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(71) Applicant: L'OREAL [FR/FR]; 14, rue Royale, 75008 Paris (FR).

(72) Inventor: BURCKBUCHLER, Virginie; 1, ave Eugene Schueller, BP22, 93601 Aulnay-sous-Bois (FR).

(74) Agent: RIVIERE, Francois; D.I.P.I., 9, rue Pierre Dreyfus, 921 10 Clichy (FR).

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(54) Title: PROCESS FOR TREATING KERATIN FIBRES WITH A COMPOSITION COMPRISING A CROSSLINKING AGENT AND A STEAM IRON

(57) Abstract: The present invention relates to a process for treating keratin fibres, especially human keratin fibres such as the hair, employing i) a step of applying at least one crosslinking agent which contains at least one (thio)carbonyl group and ii) a step of straightening/relaxing by means of a steam iron, in particular a steam iron, in particular, i) is applied first then secondly ii) the steam iron is applied without an intermediate step of rinsing, especially in water.

## PROCESS FOR TREATING KERATIN FIBRES WITH A COMPOSITION COMPRISING A CROSSLINKING AGENT AND A STEAM IRON

The present invention relates to a process for treating keratin fibres, especially  
5 human keratin fibres such as the hair, employing i) a step of applying at least one  
crosslinking agent which contains at least one (thio)carbonyl group and ii) a step of  
straightening/relaxing by means of a steam iron, in particular a steam straightening  
iron, in particular, i) is applied first then secondly ii) the steam straightening iron is  
applied without an intermediate step of rinsing, especially in water.

10 In the hair field, consumers wish to have available compositions which make it  
possible to introduce a temporary change to their head of hair, while targeting good  
shape retention of the effect produced. In general, it is desired for the change to  
withstand shampooing for at least fifteen days or even more, depending on the nature  
of said change.

15 Heat treatments are generally used to modify the shape of the head of hair in a  
long-lasting manner. These treatments allow a visual modification of the appearance of  
the hairstyle, combining a decrease in the degree of frizziness, a reduction in overall  
volume of the head of hair, a decrease in little curls, a gain in manageability, a  
straighter overall appearance, a substantial gain in sheen, and a resistance to humidity  
20 and to heat in order to maintain the hairstyle throughout the day.

Moreover, this type of treatment has the advantage of facilitating the daily  
maintenance of the head of hair, with the use of fewer care products, in particular rinse-  
out care products such as conditioners or masks, or leave-in care products such as  
sera, care creams or balms, or taming mousses. Drying of the hair is facilitated, with a  
25 much shortened blow-drying time and a decrease in the daily use of flat tongs, in terms  
both of time and intensity. This thus makes it possible to limit the risks of damaging the  
hair through combined factors of mechanical and thermal stress.

Several techniques are combined with these heat treatments. A first technique is  
based on the use of compositions based on thiol-based reducing agents. These  
30 techniques require strict adherence to the application conditions recommended by the  
suppliers, in particular in terms of amounts and leave-in time. In addition, they may be  
contraindicated on hair that is too sensitised and may not be compatible with the same-  
day application of other treatments, such as dyeing or bleaching operations. Moreover,  
they smell unpleasant.

35 Another technique is based on the use of compositions based on formalol (or  
formaldehyde) and derivatives thereof. These treatments have the particularity of being  
robust, perfectly compatible with all the other conventional hair treatments, such as the  
thiol-based straightening operations previously mentioned, alkaline relaxing operations,  
dyeing or bleaching operations of all types, carried out before or after. They provide the  
40 hair with excellent manageability, a very bright sheen and easy daily care. The  
"serpentine" movement of the hair is also characteristic of these treatments. However,

in the event of repeated applications, further damage to the hair occurs, which can lead to breaking of the hairs. Furthermore, for toxicological reasons, the use of some of these compounds is now prohibited and/or regulated. It is therefore increasingly sought to avoid the use of such substances, which may prove to be aggressive to the hair and other keratin materials.

Another technique is based on the use of compositions based on acids, and quite particularly on the use of glyoxylic acid. Patent application WO 201 1/104282 thus proposed a novel process for semi-permanently straightening the hair, which consists in applying an alpha-keto acid or a-keto acid solution to the hair for 15 to 120 minutes, then drying and, finally, straightening the head of hair with an iron at a temperature of approximately 200°C. The a-keto acid used is preferably glyoxylic acid.

However, it has been noted that glyoxylic acid may not be well tolerated, in particular when the scalp is sensitive and/or irritated. Its volatility, amplified by the use of heat from the iron, can also be a problem. Furthermore, the compositions of the prior art may adversely affect the hair and/or adversely affect its colour.

Treatments using a composition comprising a base combined with a heat treatment have also been proposed for straightening the hair. Such treatments make it possible to obtain good relaxing of curls, but can lead to modifications of the hair fibre. Document EP 1837010 especially describes a straightening/relaxing process using a composition comprising sodium hydroxide and a heat treatment. Document WO 2007/144707 describes a straightening/relaxing process using a composition comprising a non-hydroxylated base such as monoethanolamine (MEA) or ethylenediamine, combined with a heat treatment. Document WO 2009/1 17344 also describes a straightening/relaxing process using a composition comprising a non-hydroxylated base and a protein-denaturing agent, combined with a heat treatment.

In order to limit hair fibre modifications, it has also been proposed to use compositions comprising weak acids at alkaline pH, combined with a heat treatment. Document WO 2010/049434 describes, for example, a straightening/relaxing process in which a composition comprising a dicarboxylic acid, such as maleic acid, and heat treatment are applied.

There is still a need to develop a process for treating the hair, especially a straightening/relaxing process which makes it possible to straighten/relax and/or reduce the frizziness of the hair in an effective and long-lasting manner while limiting the degradation of the hair. A process is especially sought which makes it possible to achieve good relaxation of curls, which if possible is long lasting.

This (these) technical problem(s) has (have) been solved by a process for treating keratin fibres, especially human keratin fibres such as the hair, employing:

- i) a step of applying at least one crosslinking agent which contains at least one (thio)carbonyl group; and

ii) a step of straightening/relaxing by means of a steam iron, in particular a steam straightening iron at a temperature of greater than or equal to 100°C; in particular, i) is applied first then secondly ii) the steam straightening iron is applied without an intermediate step of rinsing, especially in water.

5 The process of the invention makes it possible in particular to obtain good long-lasting relaxation of curls, while limiting the degradation of the keratin fibres. Moreover, this process makes it possible to obtain shiny, manageable keratin fibres, with a very pleasant feel or even repair of the keratin fibres. The "*serpentine*" movement of the keratin fibres following treatment with the process of the invention is characteristic of  
10 Brazilian hair straightening processes, without employing products such as formol. In addition, the process of the invention enables a significant reduction in the volume of the keratin fibres following treatment, straightening and relaxing.

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

15 Within the context of the present invention, and unless otherwise indicated, the following definitions apply:

- a "*hydrocarbon-based chain*" is "*unsaturated*" when it comprises one or more unsaturations, i.e. double bonds and/or one or more triple bonds;
- the "*aryl*" or "*heteroaryl*" radicals or the aryl or heteroaryl part of a radical may be  
20 substituted by at least one substituent borne by a carbon atom, chosen from:
  - a  $C_i-C_8$  alkyl radical optionally substituted by one or more radicals chosen from the radicals hydroxyl,  $C_i-C_2$  alkoxy,  $C_2-C_4$  (poly)hydroxyalkoxy, acylamino or amino substituted by two identical or different  $C_1-C_4$  alkyl radicals which optionally bear at least one hydroxyl group or it being possible for the two  
25 radicals to form, with the nitrogen atom to which they are attached, a saturated or unsaturated and optionally substituted 5- to 7-membered and preferably 5- or 6-membered heterocycle optionally comprising another nitrogen or non-nitrogen heteroatom;
  - a halogen atom, such as chlorine, fluorine or bromine;
  - a hydroxyl group;
  - a  $C_1-C_2$  alkoxy radical;
  - a  $C_2-C_4$  (poly)hydroxyalkoxy radical;
  - an amino radical;
  - nitro or nitroso;
  - a 5- or 6-membered heterocycloalkyl radical;
  - an optionally cationic 5- or 6-membered heteroaryl radical, preferentially imidazolium, optionally substituted by a  $(C_rC_4)$ alkyl radical, preferentially methyl;
  - an amino radical substituted by one or two  $C_i-C_6$  alkyl radicals, which may be  
40 identical or different, optionally bearing at least: i) one hydroxyl group, ii) one amino group, optionally substituted by one or two optionally substituted  $C_1-C_3$

alkyl radicals, said alkyl radicals possibly forming, with the nitrogen atom to which they are attached, a saturated or unsaturated, optionally substituted 5- to 7-membered heterocycle optionally comprising at least one other nitrogen or non-nitrogen heteroatom;

- 5
- ◆ an acylamino radical (-N(R)-C(O)-R') in which the radical R is a hydrogen atom or a C<sub>i</sub>-C<sub>4</sub> alkyl radical optionally bearing at least one hydroxyl group and the radical R' is a C<sub>i</sub>-C<sub>2</sub> alkyl radical;
  - ◆ a carbamoyl radical ((R)<sub>2</sub>N-C(O)-) in which the radicals R, which are identical or different, represent a hydrogen atom or a C<sub>1</sub>-C<sub>4</sub> alkyl radical optionally bearing at least one hydroxyl group;

10

  - ◆ a carboxylic acid or ester radical, (-O-C(O)R') or (-C(O)OR'), in which the radical R' is a hydrogen atom or a C<sub>1</sub>-C<sub>4</sub> alkyl radical optionally bearing at least one hydroxyl group, and the radical R is a C<sub>i</sub>-C<sub>2</sub> alkyl radical;
  - ◆ the carboxylic radical possibly being in acid or salified form (preferably with an alkali metal or a substituted or unsubstituted ammonium);

15

  - ◆ an alkylsulfonamino radical (R'S(O)<sub>2</sub>-N(R)-) in which the radical R represents a hydrogen atom or a C<sub>1</sub>-C<sub>4</sub> alkyl radical optionally bearing at least one hydroxyl group and the radical R' represents a C<sub>1</sub>-C<sub>4</sub> alkyl radical, or a phenyl radical;

20

  - ◆ an aminosulfonyl radical ((R)<sub>2</sub>N-S(O)<sub>2</sub>-) in which the radicals R, which are identical or different, represent a hydrogen atom or a C<sub>1</sub>-C<sub>4</sub> alkyl radical optionally bearing at least one hydroxyl group;
    - a cyano group (CN);
    - a (poly)haloalkyl group, preferentially trifluoromethyl (CF<sub>3</sub>);

25

    - the cyclic or heterocyclic part of a non-aromatic radical of heterocycloalkyl type may be substituted by at least one substituent borne by a carbon atom, chosen from the groups:
      - hydroxyl;
      - C<sub>i</sub>-C<sub>4</sub> alkoxy or C<sub>2</sub>-C<sub>4</sub> (poly)hydroxyalkoxy;

30

      - alkylcarbonylamino ((RC(O)-NR'-) in which the radical R' is a hydrogen atom or a C<sub>i</sub>-C<sub>4</sub> alkyl radical optionally bearing at least one hydroxyl group, and the radical R is a C<sub>1</sub>-C<sub>2</sub> alkyl radical or an amino radical substituted by two identical or different C<sub>1</sub>-C<sub>4</sub> alkyl groups optionally bearing at least one hydroxyl group, said alkyl radicals possibly forming, with the nitrogen atom to which they are attached, a saturated or unsaturated, optionally substituted 5- to 7-membered heterocycle optionally comprising at least one other nitrogen or non-nitrogen heteroatom;

35

      - alkylcarbonyloxy ((RC(O)-O-) in which the radical R is a C<sub>1</sub>-C<sub>4</sub> alkyl radical or an amino radical substituted by two identical or different C<sub>1</sub>-C<sub>4</sub> alkyl groups optionally bearing at least one hydroxyl group, said alkyl radicals possibly forming, with the nitrogen atom to which they are attached, a saturated or

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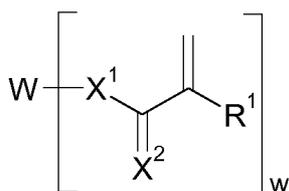
- unsaturated, optionally substituted 5- to 7-membered heterocycle, optionally comprising at least one other nitrogen or non-nitrogen heteroatom;
- alkoxy carbonyl ((RO-C(O)-) in which the radical R is a C<sub>i</sub>-C<sub>4</sub> alkyl radical or an amino radical substituted by two identical or different C<sub>1</sub>-C<sub>4</sub> alkyl groups optionally bearing at least one hydroxyl group, said alkyl radicals possibly forming, with the nitrogen atom to which they are attached, a saturated or unsaturated, optionally substituted 5- to 7-membered heterocycle, optionally comprising at least one other nitrogen or non-nitrogen heteroatom;
  - a cyclic or heterocyclic radical or a non-aromatic part of an aryl or heteroaryl radical may also be substituted by one or more oxo groups;
  - an "aryP" radical represents a monocyclic or fused or non-fused polycyclic group comprising from 6 to 22 carbon atoms, at least one ring of which is aromatic; the aryl radical is in particular a phenyl, biphenyl, naphthyl, indenyl, anthracenyl or tetrahydronaphthyl and more preferentially phenyl or tetrahydronaphthyl;
  - a "heteroaryP" radical represents a 5- to 22-membered, monocyclic or fused or non-fused polycyclic group, comprising from 1 to 6 heteroatoms chosen from nitrogen, oxygen, sulfur and selenium atoms, at least one ring of which is aromatic; preferentially, a heteroaryl radical is chosen from acridinyl, benzimidazolyl, benzobistriazolyl, benzopyrazolyl, benzopyridazinyl, benzoquinolyl, benzothiazolyl, benzotriazolyl, benzoxazolyl, pyridinyl, tetrazolyl, dihydrothiazolyl, imidazopyridinyl, imidazolyl, indolyl, isoquinolyl, naphthoimidazolyl, naphthoxazolyl, naphthopyrazolyl, oxadiazolyl, oxazolyl, oxazolopyridyl, phenazinyl, phenoxazolyl, pyrazinyl, pyrazolyl, pyrilyl, pyrazoyltriazyl, pyridyl, pyridinoimidazolyl, pyrrolyl, quinolyl, tetrazolyl, thiadiazolyl, thiazolyl, thiazolopyridinyl, thiazoylimidazolyl, thiopyrylyl, triazolyl, xanthyl and the ammonium salt thereof;
  - a "cyclic" radical is a "cycloalkyl" radical, i.e. a non-aromatic monocyclic or fused or non-fused polycyclic radical containing from 5 to 22 carbon atoms, which may comprise one or more unsaturations, such as cyclohexyl or cyclopentyl;
  - a "heterocyclic" radical or "heterocycloalkyl" is a saturated or unsaturated non-aromatic, monocyclic or fused or non-fused polycyclic 5- to 22-membered radical, comprising from 1 to 6 heteroatoms chosen from nitrogen, oxygen, sulfur and selenium atoms, morpholinyl, thiomorpholinyl, piperidinyl, piperazinyl, pyrrolidinyl, tetrahydrofuranyl, tetrahydrothiophenyl, azepanyl, thioazepanyl; preferentially pyrrolidinyl and morpholino;
  - an "alkyl" radical is a C<sub>i</sub>-C<sub>8</sub>, particularly C<sub>1</sub>-C<sub>4</sub> hydrocarbon-based radical such as methyl or ethyl;
  - an "alkenyl" radical is a linear or branched C<sub>2</sub>-C<sub>10</sub> hydrocarbon-based radical comprising one or more conjugated or unconjugated double bonds, in particular comprising one, two or three double bonds, preferentially only one double bond;
  - the term "optionally substituted" attributed to the alkyl or alkenyl radical implies that said alkyl radical may be substituted by one or more radicals chosen from the

- following radicals: i) hydroxyl, ii) C1-C4 alkoxy, iii) acylamino, iv) amino optionally substituted by one or two identical or different C1-C4 alkyl radicals, said alkyl radicals possibly forming, with the nitrogen atom that bears them, a 5- to 7-membered heterocycle, optionally comprising another nitrogen or non-nitrogen heteroatom, v) phenyl, vi) (CrC<sub>6</sub>)alkoxycarbonyl, vii) (CrC<sub>6</sub>)alkylcarbonyloxy, viii) H-C(O)-O-;
- 5
- an "*alkoxy*" radical is an alkyl-oxy or alkyl-O- radical for which the alkyl radical is a linear or branched CrC<sub>8</sub>, particularly C1-C4 hydrocarbon-based radical; such as methoxy or ethoxy, and when the alkoxy group is optionally substituted, this implies
  - 10 that the alkyl group is optionally substituted as defined above;
  - a "*(poly)haloalkyl*" radical is an "*alkyl*" radical as defined above, in which one or more hydrogen atoms are substituted or replaced with one or more halogen atoms such as the fluorine, chlorine or bromine atom; a polyhaloalkyl that may be mentioned is the trifluoromethyl group;
  - 15 - an "*alkylthio*" radical is an alkyl-S- radical for which the alkyl radical is a linear or branched Ci-C<sub>8</sub>, particularly C1-C4 hydrocarbon-based radical; such as methylthio or ethylthio, and when the alkylthio group is optionally substituted, this implies that the alkyl group is optionally substituted as defined above;
  - an anionic counterion is organic or mineral, preferentially chosen from halide anions such as Cl<sup>-</sup>, Br<sup>-</sup> or I<sup>-</sup>, and organic anions such as mesylates;
  - 20 - when the expression "*at least one*" is used, "*one or more*" is implied;
  - the limit values delimiting the extent of a range of values are included in this range of values.
- 25 i) *(thio)carbonyl group(s)-containing crosslinking agent*

The process for treating keratin fibres of the invention employs i) a step of applying at least one crosslinking agent which comprises one or more (thio)carbonyl group(s), i.e. one or more groups chosen from carbonyl C=O and thiocarbonyl C=S.

30 "*Crosslinking agent*" or "*polymer network*" are intended to mean a chemical agent which is used in polymer chemistry to form three-dimensional polymer networks, also referred to as crosslinking. Crosslinking reactions are carried out using a crosslinking agent chemically or physically (light, heat), creating macromolecular networks between the polymers.

35 According to one embodiment of the invention, the (thio)carbonyl groups-containing crosslinking agent(s) is(are) selected from that(those) of formula (I):

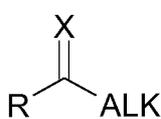


in which formulae (I):

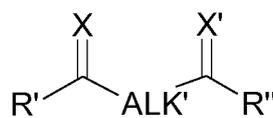
- **W** represents:
  - i) either an optionally substituted (hetero)aryl or optionally substituted (hetero)cycloalkyl group, and preferably represents a 5- or 6-membered phenyl or heteroaryl such as pyridinyl or 5- to 8-membered heterocycloalkyl comprising at least one oxygen atom, such as tetrahydrofuryl, piperazinyl or hexahydrofuro[3,2-b]furanlyl,
  - ii) or a  $^*-\text{A}-(\text{CR}^2\text{R}^3)_x-\text{A}^*$  group, where  $w$  is equal to 2, with  $\text{R}^2$  and  $\text{R}^3$ , which are identical or different, representing a hydrogen atom or a  $(\text{CrC}_6)$ alkyl group such as methyl,  $x$  represents an integer of between 0 and 10 inclusive, preferably  $x$  is equal to 1,  $*$  represents the point of attachment to the  $-\text{X}^1-\text{C}(\text{X}^2)-\text{C}(=\text{CH}_2)-\text{R}^1$  groups and **A** represents an optionally substituted (hetero)aryl or optionally substituted (hetero)cycloalkyl group, preferably **A** represents a phenyl;
  - iii) or a linear or branched polyvalent, preferably divalent or trivalent, saturated or unsaturated, preferably saturated, hydrocarbon-based chain, optionally substituted, preferably by a hydroxyl group or a phenyl group, and comprising from 1 to 20 carbon atoms;
- $\text{R}^1$  represents a hydrogen atom or a  $(\text{CrC}_4)$ alkyl group, preferably  $\text{R}^1$  represents a methyl group ;
- $\text{X}^1$  represents an oxygen atom, a sulfur atom, or a  $-\text{N}(\text{R}^1)-$  group with  $\text{R}^1$  as defined above, preferably  $\text{X}^1$  represents an oxygen atom or a  $-\text{N}(\text{R}^1)-$  group with  $\text{R}^1$  as defined above ;
- $\text{X}^2$  represents an oxygen atom or a sulfur atom, preferably  $\text{X}^2$  represents an oxygen atom ;
- $w$  represents an integer of between 2 and 10 inclusive, more particularly between 2 and 5, such that  $w = 2$  or 3.

In particular, **W** represents a  $\text{CrC}_6$  divalent or **c-i-c-io** trivalent alkyl group.

According to another embodiment of the invention, the (thio)carbonyl groups-containing crosslinking agent(s) is(are) selected from that(those) of formula (II) or (III):



(II)



(III)

and also the organic or mineral acid or base salts thereof, the tautomers thereof, and the solvates thereof such as hydrates;

in which formulae (II) and (III):

- 5 • **X** and **X'**, which are identical or different, preferably identical, represent an oxygen atom or a sulfur atom, preferably oxygen;
- **ALK** represents a linear or branched hydrocarbon-based chain comprising from 1 to 10 carbon atoms, which is saturated or unsaturated, in particular with 1 to 3 conjugated or unconjugated unsaturations; said chain is optionally substituted by one or more groups chosen from:
  - 10 a) a hydroxyl group;
  - b) a  $-C(X)-OR_b$  group with X as defined above, and  $R_b$  representing a hydrogen atom, an alkali metal or an alkaline earth metal, and
  - c) a saturated or unsaturated, non-aromatic 4- to 8-membered heterocyclic lactone group which may optionally be substituted especially by one or more hydroxyl groups ; preferably the non-aromatic 4- to 8-membered heterocyclic lactone group is saturated ;
- 15 • **ALK'** represents a linear or branched divalent hydrocarbon-based chain comprising from 1 to 10 carbon atoms, which is saturated or unsaturated, in particular with 1 to 3 conjugated or unconjugated unsaturations;
- 20 • **R** represents i) a hydrogen atom or ii) an  $OR_a$  group with  $R_a$  representing a hydrogen atom, an alkali metal or an alkaline earth metal, or a (**CrC**<sub>6</sub>)alkyl, (**C**<sub>2</sub>-**C**<sub>6</sub>)alkenyl, or (**C**<sub>2</sub>-**C**<sub>6</sub>)alkynyl group; preferably, R represents a hydrogen atom or an  $OR_a$  group with  $R_a$  representing a hydrogen atom or an alkali metal or alkaline earth metal;
- 25 • **R'** and **R''** which are identical or different, represent a group chosen from:
  - **ALK''-0-** with **ALK''** representing a linear or branched hydrocarbon-based chain comprising from 1 to 10 carbon atoms, and optionally from 1 to 3 conjugated or unconjugated unsaturations; preferably, **ALK''** represents a (**CrC**<sub>6</sub>)alkyl, (**C**<sub>2</sub>-**C**<sub>6</sub>)alkenyl or (**C**<sub>2</sub>-**C**<sub>6</sub>)alkynyl group;
  - 30 - **-C(0)-OR<sub>b</sub>** with  $R_b$  representing a hydrogen atom, an alkali metal or an alkaline earth metal;
  - an  $NR_cR_d$  amino group with  $R_c$  and  $R_d$ , which are identical or different, representing a hydrogen atom or a (**CrC**<sub>6</sub>)alkyl, (**C**<sub>2</sub>-**C**<sub>6</sub>)alkenyl, or (**C**<sub>2</sub>-**C**<sub>6</sub>)alkynyl group, preferably  $NH_2$ ;
- 35 it being understood that **ALK'**, **R'** or **R''** contains at least one group comprising at least one unsaturation.

40 According to one particular embodiment of the invention, the (thio)carbonyl group(s)-containing crosslinking agent(s) is(are) selected from that(those) of formula (II).

According to one particular embodiment of the invention, the (thio)carbonyl group(s)-containing crosslinking agent(s) of formula **(II)** is(are) such that **R** represents i) a hydrogen atom.

According to another particular variant of the invention, the (thio)carbonyl group(s)-containing agent(s) of formula **(II)** is(are) such that **R** represents ii) an  $OR_a$  group with  $R_a$  representing a hydrogen atom, an alkali metal, an alkaline earth metal, or a **(CrC<sub>4</sub>)**alkyl group; preferably, **R** represents a hydrogen atom or an  $OR_a$  group with  $R_a$  representing a hydrogen atom, an alkali metal or an alkaline earth metal.

According to a preferred embodiment of the invention, the (thio)carbonyl group(s)-containing agent(s) of formula **(II)** is(are) such that **ALK** represents a **(CrC<sub>6</sub>)**alkyl group optionally substituted by one or more groups chosen from:

- a) hydroxy;
- b)  $-C(O)-OR_b$  with  $R_b$  representing a hydrogen atom, an alkali metal or an alkaline earth metal; and
- c) a **4-** to **6-**membered lactone heterocycle which may optionally be substituted by one to three hydroxyl groups, preferably the **4-** to **6-**membered heterocyclic lactone group is saturated.

In particular, **ALK** is substituted by one or more groups chosen from a) and c) as defined above.

According to one particular embodiment of the invention, the (thio)carbonyl group(s)-containing agent(s) of formula **(II)** is(are) such that **X** represents an oxygen atom.

According to one particular embodiment of the invention, the (thio)carbonyl group(s)-containing crosslinking agent(s) is(are) of formula **(III)**.

According to one particular embodiment of the invention, the (thio)carbonyl group(s)-containing agent(s) of formula **(III)** is(are) such that **R'** and **R''**, which are identical or different, represent  $ALK''-O-$  with  $ALK''$  as defined above; preferably,  $ALK''$  are identical and represent a **(CrC<sub>6</sub>)**alkyl, or  $(C_2-C_6)$ alkenyl group.

According to another particular embodiment of the invention, the (thio)carbonyl group(s)-containing agent(s) of formula **(III)** is(are) such that **R'** and **R''**, which are identical or different, represent:

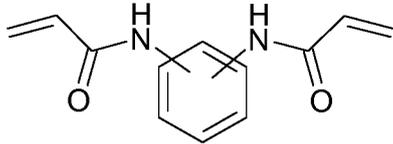
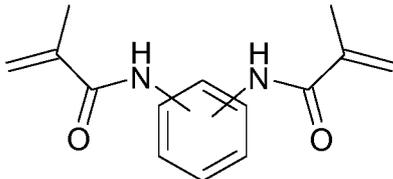
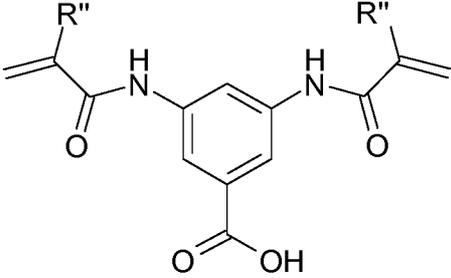
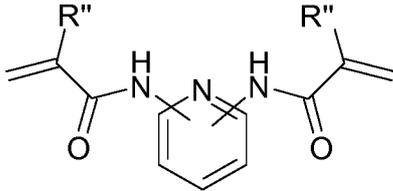
- $-C(O)-OR_b$  with  $R_b$  representing a hydrogen atom, an alkali metal or an alkaline earth metal;
- an  $NR_cR_d$  amino group with  $R_c$  and  $R_d$ , which are identical or different, representing a hydrogen atom or a **(CrC<sub>6</sub>)**alkyl,  $(C_2-C_6)$ alkenyl, or  $(C_2-C_6)$ alkynyl group, preferably an amino group  $NH_2$ .

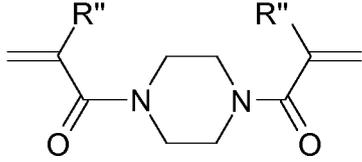
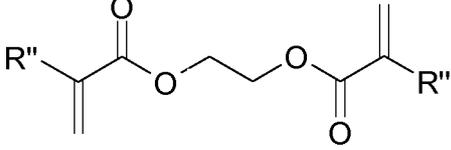
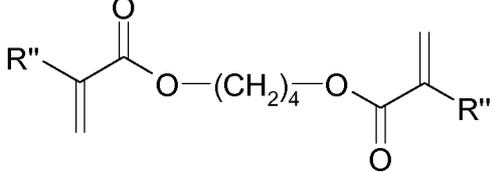
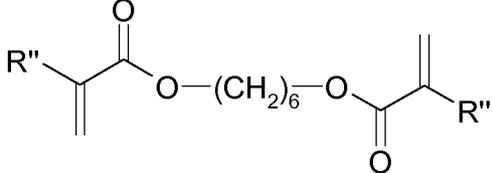
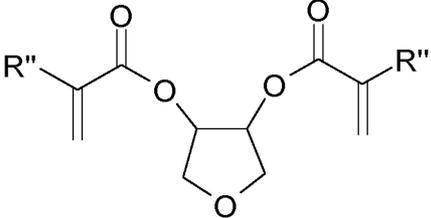
According to one particular embodiment of the invention, the (thio)carbonyl group(s)-containing agent(s) of formula **(III)** is(are) such that **ALK'** represents a linear or branched divalent hydrocarbon-based chain comprising from 1 to 6 carbon atoms, unsaturated with **1** to **3** conjugated or unconjugated unsaturations.

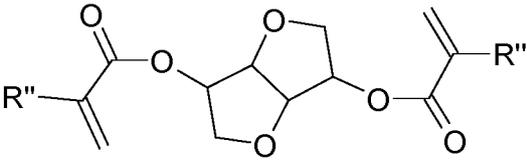
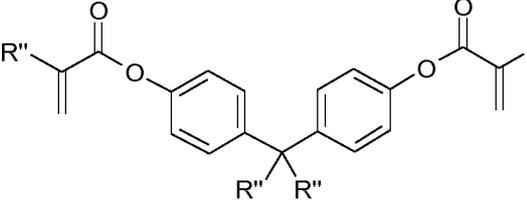
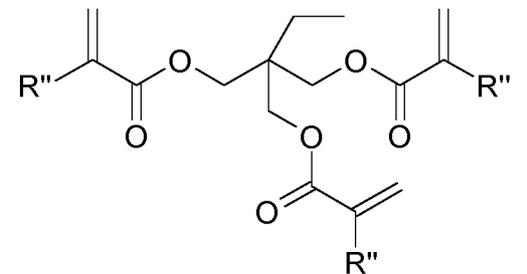
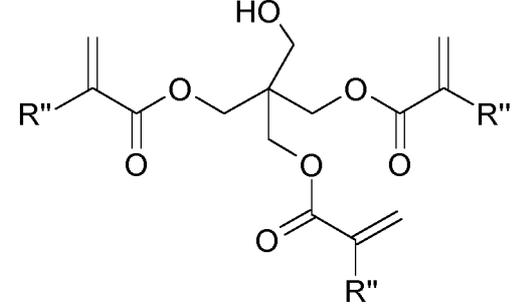
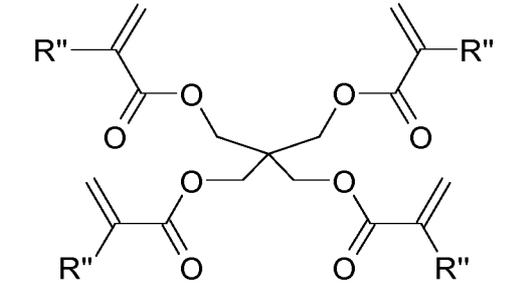
Preferably, **ALK'** represents a (C<sub>2</sub>-C<sub>6</sub>)alkenylene, or (C<sub>2</sub>-C<sub>6</sub>)alkynylene, more preferentially (C<sub>2</sub>-C<sub>6</sub>)alkenylene, even more preferentially (C<sub>2</sub>-C<sub>4</sub>)alkenylene group such as ethylene -CH=CH-.

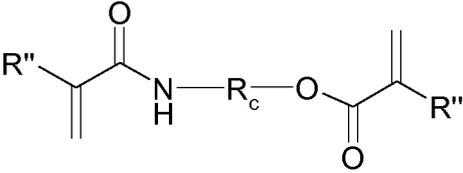
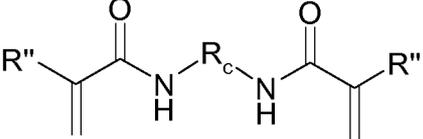
According to one particular embodiment of the invention, the (thio)carbonyl group(s)-containing agent(s) of formula (III) is(are) such that **X** and **X'** represents an oxygen atom.

According to a preferred variant of the invention, the (thio)carbonyl groups-containing crosslinking agent(s) is(are) chosen from the compounds of formula (I) and in particular 1 to 16 from the table below, and also the optical and geometric isomers thereof, the tautomers and mineral or organic acid or base salts thereof:

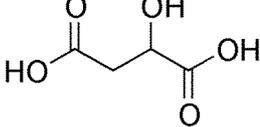
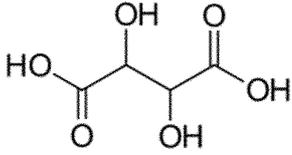
Name	Abbreviation/ no.	Structure
1,3-phenylenediacrylamide; 1,4-phenylenediacrylamide	<u>1</u>	
<i>N,N'</i> -1,3-phenylenebis(2-methyl-2-propenamide); <i>N,N'</i> -1,4-phenylenebis(2-methyl-2-propenamide)	<u>2</u>	
3,5-Bisacrylamido benzoic acid with R'' identical and equal to H; and 3,5-bismethylacrylamido-benzoic acid with R'' identical and equal to CH <sub>3</sub>	<u>3</u>	 R'' = H or CH <sub>3</sub>
2,6-bisacryloylamidopyridine with R'' identical and equal to H; 2,6-bismethylacryloylamidopyridine with R'' identical and equal to CH <sub>3</sub>	<u>4</u>	 R'' = H or CH <sub>3</sub>

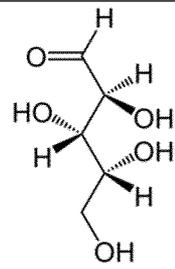
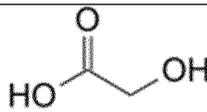
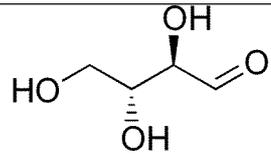
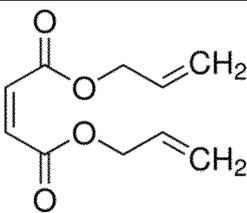
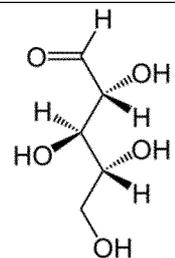
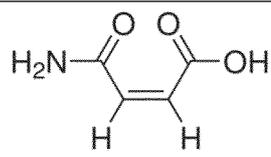
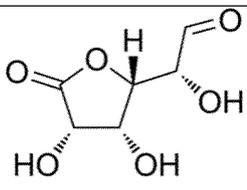
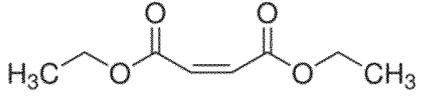
<p>1,4-diacryloylpiperazine with R'' identical and equal to H;</p> <p>1,4-dimethylacryloylpiperazine with R'' identical and equal to CH<sub>3</sub></p>	<p>(DAP)</p> <p><u>5</u></p>	 <p>R'' = H or CH<sub>3</sub></p>
<p>Ethylene glycol dimethacrylate with R'' identical and equal to CH<sub>3</sub> (EGDMA); ethylene glycol diacrylate with R'' identical and equal to H</p>	<p>(EGDMA)</p> <p><u>6</u></p>	 <p>R'' = H or CH<sub>3</sub></p>
<p>Tetramethylene dimethacrylate with R'' identical and equal to CH<sub>3</sub>; tetramethylene diacrylate with R'' identical and equal to H</p>	<p>(TDMA)</p> <p><u>7</u></p>	 <p>R'' = H or CH<sub>3</sub></p>
<p>Hexamethylene dimethacrylate with R'' identical and equal to CH<sub>3</sub> and hexamethylene diacrylate with R'' identical and equal to H</p>	<p><u>8</u></p>	 <p>R'' = H or CH<sub>3</sub></p>
<p>Anhydroerythritol dimethacrylate with R'' identical and equal to CH<sub>3</sub> and anhydroerythritol diacrylate with R'' identical and equal to H</p>	<p><u>9</u></p>	 <p>R'' = H or CH<sub>3</sub></p>

<p>1,4:3,6-Dianhydro-p-sorbitol-2,5-dimethacrylate with R'' identical and equal to CH<sub>3</sub>; 1,4:3,6-dianhydro-p-sorbitol-2,5-diacrylate with R'' identical and equal to H</p>	<p><b><u>10</u></b></p>	 <p>R'' = H or CH<sub>3</sub></p>
<p>Isopropenebis(1,4-phenylene) dimethacrylate with R'' identical and equal to CH<sub>3</sub>; isopropenebis(1,4-phenylene) diacrylate with R'' identical and equal to H</p>	<p><b><u>11</u></b></p>	 <p>R'' = H or CH<sub>3</sub></p>
<p>2,2-bis(Hydroxymethyl)butanol trimethacrylate with R'' identical and equal to CH<sub>3</sub> (TRIM); 2,2-bis(hydroxymethyl)butanol triacrylate with R'' identical and equal to H</p>	<p>(TRIM) <b><u>12</u></b></p>	 <p>R'' = H or CH<sub>3</sub></p>
<p>Pentaerythritol triacrylate with R'' identical and equal to H; Pentaerythritol trimethacrylate with R'' identical and equal to CH<sub>3</sub></p>	<p><b><u>13</u></b></p>	 <p>R'' = H or CH<sub>3</sub></p>
<p>Pentaerythritol tetraacrylate with R'' identical and equal to H (PETRA); Pentaerythritol tetramethacrylate with R'' identical and equal to CH<sub>3</sub></p>	<p>(PETRA) <b><u>14</u></b></p>	 <p>R'' = H or CH<sub>3</sub></p>

<p><i>N,O</i>-bismethacryloylethanolamine with <math>R_c</math> equal to ethylene and <math>R''</math> identical and equal to <math>CH_3</math></p>	<p>(NOBE) <b><u>15</u></b></p>	 <p><math>R_c = (C_1-C_6)</math>alkylene such as ethylene <math>R'' = H</math> or <math>CH_3</math></p>
<p><i>N,N'</i>-methylenebisacrylamide with <math>R_c = CH_2</math> (MDAA); or <i>N,N'</i>-1,2-ethanediylbis(2-methyl-2-propenamamide) <i>N,N'</i>-ethylenebisacrylamide with <math>R_c = CH_2-CH_2</math>; <i>N,N'</i>-butylenebisacrylamide with <math>R_c = CH_2-CH_2-CH_2-CH_2</math>; <i>N,N'</i>-hexylenebisacrylamide with <math>R_c = CH_2-CH_2-CH_2-CH_2-CH_2-CH_2</math></p>	<p>(MDAA) <b><u>16</u></b></p>	 <p><math>R_c = (C_1-C_6)</math>alkylene <math>R'' = H</math> or <math>CH_3</math></p>

According to a preferred variant of the invention, the (thio)carbonyl group(s)-containing crosslinking agent(s) is(are) chosen from the compounds of formula (II) or (III) and in particular **17** to **26** from the table below, and also the optical and geometric isomers thereof, the tautomers and mineral or organic acid or base salts thereof:

Name	No.	Structure
Malic acid	<b><u>17</u></b>	
Tartaric acid	<b><u>18</u></b>	

Lyxose	<u>19</u>	
Glycolic acid	<u>20</u>	
Erythrose	<u>21</u>	
Diallyl maleate	<u>22</u>	
Ribose	<u>23</u>	
Maleamic acid	<u>24</u>	
Glucoronolactone	<u>25</u>	
Diethyl maleate	<u>26</u>	

Particularly the (thio)carbonyl group(s)-containing crosslinking agent(s) is(are) chosen from malic acid **17**, erythrose **21** maleamic acid **24** and diethyl maleate **26** especially in presence of steam, more especially for curl relaxation.

Preferably the (thio)carbonyl group(s)-containing crosslinking agent(s) is(are)  
5 chosen from lyxose **19**, ribose **23**, tartaric acid **18**, glycolic acid **20**, and maleamic acid **24** especially in presence of steam, more especially for soft touch.

According to another preferred embodiment the (thio)carbonyl group(s)-containing crosslinking agent(s) is(are) chosen from lyxose **19**, D-glucoronolactone **25**, erythrose **21**.

10 According to one particular embodiment of the invention, the (thio)carbonyl group(s)-containing crosslinking agent(s) as defined above is(are) in a cosmetic composition, in an amount of between 1% and 80% by weight of the composition which comprises it(them), more particularly in an amount of between 3% and 50% by weight, preferentially between 5% and 30% by weight, more preferentially between 7% and 20%  
15 by weight, such as 10% by weight relative to the total weight of the composition comprising it(them).

#### Cosmetic composition

The composition used in the process of the invention may be aqueous or  
20 anhydrous. It is preferably aqueous and then comprises water at a concentration ranging from 10% to 99%, better still from 30% to 99% and even better still from 50% to 98% by weight relative to the total weight of the composition. The composition is especially aqueous when it comprises one or more (thio)carbonyl group(s)-containing crosslinking agent(s) of formula (II) as defined above.

25 The composition may especially comprise one or more organic water-soluble solvents such as  $C_1$ - $C_7$  alcohols; mention may especially be made of  $C_1$ - $C_7$  aliphatic monoalcohols, for example ethanol, or  $C_6$ - $C_7$  aromatic alcohols, such as benzyl alcohol, which may be employed alone or as a mixture with water.

According to one particular embodiment of the invention, the (thio)carbonyl  
30 group(s)-containing crosslinking agent(s), especially of formula (III), are in an aqueous-alcoholic, or even alcoholic, composition, i.e. which comprises, as predominant solvent, aliphatic monoalcohols such as ethanol.

According to one variant, the cosmetic composition comprises at least one lipophilic, aprotic and/or apolar organic solvent which is liquid at room temperature  
35 ( $25^{\circ}\text{C}$ ) and at atmospheric pressure, in particular an oil such as isododecane.

The composition used in the process of the invention may also comprise at least one customary cosmetic ingredient, especially chosen from propellants; solid fatty substances and especially  $C_8$ - $C_{40}$  esters,  $C_8$ - $C_{40}$  acids; aliphatic  $C_8$ - $C_{40}$  alcohols,

5 sunscreens; moisturizers; antidandruff agents; antioxidants; chelating agents; nacreous agents and opacifiers; plasticizers or coalescers; fillers; polymeric or non-polymeric thickeners or gelling agents other than the cellulose-based polymers already mentioned; emulsifiers; polymers, in particular conditioning or styling polymers; fragrances; silanes; crosslinking agents. The composition can, of course, comprise several cosmetic ingredients appearing in the above list.

10 Depending on their nature and the purpose of the composition, the normal cosmetic ingredients can be present in normal amounts which can be easily determined by those skilled in the art and which can be, for each ingredient, between 0.01% and 80% by weight. Those skilled in the art will take care to choose the ingredients included in the composition, and also the amounts thereof, such that they do not harm the properties of the compositions of the present invention.

15 The composition(s) used in the process according to the invention may be in any of the formulation forms conventionally used, and especially in the form of an aqueous, alcoholic or aqueous-alcoholic, or oily solution or suspension; a solution or a dispersion of the lotion or serum type; an emulsion, especially of liquid or semi-liquid consistency, of the O/W, W/O or multiple type; a suspension or emulsion of soft consistency of cream (O/W) or (W/O) type; an aqueous or anhydrous gel, or any other cosmetic form.

20 These compositions may be packaged in pump-action bottles or in aerosol containers, so as to apply the composition in vaporized (lacquer) form or in the form of a mousse. Such packaging forms are indicated, for example, when it is desired to obtain a spray or a mousse, for treating the hair. In these cases, the composition preferably comprises at least one propellant.

25 The (thio)carbonyl group(s)-containing crosslinking agent(s) as defined above may be applied to dry or wet hair, preferably to dry hair.

30 The bath ratio of the composition applied which comprises the (thio)carbonyl group(s)-containing crosslinking agent(s) as defined above may vary from 0.1 to 10, more particularly from 0.2 to 5, and preferably between 0.5 and 3. The term "bath ratio" is intended to mean the ratio between the total weight of the applied composition and the total weight of keratin fibres to be treated.

*ii) Steam iron step*

35 The process for treating keratin fibres according to the invention comprises a step of straightening/relaxing the keratin fibres with a steam iron, i.e. an "iron" which comprises a device which emits steam and which applies this steam before, during or after the straightening/relaxing, preferably before the step of straightening/relaxing and more preferentially just before the step of straightening/relaxing (0.5 to 10 seconds before).

40 For the purposes of the present invention, the term "iron" is intended to mean a device for heating keratin fibres by placing said fibres and the heating device in contact

with one another. The end of the iron which comes into contact with the keratin fibres generally has two flat surfaces. These two surfaces may be made of metal or ceramic. In particular, these two surfaces may be smooth or crimped or curved.

5 According to a particular embodiment, the iron of the steam iron is at a temperature of between 65°C and 250°C, particularly between 80°C and 230°C, more particularly greater than or equal to 100°C and preferentially between 100°C and 190°C. Preferably, step ii) of the process for treating keratin fibres is carried out at a temperature ranging from 150°C to 220°C, preferably ranging from 160°C to 220°C, preferentially ranging from 160°C to 210°C, especially ranging from 180°C to 200°C.

10 As examples of irons that may be used in the straightening process according to the invention, mention may be made of any type of steam flat iron, and in particular, nonlimitingly, those described in patents US 5 957 140 and US 5 046 516.

The steam iron may be applied by successive separate strokes lasting a few seconds or by gradual movement or sliding along the tresses of keratin fibres, especially of hair.

15 Preferably, the steam iron is applied in the process according to the invention with a continuous movement from the root to the tip of the hair, in one or more passes, in particular in two to twenty passes. The duration of each pass of the steam iron may range from 2 seconds to 1 minute.

20 Advantageously, steam is applied to keratin fibres, especially the hair, according to a flow rate of less than 5 g/min, especially of between 1 and 4 g/min.

Steam may be applied using any device known per se for generating the amount of steam of use in the process of the invention. According to a particular embodiment, this device is portable, that is to say that the tank which makes it possible to generate the steam is in contact with the part of the device comprising the orifices for dispensing the steam.

The step of application of the steam may be carried out before, during or after the heating step, and preferably before and more preferentially just before the step of straightening/relaxing (0.5 to 10 seconds before).

30 Preferably, the step of straightening/relaxing the keratin fibres is carried out for a time that may range from 2 seconds to 30 minutes, and preferentially from 2 seconds to 20 minutes, better still from 2 seconds to 10 minutes, better still from 2 seconds to 5 minutes and even better still from 2 seconds to 2 minutes.

Preferably, step ii) is carried out with a steam straightener device.

35 The process according to the invention may also comprise an additional step of drying the keratin fibres, after step i) and before step ii). The drying step may be carried out by means of a hairdryer, a hood or else natural drying. The drying step is advantageously carried out at a temperature ranging from 20 to 70°C.

40 After the step of straightening/relaxing using the steam iron, the keratin fibres may be optionally rinsed with water or washed with a shampoo. The keratin fibres are then optionally dried using a hairdryer or a hood or in the open air.

According to one embodiment, the process according to the invention is carried out on natural keratin fibres, especially natural hair.

According to another embodiment, the process according to the invention is carried out on damaged keratin fibres, especially damaged hair. The term "damaged hair" is intended to mean dry or coarse or brittle or split or limp hair.

The treatment process according to the invention is particularly carried out on sensitized human keratin fibres, especially hair, such as bleached, relaxed or permanent-waved fibres.

The process according to the invention may be carried out on keratin fibres, especially hair, which is dry or wet. Preferentially, the process is carried out on natural keratin fibres.

After step i) of the process of the invention, and before carrying out step ii), it is possible to leave the crosslinking agent(s) which contain(s) at least one (thio)carbonyl group or the composition containing it(them) applied for a duration ranging from 1 to 60 minutes, preferably ranging from 2 to 50 minutes and preferentially ranging from 5 to 45 minutes. The leave-in time may take place at a temperature ranging from 15°C to 45°C, preferably at room temperature (25°C).

The cosmetic composition which contains at least one crosslinking agent which comprises at least one (thio)carbonyl group as described above is advantageously applied to the keratin fibres in an amount ranging from 0.1 to 10 grams, preferably from 0.2 to 5 grams of composition per gram of keratin fibres.

After application of the cosmetic composition containing at least one crosslinking agent which contains at least one (thio)carbonyl group to the keratin fibres, the latter may be wrung out to remove the excess composition or else washed with water or with a shampoo.

The treatment process according to the invention may be carried out before, during and/or after an additional process of cosmetic treatment of the keratin fibres, such as a process for temporarily shaping (shaping with curlers, a crimping iron or a straightening iron) or a process for durably shaping (permanent-waving or relaxing) the keratin fibres.

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

The amounts indicated in the examples are expressed as percentage by weight.

a). Protocol for preparing the compositions of the process of the invention:

35

Malic acid 17, lyxose 19, erythrose 21, ribose 23, D-gluconolactone 25, tartaric acid 18, and glycolic acid 20 are tested in solution at 10 % by weight in water at spontaneous pH.

Maleamic acid 24 and diethyl maleate 26 are tested at 10% by weight in ethanol, and diallyl maleate 22 is tested at 10% in isododecane.

40

b). Protocol for evaluating the technical effect (stability, performance during/after application, texture)

Each composition produced in the above preparation protocol a) was tested on 4  
5 locks of DARK BROWN 936 type IV hair: 2 natural locks and 2 bleached locks  
according to the straightening treatment protocols.

In order to quantify the contribution of steam, for each crosslinker and each type  
of lock (natural or bleached): one lock was straightened with a steampod LP8500  
Go/7PO steam device from Rowenta, and the other was straightened with this same  
10 device used as a conventional straightening iron (without steam = comparative 1)  
under the same experimental conditions.

Equivalent straightening conditions were applied, i.e: 1 pass of steam iron = 3  
passes of iron, and not equivalent numbers of passes.

The operating conditions followed are as follows:

- 15 - Conventional straightening iron (comparative 2): 10 passes at 210°C.  
- Steam iron: 3 slow passes at 210°C.

*B1) Protocol for conventional straightening iron (comparative 1)*

The locks were wetted by 5 passes under water at 37°C then were placed in a  
20 glass chute.

0.054 g of crosslinking agent to be tested were introduced into an 8 ml flask with  
5.4 g of solvent (water, ethanol or isododecane), i.e. 5.454 g of compositions which  
were prepared according to a) above.

The compositions were then applied to each lock and left on for 15 minutes at  
25 room temperature. The treated locks were then wrung out.

*B2) Protocol for Brazilian straightening with conventional iron:*

The locks of keratin fibres were combed, then were subjected to 5 successive  
blow drying passes, at position 2 (80 °C) of the hairdryer, with a round brush of medium  
30 diameter. Each of the locks was then separated into 2. Each part was subjected to 10  
passes with the straightening iron using a comb on each half, then 2/3 passes over all  
of it.

The locks were then washed with a shampoo such as Ultra-Doux camomile and  
blossom honey.

35 Each lock was then pressed at various points so as not to interfere with the curl,  
then dried flat.

*B3) Protocol with iron and steam*

The locks were wetted by 5 passes under water at 37°C then were placed in a  
40 glass chute.

0.054 g of crosslinking agent to be tested were introduced into an 8 ml flask with 5.4 g of solvent (water, ethanol or isododecane), i.e. 5.454 g of compositions which were prepared according to a) above.

The compositions were then applied to each lock and left in for 15 minutes at room temperature. The treated locks were then wrung out.

*B4) Protocol for Brazilian straightening with steam iron:*

The locks of keratin fibres were combed, then were subjected to 5 successive blow drying passes, at position 2 (80 °C) of the hairdryer, with a round brush of medium diameter. Each of the locks was then separated into 2. Each part was subjected to 3 15-second passes (27 cm long lock) with the steam iron on each half, then 2/3 passes over all of it.

The locks were then washed with a shampoo such as Ultra-Doux camomile and blossom honey.

Each lock was then pressed at various points so as not to interfere with the curl, then dried flat.

c). Results of the evaluation:

The vitro orientation tests were evaluated on the following 4 criteria: curl relaxation, feel, manageability and durability.

The means of the performance of the crosslinking agents with steam iron (invention) and with conventional iron have been compiled in the tables below:

Inventive process vs comparative process	Rating for property of "immediate straightening" / curl relaxation
Malic acid <u>17</u> + steam iron (invention)	++
<i>Malic acid 17 + iron (comparative)</i>	+
Lyxose <u>19</u> + steam iron (invention)	+++
<i>Lyxose 19 + iron (comparative)</i>	++
Erythrose <u>21</u> + steam iron (invention)	+
<i>Erythrose 21 + iron (comparative)</i>	-
D-glucoronolactone <u>25</u> + steam iron (invention)	+++
<i>D-glucoronolactone 25 + iron (comparative)</i>	++
Maleamic acid <u>24</u> + steam iron (invention)	++
<i>Maleamic acid 24 + iron (comparative)</i>	+
Diethyl maleate <u>26</u> + steam iron (invention)	+
<i>Diethyl maleate 26 + iron (comparative)</i>	-

Inventive process vs comparative process	Rating for property of "soft touch" / feel
Lyxose <b>19</b> + steam iron (invention)	++
<i>Lyxose <b>19</b> + iron (comparative)</i>	+
Erythrose <b>21</b> + steam iron (invention)	+++
<i>Erythrose <b>21</b> + iron (comparative)</i>	++
Ribose <b>23</b> + steam iron (invention)	++
<i>Ribose <b>23</b> + iron (comparative)</i>	+
Tartaric acid <b>18</b> + steam iron (invention)	+
<i>Tartaric acid <b>18</b> + iron (comparative)</i>	-
Glycolic acid <b>20</b> + steam iron (invention)	++
<i>Glycolic acid <b>20</b> + iron (comparative)</i>	-
Maleamic acid <b>24</b> + steam iron (invention)	++
<i>Maleamic acid <b>24</b> + iron (comparative)</i>	+

Inventive process vs comparative process	Rating for property of "volume reduction" / manageability
Malic acid <b>17</b> + steam iron (invention)	++
<i>Malic acid <b>17</b> + iron (comparative)</i>	+
Ribose <b>23</b> + steam iron (invention)	+
<i>Ribose <b>21</b> + iron (comparative)</i>	-
Tartaric acid <b>18</b> + steam iron (invention)	+
<i>Tartaric acid <b>18</b> + iron (comparative)</i>	-
Glycolic acid <b>20</b> + steam iron (invention)	++
<i>Glycolic acid <b>20</b> + iron (comparative)</i>	-
Diallyl maleate <b>22</b> + steam iron (invention)	++
<i>Diallyl maleate <b>22</b> + iron (comparative)</i>	+
Diethyl maleate <b>26</b> + steam iron (invention)	+
<i>Diethyl maleate <b>26</b> + iron (comparative)</i>	-

Inventive process vs comparative process	Rating for property of "clear facilitation of daily hair styling" / durability
Erythrose <u>21</u> + steam iron (invention)	+++
<i>Erythrose 21 + iron (comparative)</i>	++
Ribose <u>23</u> + steam iron (invention)	++
<i>Ribose 23 + iron (comparative)</i>	-
Glycolic acid <u>20</u> + steam iron (invention)	+++
<i>Glycolic acid 20 + iron (comparative)</i>	-
Diallyl maleate <u>22</u> + steam iron (invention)	+
<i>Diallyl maleate 22 + iron (comparative)</i>	-
Maleamic acid <u>24</u> + steam iron (invention)	+
<i>Maleamic acid 24 + iron (comparative)</i>	-
Diethyl maleate <u>26</u> + steam iron (invention)	+
<i>Diethyl maleate 26 + iron (comparative)</i>	-

Key to rating:

1- no effect (-)

2- slight effect (+)

5 3- pronounced effect (++)

4- good effect (+++)

10 The process according to the invention which employs the steam iron step made it possible to obtain significant superiority in terms of the cosmetic performance obtained over all the evaluation criteria, compared to the comparison, i.e. conventional straightening iron without steam.

It became apparent that all the parameters are significantly superior with the process of the invention which employs a steam iron step, vs. the comparative process, which represents a very large gain in performance.

15 Curl relaxation is far better with the care provided to the hair with the process for treating keratin fibres of the invention than the process without steam iron. In addition, the straightening time proved to be much shorter, which made it possible, in terms of the process for treating keratin fibres, for professional hairdressers to save time and avoids additional actions for said professionals. The process according to the invention  
20 made it possible to obtain good long-lasting curl relaxation.

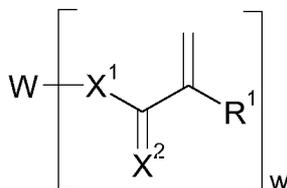
The straightening time was reduced on average by three compared to a conventional process without steam.

## CLAIMS

1. Process for treating keratin fibres, especially human keratin fibres such as the hair, employing:

- 5 i) a step of applying at least one crosslinking agent which contains at least one (thio)carbonyl group; and  
 ii) a step of straightening/relaxing by means of a steam iron;  
 in particular, i) is applied first then secondly ii) the steam straightening iron is applied without an intermediate rinsing step.

10 2. Process according to the preceding claim, wherein the (thio)carbonyl groups-containing crosslinking agent(s) is(are) selected from that(those) of formula (I):



in which formulae (I):

- **W** represents:
 

15 i) either an optionally substituted (hetero)aryl or optionally substituted (hetero)cycloalkyl group, and preferably represents a 5- or 6-membered phenyl or heteroaryl such as pyridinyl or 5- to 8-membered heterocycloalkyl comprising at least one oxygen atom, such as tetrahydrofuryl, piperazinyl or hexahydrofuro[3,2-b]furanlyl,

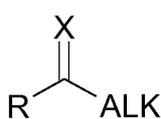
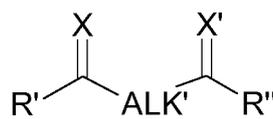
20 ii) or a  $^* -A-(CR^2R^3)_x -A^*$  group, where  $w$  is equal to 2, with  $R^2$  and  $R^3$ , which are identical or different, representing a hydrogen atom or a  $(CrC_6)$ alkyl group such as methyl,  $x$  represents an integer of between 0 and 10 inclusive, preferably  $x$  is equal to 1,  $^*$  represents the point of attachment to the  $-X^1-C(X^2)-C(=CH_2)-R^1$  groups and **A** represents an optionally substituted (hetero)aryl or optionally substituted (hetero)cycloalkyl group, preferably **A** represents a phenyl;

25 iii) or a linear or branched polyvalent, preferably divalent or trivalent, saturated or unsaturated, preferably saturated, hydrocarbon-based chain, optionally substituted, preferably by a hydroxyl group or a phenyl group, and comprising from 1 to 20 carbon atoms;
- $R^1$  represents a hydrogen atom or a  $(CrC_4)$ alkyl group, preferably  $R^1$  represents a methyl group ;
- $X^1$  represents an oxygen atom, a sulfur atom, or a  $-N(R^1)-$  group with  $R^1$  as defined above, preferably  $X^1$  represents an oxygen atom or a  $-N(R^1)-$  group with  $R^1$  as defined above ;
- 35 •  $X^2$  represents an oxygen atom or a sulfur atom, preferably  $X^2$  represents an oxygen atom ;

- **w** represents an integer of between 2 and 10 inclusive, more particularly between 2 and 5, such that  $w = 2$  or  $3$ ;

in particular **W** represents a **Ci-C<sub>6</sub>** divalent or **c-i-c-io** trivalent alkyl group.

- 5      3. Process according to either of the preceding claims, wherein the (thio)carbonyl group(s)-containing crosslinking agent(s) is(are) selected from that(those) of formula **(II)** or **(III)**:

**(II)****(III)**

and also the organic or mineral acid or base salts thereof, the tautomers thereof, and  
10 the solvates thereof such as hydrates;

in which formulae **(II)** and **(III)**:

- **X** and **X'**, which are identical or different, preferably identical, represent an oxygen atom or a sulfur atom, preferably oxygen;
- **ALK** represents a linear or branched hydrocarbon-based chain comprising from  
15 1 to 10 carbon atoms, which is saturated or unsaturated, in particular with 1 to 3 conjugated or unconjugated unsaturations; said chain is optionally substituted by one or more groups chosen from:
  - a hydroxyl group;
  - a  $-\text{C}(\text{X})-\text{OR}_b$  group with **X** as defined above, and  $\text{R}_b$  representing a hydrogen  
20 atom, an alkali metal or an alkaline earth metal, and
    - a saturated or unsaturated, non-aromatic 4- to 8-membered heterocyclic lactone group which may optionally be substituted especially by one or more hydroxyl groups ; preferably the non-aromatic 4- to 8-membered heterocyclic lactone group is saturated ;
- **ALK'** represents a linear or branched divalent hydrocarbon-based chain comprising from 1 to 10 carbon atoms, which is saturated or unsaturated, in particular with 1 to 3 conjugated or unconjugated unsaturations;
- **R** represents i) a hydrogen atom or ii) an  $\text{OR}_a$  group with  $\text{R}_a$  representing a hydrogen atom, an alkali metal or an alkaline earth metal, or a **(CrC<sub>6</sub>)**alkyl, **(C<sub>2</sub>-C<sub>6</sub>)**alkenyl, or **(C<sub>2</sub>-C<sub>6</sub>)**alkynyl group; preferably, **R** represents a hydrogen atom or an  $\text{OR}_a$  group with  $\text{R}_a$  representing a hydrogen atom or an alkali metal or alkaline earth metal;
- **R'** and **R''** which are identical or different, represent a group chosen from:
  - $\text{ALK}''-0-$  with  $\text{ALK}''$  representing a linear or branched hydrocarbon-based  
35 chain comprising from 1 to 10 carbon atoms, and optionally from 1 to 3 conjugated or unconjugated unsaturations; preferably,  $\text{ALK}''$  represents a **(CrC<sub>6</sub>)**alkyl, **(C<sub>2</sub>-C<sub>6</sub>)**alkenyl or **(C<sub>2</sub>-C<sub>6</sub>)**alkynyl group;

- $-C(0)-OR_b$  with  $R_b$  representing a hydrogen atom, an alkali metal or an alkaline earth metal;
- an  $NR_cR_d$  amino group with  $R_c$  and  $R_d$ , which are identical or different, representing a hydrogen atom or a  $(CrC_6)$ alkyl,  $(C_2-C_6)$ alkenyl, or  $(C_2-C_6)$ alkynyl group, preferably  $NH_2$ ;

5 it being understood that ALK', R' or R" contains at least one group comprising at least one unsaturation.

4. Process according to any one of the preceding claims, wherein the  
10 (thio)carbonyl group(s)-containing crosslinking agent(s) is(are) selected from that(those) of formula (II) as defined in the preceding claim.

5. Process according to any one of the preceding claims, wherein the  
15 (thio)carbonyl group(s)-containing crosslinking agent(s) is(are) selected from that(those) of formula (II) as defined in the preceding claim with R representing i) a hydrogen atom.

6. Process according to any one of Claims 1 to 4, wherein the (thio)carbonyl  
20 group(s)-containing crosslinking agent(s) is(are) selected from that(those) of formula (II) as defined in Claim 3, with R representing ii) an  $OR_a$  group with  $R_a$  representing a hydrogen atom, an alkali metal, an alkaline earth metal, or a  $(CrC_4)$ alkyl group; preferably, R represents an  $OR_a$  group with  $R_a$  representing a hydrogen atom, an alkali metal or an alkaline earth metal.

7. Process according to any one of the preceding claims, wherein the  
25 (thio)carbonyl group(s)-containing crosslinking agent(s) is(are) selected from that(those) of formula (II) as defined in Claim 3, with ALK representing a  $(CrC_6)$ alkyl group optionally substituted by one or more groups chosen from:

- a) hydroxy;
- 30 b)  $-C(0)-OR_b$  with  $R_b$  representing a hydrogen atom, an alkali metal or an alkaline earth metal; and
- c) a 4- to 6-membered lactone heterocycle which may optionally be substituted by one to three hydroxyl groups ; preferably the 4- to 6-membered heterocyclic lactone group is saturated ;

35 in particular, ALK is substituted by one or more groups chosen from a) and c) as defined above.

8. Process according to any one of the preceding claims, wherein the  
40 (thio)carbonyl group(s)-containing crosslinking agent(s) is(are) selected from that(those) of formula (II) as defined in Claim 3, with X representing an oxygen atom.

9. Process according to any one of Claims 1 to 3, wherein the crosslinking agent(s) is(are) of formula (III) as defined in Claim 3.

10 5 10. Process according to any one of Claims 1 to 3 and 9, wherein the crosslinking agent(s) is(are) of formula (III) as defined in Claim 3, with  $R'$  and  $R''$ , which are identical or different, representing  $ALK''-O-$  with  $ALK''$  as defined above; preferably,  $ALK''$  are identical and represent a  $(CrC_6)$ alkyl, or  $(C_2-C_6)$ alkenyl group.

11. Process according to any one of Claims 1 to 3 and 9, wherein the crosslinking agent(s) is(are) of formula (III) as defined in Claim 3, with  $R'$  and  $R''$ , which are identical or different, representing:

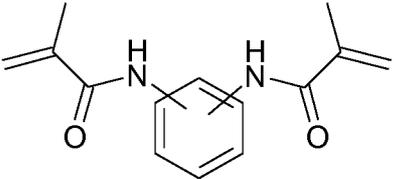
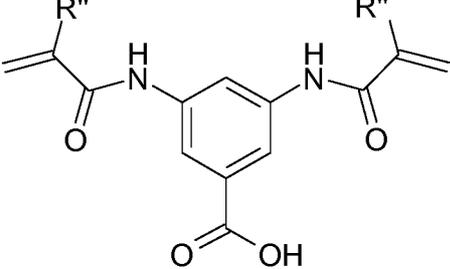
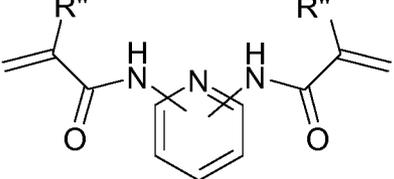
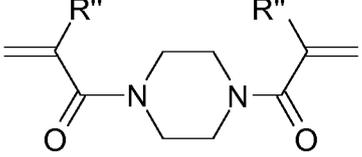
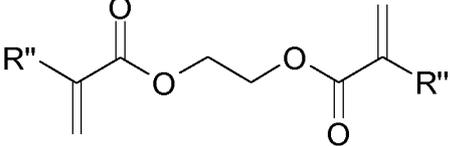
- $-C(O)-OR_b$  with  $R_b$  representing a hydrogen atom, an alkali metal or an alkaline earth metal;
- an  $NR_cR_d$  amino group with  $R_c$  and  $R_d$ , which are identical or different, representing a hydrogen atom or a  $(CrC_6)$ alkyl,  $(C_2-C_6)$ alkenyl, or  $(C_2-C_6)$ alkynyl group, preferably an amino group  $NH_2$ .

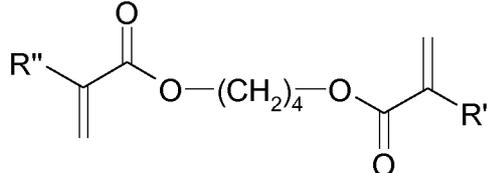
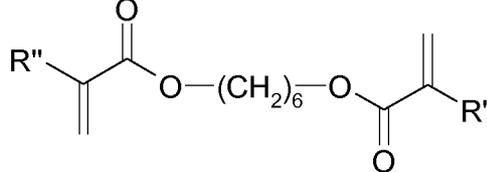
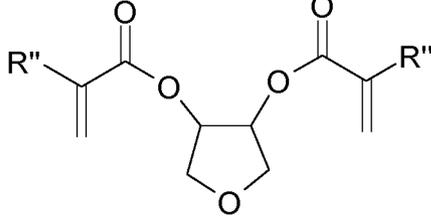
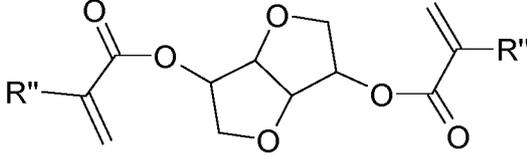
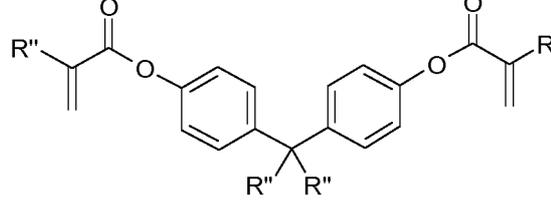
12. Process according to any one of Claims 1 to 3 and 9 to 11, wherein the crosslinking agent(s) is(are) of formula (III) as defined in Claim 3, with  $ALK'$  representing a linear or branched divalent hydrocarbon-based chain comprising from 1 to 6 carbon atoms, unsaturated with 1 to 3 conjugated or unconjugated unsaturations; preferably,  $ALK'$  represents a  $(C_2-C_6)$ alkenylene, or  $(C_2-C_6)$ alkynylene, more preferentially  $(C_2-C_6)$ alkenylene, even more preferentially  $(C_2-C_4)$ alkenylene group such as ethylene  $-CH=CH-$ .

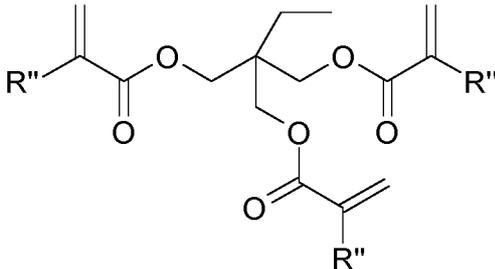
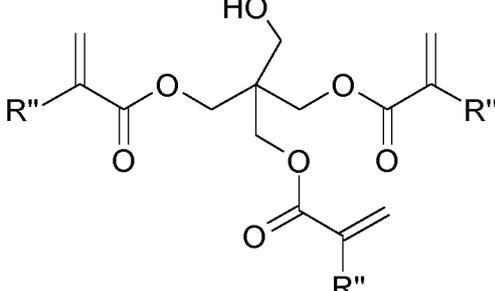
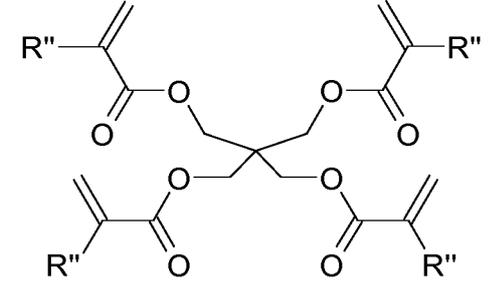
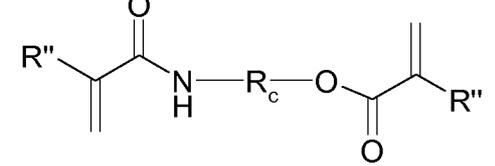
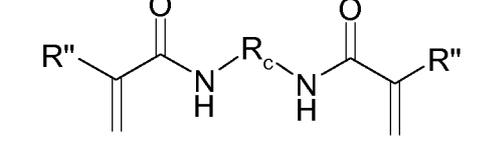
13. Process according to any one of Claims 1 to 3 and 9 to 12, wherein the crosslinking agent(s) is(are) of formula (III) as defined in Claim 3, with  $X$  and  $X'$  representing an oxygen atom.

14. Process according to any one of the preceding claims, wherein the crosslinking agent(s) is(are) of the following formula and the optical and geometric isomers thereof, the tautomers and mineral or organic acid or base salts thereof:

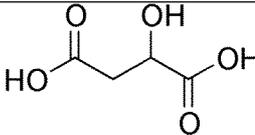
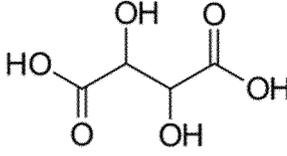
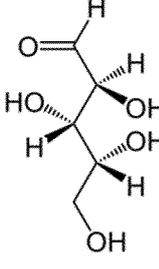
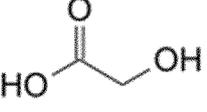
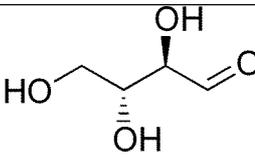
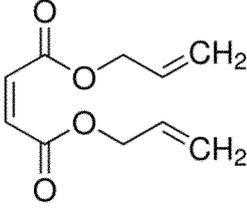
Name	Abbreviation/no.	Structure
1,3-phenylenediacrylamide; 1,4-phenylenediacrylamide	<u>1</u>	

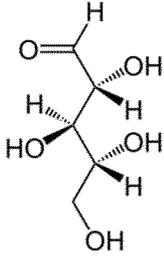
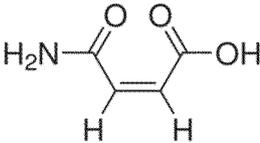
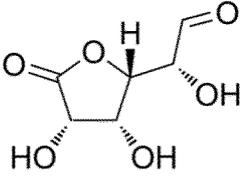
<p><i>N,N'</i>-1,3-phenylenebis(2-methyl-2-propenamide);</p> <p><i>N,N'</i>-1,4-phenylenebis(2-methyl-2-propenamide)</p>	<u>2</u>	
<p>3,5-Bisacrylamido benzoic acid with R'' identical and equal to H; and 3,5-bismethylacrylamido-benzoic acid with R'' identical and equal to CH<sub>3</sub></p>	<u>3</u>	 <p>R'' = H or CH<sub>3</sub></p>
<p>2,6-bisacryloylamidopyridine with R'' identical and equal to H;</p> <p>2,6-bismethylacryloylamidopyridine with R'' identical and equal to CH<sub>3</sub></p>	<u>4</u>	 <p>R'' = H or CH<sub>3</sub></p>
<p>1,4-diacryloylpiperazine with R'' identical and equal to H;</p> <p>1,4-dimethylacryloylpiperazine with R'' identical and equal to CH<sub>3</sub></p>	(DAP) <u>5</u>	 <p>R'' = H or CH<sub>3</sub></p>
<p>Ethylene glycol dimethacrylate with R'' identical and equal to CH<sub>3</sub> (EGDMA); ethylene glycol diacrylate with R'' identical and equal to H</p>	(EGDMA) <u>6</u>	 <p>R'' = H or CH<sub>3</sub></p>

<p>Tetramethylene dimethacrylate with R'' identical and equal to CH<sub>3</sub>; tetramethylene diacrylate with R'' identical and equal to H</p>	<p>(TDMA)</p> <p><u>7</u></p>	 <p>R'' = H or CH<sub>3</sub></p>
<p>Hexamethylene dimethacrylate with R'' identical and equal to CH<sub>3</sub> and hexamethylene diacrylate with R'' identical and equal to H</p>	<p><u>8</u></p>	 <p>R'' = H or CH<sub>3</sub></p>
<p>Anhydroerythritol dimethacrylate with R'' identical and equal to CH<sub>3</sub> and anhydroerythritol diacrylate with R'' identical and equal to H</p>	<p><u>9</u></p>	 <p>R'' = H or CH<sub>3</sub></p>
<p>1,4:3,6-Dianhydro-p-sorbitol-2,5-dimethacrylate with R'' identical and equal to CH<sub>3</sub>; 1,4:3,6-dianhydro-p-sorbitol-2,5-diacrylate with R'' identical and equal to H</p>	<p><u>10</u></p>	 <p>R'' = H or CH<sub>3</sub></p>
<p>Isopropenebis(1,4-phenylene) dimethacrylate with R'' identical and equal to CH<sub>3</sub>; isopropenebis(1,4-phenylene) diacrylate with R'' identical and equal to H</p>	<p><u>11</u></p>	 <p>R'' = H or CH<sub>3</sub></p>

<p>2,2-bis(Hydroxymethyl)butanol trimethacrylate with R'' identical and equal to CH<sub>3</sub> (TRIM); 2,2-bis(hydroxymethyl)butanol triacrylate with R'' identical and equal to H</p>	<p>(TRIM) <u>12</u></p>	 <p>R'' = H or CH<sub>3</sub></p>
<p>Pentaerythritol triacrylate with R'' identical and equal to H; Pentaerythritol trimethacrylate with R'' identical and equal to CH<sub>3</sub></p>	<p><u>13</u></p>	 <p>R'' = H or CH<sub>3</sub></p>
<p>Pentaerythritol tetraacrylate with R'' identical and equal to H (PETRA); Pentaerythritol tetramethacrylate with R'' identical and equal to CH<sub>3</sub></p>	<p>(PETRA) <u>14</u></p>	 <p>R'' = H or CH<sub>3</sub></p>
<p>N,O-bismethacryloylethanolamine with R<sub>c</sub> equal to ethylene and R'' identical and equal to CH<sub>3</sub></p>	<p>(NOBE) <u>15</u></p>	 <p>R<sub>c</sub> = (C<sub>1</sub>-C<sub>6</sub>)alkylene such as ethylene R'' = H or CH<sub>3</sub></p>
<p>N,N'-methylenebisacrylamide with R<sub>c</sub> = CH<sub>2</sub> (MDAA); or N,N'-1,2-ethanediylbis(2-methyl-2-propenamide) N,N'-ethylenebisacrylamide</p>	<p>(MDAA) <u>16</u></p>	 <p>R<sub>c</sub> = (C<sub>1</sub>-C<sub>6</sub>)alkylene</p>

with $R_c = \text{CH}_2\text{-CH}_2$ ;  <i>N,N'</i> -butylenebisacrylamide with $R_c = \text{CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2$ ;  <i>N,N'</i> -hexylenebisacrylamide with $R_c = \text{CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2$		$R'' = \text{H or CH}_3$
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Malic acid	<u>17</u>	
Tartaric acid	<u>18</u>	
Lyxose	<u>19</u>	
Glycolic acid	<u>20</u>	
Erythrose	<u>21</u>	
Diallyl maleate	<u>22</u>	

Ribose	<u>23</u>	
Maleamic acid	<u>24</u>	
Glucoronolactone	<u>25</u>	
Diethyl maleate	<u>26</u>	

15 15. Process according to any one of the preceding claims, wherein the (thio)carbonyl group(s)-containing crosslinking agent(s) as defined in any one of the preceding claims is(are) in a cosmetic composition, preferably in an amount of between 1% and 80% by weight of the composition which comprises it(them), more particularly in an amount of between 3% and 50% by weight, preferentially between 5% and 30% by weight, more preferentially between 7% and 20% by weight, such as 10% by weight relative to the total weight of the composition comprising it(them).

10 16. Process according to any one of the preceding claims, wherein, in the step ii) of straightening/relaxing by means of a steam iron, said iron being at a temperature of between 65°C and 250°C, particularly between 80°C and 230°C, more particularly greater than or equal to 100°C and preferentially between 100°C and 190°C; preferably, step ii) of the process for treating keratin fibres is carried out at a  
15 temperature ranging from 150°C to 220°C, preferably ranging from 160°C to 220°C, preferentially ranging from 160°C to 210°C, especially ranging from 180°C to 200°C.

20 17. Process according to any one of the preceding claims, wherein, in the step ii) of straightening/relaxing by means of a steam iron, said iron being applied with a continuous movement from the root to the tip of said fibres, in particular human keratin fibres such as the hair, in one or more passes, in particular in two to twenty passes, the duration of each pass of the iron may range from 2 seconds to 1 minute.

18. Process according to any one of the preceding claims, wherein, in the step ii) of straightening/relaxing by means of a steam iron, the steam having a flow rate of less than 5 g/min, in particular of between 1 and 4 g/min, preferably step ii) is carried out  
5 with a steam straightener.

INTERNATIONAL SEARCH REPORT

International application No  
PCT/EP2016/077215

A. CLASSIFICATION OF SUBJECT MATTER  
 INV. A61Q5/04 A61K8/35 A61K8/365 A61K8/42 A61K8/49  
 A61K8/60  
 ADD.  
 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)  
 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 practicable, search terms used)  
 EPO-Internal , WPI Data, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	FR 2 921 805 AI (OREAL [FR] ) 10 April 2009 (2009-04-10)	1,3-18
A	example 2 the whole document	2
X	FR 2 943 895 AI (OREAL [FR] ) 8 October 2010 (2010-10-08)	1,3-18
A	example 2 the whole document	2
X	FR 3 015 244 AI (OREAL [FR] ) 26 June 2015 (2015-06-26)	1,3-18
A	the whole document	2
A	US 2013/233333 AI (ROULET CHARLOTTE [FR] ET AL) 12 September 2013 (2013-09-12) paragraph [0401] - paragraph [0404] claim 16	1-18
	----- -/- .	

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	"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
"E" earlier application or patent but published on or after the international filing date	"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
"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)	"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
"O" document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search  2 December 2016	Date of mailing of the international search report  21/12/2016
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  Di ebol d, Al ai n

## INTERNATIONAL SEARCH REPORT

 International application No  
 PCT/EP2016/077215

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2012/312317 AI (MANNOZZI ALDERANO [IT] ) 13 December 2012 (2012-12-13) the whole document -----	1-18
A	wo 2014/118212 AI (OREAL [FR] ) 7 August 2014 (2014-08-07) the whole document -----	1-18
A	EP 0 662 314 AI (KAO CORP [JP] ) 12 July 1995 (1995-07-12) the whole document -----	1-18
A	wo 03/084490 AI (MNEMOSCI ENCE GMBH [DE] ; LENDLEIN ANDREAS [DE] ; GRASSER WERNER [DE] ; KR) 16 October 2003 (2003-10-16) the whole document -----	2
A	US 2011/251299 AI (COOK CLINTON J [US] ET AL) 13 October 2011 (2011-10-13) the whole document -----	2

## INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2016/077215

Patent document cited in search report	Publication date	Patent family member(s)	Publication date	
FR 2921805	AI	10-04-2009	CN 101808548 A	18-08-2010
			EP 2205119 AI	14-07-2010
			FR 2921805 AI	10-04-2009
			JP 2010540137 A	24-12-2010
			KR 20100063778 A	11-06-2010
			US 2010307528 AI	09-12-2010
			Wo 2009043909 AI	09-04-2009
FR 2943895	AI	08-10-2010	BR PI 1001018 A2	26-04-2011
			CN 101856172 A	13-10-2010
			CN 105831947 A	10-08-2016
			EP 2236053 AI	06-10-2010
			ES 2576735 T3	11-07-2016
			FR 2943895 AI	08-10-2010
			JP 2010241812 A	28-10-2010
			JP 2016025937 A	12-02-2016
			KR 20100110748 A	13-10-2010
			MX 338820 B	03-05-2016
			US 2010258141 AI	14-10-2010
FR 3015244	AI	26-06-2015	NONE	
US 2013233333	AI	12-09-2013	BR 112013007567 A2	26-07-2016
			CN 103140213 A	05-06-2013
			EP 2621465 A2	07-08-2013
			FR 2965481 AI	06-04-2012
			JP 2013538842 A	17-10-2013
			US 2013233333 AI	12-09-2013
			Wo 2012042019 A2	05-04-2012
US 2012312317	AI	13-12-2012	AU 2011219795 AI	18-10-2012
			BR PI 1002742 A2	29-05-2012
			BR 112012021410 A2	04-10-2016
			CN 102970962 A	13-03-2013
			EP 2538916 A2	02-01-2013
			IT 1398503 BI	01-03-2013
			JP 2013520468 A	06-06-2013
			JP 2016047851 A	07-04-2016
			RU 2012140303 A	27-03-2014
			SG 183477 AI	27-09-2012
			SG 10201406083S A	27-11-2014
US 2012312317 AI	13-12-2012			
wo 2011104282 A2	01-09-2011			
wo 2014118212	AI	07-08-2014	FR 3001385 AI	01-08-2014
			US 2016000693 AI	07-01-2016
			wo 2014118212 AI	07-08-2014
EP 0662314	AI	12-07-1995	AT 186204 T	15-11-1999
			DE 69421508 DI	09-12-1999
			DE 69421508 T2	04-05-2000
			EP 0662314 AI	12-07-1995
			JP H07165539 A	27-06-1995
wo 03084490	AI	16-10-2003	AU 2003224060 AI	20-10-2003
			AU 2003227596 AI	20-10-2003
			BR 0304411 A	27-07-2004
			BR 0304414 A	01-02-2005

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2016/077215

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
		EP 1492492 AI	05-01 -2005
		EP 1492493 AI	05-01 -2005
		JP 2005527571 A	15-09-2005
		JP 2005529095 A	29-09 -2005
		US 2005244353 AI	03-11 -2005
		US 2006140892 AI	29-06 -2006
		W0 03084489 AI	16-10-2003
		W0 03084490 AI	16-10 -2003
-----			
US 2011251299	AI	13-10-2011	NONE
-----			