -CR (R denoting C1-C4 alkyl) or -NR22(X-)r;

r denotes 0 or 1;

R22 represents an O- atom, a C1-C4 alkoxy radical or a C1-C4 alkyl radical;

R23 and R24, which may be identical or different, represent a hydrogen atom or a halogen atom chosen from chlorine, bromine, iodine and fluorine, a C1-C4 alkyl or C1-C4 alkoxy radical, or an -N02 radical;

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

with the proviso that,

if R22 denotes O-, then r denotes zero;

if K or P or M denotes -N-(Ci-C4)alkyl X-, then R23 or R24 is preferably different than a hydrogen atom;

if K denotes -NR22(X-)r, then M= P= -CH, -CR;

if M denotes -NR22(X-)r, then K= P= -CH, -CR;

if P denotes -NR22(X-)r, then K= M and denotes -CH or -CR;

if Z denotes a sulfur atom with R2i denoting C1-C4 alkyl, then R2o is other than a hydrogen atom;

if Z denotes -NR22 with R1o denoting C1-C4 alkyl, then at least one of the radicals Ris, R2o or R2i of the group of structure G2 is other than a C1-C4 alkyl radical;

the symbol J represents:

-(a) a group of structure Ji below:
in which structure $J_1$:

$R_{25}$ represents a hydrogen atom, a halogen atom chosen from chlorine, bromine, iodine and fluorine, a C1-C4 alkyl or C1-C4 alkoxy radical, an -OH, -N0$_2$, -NHR$_{28}$, -NR$_{29}$R$_{30}$ or C1-C4 -NHCOalkyl radical, or forms with $R_{26}$ a 5- or 6-membered ring optionally containing one or more heteroatoms chosen from nitrogen, oxygen and sulfur;

$R_{26}$ represents a hydrogen atom, a halogen atom chosen from chlorine, bromine, iodine and fluorine, a C1-C4 alkyl or C1-C4 alkoxy radical, or forms with $R_{27}$ or $R_{28}$ a 5- or 6-membered ring optionally containing one or more heteroatoms chosen from nitrogen, oxygen and sulfur;

$R_{27}$ represents a hydrogen atom, an -OH radical, a radical -NHR$_{28}$ or a radical -NR$_{29}$R$_{30}$;

$R_{28}$ represents a hydrogen atom, a C1-C4 alkyl radical, a C1-C4 monohydroxyalkyl, C$_2$-C4 polyhydroxyalkyl radical or a phenyl radical;

$R_{29}$ and $R_{30}$, which may be identical or different, represent a C1-C4 alkyl radical, a C1-C4 monohydroxyalkyl or C$_2$-C4 polyhydroxyalkyl radical;

-(b) a 5- or 6-membered nitrogenous heterocyclic group, which may contain other heteroatoms and/or carbonyl groups and may be substituted with one or more C1-C4 alkyl, amino or phenyl radicals, and especially a group of structure $J_2$ below:

in which structure $J_2$:

$R_{31}$ and $R_{32}$, which may be identical or different, represent a hydrogen atom, a C1-C4 alkyl radical or a phenyl radical;
Y denotes a -CO- radical or a \( \overline{\delta^n} = \) radical;

\( n = 0 \) or \( 1 \), with, when \( n \) denotes \( 1 \), \( U \) denoting a -CO- radical.

In the structures of dyes (I) to (IV) defined above, the C1-C4 alkyl or alkoxy group preferably denotes methyl, ethyl, butyl, methoxy or ethoxy.

Among the compounds of formulae (I) and (III), the following compounds are preferred:

- Disperse Red 17
- Basic Red 22
- Basic Red 76
- Basic Yellow 57
- Basic Brown 16
- Basic Brown 17
- Disperse Black 9.

Mention may also be made of 1-(4'-aminodiphenylazo)-2-methy1-4-bis (P-hydroxyethyl)amino benzene.

Among the quinone direct dyes that may be mentioned are the following dyes:
- Disperse Red 15
- Solvent Violet 13
- Disperse Violet 1
- Disperse Violet 4
- Disperse Blue 1
- Disperse Violet 8
- Disperse Blue 3
- Disperse Red 11
- Disperse Blue 7
- Basic Blue 22
- Disperse Violet 15
- Basic Blue 99

and also the following compounds:
- 1-N-methylmorpholiniumpropylamino-4-hydroxyanthraquinone
  - 1-aminopropylamino-4-methylaminoanthraquinone
  - 1-aminopropylaminoanthraquinone
  - 5-P-hydroxyethyl-1,4-diaminoanthraquinone
  - 2-aminoethylaminoanthraquinone
  - 1,4-bis (P,y-dihydroxypropylamino)anthraquinone.

Among the azine dyes that may be mentioned are the following compounds:
- Basic Blue 17
- Basic Red 2.

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 may be used according to the invention, mention may be made of the following compounds:
- 2-β-hydroxyethy lamino -5- [bis (P-4'-hydroxy ethyl) amino] - anilino - 1,4-benzoquinone
- 2-P-hydroxyethylamino -5-(2'-methoxy -4'-amino) anilino - 1,4-benzoquinone
- 3-N-(2'-chloro -4'-hydroxy)phenylacetlylamino -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.

Among the dyes of tetraazapentamethine type that may be used according to the invention, mention may be made of the following compounds given in the table below, An being defined as previously:
X represents an anion preferably chosen from chloride, iodide, methyl sulfate, ethyl sulfate, acetate and perchlorate.

Among the polychromophoric dyes, mention may be made more particularly of symmetrical or non-symmetrical azo and/or azomethine (hydrazone) di- or trichromophoric dyes comprising, on the one hand, at least one optionally fused 5- or 6-membered aromatic heterocycle, comprising at least one quaternized nitrogen atom engaged in said heterocycle and optionally at least one other heteroatom (such as nitrogen, sulfur or oxygen), and, on the other hand, at least one optionally substituted phenyl or naphthyl group, optionally bearing at least one group OR with R representing a hydrogen atom, an optionally substituted Ci-C₆ alkyl radical, an optionally substituted phenyl nucleus, or at least one group N(R')₂ with R', which may be identical or different, representing a hydrogen atom, an optionally substituted Ci-C₆ alkyl radical or an optionally substituted phenyl nucleus; the radicals R' possibly forming, with the nitrogen atom to which they are attached, a saturated 5- or 6-membered heterocycle, or alternatively one and/or both the radicals R' may each form, with the carbon atom of the aromatic ring located ortho to the nitrogen atom, a saturated 5- or 6-membered heterocycle.

Aromatic cationic heterocycles that may preferably be mentioned include 5- or 6-membered rings containing 1 to 3 nitrogen atoms and preferably 1 or 2 nitrogen atoms, one being quaternized; said heterocycle moreover being optionally fused to a benzene nucleus. It should similarly be noted that the heterocycle may optionally comprise another heteroatom other than nitrogen, for instance sulfur or oxygen.

If the heterocycles or phenyl or naphthyl groups are substituted, they are substituted, for example, with one or more Ci-Cs
alkyl radicals optionally substituted with a hydroxyl, C1-C2 alkoxy, C2-C4 hydroxyalkoxy, acetylamino or amino group substituted with one or two C1-C4 alkyl radicals optionally bearing at least one hydroxyl group, or the two radicals possibly forming, with the nitrogen atom to which they are attached, a 5- or 6-membered heterocycle, optionally comprising another heteroatom identical to or different than nitrogen; a halogen atom; a hydroxyl group; a C1-C2 alkoxy radical; a C2-C4 hydroxyalkoxy radical; an amino radical; an amino radical substituted with one or two identical or different C1-C4 alkyl radicals, optionally bearing at least one hydroxyl group.

These polychromophores are connected together by means of at least one linker optionally comprising at least one quaternized nitrogen atom that may or may not be engaged in a saturated or unsaturated, optionally aromatic heterocycle.

Preferably, the linker is a linear, branched or cyclic C1-C20 alkyl chain, optionally interrupted with at least one heteroatom (such as nitrogen or oxygen) and/or with at least one group comprising such a heteroatom (CO or SO2), optionally interrupted with at least one heterocycle that may or may not be fused to a phenyl nucleus and comprising at least one quaternized nitrogen atom engaged in said ring and optionally at least one other heteroatom (such as oxygen, nitrogen or sulfur), optionally interrupted with at least one substituted or unsubstituted phenyl or naphthyl group, optionally at least one quaternary ammonium group substituted with two optionally substituted C1-C15 alkyl groups; the linker not comprising any nitro, nitroso or peroxy groups.

The bonding between the linker and each chromophore generally takes place via a heteroatom substituent on the phenyl or naphthyl nucleus or via the quaternized nitrogen atom of the cationic heterocycle.

The dye may comprise identical or different chromophores.


It is also possible to use the cationic direct dyes mentioned in patent applications: EP 1 006 153, which describes dyes comprising two chromophores of anthraquinone type connected via a linker of cationic type; EP 1 433 472, EP 1 433 474, EP 1 433 471 and EP 1 433 473, which describe identical or different dichromophoric dyes, connected via a cationic or non-cationic linker, and also EP 6 291 333, which especially describes dyes comprising three chromophores, one of them being an anthraquinone chromophore, to which are attached two chromophores of azo or diazacarbocyanin type or an isomer thereof.

Among the natural direct dyes that may be used according to the invention, mention may be made of lawsone, juglone, alizarin, purpurin, carminic acid, kermesic acid, purpurogallin, protocatechaldehyde, indigo, isatin, curcumin, spinulosin, apigenidin and orceins. It is also possible to use extracts or decoctions containing these natural dyes and especially henna-based poultices or extracts.

When they are present, the direct dye(s) advantageously represent an amount greater than 0.0001% to 10% by weight and preferably an amount greater than 0.005% to 5% by weight relative to the total weight of the inverse emulsion (A).

According to a third embodiment of the invention, the emulsions (A) and (B) do not comprise any direct dyes or any oxidation dyes (bases and couplers), or else, if they are present, their total content does not exceed 0.005% by weight relative to the total weight of each emulsion.

In this embodiment, the agent according to the invention is advantageously used for bleaching keratin fibres.

In this embodiment, the inverse emulsion (A) may advantageously comprise one or more solid or pasty adjuvants, which are preferably pulverulent. The adjuvants may then be chosen from clays, salts other than ammonium salts, anionic, nonionic, cationic or zwitterionic surfactants, natural or synthetic thickeners, optionally modified starch, glass beads, silica, Nylon, alumina, titanium dioxide,
zeolites, poly(methyl methacrylate) (PMMA), chitosan, maltodextrin, cyclodextrin, monosaccharides or disaccharides, for instance glucose, sucrose, sorbitol or fructose, zinc oxide, zirconium oxide, silica beads, talc, borosilicates, especially of calcium, polyethylene, polytetrafluoroethylene (PTFE), cellulose and derivatives thereof, superabsorbent compounds, magnesium or calcium carbonates, polyacrylamide, porous hydroxyapatite, sawdust, fucus powder, crosslinked polyvinylpyrrolidone, calcium alginate, active charcoal, poly(vinylidene chloride/acrylonitrile) particles, especially those sold under the general name Expancel® by the company Akzo Nobel under the particular references Expancel® WE or DE, and mixtures thereof.

In general, the emulsions (A) and (B) constitute a cosmetically acceptable medium optionally comprising one or more organic solvents.

Examples of organic solvents that may be mentioned include linear or branched C₂-C₄ alkanols, such as ethanol and isopropanol; glycerol; polyols and polyol ethers, for instance 2-butoxyethanol, propylene glycol, dipropylene glycol, propylene glycol monomethyl ether, diethylene glycol monomethyl ether and monoethyl ether, and also aromatic alcohols, such as benzyl alcohol or phenoxyethanol, and mixtures thereof.

Such organic solvents may be present in proportions preferably of between 1% and 40% by weight and more preferentially between 5% and 30% by weight relative to the total weight of each composition in which they are contained.

The emulsions (A) and/or (B) according to the present invention may also comprise one or more adjuvants, chosen from those conventionally used in compositions for dyeing and/or bleaching keratin fibres, such as conditioning polymers, in particular cationic polymers, organic thickeners other than the oil thickeners defined previously, with, in particular, anionic, cationic and nonionic polymeric associative thickeners, surfactants with an HLB of less than 8, antioxidants; penetrants; sequestrants; fragrances; dispersants; film-forming agents; ceramides; preserving agents; opacifiers.

The direct emulsion (B) may also comprise thickeners as described above for the inverse emulsion (A), and also anionic,
cationic, amphoteric and nonionic surfactants such as those described above for the inverse emulsion (A).

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

A subject of the present invention is also a process for dyeing and/or bleaching keratin fibres, comprising the application to the said fibres of the agent as described above.

According to the invention, the agent applied to the keratin fibres results from the mixing of the emulsions (A) and (B), this mixing being performed either before application to the keratin fibres (extemporaneous preparation) or directly on the keratin fibres (successive application to the fibres of the emulsions (A) and (B) without intermediate rinsing).

Thus, according to a first variant of the process according to the invention, the emulsions (A), and then (B), are applied to the wet or dry keratin fibres, successively and without intermediate rinsing.

According to a second variant of the process according to the invention, a composition obtained by extemporaneous mixing, before application, of the emulsions (A) and (B) is applied to the wet or dry keratin fibres.

In this case, the time between the mixing of the emulsions (A) and (B) and the application of the mixture to the hair then preferably does not exceed 30 minutes, preferably 10 minutes and more preferably 5 minutes.

Independently of the variant used, the weight ratio of the amount of inverse emulsion (A) used to the amount of direct emulsion (B) used may range from 0.2 to 3 and preferably from 0.3 to 1.

In addition, independently of the variant used, the mixture present on the fibres (resulting either from the extemporaneous mixing of the emulsions (A) and (B), or from the successive application of these compositions) is left in place for a time, generally from about 1 minute to 1 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.

Finally, a subject of the invention is also a multi-compartment dyeing and/or bleaching device or "kit", comprising a first compartment containing an inverse emulsion (A), and a second compartment containing a direct emulsion (B), the emulsions (A) and (B) being as described above.

This device may also comprise one or more compositions for washing and/or conditioning keratin fibres, which are intended to be applied before and/or after the dyeing and/or bleaching treatment according to the invention.

This device may advantageously be equipped with a means for dispensing the desired mixture on the hair, such as the devices described in patent FR 2 586 913.

Finally, the invention relates to the use of the agent as defined above for dyeing and/or bleaching keratin fibres, in particular human keratin fibres such as the hair.

The examples that follow serve to illustrate the invention without, however, being limiting in nature.

**EXAMPLE**

The oxidation dyeing inverse emulsion (A) below was prepared (in the table below, the amounts are expressed as weight percentages):

<table>
<thead>
<tr>
<th>Inverse emulsion comprising dye precursors (weight%)</th>
<th>CI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid petroleum jelly</td>
<td>51.5</td>
</tr>
<tr>
<td>Octyldodecanol</td>
<td>9</td>
</tr>
<tr>
<td>Distearyldimethylammonium-modified hectorite</td>
<td>1.3</td>
</tr>
<tr>
<td>Propylene carbonate</td>
<td>0.45</td>
</tr>
<tr>
<td>Oleyl alcohol 10 OE (1)</td>
<td>4.3</td>
</tr>
<tr>
<td>Propylene glycol</td>
<td>2</td>
</tr>
<tr>
<td>Ethanol</td>
<td>3</td>
</tr>
<tr>
<td>Hexylene glycol</td>
<td>1</td>
</tr>
<tr>
<td>Dipropylene glycol</td>
<td>1</td>
</tr>
</tbody>
</table>
Monoethanolamine | 4
---|---
POE/POP/POE (Poloxamer 184) | 13
Ascorbic acid | 0.25
para-Phenylenediamine | 0.03
Resorcinol | 0.04
1-Hydroxy-3-amino benzene | 0.002
1-β-Hydroxyethylhyoxy-2,4-diamino benzene dihydrochloride | 0.0003
N,N-Bis(2-hydroxyethyl)-p-phenylenediamine mono hydrate sulfate | 0.006
Water | qs 100

\(^{(1)}\) HLB = 12.4
\(^{(2)}\) HLB = 15

<table>
<thead>
<tr>
<th>Oxidizing direct emulsion (weight%)</th>
<th>C2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid paraffin</td>
<td>20</td>
</tr>
<tr>
<td>C16/C18 cetylstearyl alcohol (30/70)</td>
<td>8</td>
</tr>
<tr>
<td>Cetylstearyl alcohol 33 OE</td>
<td>3</td>
</tr>
<tr>
<td>Disodium tin hexahydroxide</td>
<td>0.04</td>
</tr>
<tr>
<td>Oxyethylendated rapeseed acid amide (4 OE)</td>
<td>1.5</td>
</tr>
<tr>
<td>Vitamin E</td>
<td>0.1</td>
</tr>
<tr>
<td>Glycerol</td>
<td>1</td>
</tr>
<tr>
<td>Hydrogen peroxide</td>
<td>6</td>
</tr>
<tr>
<td>Sodium stannate hexahydrate</td>
<td>0.04</td>
</tr>
<tr>
<td>Diethylenetriaminepentaaacetic acid</td>
<td>0.015</td>
</tr>
<tr>
<td>Tetrasodium pyrophosphate decahydrate</td>
<td>0.03</td>
</tr>
<tr>
<td>Phosphoric acid</td>
<td>qs pH = 3</td>
</tr>
<tr>
<td>Demineralized water</td>
<td>qs 100</td>
</tr>
</tbody>
</table>

At the time of the use, one part by weight of the direct emulsion C1 is mixed with one part by weight of the inverse emulsion C2.

The mixture is then applied to locks of natural hair containing 90% white hairs. After a leave-on time of 30 minutes at room temperature (23°C), the hair is rinsed, washed with a standard
shampoo and then dried. An ash-golden very light blond coloration is then obtained.
CLAIMS

1. Agent for dyeing and/or bleaching keratin fibres, comprising:

- a water-in-oil inverse emulsion (A) comprising:
  - 30% to 70% by weight, relative to the weight of the emulsion (A), of one or more oils not containing any carboxylic acid functions,
  - water,
  - one or more surfactants with an HLB value of greater than or equal to 8,
- one or more basifying agents,
- an oil-in-water direct emulsion (B) comprising:
  - water,
  - one or more oils not containing any carboxylic acid functions,
  - one or more oxidizing agents,
the total amount of the said oils contained in the mixture of emulsions (A) and (B) representing at least 20% by weight relative to the total weight of the said mixture.

2. Agent according to Claim 1, characterized in that the basifying agent is chosen from aqueous ammonia, alkali metal carbonates, alkanolamines and derivatives thereof, sodium hydroxide, potassium hydroxide and the compounds of formula (I) below:

\[
\begin{align*}
\text{Rx} & \quad \text{N} & \quad \text{W} & \quad \text{N} & \quad \text{Rz} \\
\text{Ry} & \quad \text{W} & \quad \text{Rx} & \quad \text{Rz}
\end{align*}
\]

in which W is a \(\text{Ci-C}_6\) alkylene residue optionally substituted with a hydroxyl group or a \(\text{Ci-C}_6\) alkyl radical; Rx, Ry, Rz and Rt, which may be identical or different, represent a hydrogen atom or a \(\text{Ci-C}_6\) alkyl, \(\text{Ci-C}_6\) hydroxyalkyl or \(\text{Ci-C}_6\) aminoalkyl radical; and is preferably chosen from alkanolamines.

3. Agent according to either of the preceding claims, characterized in that the oxidizing agent is chosen from hydrogen peroxide, urea peroxide, alkali metal bromates or ferricyanides, peroxygenated salts, preferably alkali metal or alkaline-earth metal persulfates, perborates and percarbonates, redox enzymes, preferably
laccases, peroxidases and 2-electron oxidoreductases, optionally in the presence of the respective donor or cofactor thereof; and is preferably hydrogen peroxide.

4. Agent according to any one of the preceding claims, characterized in that the inverse emulsion (A) comprises one or more oil thickeners.

5. Agent according to the preceding claim, characterized in that the thickener present in the inverse emulsion (A) is an organophilic clay chosen from optionally modified montmorillonite, bentonite, hectorite, attapulgite and sepiolite, and mixtures thereof.

6. Agent according to either of Claims 4 and 5, characterized in that the concentration of thickener in the inverse emulsion (A) is between 0.1% and 10% by weight, preferably ranging from 0.5% to 7% by weight and more preferentially ranging from 1% to 5% by weight relative to the total weight of the inverse emulsion (A).

7. Agent according to any one of the preceding claims, characterized in that the surfactant with an HLB value of greater than or equal to 8 is anionic or nonionic, preferably nonionic.

8. Agent according to any one of the preceding claims, characterized in that the surfactant with an HLB value of greater than or equal to 8 present in the inverse emulsion (A) is chosen from oxyalkylenated nonionic surfactants preferably belonging to the following families:
   - oxyethylenated alkylphenols,
   - OE/OP condensates,
   - oxyethylenated plant oils,
   - oxyethylenated fatty alcohols,
   - fatty acid esters of polyethylene glycols,
   - polyoxyethylenated fatty acid esters of sorbitol.

9. Agent according to any one of the preceding claims, characterized in that the concentration of surfactant with an HLB value of greater than or equal to 8 present in the inverse emulsion (A) is
between 1% and 20% by weight, preferably between 1% and 15% by weight and better still from 2% to 10% by weight relative to the total weight of the inverse emulsion (A).

10. Agent according to any one of the preceding claims, characterized in that the oil(s) not containing any carboxylic acid functions are chosen from hydrocarbons, non-silicone oils of animal, plants, mineral or synthetic origin, fatty alcohols, fatty acid esters and/or fatty alcohol esters, and silicones, and mixtures thereof; preferably from liquid petroleum jelly, polydecenes, liquid esters of fatty acids and/or of fatty alcohols, and liquid fatty alcohols, and mixtures thereof; and more preferably from liquid petroleum jelly, polydecenes and liquid fatty alcohols, and mixtures thereof.

11. Agent according to any one of the preceding claims, characterized in that the emulsion (B) contains from 5% to 50% by weight and preferably from 10% to 30% by weight, relative to the total weight of the emulsion (B), of one or more oils not containing any carboxylic acid functions.

12. Agent according to any one of the preceding claims, characterized in that the total amount of oil(s) not containing any carboxylic acid functions in the mixture of the emulsions (A) and (B) represents at least 25% by weight and preferably at least 30% by weight relative to the total weight of the mixture of these two emulsions.

13. Agent according to any one of the preceding claims, characterized in that the inverse emulsion (A) also comprises one or more oxidation dyes, chosen from oxidation bases, optionally combined with one or more couplers, and/or one or more direct dyes.

14. Agent according to any one of Claims 1 to 12, characterized in that the emulsions (A) and (B) comprise a total content of direct dye or of oxidation dye precursor (bases and couplers) not exceeding 0.005% by weight relative to the weight of each emulsion.
15. Process for dyeing and/or bleaching keratin fibres, comprising the application to the said wet or dry fibres, successively and without intermediate rinsing, of the emulsions (A) and then (B) as defined in any one of the preceding claims.

16. Process for dyeing and/or bleaching keratin fibres, comprising the application to the said wet or dry fibres of a composition obtained by extemporaneous mixing of the emulsions (A) and (B) as defined in any one of Claims 1 to 14.

17. Multi-compartment dyeing and/or bleaching device or "kit", comprising a first compartment containing an inverse emulsion (A), and a second compartment containing a direct emulsion (B), the emulsions (A) and (B) being as defined in any one of Claims 1 to 14.

18. Use of the agent as defined in any one of Claims 1 to 14, for dyeing and/or bleaching keratin fibres, in particular human keratin fibres such as the hair.
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
INV. A61Q5/08 A61Q5/10 A61K8/06 A61K8/22 A61K8/31
A61K8/34 A61K8/39

B. FIELDS SEARCHED
Minimum documentation searched (classification system followed by classification symbols)
A61Q A61K

Documentation searched other than minimum documentation, to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category* Citation of document, with indication, where appropriate, of the relevant passages Relevant to claim No.

Y EP 0 823 250 A2 (SHISEIDO CO LTD [JP]) 11 February 1998 (1998-02-11) page 2, line 12 - line 14 page 2, line 30 - line 37 page 2, line 51 - line 53 page 4, line 57 - page 5, line 3 claim; example 1-18

Y WO 03/011216 A2 (PRAGMATIC VISION INTERNATIONAL [US]; Mogi LeVich Irina M [RU]) 13 February 2003 (2003-02-13) claims; examples tables 9,10 1-18

Date of the actual completion of the international search
15 March 2011

Date of mailing of the international search report
25/03/2011

Name and mailing address of the ISA
European Patent Office, P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk Tel: (+31-70) 340-2040; Fax: (+31-70) 340-3016

Authorized officer
Dehicles, Alain

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"P" document published prior to the international filing date but later than the priority date claimed
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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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"Z" document member of the same patent family

Further documents are listed in the continuation of Box C. See patent family annex.
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<td>EP 1 716 839 A1 (OREAL [FR])&lt;br&gt;2 November 2006 (2006-11-02)&lt;br&gt;paragraphs [0001], [0010] - [0012], [0019], [0020]&lt;br&gt;claims; example&lt;br&gt;-----</td>
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<td>EP 0 308 825 A1 (HENKEL KGAA [DE])&lt;br&gt;29 March 1989 (1989-03-29)&lt;br&gt;page 2, line 2 - line 4&lt;br&gt;page 2, line 23 - line 25&lt;br&gt;page 2, line 47 - page 3, line 21&lt;br&gt;claims 1-3; example&lt;br&gt;-----</td>
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