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(54) Title: METHOD AND KIT FOR ALTERING SHAPE OF HUMAN KERATIN FIBRES

(57) Abstract: A method for altering the shape of human keratin fibres is disclosed, comprising the following steps: a reducing composition (A) comprising one or more sulfur-containing reducing agent (s) is applied onto the fibres; after a leave-on time of said composition (A), a neutralizing composition (B) comprising one or more oxidizing agent (s) is applied onto the fibres; and one or more solid polyethylene wax(es), present in said composition (A) or in a separate composition (C), is (are) applied onto the fibres. Also disclosed is a multi-compartment device or kit suitable for performing the method.



## METHOD AND KIT FOR ALTERING SHAPE OF HUMAN KERATIN FIBRES

The present invention relates to a method for altering the shape of human keratinous fibres, especially a method for permanent deformation of keratinous fibres such as the hair, comprising the application onto said fibres of a reducing composition and of an oxidizing composition, wherein a solid polyoxyethylene wax is further applied onto said fibres.

The present invention also relates to a multi-compartment device or "kit" that is suitable for performing the method according to the invention.

Many people are not satisfied with the appearance of their hair, especially those people who have curly hair usually wish to acquire smooth hair, and, conversely, those people who have straight hair wish to have curly hair.

One of the techniques commonly used in order to obtain permanent deformation of the hair involves a two-step procedure, the first step of which is to reduce the disulfide bridges present in the keratinous fibres, using a composition containing a suitable reducing agent (reduction step).

Once these disulfide bridges have been reduced, the hair is then shaped in the desired manner. This shaping step may involve frizzing the hair or else smoothing it, the result being dependent on the means employed to tension the hair and on the nature of the original keratinous fibres. This tensioning operation may be carried out before, during or after the application of the reducing composition to the hair. Once this first step has been performed, a neutralizing step is necessary in order to recreate the disulfide bridges and to stabilize the shape obtained. This operation is commonly carried out using a neutralizing composition (in a step also called the setting step).

The reducing compositions intended for smoothing or perming of the hair generally include reducing agents in the form of sulfites, bisulfites, alkylphosphines or, preferably, thiols. These reducing compositions are generally in the form of a thickened or unthickened lotion, a cream or a gel.

These compositions may also comprise alkaline agents.

The neutralizing compositions contain an oxidizing agent such as for example hydrogen peroxide.

This technique allows the hair to be waved (perming procedure) and/or smoothed (straightening). The new shape imposed on the hair by a chemical treatment as described above is durable over time and resistant particularly to the action of washing with water or using shampoos, as opposed to simple, conventional techniques of temporary deformation, such as setting.

However, such technique is sometimes considered as being damaging for the hair by the consumers, in particular those having fine or sensitized hair. After treatment, the hair is sometimes brittle and difficult to disentangle, and lacks conditioning properties such as softness, smoothness and shine.

There is therefore a need to develop methods for altering the shape of keratinous fibres which are devoid of all of the drawbacks described above. In particular, there is a need to improve the existing hair deformation methods, especially in terms of conditioning of the hair.

The applicant has found that it is possible to achieve these objectives by applying onto the fibres, in the course of the treatment, one or more solid polyoxyethylene wax.

The present invention thus concerns a method for altering the shape of human keratin fibres, wherein:

- a reducing composition (A) comprising one or more sulfur-containing reducing agent(s) is applied onto the fibres;
- after a leave-on time of said composition (A), a neutralizing composition (B) comprising one or more oxidizing agent(s) is applied onto the fibres; and
- one or more solid polyethylene wax(es), present in said composition (A) or in a separate composition (C), is (are) applied onto the fibres.

The method of the invention allows achieving a permanent deformation of the keratinous fibres, especially a smoothing or perming of keratinous fibres, in a very satisfactory way, while endowing said fibres with good cosmetic properties.

The method of the present invention allows reducing the potential hair damage that may occur during the deformation treatment. The method further allows achieving a better conditioning of the fibres at the end of the treatment. In particular, the hair treated with the method of the invention is smoother, stronger (less brittle), easier to disentangle, and softer than the

hair treated with a classical method that does not involve the use of a polyoxyethylene wax.

Advantageously, such an improvement is even more noticeable when the method of the invention involves a step of heating the keratin fibres.

Other subjects, characteristics, aspects and advantages of the present invention will emerge even 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 within that range.

The expression "at least one" is equivalent to the expression "one or more".

The present invention comprises a step of application of a reducing composition (A).

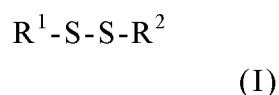
The reducing composition (A) of the present invention comprises at least one sulfur-containing reducing agent.

According to a preferred embodiment, said reducing agent is selected from the group consisting of disulfides, thiols, and mixtures thereof.

The expression "disulfide" here means a compound having at least one disulfide bond (-S-S-). As long as the disulfide includes at least one disulfide bond, the type of the disulfide is not limited.

It is preferable to use a linear organic disulfide which has a linear chemical structure.

The linear organic disulfide may be represented by the formula (I):



wherein:

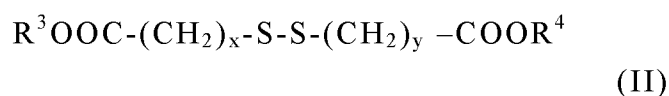
$\text{R}^1$  and  $\text{R}^2$  independently represent a linear, saturated or unsaturated hydrocarbon group, which may be interrupted by one or more hetero atoms selected from the group consisting of a sulfur atom, oxygen atom, nitrogen atom, silicon atom and phosphorous atom, and which may comprise one or more substituents selected from the group consisting of hydroxyl groups, cyano groups, ester groups, amino groups, amide groups, carbamoyl groups, carbamate groups, carboxylic acid groups, carbonate groups, hydrazinyl groups, ether groups, and ureido groups, and salts thereof.

It is possible that the linear organic disulfide compound be selected from the group consisting of dialkyldisulfides, dialkenyldisulfides,

dialkylaryldisulfides, N,N'-dithiodialkylcarboxylic acids or salts thereof (or dicarboxydisulfides or dialkoxycarbonyldisulfides), N,N'-dithiodialkyl esters, N,N'-dithiodialkyl amines and N,N'-dithiodialkyl amides.

According to a preferred embodiment, the disulfide compound is selected from N,N'-dithiodialkylcarboxylic acids or salts thereof.

As the dicarboxydisulfides or dialkoxycarbonyldisulfides, mention may be made of those represented by the following formula (II):



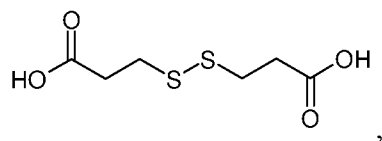
wherein:

$R^3$  and  $R^4$  independently denote a hydrogen atom, or an ammonium;

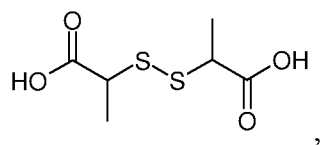
$x$  and  $y$  independently denote a number from 0 to 5, and preferably 0 to 3.

Examples of corresponding compounds include:

3,3'-dithiodipropionic acid (disulfide of mercaptopropionic acid) represented by the following formula:



2,2'-dithiodipropionic acid (dithiodilactic acid) represented by the following formula:



Diammonium dithiodiglycolate represented by the following formula:



It is preferred that the disulfide be selected from the group consisting of dithiodiglycolic acid and salts thereof.

Examples of such products are available on the market, such as the product sold by the company Evans Chemetics under the name Di-Ammonium Dithiodiglocolate 40%.

The reducing agent used in the present invention may also comprise at least one thiol.

The expression "thiol" here means a compound having at least one thiol group (-SH). As long as the thiol includes at least one thiol group, the type of the thiol is not limited.

The thiol may preferably be chosen from the group consisting of thioglycolic acid and derivatives thereof, in particular esters thereof such as glycerol or glycol monothioglycolate; thiolactic acid and derivatives thereof, in particular esters thereof such as glycerol monothiolactate; 3-mercaptopropionic acid and derivatives thereof, in particular esters thereof such as glycerol 3-mercaptopropionate and ethyleneglycol 3-mercaptopropionate; cysteamine and derivatives thereof, in particular C<sub>1-4</sub> acyl derivatives thereof such as N-acetylcysteamine and N-propionylcysteamine; mono-thioglycerol and derivatives thereof, in particular esters; cysteine and derivatives thereof, in particular esters such as N-acetylcysteine, N-alkanoylcysteine and cysteine alkyl esters; and salts thereof.

It is preferred that the at least one thiol be selected from the group consisting of thioglycolic acid, thiolactic acid, and salts thereof.

Mentions of such products may be made to the one, for example, sold under the name Thioglycolic acid by the company Bruno Bock.

Said reducing agent(s) is (are) preferably present in an amount ranging from 0.1% to 20% by weight, preferably from 0.2% to 15% by weight and more preferably from 1% to 10% by weight relative to the total weight of composition (A).

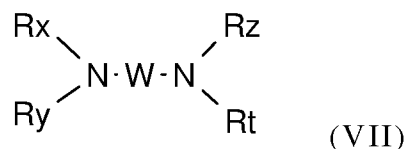
According to a preferred embodiment of the present invention, the reducing composition (A) further contains one or more alkaline agent(s).

The alkaline agent(s) used in composition (A) may be any agent capable of increasing the pH of the composition in which it is present. The alkaline agent may be a Brönsted-Lowry or Lewis base. It may be mineral or organic.

In particular, the alkaline agent(s) may be chosen from:

- a) aqueous ammonia,
- b) alkanolamines such as mono-, di- and triethanolamine, isopropanolamine and 2-amino-2-methyl-1-propanol, and also derivatives thereof,
- c) oxyethylenated and/or oxypropylenated ethylenediamines,

- d) mineral or organic hydroxides,
- e) alkali metal silicates such as sodium metasilicates,
- f) amino acids, preferably basic amino acids, such as arginine, lysine, ornithine, citrulline and histidine,
- g) carbonates and bicarbonates, particularly of a primary amine, secondary amine or tertiary amine, or of an alkali metal or alkaline-earth metal, or of ammonium, and
- h) the compounds of formula (VII) below:



in which W is a C<sub>1</sub>-C<sub>6</sub> alkylene residue optionally substituted with a hydroxyl group or a C<sub>1</sub>-C<sub>6</sub> alkyl radical; Rx, Ry, Rz and Rt, which may be identical or different, represent a hydrogen atom or a C<sub>1</sub>-C<sub>6</sub> alkyl, C<sub>1</sub>-C<sub>6</sub> hydroxyalkyl or C<sub>1</sub>-C<sub>6</sub> aminoalkyl radical.

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

The mineral or organic hydroxides are preferably chosen from hydroxides of an alkali metal, hydroxides of an alkaline-earth metal, for instance sodium hydroxide or potassium hydroxide, hydroxides of a transition metal, such as hydroxides of metals from groups III, IV, V and VI of the Periodic Table of the Elements, hydroxides of lanthanides or actinides, quaternary ammonium hydroxides and guanidinium hydroxide.

The hydroxide may be formed *in situ*, for instance guanidine hydroxide, by reacting calcium hydroxide and guanidine carbonate.

The preferred alkaline agents are in particular aqueous ammonia, ammonium carbonate, ammonium bicarbonate, arginine, monoethanolamine and 2-amino-2-methyl-1-propanol.

More preferably, the alkaline agent is ammonium bicarbonate.

Mentions may be made of the product available on the market, such as the one under the name Bicarbonate D'ammonium sold by the company Pesquisa.

The alkaline agent(s) as defined previously may represent, for example, from 0.001% to 20% by weight, and preferably from 0.005% to 10% by weight, relative to the total weight of composition (A).

The concentration of alkaline agent(s) is especially adjusted as a function of the pH desired for the composition.

Preferably, the composition (A) used in the method of the present invention has a pH ranging from 7 to 10 and more preferentially from 7 to 9.5.

The neutralizing composition (B) used in the method of the present invention comprises one or more oxidizing agents.

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

Preferably, composition (B) does not contain any peroxygenated salt.

The oxidizing agent is preferably chosen from hydrogen peroxide, sodium bromate, and mixtures thereof, and is preferably used as an aqueous solution. Thus, according to a preferred embodiment composition (B) contains water and at least one oxidizing agent chosen from hydrogen peroxide, sodium bromate, and mixtures thereof. More preferably, composition (B) contains water and sodium bromate.

The oxidizing agent(s) as defined previously may represent from 0.01% to 15% by weight and preferably from 0.1% to 10% by weight, relative to the total weight of composition (B).

When hydrogen peroxide is present in composition (B), said composition may also comprise one or more hydrogen peroxide stabilizers.

The composition (B) used according to the invention may comprise one or more pH regulators, which may be chosen from alkaline agents as described above and/or acidic agents.

The acidic agents that may be used according to the present invention may preferably be chosen from hydrochloric acid, (ortho)phosphoric acid, sulfuric acid, boric acid, and also carboxylic acids, for instance acetic acid, lactic acid or citric acid, or sulfonic acids.

Preferably, composition (B) used in the method according to the invention has a pH ranging from 1 to 10.

When hydrogen peroxide is present in composition (B), the pH of composition (B) preferably ranges from 1 to 5.

When sodium bromate is present in composition (B), preferably, the pH of composition (B) ranges from 2 to 10, more preferably from 3 to 8.

The method of the present invention involves the application onto the keratinic fibres of one or more solid polyethylene wax(es).

Said wax may be present in said composition (A) or in a separate composition (C) which is applied onto the fibres.

According to a first embodiment, said polyethylene wax is present in composition (A).

According to a second embodiment, said polyethylene wax is present in a separate composition (C) which is applied onto the fibres before the application of composition (A), after the application of composition (B), or between the application of composition (A) and the application of composition (B). In this second embodiment, composition (C) is preferably applied between the application of composition (A) and the application of composition (B), that is to say, after the application of composition (A) and before the application of composition (B).

By solid wax is meant, in the sense of the present invention, a substance which is not liquid at room temperature (25°C) and at atmospheric pressure (760 mm Hg, or  $1.013 \times 10^5$  Pa), more particularly a compound which is solid or a compound which has a viscosity of greater than 2 Pa.s at a shear rate of  $1\text{s}^{-1}$  under the aforementioned conditions.

The solid polyethylene waxes useful in the present invention have a melting temperature of greater than room temperature, preferably a melting temperature of greater than or equal to 50°C, more preferably a melting point in the range from 60 to 140°C, even more preferably in the range from 90 to 130°C.

The melting points of the wax(es) may be determined according to known methods or apparatus such as by differential scanning calorimetry, Banc Koffler device, melting point apparatus, and slip melting point measurements.

The waxes used in the method of the present invention are made of polyethylene.

According to a preferred embodiment, said polyethylene wax is under the form of a dispersion of solid particles, which means that composition (A) and/or composition (C) contain a dispersion of polyethylene wax particles.

Such particles may have an average size ranging from 1 to 100 microns, preferably from 2 to 50 microns, more preferably from 5 to 25 microns.

The term “size” as used above refers to the diameter of the particles. For non-spherical particles, the particle size refers to the largest diameter of the particles, i.e., the diameter in the dimension having the largest diameter.

Preferably, the wax particles used in the present invention have a narrow particle size distribution, that is, the average difference in the particle sizes is not more than about 20 microns, or not more than about 15 microns, or not more than about 10 microns, or not more than about 8 microns, or not more than about 6 microns, or not more than about 2 microns.

The size and the size distribution of the wax particles can be determined using the test defined in D 4464 (Standard Test Method for Particle Size Distribution of Catalytic Materials by Laser Light Scattering).

The wax particles may have any shape. The shape of the wax particles is preferably spherical, ellipsoidal or oval, and even more preferably spherical. The terms “spherical” or ellipsoidal” or “oval” as used herein also mean that the solid wax particle has a uniform and substantially spherical or ellipsoidal or oval shape. The term “substantially” as used in the context of the shape of a spherical particle means that the particle is of substantially isotropic shape, i.e., it has a relatively regular morphology. The wax particles are preferably substantially homogeneous with respect to their shape, which means that 50% or more of the wax particles are of the same (for example spherical, ellipsoidal or oval) shape.

The particle size, particle size distribution, and shape of the solid wax particle of the present disclosure may be evaluated by any known method such as in particular laser diffraction, and image analysis (optical microscopy).

Examples of commercially available polyethylene waxes useful in the present invention include the product sold under the trade name Kostene C-30 by the company Koster Keunen, and the products sold under the series name Micropoly by the company Micro Powders, such as the products Micropoly 1160S, Micropoly 200, Micropoly 220, Micropoly 230, Micropoly 250, and preferably Micropoly 1160S.

The polyethylene wax is preferably present in an amount ranging from 0.2 to 10% by weight, preferably from 0.5 to 5% by weight, with regard to the weight of the composition containing it.

When the polyethylene wax is under the form of a dispersion of solid particles, the composition containing said dispersion of polyethylene wax particles preferably further contains one or more polymeric thickening agent(s).

Such agents can be chosen from polymeric thickeners such as cellulose-based thickeners (hydroxyethylcellulose, hydroxypropylcellulose or carboxymethylcellulose); guar gum and derivatives thereof (hydroxypropyl guar); gums of microbial origin (xanthan gum, scleroglucan gum); acrylic acid or acrylamidopropanesulfonic acid crosslinked homopolymers and copolymers; and associative polymers, that is to say polymers comprising hydrophilic regions and fatty-chain hydrophobic regions (alkyl or alkenyl containing at least 10 carbon atoms) that are capable, in an aqueous medium, of reversibly combining with each other or with other molecules.

According to a preferred embodiment of the invention, the polymeric thickeners comprises at least one copolymer comprising at least one monomer of 2-acrylamido-2-methylpropanesulfonic acid (AMPS<sup>®</sup>), at least one monomer with a hydrophobic group and at least one ethylenically unsaturated monomer which does not comprise any hydrophobic groups.

Within the context of the present invention, the term "hydrophobic group" is understood to be a hydrocarbon-based, branched or unbranched, saturated or unsaturated fatty chain comprising from 6 to 50 carbon atoms.

The copolymer(s) may be crosslinked in the presence of a crosslinking agent.

The term "crosslinked copolymer" is understood to be a non-linear copolymer which is in the form of a three-dimensional network that is insoluble in water but swellable in water, leading to the production of a chemical gel.

The crosslinking agent is chosen from polyolefinically unsaturated compounds commonly used for the crosslinking of polymers obtained by radical polymerization.

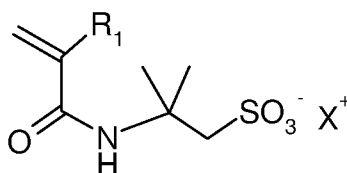
The crosslinking agent is more particularly chosen from ethylene glycol dimethacrylate, tetraallyloxyethane, ethylene glycol diacrylate, diallylurea, triallylamine, trimethylolpropane triacrylate or methylenebisacrylamide, or a mixture of these compounds.

Preferably, the crosslinking agent is trimethylolpropane triacrylate.

Preferably, the AMPS<sup>®</sup> copolymer(s) are crosslinked by a crosslinking agent, preferably trimethylolpropane triacrylate.

The 2-acrylamido-2-methylpropanesulfonic acid monomer(s) of the copolymer contained in the composition in accordance with the invention are in free form or are partially or completely neutralized by an inorganic base (sodium hydroxide, potassium hydroxide or aqueous ammonia) or an organic base, such as mono-, di- or triethanolamine, an aminomethylpropanediol, N-methylglucamine, basic amino acids, such as arginine and lysine, and the mixture of these compounds.

According to the invention, the 2-acrylamido-2-methylpropanesulfonic acid (AMPS<sup>®</sup>) monomers preferably correspond to the following general formula (1):



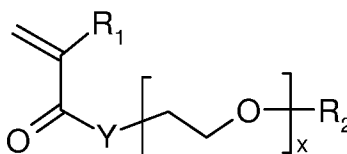
(1)

in which  $X^+$  denotes a cationic counterion, in particular an alkali metal or alkaline-earth metal, or an ammonium, preferably ammonium, or a mixture of cations;  $R_1$  denotes a hydrogen atom or a linear or branched  $C_1$ - $C_6$  alkyl radical such as methyl, and  $R_1$  preferably denotes a hydrogen atom.

Preferably, the 2-acrylamido-2-methylpropanesulfonic acid monomer(s) according to the invention are completely salified, preferably in the form of the ammonium salt.

The AMPS<sup>®</sup> copolymer(s) comprise at least one monomer with a hydrophobic group which is preferably an ethylenically unsaturated monomer comprising at least one fatty hydrocarbon-based chain comprising from 6 to 50 carbon atoms, preferably from 6 to 22 and more particularly from 12 to 18 carbon atoms.

The monomer with a hydrophobic group is preferably chosen from the acrylates or acrylamides of formula (2):



(2)

in which  $R_1$  denotes a hydrogen atom or a linear or branched  $C_1$ - $C_6$  alkyl radical, preferably methyl; Y denotes O or NH;  $R_2$  denotes a hydrocarbon-based radical comprising from 6 to 50 carbon atoms and more preferably from 6 to 22 carbon atoms and even more preferably from 12 to 18 carbon atoms; x denotes a number ranging from 0 to 100.

According to one particular embodiment of the invention, in formula (2), Y denotes an oxygen atom.

According to one particular embodiment of the invention, in formula (2), the  $R_1$  group represents a methyl.

According to one particular embodiment of the invention, x represents an integer between 3 and 25, and x is preferably equal to 4.

According to one particular embodiment of the invention, in formula (2), the  $R_2$  group represents an alkyl radical comprising from 12 to 18 carbon atoms.

According to one even more preferred embodiment of the invention, in formula (2), Y denotes an oxygen atom, the  $R_1$  group represents a methyl, the  $R_2$  group represents an alkyl radical comprising from 12 to 18 carbon atoms, and x represents an integer between 3 and 25, and x is preferably equal to 4.

According to one particular embodiment of the invention, the hydrophobic monomer of formula (2) is tetraethoxylated (4EO) lauryl methacrylate, corresponding to the compound of formula (2) in which the Y group denotes O, the  $R_2$  group represents an alkyl radical comprising 12 carbon atoms and x is equal to 4.

Preferably, the monomer with a hydrophobic group is tetraethoxylated lauryl methacrylate.

According to one particular embodiment of the invention, the AMPS<sup>®</sup> copolymer may comprise at least one monomer of formula (2) in which x is equal to 0, with Y representing an oxygen atom, the  $R_1$  group representing a methyl, and the  $R_2$  group representing an alkyl radical comprising from 12 to 18 carbon atoms.

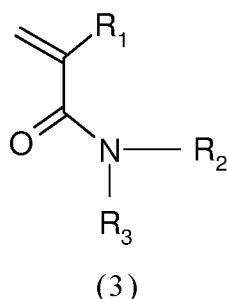
In this embodiment, the monomer with a hydrophobic group is preferably lauryl methacrylate.

According to one particular embodiment, the AMPS<sup>®</sup> copolymer comprises at least one monomer of formula (2) in which x is equal to 0, with Y preferably denoting an oxygen atom, the  $R_1$  group representing a methyl, and the  $R_2$  group representing an alkyl radical comprising from 12 to 18

carbon atoms, and at least one monomer of formula (2) in which Y denotes an oxygen atom, the  $R_1$  group represents a methyl, the  $R_2$  group represents an alkyl radical comprising from 12 to 18 carbon atoms, and x represents an integer between 3 and 25, and x is preferably equal to 4.

Preferably, the AMPS<sup>®</sup> copolymer comprises, as monomers with a hydrophobic group, lauryl methacrylate and tetraethoxylated lauryl methacrylate.

The AMPS<sup>®</sup> copolymer(s) also comprise at least one ethylenically unsaturated monomer, which does not comprise any hydrophobic groups, preferably corresponding to the following general formula (3):



in which  $R_1$  denotes a hydrogen atom or a linear or branched  $C_1$ - $C_4$  alkyl radical,  $R_1$  preferably denotes a hydrogen atom,  $R_2$  denotes a linear or branched  $C_1$ - $C_4$  alkyl radical and  $R_3$  denotes a linear or branched  $C_1$ - $C_4$  alkyl radical and  $R_2$  and  $R_3$  preferably denote a methyl.

The ethylenically unsaturated monomer which does not comprise any hydrophobic groups is chosen from (meth)acrylamides such as acrylamide, (meth)acrylic acids and the esters ((meth)acrylates) thereof, such as 2-hydroxyethyl acrylate, vinylpyrrolidones, N-( $C_1$ - $C_4$ )alkylacrylamides, and N,N-di( $C_1$ - $C_4$ )alkylacrylamides such as N,N-dimethylacrylamide.

Preferably, the ethylenically unsaturated monomer which does not comprise any hydrophobic groups is N,N-dimethylacrylamide.

Preferably, the AMPS<sup>®</sup> copolymer is chosen from the copolymers of 2-acrylamido-2-methylpropanesulfonic acid, preferably completely salified with ammonium (ammonium acryloyl dimethyl taurate), of N,N-dimethylacrylamide, of tetraethoxylated lauryl methacrylate and of lauryl methacrylate, preferably crosslinked, such as for example the copolymer sold under the name Sepimax zen by Seppic, with INCI name Polyacrylate crosspolymer-6.

The content of the polymeric thickening agent(s) if they are present, usually ranges from 0.01% to 10% by weight relative to the weight of the

composition containing it (them), preferably from 0.05% to 5% by weight and even more preferably from 0.1 to 2% by weight.

The compositions (A), (B) and (C) used in the method of the present invention advantageously comprise water or a mixture of water and of one or more cosmetically acceptable solvents chosen from C<sub>1</sub>-C<sub>4</sub> lower alcohols, such as ethanol, isopropanol, tert-butanol or n-butanol, polyols such as propylene glycol, polyol ethers, C<sub>5</sub>-C<sub>10</sub> alkanes, C<sub>3</sub>-C<sub>4</sub> ketones, such as acetone and methyl ethyl ketone, C<sub>1</sub>-C<sub>4</sub> alkyl acetates, such as methyl acetate, ethyl acetate and butyl acetate, dimethoxyethane and diethoxyethane, and mixtures thereof.

The compositions (A), (B) and (C) used in the method of the present invention may further comprise one or more surfactants, that can be chosen from anionic, amphoteric, zwitterionic, cationic and nonionic surfactants, and preferentially nonionic surfactants.

According to a preferred embodiment, one or more of composition(s) (A), (B) and (C) used in the method of the present invention further comprises at least one nonionic surfactant.

Examples of nonionic surfactants that may be used in the compositions used in the present invention are described, for example, in the "Handbook of Surfactants" by M.R. Porter, published by Blackie & Son (Glasgow and London), 1991, pp. 116-178.

Mention may be made of oxyalkylenated nonionic surfactants such as in particular:

- oxyalkylenated (C<sub>8</sub>-C<sub>24</sub>)alkylphenols;
- saturated or unsaturated, linear or branched, oxyalkylenated C<sub>8</sub>-C<sub>30</sub> alcohols;
- saturated or unsaturated, linear or branched, oxyalkylenated C<sub>8</sub>-C<sub>30</sub> amides;
- esters of saturated or unsaturated, linear or branched, C<sub>8</sub>-C<sub>30</sub> acids and of polyethylene glycols;
- polyoxyethylenated esters of saturated or unsaturated, linear or branched, C<sub>8</sub>-C<sub>30</sub> acids and of sorbitol;
- esters of fatty acids and of sucrose;
- (C<sub>8</sub>-C<sub>30</sub>)alkylpolyglycosides, (C<sub>8</sub>-C<sub>30</sub>)alkenylpolyglycosides, which are optionally oxyalkylenated (0 to 10 oxyalkylene units) and which comprise 1 to 15 glucose units, (C<sub>8</sub>-C<sub>30</sub>)alkylglucoside esters;
- saturated or unsaturated, oxyethylenated plant oils;

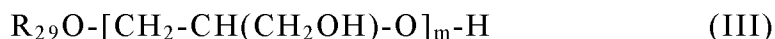
- condensates of ethylene oxide and/or of propylene oxide, inter alia, alone or as mixtures;
- N-(C<sub>8</sub>-C<sub>30</sub>)alkylglucamine derivatives and N-(C<sub>8</sub>-C<sub>30</sub>)acylmethylglucamine derivatives;
- aldobionamides;
- amine oxides;
- oxyethylenated and/or oxypropylenated silicones;

the surfactants containing a number of moles of ethylene oxide and/or of propylene oxide ranging advantageously from 1 to 100, more particularly from 2 to 100, preferably from 2 to 50 and more advantageously from 2 to 30. Advantageously, the nonionic surfactants do not comprise any oxypropylene units.

In accordance with a preferred embodiment of the invention, the oxyalkylenated nonionic surfactants are chosen from oxyethylenated C<sub>8</sub>-C<sub>30</sub> alcohols comprising from 1 to 100 mol and more particularly from 2 to 100 mol of ethylene oxide; polyoxyethylenated esters of saturated or unsaturated, linear or branched C<sub>8</sub>-C<sub>30</sub> acids and of sorbitan comprising from 1 to 100 mol and better still from 2 to 100 mol of ethylene oxide.

As examples of monoglycerolated or polyglycerolated nonionic surfactants, monoglycerolated or polyglycerolated C<sub>8</sub>-C<sub>40</sub> alcohols are preferably used.

In particular, the monoglycerolated or polyglycerolated C<sub>8</sub>-C<sub>40</sub> alcohols correspond to formula (III) below:



in which formula (III):

- R<sub>29</sub> represents a linear or branched C<sub>8</sub>-C<sub>40</sub> and preferably C<sub>8</sub>-C<sub>30</sub> alkyl or alkenyl radical; and
- m represents a number ranging from 1 to 30 and preferably from 1 to 10.

As examples of compounds of formula (III) that are suitable for use in the context of the invention, mention may be made of lauryl alcohol containing 4 mol of glycerol (INCI name: Polyglyceryl-4 Lauryl Ether), lauryl alcohol containing 1.5 mol of glycerol, oleyl alcohol containing 4 mol of glycerol (INCI name: Polyglyceryl-4 Oleyl Ether), oleyl alcohol containing 2 mol of glycerol (INCI name: Polyglyceryl-2 Oleyl Ether),

cetearyl alcohol comprising 2 mol of glycerol, cetearyl alcohol comprising 6 mol of glycerol, oleocetyl alcohol comprising 6 mol of glycerol and octadecanol comprising 6 mol of glycerol.

The alcohol of formula (III) may represent a mixture of alcohols in the same way that the value of  $m$  represents a statistical value, which means that, in a commercial product, several species of polyglycerolated fatty alcohols may coexist in the form of a mixture.

Further preferred nonionic surfactants are chosen from polyoxyethylenated sorbitol esters, polyoxyethylenated fatty alcohols, alkylpolyglucosides, and mixtures thereof.

The surfactant(s) may be present in anyone of compositions (A), (B), or (C) according to the invention in a content ranging from 0.1% to 20% by weight and better still from 0.5% to 10% by weight relative to the total weight of the each composition containing them.

According to a preferred embodiment, the method according to the invention comprises the following steps:

- applying the reducing composition (A) as described previously to wet or dry hair, and then
- leaving composition (A) to stand on the hair, during a leave-on time ranging from 1 to 60 minutes and preferably from 2 to 30 minutes, and then
  - optionally rinsing the hair with water,
  - optionally rubbing and/or disentangling the hair, and then
- applying the neutralizing composition (B) as described previously, to the wet hair, and then
- leaving composition (B) to stand on the hair, during a leave-on time ranging from 30 seconds to 15 minutes and preferably from 1 to 10 minutes, and then
- rinsing the hair with water.

Preferably, the hair is rinsed between application of composition (A) and composition (B).

The hair may then be dried, for example by means of a drying hood or a hairdryer, or may be left in the open air.

When the polyethylene wax is applied in a separate composition (C), such composition (C) can be applied at any stage of the method, and preferably between application of composition (A) and application of composition (B).

Even more preferably, a heating step is performed after application of the composition (C).

Thus, according to a particularly preferred embodiment of the invention, the method comprises the following steps:

- applying the reducing composition (A) onto the hair, and then
- leaving composition (A) to stand on the hair, during a leave-on time ranging from 1 to 60 minutes and preferably from 2 to 30 minutes, and then
- rinsing the hair with water, then
- applying composition (C) onto the hair, then
- heating the hair at a temperature ranging from 80 to 160°C, preferably from 100 to 140°C, and even more preferably of 120°C, then
- applying the neutralizing composition (B) onto the hair,
- leaving composition (B) to stand on the hair, during a leave-on time ranging from 30 seconds to 15 minutes and preferably from 1 to 10 minutes, and then
- rinsing the hair with water.

In order to obtain a substantial alteration of the shape of the keratinous fibres, the method of the invention preferably includes placing said fibres under mechanical tension. The mechanical tension can be applied during all steps of the claimed method, or during particular steps thereof.

According to a preferred embodiment, the fibres are placed under mechanical tension at least when they are in contact with the reducing composition (A), as this composition is applied in order to reduce the disulfide links in the keratin. In this embodiment the keratinous fibres are placed under mechanical tension before, during or after application of the reducing composition (A).

When a perming operation is desired, preference is given to using mechanical hair-shaping means such as curlers in order to place the keratinous fibres under tension. The reducing composition (A) according to the invention can be applied before, during or after said hair-shaping means, preferably after.

The reducing composition (A) may be applied to wetted hair which has been wound beforehand onto rollers with a diameter of from 2 to 30 mm. The reducing composition may also be applied in line with the winding of the hair.

Following application of the reducing composition according to the invention, it is also possible to subject the whole hair to a heat treatment by

heating at a temperature of between 30 and 250°C for all or part of the leave-on time. In practice, this operation may be performed using a hairstyling hood, a hairdryer, a round or flat iron, an infrared ray dispenser and other heating appliances.

In particular it is possible, both as heating means and as hair-shaping means, to use heating tongs at a temperature of between 60 and 230°C, and preferably between 120 and 230°C, the heating tongs being preferably used after the step of interim rinsing following the application of the reducing composition.

The curler itself may be a heating means.

In the case of a hair relaxing or straightening process, after the reducing composition (A) is applied to the hair, the hair can then be subjected to mechanical deformation for fixing the hair in its new shape, by means of a hair straightening operation, with a wide-toothed comb, with the back of a comb, by hand or with a brush.

This application may also be followed with a heating treatment, especially using an iron.

The straightening of the hair may also be performed, totally or partly, using a heating iron at between 60 and 230°C and preferably between 120 and 230°C.

After the permanent deformation treatment method has been performed, the keratinous fibres are preferably rinsed thoroughly, generally with water.

The keratinous fibres may then be washed with a shampoo, rinsed and dried or left to dry.

The permanent deformation treatment method is preferably a method of perming human keratinous fibres such as the hair.

At last, the present invention concerns a kit for altering the shape of human keratin fibres, comprising at least two compartments:

- a first compartment containing a reducing composition (A) as described above; and
- a second compartment containing a neutralizing composition (B) as described above.

According to a first embodiment, the kit of the invention contains at least two compartments and the composition (A) contains one or more solid polyethylene wax(es) as described above.

According to a second embodiment, the kit of the invention contains at least three compartments, namely, a first and a second compartment as defined above, and a third compartment containing a composition (C) comprising one or more solid polyethylene wax(es) as described above.

The kit thus contains compositions (A), (B) and optionally (C) used in the invention packaged in separate compartments. The kit may further contain suitable identical or different application means, such as fine brushes, coarse brushes or sponges.

The abovementioned kit may also be equipped with means for dispensing the desired mixture on the hair, such as, for instance the device described in patent FR 2 586 913.

The examples that follow are given purely as illustrations of the present invention.

#### EXAMPLES:

The compositions containing the ingredients hereunder were prepared, with all amounts expressed by percentages by weight of active matter with regard to the total weight of each composition.

Reducing composition (A):

|                                                                                                       |           |
|-------------------------------------------------------------------------------------------------------|-----------|
| PPG-5-CETETH-20 (SP Procetyl AWS from Croda)                                                          | 3         |
| MINERAL OIL (Marcol from Exxonmobil Chemical)                                                         | 4         |
| CETEARYL ALCOHOL (and) CETETH-10 PHOSPHATE<br>(Crodafos CES from Croda, with 75% of cetearyl alcohol) | 3.5       |
| CETEARYL ALCOHOL (Lanette O OR from Basf)                                                             | 5.0       |
| THIOGLYCOLIC ACID (Thioglycolic acid from Bruno Bock)                                                 | 9         |
| ETHANOLAMINE                                                                                          | 12.8      |
| EDTA                                                                                                  | 0.1       |
| DIAMMONIUM DITHIODIGLYCOLATE (Di-Ammonium<br>Dithiodiglocolate 40% from Evans Chemetics)              | 1.0       |
| AMMONIUM BICARBONATE (Bicarbonate D'ammonium<br>from Pesquisa)                                        | 2.30      |
| FRAGRANCE                                                                                             | 0.60      |
| WATER                                                                                                 | QS to 100 |

Neutralizing composition (B):

|                                                                                |           |
|--------------------------------------------------------------------------------|-----------|
| SODIUM BROMATE (Sodium Bromate from Bromine)                                   | 8.00      |
| TRISODIUM PHOSPHATE (Trisodium Phosphate from<br>Merck)                        | 0.50      |
| SODIUM PHOSPHATE (Sodium dihydrogenphosphate<br>dihydrate from Kokusan Kagaku) | 0.30      |
| LAURAMINE OXIDE (30% of lauramine oxide, Aromox<br>MCD-W from Akzo Nobel)      | 0.6       |
| POLYQUATERNIUM-6 (40% active ingredient, Merquart<br>100 from Nalco)           | 0.08      |
| PHENOXYETHANOL                                                                 | 0.04      |
| CITRIC ACID                                                                    | 0.43      |
| WATER                                                                          | QS to 100 |

Compositions (C), (D), and (C')

|                                 | (C)<br>Invention | (D)<br>Comparative | (C')<br>Comparative |
|---------------------------------|------------------|--------------------|---------------------|
| Polyethylene wax (1)            | 1                | 0                  | 0                   |
| Wax silicone (1')               | 0                | 0                  | 1                   |
| Polyacrylate crosspolymer-6 (2) | 0.2              | 0.2                | 0.2                 |
| Water                           | 98.8             | 99.8               | 98.8                |

(1) Sold under the name Micropoly 1160S by the company Micro Powders

(2) Sold under the name Sepimax ZEN by the company Seppic

(1') Sold under the name SF 1642 by the company MOMENTIVE

Composition (C) is used in the method of the invention, whereas compositions (D) and (C') are used in comparative methods, as described below.

18 natural or slightly bleached hair swatches were cleaned with a commercial shampoo, and divided into two equivalent groups.

All the swatches were dried by hair dryer, (60°C for 15-20min), then put it in oven (temp. 25°C, RH 50%) overnight.

A first group of 6 swatches (Group 1) was treated according to the following protocol in accordance with the present invention:

The reducing composition (A) was applied onto the swatches, in an amount of 2g of composition per g of swatch. The composition was left on for 15 min, and then rinsed off with water.

Then composition (C) was applied onto the swatches, in an amount of 0.4g of composition per g of swatch. The hair was then would on rods and heated at 120°C for 10 min. After cooling down, the hair was straightened using a flat iron at 230°C during 30s.

Then neutralizing composition (B) was applied onto the swatches in an amount of 2g of composition per g of swatch. The composition was left on for 10 min.

Then the swatches were rinsed thoroughly with water and left to dry, and then put in oven overnight (temp. 25°C, relative humidity 50%).

A second group of 12 swatches was treated according to the following comparative protocol:

The reducing composition (A) was applied onto the swatches, in an amount of 2g of composition per g of swatch. The composition was left on for 15 min, and then rinsed off with water.

Then composition (D) or (C') was applied onto the swatches, in an amount of 0.4g of composition per g of swatch. A group of 6 swatches (Group 2) were treated with composition (D) and a group of 6 swatches (Group 3) were treated with composition (C').

The hair was then wound on rods and heated at 120°C for 10 min. After cooling down, the hair was straightened using a flat iron at 230°C during 30s.

Then neutralizing composition (B) was applied onto the swatches in an amount of 2g of composition per g of swatch. The composition was left on for 10 min.

Then the swatches were rinsed thoroughly with water and left to dry, and then put in oven overnight (temp. 25°C, relative humidity 50%).

Sliding tests were conducted on the swatches in dry state just after the above protocols.

#### Measurement principle:

The force needed to make each hair swatch slide between 2 others is measured. 2 swatches are put in parallel, the third swatch is put reversedly. The first 2 swatches are fixed, then the third swatch is pulled and the strength is measured. The measurement is realized from roots to tips.

The average force is calculated and the evolution of the sliding force is recorded to quantify the surface state (homogeneous or heterogeneous) along the fiber (from roots to tips). The sliding force is representative of the smoothness of the hair.

The average sliding forces obtained are detailed in the table hereunder:

|                                                                                   | Average sliding force |
|-----------------------------------------------------------------------------------|-----------------------|
| Group 1 - Swatches treated with the method of the invention using composition (C) | $0.36 \pm 0.02$       |
| Group 2 - Swatches treated with the comparative method using composition (D)      | $0.44 \pm 0.03$       |

The results above show that the hair treated with the method of the present invention exhibit lower sliding forces, which means that the hair is significantly smoother, with a 22% of improvement in terms of smoothness ( $0.44-0.36/0.36$ ).

Tensile tests were conducted on the dried hair swatches, using the tensile testing machine produced by the company Dia-stron (Dia-stron extensometer, MTT type model).

#### Measurement principle:

The hair fibres are attached between two brass cylinders. The length of the working area is 30 mm. 50 fibres are recommended per series.

Measurements are carried out in water. The hair fibres are therefore immersed in distilled water at least half an hour prior to measurement and during measurement. For this test, the humidity is not a factor.

The fiber is threaded into two small brass cylinders then crimped using a hydraulic press in order to compress the cylinders onto the fibers at a pressure of 150 bars:

1. Thread a fiber into 2 small brass cylinders and slide the cylinders to the centre of the fibre.
2. Place the fibre on the press holder and fix it in tight between the two white rubber slots available for this purpose.
3. Slide the cylinders so as to place them in the press holder slots.
4. As the press holder can take up to two fibres, repeat steps 1 to 3 twice (for two samples).

5. Open the protective Plexiglas cover.
6. Place the press holder under the press and close the protective Plexiglas cover.
7. Crimp the fibres by pumping up to 150 bars. Any excess pressure is automatically evacuated.
8. Turn the wheel near the manometer to depressurize.
9. Open the Plexiglas cover and remove the press holder.
10. Take the fibre by the ends and remove it from the rubber slots without stretching it.
11. Using a scalpel (or scissors), cut any hair or rubber sticking out from each end of the sample.
12. Identify the sample using a permanent marker.

The cross-section of 10 each fibre must be determined before calculating the strain and tensile modulus on the basis of the tensile forces. This can be done using the FDAS765 (Fiber Dimensional Automatic System marketed by Dia-stron) via a sample loader which is able to measure up to 50 specimens automatically. This device is placed in a glove box so that the dimensions can be measured at 80% RH in the tensile tests. The specimens must be kept in the same conditions at least overnight before measuring the dimensions.

The measurement parameters are as follows:

- Preload: 2 gmf (20 mN)
- Speed: 10 mm/mn

The average results obtained are detailed in the table hereunder:

|                                                                                   | Value of Tensile test,<br>Break stress, Mpa |
|-----------------------------------------------------------------------------------|---------------------------------------------|
| Group 1 - Swatches treated with the method of the invention using composition (C) | 143                                         |
| Group 2 - Swatches treated with the comparative method using composition (D)      | 133                                         |
| Group 3 - Swatches treated with the comparative method using composition (C')     | 133                                         |

The results above show that the hair treated with the method of the present invention exhibit higher tensile strength, which means that the hair fibers are significantly stronger.

## CLAIMS

1. A method for altering the shape of human keratin fibres, wherein:
- 5           - a reducing composition (A) comprising one or more sulfur-containing reducing agent(s) is applied onto the fibres;
- after a leave-on time of said composition (A), a neutralizing composition (B) comprising one or more oxidizing agent(s) is applied onto the fibres; and
- 10           - one or more solid polyethylene wax(es), present in said composition (A) or in a separate composition (C), is (are) applied onto the fibres.
2. Method according to claim 1, wherein said polyethylene wax is present in composition (A).
- 15           3. Method according to claim 1, wherein said polyethylene wax is present in a separate composition (C) which is applied onto the fibres before the application of composition (A), after the application of composition (B), or between the application of composition (A) and the application of composition (B); and preferably between the
- 20           application of composition (A) and the application of composition (B).
4. Method according to any one of the preceding claims, characterized in that said polyethylene wax has a melting temperature of greater than or equal to 50°C, more preferably a melting temperature in the range from 60 to 140°C, even more preferably in
- 25           the range from 90 to 130°C.
5. Method according to any one of the preceding claims, characterized in that said polyethylene wax is under the form of a dispersion of solid particles having an average size ranging from 1 to 100 microns, preferably from 2 to 50 microns, more preferably from 5
- 30           to 25 microns.
6. Method according to the preceding claim, characterized in that the composition containing the dispersion of polyethylene wax further contains one or more polymeric thickening agent(s), preferably

chosen from cellulose-based thickeners; guar gum and derivatives thereof; gums of microbial origin; acrylic acid or acrylamidopropanesulfonic acid crosslinked homopolymers and copolymers; and associative polymers.

5           7. Method according to the preceding claim, characterized in that the polymeric thickening agent(s) is (are) chosen from copolymer(s) comprising at least one monomer of 2-acrylamido-2-methylpropanesulfonic acid, at least one monomer with a hydrophobic group and at least one ethylenically unsaturated monomer which does  
10           not comprise any hydrophobic groups; and preferably from crosslinked copolymers of salified 2-acrylamido-2-methylpropanesulfonic acid, of N,N-dimethylacrylamide, of tetraethoxylated lauryl methacrylate and of lauryl methacrylate.

15           8. Method according to any one of the preceding claims, characterized in that said polyethylene wax is present in an amount ranging from 0.2 to 10% by weight, preferably from 0.5 to 5% by weight, with regard to the weight of the composition containing it.

20           9. Method according to any one of the preceding claims, characterized in that said sulfur-containing reducing agent(s) are chosen from linear organic disulfides, thiols and mixtures thereof.

25           10. Method according to the preceding claim, characterized in that said linear organic disulfides are chosen from dialkyldisulfides, dialkenyldisulfides, dialkylaryldisulfides, N,N'-dithiodialkylcarboxylic acids and salts thereof, N,N'-dithiodialkyl  
esters, N,N'-dithiodialkyl amines and N,N'-dithiodialkyl amides, preferably from N,N'-dithiodialkylcarboxylic acids and salts thereof, and even more preferably from dithiodiglycolic acid and salts thereof.

30           11. Method according to claim 9, characterized in that said thiols are chosen from thioglycolic acid and esters thereof; thiolactic acid and esters thereof; 3-mercaptopropionic acid and esters thereof; cysteamine and C<sub>1-4</sub> acyl derivatives thereof; mono-thioglycerol and esters thereof; cysteine, N-alkanoylcysteine, esters thereof and salts thereof; and preferably from thioglycolic acid, thiolactic acid, and salts thereof.

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12. Method according to any one of the preceding claims, characterized in that said sulfur-containing reducing agent(s) are present in an amount ranging from 0.1% to 20% by weight, preferably from 0.2% to 15% by weight and more preferably from 1 to 10% by weight relative to the total weight of composition (A).

13. Method according to any one of the preceding claim, wherein composition (A) further contains one or more alkaline agent, preferably chosen from:

- a) aqueous ammonia,
- b) alkanolamines and derivatives thereof,
- c) oxyethylenated and/or oxypropylenated ethylenediamines,
- d) mineral or organic hydroxides,
- e) alkali metal silicates,
- f) amino acids, which are preferably basic amino acids,
- g) carbonates and bicarbonates, particularly of a primary amine, secondary amine or tertiary amine, or of an alkali metal or alkaline-earth metal, or of ammonium, and
- h) the compounds of formula (VII) below:



in which W is a C<sub>1</sub>-C<sub>6</sub> alkylene residue optionally substituted with a hydroxyl group or a C<sub>1</sub>-C<sub>6</sub> alkyl radical; Rx, Ry, Rz and Rt, which may be identical or different, represent a hydrogen atom or a C<sub>1</sub>-C<sub>6</sub> alkyl, C<sub>1</sub>-C<sub>6</sub> hydroxyalkyl or C<sub>1</sub>-C<sub>6</sub> aminoalkyl radical.

14. Method according to any one of the preceding claims, characterized in that said oxidizing agent(s) are chosen from hydrogen peroxide, urea peroxide, alkali metal bromates or ferricyanides, peroxygenated salts, for instance persulfates, perborates, peracids and precursors thereof, alkali metal or alkaline-earth metal percarbonates, and mixtures thereof, and more preferably from hydrogen peroxide, sodium bromate and mixtures thereof.

15. Method according to any one of the preceding claims, characterized in that said oxidizing agent(s) represent from 0.01% to

15% by weight and preferably from 0.1% to 10% by weight, relative to the total weight of composition (B).

16. Method according to any one of the preceding claims, characterized in that it comprises the following steps:

- 5           - applying the reducing composition (A) onto the hair, and then
- leaving composition (A) to stand on the hair, during a leave-on time ranging from 1 to 60 minutes, and then
- rinsing the hair with water, then
- applying composition (C) onto the hair, then
- 10          - heating the hair at a temperature ranging from 80 to 160°C, preferably from 100 to 140°C, and even more preferably of 120°C, then
- applying the neutralizing composition (B) onto the hair,
- leaving composition (B) to stand on the hair, during a leave-on time ranging from 30 seconds to 15 minutes, and then
- 15          - rinsing the hair with water.

17. Kit for altering the shape of human keratin fibres, comprising at least two compartments:

- 20          - a first compartment containing a reducing composition (A) as defined in anyone of claims 1 to 13; and
- a second compartment containing a neutralizing composition (B) as defined in anyone of claims 1, 14 and 15,
- one or more solid polyethylene wax being present in said composition (A) or in a separate composition (C) that is stored in a
- 25          third compartment.

# INTERNATIONAL SEARCH REPORT

International application No.

**PCT/CN2016/108439**

## A. CLASSIFICATION OF SUBJECT MATTER

A61K 8/23(2006.01)i; A61K 8/33(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

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 practicable, search terms used)

CNABS,DWPI,CNXT,EPTXT,USTXT,WOTXT,CNKI,WANFANG,ISI-WEB OF KNOWLEDGE,GOOGLE SCHOLAR:  
keratin fibre,keratin fiber,deform,deforming,shape,shaping,reshape,reshaping,deformation,hair,reducing agent,neutralizing agent,polyethylene wax,oxidizing agent

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages                                                                             | Relevant to claim No. |
|-----------|----------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------|
| Y         | US 6471953 B1 (LYLAN, N'GUYEN ET AL.) 29 October 2002 (2002-10-29)<br>see the whole document, especially the abstract, description, column 14, and claims 1-34 | 1-17                  |
| Y         | US 2006120984 A1 (SANDRINE, DECOSTER ET AL.) 08 June 2006 (2006-06-08)<br>see the whole document, especially claims 96, 171 and 177                            | 1-17                  |
| A         | WO 2013011116 A2 (OREAL ET AL.) 24 January 2013 (2013-01-24)<br>see the whole document                                                                         | 1-17                  |
| A         | WO 2006013412 A1 (OREAL ET AL.) 09 February 2006 (2006-02-09)<br>see the whole document                                                                        | 1-17                  |

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

\* Special categories of cited documents:

“A” document defining the general state of the art which is not considered to be of particular relevance

“E” earlier application or patent but published on or after the international filing date

“L” document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

“O” document referring to an oral disclosure, use, exhibition or other means

“P” document published prior to the international filing date but later than the priority date claimed

“T” later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

“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

“Y” document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

“&” document member of the same patent family

Date of the actual completion of the international search

**31 August 2017**

Date of mailing of the international search report

**15 September 2017**

Name and mailing address of the ISA/CN

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**INTERNATIONAL SEARCH REPORT**  
**Information on patent family members**

International application No.

**PCT/CN2016/108439**

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