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(54) Title: COSMETIC PROCESS FOR ATTENUATING WRINKLES

(57) Abstract: The invention relates to a cosmetic process for caring for wrinkled skin, comprising: the topical application to the skin of a thiol or of a composition, in particular a cosmetic composition, containing same, leaving it on for a period ranging from 1 minute to one hour, followed by the application to the treated skin of a composition, in particular a cosmetic composition, comprising a polysaccharide polymer grafted with (meth)acrylate groups.
Cosmetic process for attenuating wrinkles

The present invention relates to a skincare process, in particular a cosmetic skincare process, intended to attenuate wrinkles, comprising the application to the skin of a particular thiol compound, and then of a polysaccharide polymer grafted with (meth)acrylate groups.

During the ageing process, various signs appear on the skin, which are very characteristic of this ageing, resulting in particular in a modification of skin structure and functions. The main clinical signs of skin ageing are in particular the appearance of fine lines and deep wrinkles, which increase with age.

It is known practice to treat these signs of ageing using cosmetic or dermatological compositions containing active agents capable of combating ageing, such as a-hydroxy acids, β-hydroxy acids and retinoids. These active agents act on wrinkles by eliminating dead skin cells and by accelerating the cell renewal process. However, these active agents have the drawback of only being effective for the treatment of wrinkles after a certain application time. However, it is increasingly sought to obtain an immediate effect of the active agents used, rapidly resulting in smoothing out of wrinkles and fine lines and in the disappearance of the signs of fatigue.

The inventors have discovered that by applying to the skin first a thiol and then a polysaccharide polymer grafted with (meth)acrylate groups, such a process results in a film-forming deposit on the skin which has a good tensioning effect on the skin, thus making it possible to immediately attenuate wrinkles on the skin. Furthermore, this tensioning effect exhibits good water resistance, and therefore good persistence with respect to water.

Polymers of hyaluronic acid grafted with (meth)acrylate groups are described in document WO 2007/106738 and the publications J. Burdick et al "Controlled degradation and mechanical behavior photopolymerized hyaluronic acid networks", Biomacromolecules, 2005, 6, pages 386-391; Mark Grinstaff "Photocrosslinkable polysaccharides for in situ hydrogel formation", Journal of biomedical materials research, 2001 , volume 55, Issue 2, pages 115-121. They have been used to form hydrogels after crosslinking.

Polymers of dextran grafted with methacrylate groups are described in document WO 2010/083039. They are used in combination with riboflavin and arginine or chitosan for forming, after crosslinking under UV exposure or exposure to visible light, hydrogels which are applied to the skin.

Carrageenans are known for their skin tensioning properties, in particular in document FR-A-2838343.

More specifically, a subject of the present invention is a process, in particular a cosmetic process, for caring for the skin, more particularly facial skin, in particular wrinkled skin, comprising:

the topical application to the skin of at least one thiol, preferably one thiol, or of a composition, in particular a cosmetic composition, containing same (composition A), leaving it on for a period ranging from 1 minute to one hour,

followed by the application to the treated skin of a composition, in particular a cosmetic composition, comprising at least one polysaccharide polymer grafted with (meth)acrylate groups (composition B).

A subject of the invention is also a kit comprising a first composition (composition B), which is in particular a cosmetic composition, comprising at least one grafted polysaccharide polymer as previously defined and a second composition (composition A), which is in particular a cosmetic composition, comprising at least one thiol compound as previously defined, the first and second compositions each being packaged in a distinct packaging assembly.

The composition packaging assembly is, in a known manner, any packaging that is suitable for storing cosmetic compositions (in particular a bottle, tube, spray bottle or aerosol bottle).

Such a kit allows the skin treatment process according to the invention to be performed.

The process according to the invention is in particular intended for smoothing out wrinkled human facial and/or body skin, in particular for reducing or effacing wrinkles and/or fine lines on the skin.

The tensioning effect may be characterized by means of an in vitro retraction test as described in Examples 1 to 7.

The term "a thiol" or "a thiol compound" will subsequently be used without implied distinction to denote the thiol compound used according to the invention.
The thiol used in the process according to the invention is a compound comprising one or more thiol groups (SH). This thiol may be a monothiol or a polythiol as described hereinafter.

The term "polythiol" is intended to mean any compound bearing two or more than two thiol groups SH. It may be a non-polymeric organic molecule bearing two or more than two thiol groups, or a polymer bearing two or more than two thiol groups.

The thiol group according to the invention must not contain vinyl (C=) (non-aromatic) or acetylenic (C=C) functions. The polythiol compound may be aromatic or heteroaromatic or may contain an aromatic radical.

The thiol compound used according to the invention may also contain one or more heteroatoms chosen from O, N and S and/or one or more functions chosen from ester, ketone, amide, urea and isocyanurate functions.

Preferably, the polythiol compound according to the invention may also contain one or more heteroatoms chosen from O, N and S and/or one or more functions chosen from ester and ketone functions.

The thiol compound according to the invention denotes a non-polymeric organic compound and can be represented by formula (I)

$$W(SH)_n$$

(I)

in which n denotes an integer greater than or equal to 1, preferably between 1 and 10, preferably between 1 and 4 (limits included), and W denotes a linear or branched or (hetero)cyclic, saturated C_{2n-2}C_{60} monovalent \((n = 1)\) or multivalent (at least divalent) \((n > 1)\) radical, an aromatic radical or a heteroaromatic cyclic radical, it being possible for W to also contain one or more heteroatoms such as O, N, S or Si and/or one or more functions chosen from carboxylic acid, ester, ketone, amide, urea and isocyanurate functions, preferably ester, ketone and carboxylic acid functions, and/or to be substituted with one or more linear or branched C_{1-1}C_{10} alkyl, hydroxyl, amino, (C_{1-6} alkyl) amino, carboxylic acid, carboxylate, or linear or branched C_{1-1}C_{10} alkoxy groups, it being understood that, when the W radical is substituted, the thiol functions can be borne by the substituent(s).

The term "cyclic radical" is intended to mean a hydrocarbon-based saturated monocyclic or heterocyclic radical, a saturated or aromatic polycyclic radical, for example biphenyl, or condensed rings, for instance the naphthyl radical.
The molar mass of the compounds of formula (I) is generally between 70 and 1500 g/mol and preferably between 70 and 500 g/mol.

According to a first embodiment, the thiol compound of formula (I) is a monothiol: \( n = 1 \) and \( W \) is a monovalent radical.

Preferably, according to this first embodiment, \( W \) denotes a linear or branched saturated, or aromatic, \( \text{C}_2\text{C}_\to \) monovalent radical, it being possible for \( W \) to also contain one or more heteroatoms such as O, N, S or Si, and/or one or more functions chosen from carboxylic acid, ester and amide functions, and/or to be substituted with one or more linear or branched \( \text{Cl-C}_4 \) alkyl, hydroxyl, amino, \( \text{(Cl-C}_3 \text{ alkyl)} \) amino, carboxylic acid, carboxylate, or linear or branched \( \text{Cl-C}_4 \) alkoxy groups, it being understood that, when the \( W \) radical is substituted, the thiol functions can be borne by the substituent(s).

According to this embodiment, the monothiol compound may be chosen, for example, from thioglycolic acid, thiolactic acid, thiamalic acid, 2-mercaptoacetic acid, 3-mercaptopropionic acid, thiosalicylic acid, thiopropionic acid, glutathione, cysteine, N-acetyl cysteine, homocysteine and mercaptoacetic acid, and \( \text{Cl-C}_4 \) alcohol esters thereof, cysteamine, N-acetyl cysteamine, thioglycerol, 2-mercaptoethanol, 1-mercapto-2-propanol, 3-mercapto-1-propanol, 2-(trimethylsilyl)ethanethiol, (3-mercaptomethyl)trithioxsilane, the compounds of formula \( \text{HS-(CH}_2)_n\text{-NH-(CH}_2)_m\text{-NH}_2 \), \( n \) and \( m \) being integers ranging from 1 to 4, ortho-aminothiophenol, meta-aminothiophenol, and para-aminothiophenol.

Preferably, according to this embodiment, the thiol (I) is chosen from cysteine, cysteamine, thioglycolic acid and (3-mercaptomethyl)trithioxsilane.

According to a second embodiment, the thiol compound of formula (I) is such that \( n=2 \) (dithiol) and \( W \) denotes a linear or branched \( \text{C}_2\text{C}_\to \), preferably \( \text{C}_2\text{C}_2 \), hydrocarbon-based saturated divalent radical.

According to this embodiment, the polythiol compound of the invention denotes, for example

- 1,2-ethanediethyl, 1,2-propanediethyl, 1,3-propanediethyl, 1,4-butanediethyl, 1,6-hexanediethyl, 1,7-heptanediethyl, 1,8-octanediethyl, 1,9-nonanediethyl, 1,10-decanediethyl, 1,12-dodecanediethyl, 2,2-dimethyl-1,3-propanediethyl, 3-methyl-1,5-pentanediethyl, or 2-methyl-1,8-octanediethyl.
According to a third embodiment, the compound comprising a thiol unit, of formula (I),
is such that \( n = 3 \) and \( W \) denotes a linear or branched \( \text{C}_3-\text{C}_{20} \), preferably linear or branched \( \text{C}_2-\text{C}_{12} \), hydrocarbon-based saturated trivalent radical.

According to this embodiment, the compound comprising a thiol unit can be chosen, for example, from 1,1,1-tris(mercaptomethy)ethane, 2-ethyl-2-mercaptomethyl-1,3-propanedithiol, and 1,2,3-propanetriol.

According to a fourth embodiment, the compound comprising a thiol unit, of formula (I),
is such that \( n = 2 \) or 3 and \( W \) denotes a linear or branched \( \text{C}_3-\text{C}_{20} \), preferably linear or branched \( \text{C}_2-\text{C}_{12} \), hydrocarbon-based saturated divalent or trivalent radical, said radical containing one or more non-adjacent heteroatom(s) chosen from O and S.

According to this embodiment, the compound comprising a thiol unit can be chosen, for example, from

\[
\text{bis(mercapto(C}_2-\text{C}_{12})\text{alkyl) ethers and sulfides, such as bis(2-mercaptoethyl) ether, bis(2-mercaptoethyl)sulfide, bis(2-mercaptoethylthio-3-mercapto} \text{propane)sulfide,}
\]

\[
0 \quad \text{bis(2-mercapto((C}_3-\text{C}_5)\text{alkyl})thio)} \quad (\text{CrC}_3-\text{C}_5)\text{alkanes or bis(2-mercapto((C}_3-\text{C}_5)\text{alkyl})thio)} \quad (\text{C}_3-\text{C}_5)\text{mercaptoalkanes, for instance}} \quad \text{bis(2-mercaptoethylthio)methane, 1,2-bis(2-mercaptoethylthio)ethane, 1,3-bis(2-mercaptoethylthio)propane, 1,2-bis(2-mercaptoethylthio)propanethiol, 1,2-bis(2-mercaptoethylthio)thio-3-mercapto} \text{propane, or 1,2,3-tris(2-mercaptoethylthio)propane.}
\]

Preferably, according to this embodiment, the compound (I) is chosen from 1,2-bis(2-mercaptoethylthio)propanethiol, 1,2,3-tris(2-mercaptoethylthio)propane, and tetrakis(2-mercaptoethylthiomethyl)methane.

According to a fifth embodiment, the compound comprising a thiol unit, of formula (I),
is such that \( n \) denotes an integer greater than or equal to 2 and \( W \) denotes a linear or branched \( \text{C}_3-\text{C}_{20} \), preferably linear or branched \( \text{C}_2-\text{C}_{12} \), hydrocarbon-based saturated multivalent (at least divalent) radical, said radical containing at least one ester function.

According to this embodiment, the compound comprising a thiol unit can be chosen, for example, from

- esters of polyols (glycols, triols, tetraols, pentaols, hexaols) and of \( \text{C}_5-\text{C}_6 \) mercaptocarboxylic acid, such as ethylene glycol bis(2-mercaptoacetate),
  - ethylene glycol bis(3-mercaptopropionate),
  - ethylene glycol bis(thioglycolate),
  - trimethylolpropane tris(thioglycolate),
  - trimethylolpropane tris(beta-mercaptopropionate),
  - pentaerythritol tetras(thioglycolate),
  - pentaerythritol tetras(beta-mercaptopropionate),
  - dipentaerythritol hexakis(beta-mercaptopropionate),
  - trimethylolpropane tris(2-mercaptoacetate),
  - trimethylolpropane tris(3-mercaptopropionate),
pentaerythritol tetrakis(2-mercaptoacetate), pentaerythritol tetrakis(3-mercaptobutanate), and dipentaerythritol hex-3-mercaptopropionate.

Preferably, according to this embodiment, the compound comprising a thiol unit is chosen from trimethylolpropane tris(2-mercaptoacetate), trimethylolpropane tris(3-mercaptopropionate), pentaerythritol tetrakis(2-mercaptoacetate), pentaerythritol tetrakis(3-mercaptobutanate), and dipentaerythritol hex-3-mercaptopropionate.

Particularly preferably, the compound comprising a thiol unit is pentaerythritol tetrakis(3-mercaptopropionate).

According to a sixth embodiment, the compound comprising a thiol unit, of formula (I), is such that \( n = 4 \) and \( W \) denotes a branched \( C_4-C_{20} \), preferably \( C_8-C_{14} \), hydrocarbon-based saturated tetravalent radical interrupted with one or more non-adjacent sulfur atoms.

According to this embodiment, the compound comprising a thiol unit can be chosen, for example, from tetrakis(2-mercaptoethylthiomethyl)methane and bis-(2-mercaptoethylthio-3-mercaptopropane)sulfide.

According to a seventh embodiment, the compound comprising a thiol unit, of formula (I), is such that \( n = 2 \) and \( W \) denotes a hydrocarbon-based cyclic divalent radical optionally containing one or more non-adjacent sulfur atoms, optionally substituted with one or more linear or branched \( C_1-C_{10} \) alkyl radicals.

According to this embodiment, the compound comprising a thiol unit can be chosen, for example, from 1,4-cyclohexanedithiol, 1,4-bis(mercaptomethyl)cyclohexane, 1,1-cyclohexanediethiol, 1,2-cyclohexanedithiol, 1,1-bis(mercaptomethyl)cyclohexane, and 2,5-dimercapto-1,4-dithiane.

According to an eighth embodiment, the compound comprising a thiol unit, of formula (I), is such that \( n = 3 \) and \( W \) denotes a substituted isocyanurate-type cyclic radical.

According to this embodiment, the compound comprising a thiol unit can be chosen, for example, from polythiols of the isocyanurate class, described in patents US 3 676 440 and US 201 1 023 0585, such as tris((mercaptopropionyloxy)ethyl)isocyanurate.

According to this embodiment, the compound comprising a thiol unit denotes tris((mercaptopropionyloxy)ethyl)isocyanurate.
According to a ninth embodiment, the compound comprising a thiol unit, of formula (I), is such that \( n = 2 \) or 3 or 4 and \( W \) denotes an aromatic radical optionally substituted with one or more identical or different radicals of \( \text{C}_1-\text{C}_{10} \) alkyl or \( \text{C}_1-\text{C}_{10} \) alkoxy type, it being understood that, when the \( W \) radical is substituted, the thiol functions can be borne by the substituent(s).

According to this embodiment, the compound comprising a thiol unit can be chosen, for example, from

1.2-dimercaptobenzene, 1,3-dimercaptobenzene,
1,4-dimercaptobenzene, 1,2-bis(mercaptomethyl)benzene,
1,3-bis(mercaptomethyl)benzene,
1,4-bis(mercaptomethyl)benzene,
1,2-bis(2-mercaptoethyl)benzene,
1,3-bis(2-mercaptoethyl)benzene,
1,4-bis(2-mercaptoethyl)benzene,
1,2-bis(2-mercaptoethyleneoxy)benzene,
1,3-bis(2-mercaptoethyleneoxy)benzene,
1,4-bis(2-mercaptoethyleneoxy)benzene,
1,2,3-trimercaptobenzene,
1,2,4-trimercaptobenzene,
1,3,5-trimercaptobenzene,
1,2,3-tris(mercaptomethyl)benzene,
1,2,4-tris(mercaptomethyl)benzene,
1,3,5-tris(mercaptomethyl)benzene,
1,2,3-tris(2-mercaptoethyl)benzene,
1,2,4-tris(2-mercaptoethyl)benzene,
1,3,5-tris(2-mercaptoethyl)benzene,
1,2,3-tris(2-mercaptoethyleneoxy)benzene,
1,2,4-tris(2-mercaptoethyleneoxy)benzene,
1,3,5-tris(2-mercaptoethyleneoxy)benzene,
1,2,3,4-tetramercaptobenzene,
1,2,3,5-tetramercaptobenzene,
1,2,4,5-tetramercaptobenzene,
1,2,3,4-tetrakis(mercaptomethyl)benzene,
1,2,3,5-tetrakis(mercaptomethyl)benzene,
1,2,4,5-tetrakis(mercaptomethyl)benzene,
1,2,3,4-tetrakis(2-mercaptoethyl)benzene,
1,2,3,5-tetrakis(2-mercaptoethyl)benzene,
1,2,4,5-tetrakis(2-mercaptoethyl)benzene,
1,2,3,4-tetrakis(2-mercaptoethyleneoxy)benzene,
1,2,3,5-tetrakis(2-mercaptoethyleneoxy)benzene,
1,2,4,5-tetrakis(2-mercaptoethylenglyoxy)benzene,
2,2'-dimercaptobiphenyl,
4,4'-dimercaptobiphenyl,
4,4'-dimercaptobibenzyl,
2,5-toluenedithiol,
3,4-toluenedithiol,
1,4-naphthalenedithiol,
1,5-naphthalenedithiol,
2,6-naphthalenedithiol,
2,7-naphthalenedithiol,
2,4-dimethylbenzene-1,3-dithiol,
4,5-dimethylbenzene-1,3-dithiol,
9,10-anthracenedimethanethiol,
1,3-bis(2-mercaptoethylthio)benzene,
1,4-bis(2-mercaptoethylthio)benzene,
1,2-bis(2-mercaptoethylthiomethyl)benzene,
1,3-bis(2-mercaptoethylthiomethyl)benzene,
1,4-bis(2-mercaptoethylthiomethyl)benzene,
1,2,3-tris(2-mercaptoethylthio)benzene,
1,2,4-tris(2-mercaptoethylthio)benzene,
1,3,5-tris(2-mercaptoethylthio)benzene,
1,2,3,4-tetrakis(2-mercaptoethylthio)benzene,
1,2,3,5-tetrakis(2-mercaptoethylthio)benzene,
1,2,4,5-tetrakis(2-mercaptoethylthio)benzene,
3,4-thiophenedithiol.

According to this embodiment, the compound (I) is chosen from 1,2,3-trimercaptobenzene, 1,2,4-trimercaptobenzene, 1,3,5-trimercaptobenzene, 1,2,3-tris(mercaptomethyl)benzene, 1,2,4-tris(mercaptomethyl)benzene, 1,3,5-tris(mercaptomethyl)benzene, 1,2,3-tris(2-mercaptoethyl)benzene, 1,2,4-tris(2-mercaptoethyl)benzene, 1,3,5-tris(2-mercaptoethyl)benzene, 1,2,3,4-tris(2-mercaptoethylenglyoxy)benzene, 1,2,4,5-tetramercaptobenzene, 1,2,3,5-tetramercaptobenzene, 1,2,3,4-tetramercaptobenzene, 1,2,3,5-tetramercaptobenzene, 1,2,3,4,5-tetramercaptobenzene, 1,2,3,5-tetramercaptobenzene, 1,2,4,5-tetramercaptobenzene, 1,2,3,4,5-tetramercaptobenzene, 1,2,3,5-tetramercaptobenzene, 1,2,4,5-tetramercaptobenzene, 1,2,3,4,5-tetramercaptobenzene, 1,2,3,5-tetramercaptobenzene, 1,2,4,5-tetramercaptobenzene, 1,2,3,4,5-tetramercaptobenzene, 1,2,3,5-tetramercaptobenzene, 1,2,4,5-tetramercaptobenzene, 1,2,3,4,5-tetramercaptobenzene, 1,2,3,5-tetramercaptobenzene, 1,2,4,5-tetramercaptobenzene, 1,2,3,4,5-tetramercaptobenzene, 1,2,3,5-tetramercaptobenzene, 1,2,4,5-tetramercaptobenzene, 1,2,3,4,5-tetramercaptobenzene, 1,2,3,5-tetramercaptobenzene, 1,2,4,5-tetramercaptobenzene, 1,2,3,4,5-tetramercaptobenzene, 1,2,3,5-tetramercaptobenzene, 1,2,4,5-tetramercaptobenzene, 1,2,3,4,5-tetramercaptobenzene, 1,2,3,5-tetramercaptobenzene, 1,2,4,5-tetramercaptobenzene, 1,2,3,4,5-tetramercaptobenzene, 1,2,3,5-tetramercaptobenzene, 1,2,4,5-tetramercaptobenzene, 1,2,3,4,5-tetramercaptobenzene, 1,2,3,5-tetramercaptobenzene, 1,2,4,5-tetramercaptobenzene, 1,2,3,4,5-tetramercaptobenzene, 1,2,3,5-tetramercaptobenzene, 1,2,4,5-tetramercaptobenzene, 1,2,3,4,5-tetramercaptobenzene, 1,2,3,5-tetramercaptobenzene, 1,2,4,5-tetramercaptobenzene, 1,2,3,4,5-tetramercaptobenzene, 1,2,3,5-tetramercaptobenzene, 1,2,4,5-tetramercaptobenzene, 1,2,3,4,5-tetramercaptobenzene, 1,2,3,5-tetramercaptobenzene, 1,2,4,5-tetramercaptobenzene, 1,2,3,4,5-tetramercaptobenzene, 1,2,3,5-tetramercaptobenzene, 1,2,4,5-tetramercaptobenzene, 1,2,3,4,5-tetramercaptobenzene, 1,2,3,5-tetramercaptobenzene, 1,2,4,5-tetramercaptobenzene, 1,2,3,4,5-tetramercaptobenzene, 1,2,3,5-tetramercaptobenzene, 1,2,4,5-tetramercaptobenzene, 1,2,3,4,5-tetramercaptobenzene, 1,2,3,5-tetramercaptobenzene, 1,2,4,5-tetramercaptobenzene, 1,2,3,4,5-tetramercaptobenzene, 1,2,3,5-tetramercaptobenzene, 1,2,4,5-tetramercaptobenzene, 1,2,3,4,5-tetramercaptobenzene, 1,2,3,5-tetramercaptobenzene, 1,2,4,5-tetramercaptobenzene, 1,2,3,4,5-tetramercaptobenzene, 1,2,3,5-tetramercaptobenzene, 1,2,4,5-tetramercaptobenzene, 1,2,3,4,5-tetramercaptobenzene, 1,2,3,5-tetramercaptobenzene, 1,2,4,5-tetramercaptobenzene, 1,2,3,4,5-tetramercaptobenzene, 1,2,3,5-tetramercaptobenzene, 1,2,4,5-tetramercaptobenzene, 1,2,3,4,5-tetramercaptobenzene, 1,2,3,5-tetramercaptobenzene, 1,2,4,5-tetramercaptobenzene, 1,2,3,4,5-tetramercaptobenzene, 1,2,3,5-tetramercaptobenzene, 1,2,4,5-tetramercaptobenzene, 1,2,3,4,5-tetramercaptobenzene, 1,2,3,5-tetramercaptobenzene, 1,2,4,5-tetramercaptobenzene, 1,2,3,4,5-tetramercaptobenzene, 1,2,3,5-tetramercaptobenzene, 1,2,4,5-tetramercaptobenzene, 1,2,3,4,5-tetramercaptobenzene, 1,2,3,5-tetramercaptobenzene, 1,2,4,5-tetramercaptobenzene, 1,2,3,4,5-tetramercaptobenzene, 1,2,3,5-tetramercaptobenzene, 1,2,4,5-tetramercaptobenzene, 1,2,3,4,5-tetramercaptobenzene, 1,2,3,5-tetra...
1,2,3,5-tetrakis(2-mercaptoethylthio) benzene, 1,2,4,5-tetrakis(2-mercaptoethylthio)benzene and 3,4-thiophenedithiol.

According to a tenth embodiment, the compound comprising a thiol unit, of formula (I), is such that $n = 2$ or 3 or 4 and W denotes a triglyceride of a fatty acid or a vegetable oil, optionally substituted, it being understood that, when the W radical is substituted, the thiol functions can be borne by the substituent(s).

According to this embodiment, the compound comprising a thiol unit can be chosen, for example, from triglycerides of fatty acids or vegetable oils modified with thiol groups by chemical reaction, for instance thiolated soybean oils and hydroxylated and thiolated soybean oils, in particular the polymercaptan® products from the company Chevron Phillips, such as polymercaptan 358 (mercaptanized soybean oil) and polymercaptan 407 (mercapto hydroxy soybean oil).

According to an eleventh embodiment, the compound comprising a thiol unit, of formula (I), is such that $n = 2$ and W denotes a C$_2$-C$_6$ hydrocarbon-based saturated divalent radical substituted with one or more hydroxyl groups.

According to this embodiment, the compound comprising a thiol unit can be chosen, for example, from dithopthreitol and 2,3-dimercapto-1-propanol.

According to a twelfth embodiment, the compound comprising a thiol unit, of formula (I), is such that $n = 2$ and W denotes a C$_2$-C$_6$ hydrocarbon-based saturated divalent radical substituted with one or more carboxylic acid groups or carboxylate groups (C$_2$-C$_6$ ester group).

According to this embodiment, the compound comprising a thiol unit, of formula (I), may be meso-2,3-dimercaptosuccinic acid or C$_1$-C$_4$ alcohol esters thereof.

According to this first variant, the compounds of formula (I) for which $n$ denotes an integer ranging from 1 to 4 (limits included) will be preferred.

Preferably, according to this variant, the compounds of formula (I) are chosen from the compounds of the first embodiment, such as, in particular, thioglycolic acid, thiolactic acid, thiomalic acid, 2-mercaptopropionic acid, 3-mercaptopropionic acid, thiosalicylic acid, thiopropionic acid, glutathione, cysteine, N-acetyl cysteine, homocysteine and...
mercaptosuccinic acid, and C1-C4 alcohol esters thereof, cysteamine, N-acetyl
cysteamine, thioglycerol, 2-mercaptoethanol, 1-mercapto-2-propanol and 3-mercapto-
1-propanol, and C1-C4 esters thereof, 2-(trimethylsilyl)ethanethiol,
(3-mercaptocropl)triethoxysilane,
the compounds of formula HS-(CH₂)ₙ-NH-(CH₂)ₘ-NH₂, n and m being integers ranging
from 1 to 4, ortho-aminothiophenol, meta-aminothiophenol, and para-aminothiophenol;
or from the compounds of the fifth embodiment, such as, in particular,
trimethylolpropane tris(2-mercaptoacetate), trimethylolpropane
tris(3-mercaptopropionate), pentaerythritol tetrakis(2-mercaptoacetate), pentaerythritol
tetrakis(3-mercaptopropionate), pentaerythritol tetrakis(3-mercaptopentanate) or
dipentaerythritol hex-3-mercaptopropionate, and more particularly pentaerythritol
tetrakis(3-mercaptopropionate); or from the compounds of the eleventh embodiment,
such as, in particular, dithiothreitol.

Particularly preferably, according to this variant, the compounds of formula (I) denote
cysteine, thioglycolic acid, (3-mercaptocropl)triethoxysilane, pentaerythritol tetrakis(3-
mercaptopropionate) and dithiothreitol.

According to a second variant, the thiol compound used according to the invention
denotes a polymeric compound and can be represented by formula (II)

\[ \text{POL(SH)}ₙ \] (II)
in which \( n \) denotes an integer greater than or equal to 5, preferably between 5 and
5000, preferably between 5 and 1000,
and POL denotes a multivalent (at least pentavalent) carbon-based or silicone
polymeric radical, it being possible for POL to also contain one or more heteroatoms
such as O, N or S, and/or one or more functions chosen from ester, ketone, amide,
urea and carbamate functions, and/or to be substituted with one or more linear or
branched C1-C10 alkyl or linear or branched C1-C10 alkoxy groups, it being understood
that, when POL is substituted, the thiol functions can be borne by the substituent(s).

The molar mass of the compounds of formula (II) is generally between 500 and
400 000 g/mol and preferably between 500 and 150 000 g/mol.

POL can denote a multivalent radical of homopolymer or copolymer type;
POL can denote a polymeric radical of star, comb, brush or dendritic type.
The POL radical may be of natural origin (such as polysaccharides, peptides) or
synthetic origin (such as acrylic polymers, polyesters, polyglycols).
The thiol functions (-SH) may be end and/or pendant groups.
According to a first embodiment, the thiolated compound of formula (II) is such that
POL denotes a hydrocarbon-based polymeric radical.
As an example, mention may be made of the polymers described in the following
articles: Polymers containing groups of biological activity, CG Overberger et al,
Polytechnic Institute of Brooklyn,

In particular, mention may be made of the compounds comprising a thiol unit, of
formula (II), such as poly(vinylmercaptan), poly(4-mercaptostyrene),
poly(vinylbenzylmercaptan), poly(4-mercaptostyrene)-co-poly(methyl methacrylate),
and also polymers containing amide functions in the polymer, such as poly(thiolated
hexamethylene adipamide).

The compounds of formula (II) also denote proteins and peptides with thiol units, for
instance the structures represented in the following table:

```
     -CH₂-CH₂-  -CH₂-CH₂-  -CH₂-CH₂-  -CH₂-CH₂-
       \    \    \       \       \       \       \       
         \    \    \       \       \       \       \       
          \    \    \       \       \       \       \       
             \    \    \       \       \       \       \       
                 \    \    \       \       \       \       \       
                           \    \    \       \       \       \       \       
                                           \    \    \       \       \       \       \       
                                                   \    \    \       \       \       \       \       
                                                                 \    \    \       \       \       \       \       
                                                                                                                                                  
```

According to a first embodiment, the thiolated compound of formula (II) is such that
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and also polymers containing amide functions in the polymer, such as poly(thiolated
hexamethylene adipamide).

The compounds of formula (II) also denote proteins and peptides with thiol units, for
instance the structures represented in the following table:
The thiolated compound of formula (II) also denotes the compounds of formula (II) such that POL denotes a radical termed dendrimer or polymer which is branched or hyperbranched, and the thiol groups are end groups. As examples, mention may be made of the polymers described in the article Progress in Organic Coatings, Volume 63, Issue 1, July 2008, pages 100-109.

As an example of the synthesis of such polymers, mention may be made of the synthesis described in said article, where the Boltorn H40 polymer is converted into a thiolated polymer of formula (II) according to the scheme below:

The structure of the thiolated polymer (II) obtained is given below:
The compound comprising a thiol unit, of formula (II), may also denote a hyperbranched or dendritic polymer modified with thiol functions, as described in application FR 2 761 691.

Polymers of polypropylene ether glycol bis(beta-mercaptopropionate) type can also be used. They are prepared from polypropylene ether glycol (e.g., Pluracol P201, Wyandotte Chemical Corp.) and beta-mercaptopropionic acid by esterification reaction and are known to those skilled in the art. Some polymers comprising a thiol unit, of formula (II), are also commercially available, such as the Thiocure® products from the company Bruno Brock, Thiocure® ETTMP 1300 (Ethoxylated-Trimethylolpropane Tri-3-Mercaptopropionate (CAS# 345352-19-4) and Thiocure® ETTMP 700 (Ethoxylated-Trimethylolpropane Tri-3-Mercaptopropionate (CAS# 345352-19-4);
According to a second embodiment, the compound of formula (II) is such that POL denotes a silicone-based polymeric radical. Among the polythiol inorganic polymers, mention may be made of silicone polythiols.

The silicone polythiols are in particular polydimethylsiloxanes comprising two or more than two thiol groups such as, for example, the SMS-022, SMS 042 and SMS 992 products sold by the company Gelest Inc.

Preferably, the thiol is chosen from the thiol compounds of formula (I) with \( n = 1 \) and \( W \) denoting a linear or branched saturated \( \text{C}_2-\text{C}_{20} \) monovalent radical, or an aromatic radical, it being possible for \( W \) to also contain one or more heteroatoms such as \( \text{O}, \text{N}, \text{S} \) or \( \text{Si} \), and/or one or more functions chosen from carboxylic acid, ester and amide functions, and/or to be substituted with one or more linear or branched \( \text{C}_1-\text{C}_4 \) alkyl, hydroxyl, amino, \( \left( \text{C}_1-\text{C}_6 \right) \) alkyl) amino, carboxylic acid, carboxylate, or linear or branched \( \text{C}_1-\text{C}_4 \) alkoxy groups, it being understood that, when the \( W \) radical is substituted, the thiol functions can be borne by the substituent(s).

In particular, the monothiol compound is chosen from thioglycolic acid, thiolactic acid, thiolic acid, 2-mercaptocoproplonic acid, 3-mercaptoproplonic acid, thiosalicnylic acid, thioproplonic acid, glutathione, cysteine, N-acetyl cysteine, homocysteine and mercaptosuccinic acid, and \( \text{C}_1-\text{C}_4 \) alcohol esters thereof; cysteamine, N-acetyl cysteamine,
thioglycerol, 2-mercaptoethanol, 1-mercapto-2-propanol and 3-mercapto-1-propanol, and C₁-C₄ esters thereof, 2-(trimethylsilyl)ethanethiol, (3-mercaptopropyl)triethoxysilane, the compounds of formula:

$$\text{HS}-\left(\text{CH}_2\right)_n\text{NH}-\left(\text{CH}_2\right)_m\text{NH}_2, n \text{ and } m \text{ being integers ranging from } 1 \text{ to } 4,$$

ortho-aminothiophenol, meta-aminothiophenol and para-aminothiophenol.

Particularly preferably, the thiol (I) is chosen from cysteine, cysteamine, thioglycolic acid and (3-mercaptopropyl)triethoxysilane.

Preferably, the thiol is chosen from cysteine, cysteamine, thioglycolic acid, (3-mercaptopropyl)triethoxysilane, dithiothreitol and pentaerythritol tetra(3-mercaptopropionate).

The thiol may be present in composition A used according to the invention in a content ranging from 0.1% to 100% by weight, relative to the total weight of the composition, and preferably ranging from 1% to 10% by weight.

The thiol (or the mixture of thiols) or composition A containing same, applied to the skin, is left on for a period ranging from 1 minute to one hour, preferably ranging from 3 to 30 minutes, and preferentially ranging from 5 to 15 minutes.

After the step of applying the thiol to the skin, a step of rinsing with water, optionally as a mixture with a surfactant, can be carried out. The known surfactants suitable for cleansing the skin may be used. The rinsing step is advantageously carried out when a thiol of formula (I) (in particular for a monothiol (I) with \(n = 1\)) is applied to the skin.

A step of removing the excess water at the surface of the treated skin can then be carried out, for example using a towel or an absorbent paper.

The step of applying a composition, in particular a cosmetic composition, comprising the polysaccharide polymer grafted with (meth)acrylate groups is then carried out.

According to a first embodiment of the process according to the invention, the process comprises the following steps (in the order indicated):

topical application to the skin of a thiol of formula (I) or of a composition comprising same, leaving it on for a period ranging from 1 minute to 1 hour;
optional performing of a step of rinsing with water or a mixture of water and surfactant;
optional performing of a step of removing the excess water at the surface of the skin;
than application to the treated skin of a composition comprising the polysaccharide grafted with (meth)acrylate groups.

Advantageously, the process is performed with the rinsing step.
According to a second embodiment of the process according to the invention, the process comprises the following steps (in the order indicated):
topical application to the skin of a thiol polymer of formula (II) or of a composition comprising same, leaving it on for a period ranging from 1 minute to 1 hour;
optional performing of a step of rinsing with water or a mixture of water and surfactant;
optional performing of a step of removing the excess water at the surface of the skin;
then application to the treated skin of a composition comprising the polysaccharide grafted with (meth)acrylate groups.
Advantageously, the process is performed without rinsing step.

The term "polysaccharide grafted with (meth)acrylate groups" is intended to mean a polysaccharide of which all or some free hydroxyl groups have been esterified so as to form (meth)acrylate ester groups.

The grafted polysaccharide used according to the invention may be chosen from (meth)acrylate-grafted hyaluronic acid, (meth)acrylate-grafted dextran and (meth)acrylate-grafted carrageenan, such as those described hereinafter.

Advantageously, the (meth)acrylate-grafted polysaccharide has a weight-average molecular weight ranging from 5000 to 1 000 000 daltons, preferably ranging from 10 000 to 500 000 daltons, and even more preferentially ranging from 15 000 to 350 000 daltons.

According to a first embodiment of the process according to the invention, the grafted polysaccharide may be a (meth)acrylate-grafted hyaluronic acid.

Hyaluronic acid is a linear glycosaminoglycan composed of repeating D-glucuronic acid and N-acetyl-D-glucosamine units linked together via alternating beta-1,4 and beta-1,3 glycosidic linkages.

Preferably, the grafted hyaluronic acid polymer has a weight-average molecular weight ranging from 5000 to 1 000 000 daltons, more preferentially ranging from 10 000 to 500 000 daltons, and even more preferentially ranging from 15 000 to 350 000 daltons.
The molecular weight can be determined in particular by liquid chromatography, the eluent being 0.1 M sodium chloride and 330 mg/l of sodium azide in water, with dextran as standard, and Wyatt Optilab T-Rex refractometer and Wyatt Dawn-Heleos light scattering detectors.
Advantageously, the grafted hyaluronic acid polymer has a degree of grafting with (meth)acrylate groups ranging from 10% to 80% or 20% to 80%, preferably ranging from 40% to 70%, and preferentially ranging from 45% to 65%. The degree of grafting corresponds to the mole percentage of hydroxyl groups of the hyaluronic acid which are grafted with a (meth)acrylate group.

By way of example, a degree of grafting of 50% corresponds to 2 acrylate groups grafted onto the 4 hydroxyls of the repeating unit of the hyaluronic acid.

The grafting of hyaluronic acid with (meth)acrylate groups results from the presence of a (meth)acrylate ester group formed with the free hydroxyls of hyaluronic acid.

Preferably, the hyaluronic acid is grafted with acrylate groups.

The hyaluronic acid grafted with (meth)acrylate groups can be obtained by reaction of the hyaluronic acid with (meth)acrylic anhydride. The reaction is advantageously carried out in a basic aqueous medium, in particular in the presence of an organic or inorganic base such as, for example, sodium hydroxide. Preferably, the reaction is carried out at a temperature ranging from 5 to 10°C, in particular for a period of time ranging from 24 hours to 48 hours.

Various degrees of grafting with the (meth)acrylate groups can be obtained by varying the amount of (meth)acrylic anhydride used proportionally to the amount of hyaluronic acid.

According to a second embodiment of the process according to the invention, the grafted polysaccharide may be a (meth)acrylate-grafted dextran.

Dextran is a branched polysaccharide of d-glucose (dextrose) which has a linear backbone, the glucose s of which are linked to one another by alpha-1,6 linkages; it has branched chains consisting of d-glucose linked to one another by alpha-1,2 or -1,3 or -1,4 linkages.
Preferably, the grafted dextran polymer has a weight-average molecular weight ranging from 10 000 to 1 000 000 daltons, more preferentially ranging from 10 000 to 500 000 daltons, and even more preferentially ranging from 15 000 to 350 000 daltons.

The weight-average molecular weight can in particular be determined by liquid chromatography by gel permeation or by size exclusion chromatography.

Advantageously, the grafted dextran polymer has a degree of grafting with (meth)acrylate groups ranging from 2% to 70%, preferably ranging from 3% to 65%, and preferentially ranging from 5% to 60%. The degree of grafting corresponds to the mole percentage of hydroxyl groups of the dextran which are grafted with a (meth)acrylate group.

By way of example, a degree of grafting of 50% corresponds to 1.5 acrylate groups grafted onto the 3 hydroxyls of the repeating unit of the dextran.

The grafting of dextran with (meth)acrylate groups results from the presence of a (meth)acrylate ester group formed with the free hydroxyls of dextran.

Preferably, the dextran is grafted with methacrylate groups.

The dextran grafted with (meth)acrylate groups can be obtained by reaction of the dextran with (meth)acrylic anhydride. The reaction is advantageously carried out in an aprotic polar solvent (for example dimethylformamide, N-methylpyrrolidine, N-ethylpyrrolidine), in particular in the presence of a non-nucleophilic organic or inorganic base, for instance tertiary amines (such as triethanolamine). Preferably, the reaction is carried out at a temperature ranging from 20 to 100°C, in particular for a period of time ranging from 1 to 12 hours.
Various degrees of grafting with the (meth)acrylate groups can be obtained by varying the amount of (meth)acrylic anhydride used proportionally to the amount of dextran, and also the reaction conditions, such as the reaction temperature and time.

According to a third embodiment of the process according to the invention, the grafted polysaccharide may be a (meth)acrylate-grafted carrageenan.

Carrageenans are sulfated polysaccharides which constitute the cell walls of various red algae, from which they can be obtained. Among these red algae, mention may be made, in a non-limiting manner, of Kappaphycus alvarezii, Eucheuma denticulatum, Eucheuma spinosum, Chondrus crispus, Betaphycus gelatinum, Gigartina skottsbergii, Gigartina canaliculata, Sarcothalia crispa, Mazzaella laminaroides, Hypnea musciformis, Mastocarpus stellatus and Iridaea cordata. They comprise long galactan chains, made up of disaccharide units. These polysaccharides are composed of alternating (1→3) β-D-galactopyranose (G unit) and (1→4) α-galactopyranose (D unit) or 3,6-anhydro-α-D-galactopyranose (AnGal unit). Each sugar unit can be sulfated one or more times in position 2, 3, 4 or 6. Methyl and pyruvic acid groups and also other sugar units grafted onto the base structures previously described can also be found. The carrageenans were initially subdivided into subfamilies according to their solubility in KCl, then according to the number and position of the sulfate groups and the presence of 3',6'-anhydro bridges on the galactopyranosyl residues. There are at least about 15 carrageenans listed, the structure of which depends on the alga of origin and the extraction method. Among the most common, mention may be made of the carrageenans below:

\[
\text{\textit{µ- Carrageenan}} \quad (1\rightarrow3) \beta\text{-D-galactopyranose-4-sulfate-(1}\rightarrow4)\alpha\text{-D-galactopyranose-6-sulfate}
\]

\[
\text{\textit{K- Carrageenan}} \quad (1\rightarrow3) \beta\text{-D-galactopyranose-4-sulfate-(1}\rightarrow4)3,6\text{-anhydro-}\alpha\text{-D-galactopyranose}
\]

\[
\text{\textit{v- Carrageenan}} \quad (1\rightarrow3) 3\text{-D-galactopyranose-4-sulfate-(1}\rightarrow4)\alpha\text{-D-galactopyranose-2,6-disulfate}
\]

\[
\text{\textit{v- Carrageenan}} \quad (1\rightarrow3) P\text{-D-galactopyranose-4-sulfate-(1}\rightarrow4)3,6\text{-anhydro-}\alpha\text{-D-galactopyranose-2-sulfate}
\]
These carrageenans are thus often obtained in the form of mixtures of different structures such as, and in a non-limiting manner, mixtures of κβ, κι, κμ forms. The carrageenans that can be used may in particular be chosen from carrageenans of μ, κ, ν, λ, and θ type. Carrageenans that are particularly suitable for implementing the invention are carrageenans of μ, ν and λ type. Lambda carrageenan is preferably used.

The carrageenans of the present invention can be used in acid form or in salified form. By way of acceptable salts, mention may be made, in a non-limiting manner, of lithium, sodium, potassium, calcium, zinc or ammonium salts.

Preferably, the grafted carrageenan polymer has a weight-average molecular weight ranging from 10 000 to 1 000 000 daltons, more preferentially ranging from 10 000 to 500 000 daltons, and even more preferentially ranging from 15 000 to 350 000 daltons.

The molecular weight can be determined in particular by liquid chromatography, the eluent being 0.1 M sodium chloride and 330 mg/l of sodium azide in water, with dextran as standard, and Wyatt Optilab T-Rex refractometer and Wyatt Dawn-Heleos I light scattering detectors.

Advantageously, the grafted carrageenan polymer has a degree of grafting with (meth)acrylate groups ranging from 2% to 60%, preferably ranging from 2% to 50%, and preferentially ranging from 5% to 30%. The degree of grafting corresponds to the mole percentage of hydroxyl groups of the carrageenan which are grafted with a (meth)acrylate group.

By way of example, a degree of grafting of 50% corresponds to 1.5 acrylate groups grafted onto the 3 hydroxyls of the repeating unit of the carrageenan.

The grafting of the carrageenan with (meth)acrylate groups results from the presence of a (meth)acrylate ester group formed with the free hydroxyls of the carrageenan.

Preferably, the carrageenan is grafted with acrylate groups.
The carrageenan grafted with (meth)acrylate groups can be obtained by reaction of the carrageenan with (meth)acrylic anhydride. The reaction is advantageously carried out in a basic aqueous medium, in particular in the presence of an organic or inorganic base such as, for example, sodium hydroxide. Preferably, the reaction is carried out at a temperature ranging from 5 to 10°C, in particular for a period of time ranging from 24 hours to 48 hours.

Various degrees of grafting with the (meth)acrylate groups can be obtained by varying the amount of (meth)acrylic anhydride used proportionally to the amount of carrageenan.

Advantageously, a carrageenan chosen from μ-carrageenan, λ-carrageenan, ν-carrageenans, and preferably λ-carrageenan, is used.

The polysaccharide polymer grafted with (meth)acrylate groups as previously defined may be present in composition B used according to the invention in a content ranging from 0.1% to 10% by weight, relative to the total weight of the composition, preferably from 0.5% to 10% by weight of active material, preferentially ranging from 1% to 8% by weight, and more preferentially ranging from 1% to 6% by weight.

Advantageously, the grafted polysaccharide is chosen from acrylate-grafted hyaluronic acid, methacrylate-grafted dextran and acrylate-grafted carrageenan.

When the grafted dextran comprises methacrylate groups, a catalyst can be used in the presence of the thiol compound.

The catalyst can be chosen from the catalysts described in the articles *Tetrahedron Letters* 48 (2007), pages 141-143, and *Tetrahedron Letters* 46 (2005), pages 8329-8331, and also in the articles cited in these two articles.

As an example of a catalyst, mention may be made of Lewis acids, such as boric acid, aluminium chloride or cerium chloride, and also phosphines, such as trimethylphosphine (trialkylphosphine), phenyldimethylphosphine.
(dialkylarylphosphine), diphenylmethylphosphine (alkyldiarylphosphine), triphenylphosphine (triarylphosphine), tricarboxyethylphosphine, and the oxide equivalents.

Compositions A and/or B used according to the invention are generally suitable for topical application to the skin and thus generally comprise a physiologically acceptable medium, i.e. a medium that is compatible with the skin and/or skin appendages. It is preferably a cosmetically acceptable medium, i.e. a medium which has a pleasant colour, odour and feel and which does not cause any unacceptable discomfort (stinging, tautness or redness) liable to discourage the consumer from using this composition.

The compositions used according to the invention may be in any galenic form conventionally used for a topical application and especially in the form of dispersions of aqueous gel or lotion type, emulsions of liquid or semi-liquid consistency of the milk type, obtained by dispersing a fatty phase in an aqueous phase (O/W) or vice versa (W/O), or suspensions or emulsions of soft, semi-solid or solid consistency of the cream or gel type, or alternatively multiple emulsions (W/O/W or C7W/O), microemulsions, vesicular dispersions of ionic and/or non-ionic type, or wax/aqueous phase dispersions. These compositions are prepared according to the usual methods.

According to one preferred embodiment of the invention, compositions A and/or B are in the form of an O/W emulsion or an aqueous gel.

Advantageously, composition A and/or B used according to the invention comprises water, in particular in a content which can range from 10% to 99% by weight and preferably ranging from 50% to 99% by weight, relative to the total weight of the composition.

Compositions A and/or B used according to the invention may also contain one or more adjuvants commonly used in the cosmetics field, such as emulsifiers, preservatives, sequestering agents, fragrances, thickeners, oils, waxes or film-forming polymers.

Needless to say, those skilled in the art will take care to select this or these optional additional compound(s), and/or the amount thereof, such that the properties of the composition(s) used according to the invention are not, or are not substantially, adversely affected by the envisaged addition.

The application of the cosmetic composition(s) used according to the invention is carried out according to the usual techniques, for example by application (in particular of creams, gels, sera or lotions) to the skin intended to be treated, in particular facial
and/or neck skin, especially the skin of the area around the eyes. In the context of this process, composition A and/or B may, for example, be a care composition.

According to one embodiment of the process according to the invention, the thiol compound(s), or a cosmetic composition A containing same, is (are) first applied to the skin, and left to act for a period ranging from 1 minute to one hour, rinsing is optionally carried out with water or a mixture of water and surfactant, and then composition B, which is in particular a cosmetic composition, comprising the (meth)acrylate-grafted polysaccharide polymer(s), is applied to the treated skin.

Advantageously, composition A comprising the thiol used in the process according to the invention is an aqueous composition having a pH ranging from 5 to 10.5, preferably ranging from 6 to 9, and preferentially ranging from 7 to 8.5.

The invention will now be described with reference to the examples that follow, which are given as non-limiting illustrations.

**Synthesis example 1 (polymer 1):** Hyaluronic acid 60% functionalized with acrylic anhydride

In a thermostated reactor, 5 g of hyaluronic acid (Hyacare® 50 from Evonik) were dissolved in 100 ml of water and the mixture was maintained at a temperature of 7°C, then 14.8 g of acrylic anhydride were added dropwise over the course of approximately 2 min. The pH was adjusted to 7.7 by slowly adding (over the course of approximately one hour) sodium hydroxide at 30% in water (7 M). The mixture was left to react for 24 hours.

The mixture obtained was purified by dialysis (polymer in 150 ml of water, 3.3% by weight) on a Spectra/Por® 15 kDa membrane for 5 days in 5 litres of water (water changed 4 times, i.e. 20 litres in total), then the mixture of the purified fraction was lyophilized by freezing with a bath of dry ice + acetone at -80°C, then by placing the frozen mixture in a lyophilization apparatus for 4 days. 2.5 g of a white solid were obtained.

Analyses:

$^1$H NMR D$_2$O : 2.45 (7.36/3) OH units functionalized for 4 OH units available.

The hyaluronic acid obtained is 60%-functionalized with acrylate groups.
**Synthesis example 2 (polymer 2):** Dextran 33%-functionalized with methacrylate groups

10 g of dextran (sold under the reference 406261000 by the company Acros) were suspended in 40 ml of a lithium chloride/dimethylformamide mixture (at 10% by weight of LiCl) and the suspension was heated to 100°C. 20 ml of the lithium chloride/dimethylformamide mixture were added until complete dissolution of the dextran. The mixture was then cooled to 80°C, then 0.56 g of triethanolamine was added, the mixture was stirred for 15 minutes at 80°C, then 8.55 g of methacrylic anhydride were slowly added (10 minutes). The mixture was left to stir for 5 hours at 70°C and then left to return to ambient temperature (25°C). The reaction mixture was then poured into 150 ml of isopropanol, stirred for 1 hour and then filtered. 11.8 g of a white solid were obtained.

Analyses:
$^1$H NMR $\text{D}_2\text{O}$ : 1 OH unit functionalized for 3 OH units available.
The dextran obtained is 33%-functionalized with acrylate groups.

**Synthesis example 3 (polymer 3):** Dextran 50%-functionalized with methacrylate groups

10 g of dextran (sold under the reference 406261000 by the company Acros) were suspended in 40 ml of a lithium chloride/dimethylformamide mixture (at 10% by weight of LiCl) and the suspension was heated to 100°C. 20 ml of the lithium chloride/dimethylformamide mixture were added until complete dissolution of the dextran. The mixture was then cooled to 80°C, then 0.56 g of triethanolamine was added, the mixture was stirred for 15 minutes at 80°C, then 8.55 g of methacrylic anhydride were slowly added (10 minutes). The mixture was left to stir for 5 hours at 80°C and was then left to return to ambient temperature (25°C). The reaction mixture was then poured into 150 ml of isopropanol, stirred for 1 hour and then filtered. 13.4 g of a white solid were obtained.

Analyses:
$^1$H NMR $\text{D}_2\text{O}$ : 1.5 OH units functionalized for 3 OH units available.
The dextran obtained is 50%-functionalized with methacrylate groups.

**Synthesis example 4 (polymer 4):** Carrageenan 15% functionalized with acrylic anhydride
In a thermostated reactor, 5 g of carrageenan (lambda form) (Satiagum UTC 10 from Cargill) were dissolved in 100 ml of water and the mixture was maintained at a temperature of 7°C, then 10.7 g of acrylic anhydride were added dropwise over the course of approximately 2 min. The pH was adjusted to 7.7 by slowly adding (over the course of approximately one hour) sodium hydroxide at 30% in water (7 M). The mixture was left to react for 24 hours.

The mixture obtained was purified by dialysis (polymer in 150 ml of water, 3.3% by weight) on a Spectra/Por® 15 kDa membrane for 5 days in 5 litres of water (water changed 4 times, i.e. 20 litres in total), then the mixture of the purified fraction was lyophilized by freezing with a bath of dry ice + acetone at -80°C, then by placing the frozen mixture in a lyophilization apparatus for 4 days.

3.7 g of a white solid were obtained.

Analyses:
$^1$H NMR D$_2$O: 0.44 OH units functionalized for 3 OH units available.
The carrageenan obtained is 10%-functionalized with acrylate groups.

**Examples 1 to 7:**

**Demonstration of the tensioning effect of the process carried out on stratum corneum**

This test consists in comparing, in vitro, the tensioning capacity obtained with the sequenced application of the thiol and of the polymer to be evaluated with respect to a reference tensioning polymer: Hybridur® 875 polymer dispersion from Air Products (aqueous dispersion at 40% by weight of particles of an interpenetrated network of polyurethane and acrylic polymers).

**Preparation of the substrate**

Pieces of human stratum corneum are stuck onto Scotch tape (reference 1526886 from the company Office Depot), taking care that the external surface of the stratum corneum is not in contact directly on the Scotch tape. The substrates are then cut into a size approximately 4 cm long and 1 cm wide and used with the Scotch tape in the lower part and the external surface of the stratum corneum in the upper part.

**Application of the compounds**

On the horizontally positioned substrates, a solution containing the thiol was deposited on the free stratum corneum face. After waiting for 5 minutes, rinsing was then carried out with 5 ml of osmosed water. The excess water at the surface was then removed.
with absorbent paper. A solution containing the test polymer was then applied. After drying for 5 minutes, the substrates were held in the vertical position for 3 hours at ambient temperature (approximately 22°C / 45% RH), then the curving of the substrate treated was observed.

A substrate was treated with Hybridur® 875 (without pretreatment with a thiol). An aqueous solution containing 7% AM of Hybridur® 875 polymer was applied and then allowed to dry for 5 minutes. The substrate was then held in the vertical position for 3 hours at ambient temperature (22°C / 45% RH) so as to thus obtain a reference tensioning substrate.

The curving of the substrate treated with the polymers was observed in comparison with that obtained for the control (Hybridur® 875).

The persistence of the tensioning effect was evaluated by rinsing the treated substrates with a 0.9 M aqueous NaCl solution (10 ml of the saline solution are projected onto the substrates at a distance of 5 cm using a pipette). The surfaces of the substrates were lightly rubbed with the fingers and then allowed to dry for 3 h before again observing the tensioning effect (the curving).

The following treatments were carried out:

<table>
<thead>
<tr>
<th>Example</th>
<th>Basecoat</th>
<th>Topcoat</th>
</tr>
</thead>
<tbody>
<tr>
<td>reference</td>
<td>50 µl of an aqueous solution of Hybridur 875 at 7% am in weight</td>
<td>nothing</td>
</tr>
<tr>
<td>1b''</td>
<td>25 µl of a solution of dithiothreitol at 5% in weight in water (pH 8 adjusted with aqueous ammonia)</td>
<td>50 µl of a solution of the polymer P1 at 3% am in weight in water</td>
</tr>
<tr>
<td>1c''</td>
<td>10 µl of a solution of pentaerythritol tetra(3-mercaptopropionate) at 10% in weight in DMSO/28% aqueous ammonia (99/1 v/v)</td>
<td>50 µl of a solution of the polymer P1 at 3% am in weight in water</td>
</tr>
<tr>
<td>1d''</td>
<td>50 µl of a solution of cysteine at 5% in weight in water (pH 8 adjusted with aqueous ammonia)</td>
<td>50 µl of a solution of the polymer P1 at 3% am in weight in water</td>
</tr>
<tr>
<td>1e''</td>
<td>25 µl of a solution of thioglycolic acid at 5% in weight in water (pH 8 adjusted with aqueous ammonia)</td>
<td>50 µl of a solution of the polymer P1 at 3% am in weight in water</td>
</tr>
<tr>
<td></td>
<td>25 µl of a solution of (3-mercaptopropyl)triethoxysilane at 5% in weight in water</td>
<td>50 µl of a solution of the polymer P1 at 3% am in weight in water</td>
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The following results were obtained:

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<th>Example</th>
<th>Tensioning effect before persistence test</th>
<th>Tensioning effect after persistence test</th>
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<td>reference</td>
<td>Good</td>
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<tr>
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</tr>
<tr>
<td>4c&quot;</td>
<td>Good</td>
<td>good</td>
</tr>
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The results obtained show that the acrylate-grafted hyaluronic acid polymers P1 (Examples 1a" to 1f"), the methacrylate-grafted dextran P2 (Example 2c") and the acrylate-grafted carrageenan P4 (Example 4c"), applied to the skin after the application of a thiol, have a good tensioning effect, including after rinsing with the saline solution. The persistent tensioning effect obtained is greater than that of the reference.

**Example 8:**

A skin pretreatment composition is prepared by mixing the following ingredients:

- Thioglycolic acid 9 g
- Aqueous ammonia q s pH 8
- Hydroxyethylcellulose
This composition is applied to the skin (approximately 20 mg of composition per cm² of skin treated). After having allowed the composition to act for approximately 5 minutes, the skin is thoroughly rinsed with water and then the following composition is applied:

**Example 9:**

A skin pretreatment composition is prepared according to the invention by mixing the following ingredients:

Thioglycolic acid 5 g
Aqueous ammonia qs pH 8
Hydroxyethylcellulose
(Natroso® 250 HHR CS from Ashland) 0.5 g
Fragrance qs
Preservative qs
Water qs 100 g

This composition is applied to the skin (approximately 20 mg of composition per cm² of skin treated). After having allowed the composition to act for approximately 5 minutes, the skin is thoroughly rinsed with water and then the following composition is applied:
Polymer of Example 2 1 g
Hydroxyethylcellulose
(Natrosol® 250 HHR CS from Ashland) 0.5 g
Tricarboxyethylphosphine 0.1 g
Sodium hydroxide qs pH 7
Preservatives qs
Water qs 100 g

A similar composition is also prepared using the polymer of Example 3.

The composition obtained, applied to the face (approximately 20 mg of composition per cm² of skin treated), makes it possible to effectively smooth out the wrinkles.
CLAIMS

1. Process, in particular cosmetic process, for caring for the skin, more particularly facial skin, in particular wrinkled skin, comprising:
the topical application to the skin of at least one thiol or of a composition, in particular a cosmetic composition, containing same, leaving it on for a period ranging from 1 minute to to one hour,
followed by the application to the treated skin of a composition, in particular a cosmetic composition, comprising a polysaccharide polymer grafted with (meth)acrylate groups.

2. Process according to the preceding claim, characterized in that the grafted polysaccharide polymer has a degree of grafting ranging from 10% to 80%, preferably ranging from 40% to 70%.

3. Process according to either of the preceding claims, characterized in that the grafted polysaccharide polymer is chosen from (meth)acrylate-grafted hyaluronic acid, (meth)acrylate-grafted dextran and (meth)acrylate-grafted carrageenan.

4. Process according to one of the preceding claims, characterized in that the grafted polysaccharide polymer is chosen from hyaluronic acid grafted with acrylate groups, dextran grafted with methacrylate groups and carrageenan grafted with acrylate groups.

5. Process according to any one of the preceding claims, characterized in that the grafted polysaccharide polymer has a weight-average molecular weight ranging from 5000 to 1 000 000 daltons, preferably ranging from 10 000 to 500 000 daltons, preferentially ranging from 15 000 to 350 000 daltons.

6. Process according to any one of the preceding claims, characterized in that the grafted polysaccharide polymer is present in the composition in a content ranging from 0.1% to 10% by weight, relative to the total weight of the composition, preferably from 0.5% to 10% by weight of active material, preferentially ranging from 1% to 8% by weight, and more preferentially ranging from 1% to 6% by weight.

7. Process according to any one of the preceding claims, characterized in that the crosslinking thiol is chosen from:
(i) the non-polymeric organic compounds of formula (I)
\[ W(SH)_n \]
in which \( n \) denotes an integer greater than or equal to 1, preferably between 1 and 10, preferably between 1 and 4, and \( W \) denotes a linear or branched or (hetero)cyclic, saturated \( C_{2-6} \) mono-, di-, tri-, tetra- or polycyclic monovalent \((n = 1)\) or poly- or multivalent \((n > 1)\) radical, an aromatic radical or a heteroaromatic cyclic radical, it being possible for \( W \) to also contain one or more heteroatoms such as \( O, N, S \) or \( Si \) and/or one or more functions chosen from carboxylic acid, ester, ketone, amide, urea and isocyanurate functions, preferably ester, ketone and carboxylic acid functions, and/or to be substituted with one or more linear or branched \( C_{1-10} \) alkyl, hydroxyl, amino, \((C_1-C_6 \) alkyl) amino, carboxylic acid, carboxylate, or linear or branched \( C_{1-10} \) alkoxy groups, it being understood that, when the \( W \) radical is substituted, the thiol functions can be borne by the substituent(s);

(ii) the polymeric compounds of formula \((II)\):

\[
\text{POL(SH)}_n
\]

in which \( n \) denotes an integer greater than or equal to 5, preferably between 5 and 5000, preferably between 5 and 1000, and \( \text{POL} \) denotes a multivalent \((\text{at least pentavalent})\) carbon-based or silicone polymeric radical, it being possible for \( \text{POL} \) to also contain one or more heteroatoms such as \( O, N \) or \( S \), and/or one or more functions chosen from ester, ketone, amide, urea and carbamate functions, and/or to be substituted with one or more linear or branched \( C_{1-10} \) alkyl or linear or branched \( C_{1-10} \) alkoxy groups, it being understood that, when \( \text{POL} \) is substituted, the thiol functions can be borne by the substituent(s).

8. Process according to the preceding claim, characterized in that the thiol compound (i) has a molar mass of between 70 and 1500 g/mol and preferably between 70 and 500 g/mol.

9. Process according to any one of the preceding claims, characterized in that the thiol compound is chosen from:

thioglycolic acid, thiolactic acid, thiomalic acid, 2-mercaptobobalic acid, 3-mercaptobobalic acid, thiosalicic acid, thiobonic acid, glutathione, cysteine, \( N \)-acetyl cysteine, homocysteine and mercaptosuccinic acid, and \( C_1-C_4 \) alcohol esters thereof, cysteamine, \( N \)-acetyl cysteamine, thioglycerol, 2-mercaptoethanol, 1-mercapto-2-propanol, 1-mercapto-2-propanol, 2-(trimethylsilyl)ethanethiol, \((3\)-mercaptobobalyl)triethoxysilane,

the compounds of formula \( HS-(\text{CH}_2)_n\text{NH}-(\text{CH}_2)_m\text{NH}_2 \), \( n \) and \( m \) being integers ranging from 1 to 4, ortho-aminothiophenol, meta-aminothiophenol and para-aminothiophenol; 1,2-ethanedithiol, 1,2-propanedithiol, 1,3-propanedithiol, 1,4-butandithiol, 1,6-hexanedithiol, 1,7-heptanedithiol, 1,8-octanedithiol, 1,9-nonanedithiol, 1,10-
decanedithiol, 1,12-dodecanedithiol, 2,2-dimethyl-1,3-propanedithiol, 3-methyl-1,5-pentanedithiol, or 2-methyl-1,8-octanediol;
1,1,1-tris(mercaptopropyl)ethane, 2-ethyl-2-mercaptopropyl-1,3-propanedithiol, 1,2,3-propanetethiol;
bis(2-mercaptoethyl) ether, bis(2-mercaptoethyl)sulfide, bis-(2-mercaptoethylthio-3-mercaptopropane)sulfide;
bis(2-mercaptoethylthio)methane, 1,2-bis(2-mercaptoethylthio)ethane, 1,3-bis(2-mercaptoethylthio)propane, 1,2-bis(2-mercaptoethylthio)propanethiol, 1,2-bis(2-mercaptoethylthio)thio-3-mercaptopropane, 1,2,3-tris(2-mercaptoethylthio)propane;
ethylene glycol bis(2-mercaptoacetate), ethylene glycol bis(3-mercaptopropionate), ethylene glycol bis(thioglycolate), trimethylolpropane tris(thioglycolate), trimethylolpropane tris(beta-mercaptopropionate), pentaerythritol tetrakis(thioglycolate), pentaerythritol tetrakis(beta-mercaptopropionate), trimethylolpropane tris(2-mercaptoacetate), trimethylolpropane tris(3-mercaptopropionate), pentaerythritol tetrakis(2-mercaptoacetate), pentaerythritol tetrakis(3-mercaptopropionate), pentaerythritol tetrakis(3-mercaptobutanate), dipentaerythritol hex-3-mercaptopropionate;
tetrakis(2-mercaptoethylthiomethyl)methane, bis(2-mercaptoethylthio-3-mercaptopropane)sulfide;
1,4-cyclohexane dithiol, 1,4-bis(mercaptopropyl)cyclohexane, 1,1-cyclohexanedithiol, 1,2-cyclohexanedithiol, 1,1-bis(mercaptopropyl)cyclohexane, 2,5-dimercapto-1,4-dithiane;
tris((mercaptopropionyloxy)ethyl)isocyanurate;
1,2-dimercapto benzene, 1,3-dimercapto benzene,
1,4-dimercapto benzene, 1,2-bis(mercaptopropynyl)benzene,
1,3-bis(mercaptopropynyl)benzene,
1,4-bis(mercaptopropynyl)benzene,
1,2-bis(2-mercaptopropynyl)benzene,
1,3-bis(2-mercaptopropynyl)benzene,
1,4-bis(2-mercaptopropynyl)benzene,
1,2-bis(2-mercaptopropynyl)benzene,
1,3-bis(2-mercaptopropynyl)benzene,
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1,2,3-trimercapto benzene,
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1.2.3,5-tetrakis(2-mercaptoethyl)benzene,
1.2.4,5-tetrakis(2-mercaptoethyl)benzene,
1.2.3,4-tetrakis(2-mercaptoethylthio)benzene,
1.2.3,5-tetrakis(2-mercaptoethylthio)benzene,
1.2,4,5-tetrakis(2-mercaptoethylthio)benzene,
2,2'-dimercaptobiphenyl,
4,4'-dimercaptobiphenyl,
4,4'-dimercaptobenzyl,
2,5-toluenedithiol,
3,4-toluenedithiol,
1,4-naphthalenedithiol,
1,5-naphthalenedithiol,
2,6-naphthalenedithiol,
2,7-naphthalenedithiol,
2,4-dimethylbenzene-1,3-dithiol,
4,5-dimethylbenzene-1,3-dithiol,
9,10-anthracenedimethanethiol,
1.3-bis(2-mercaptoethylthio)benzene,
1.4-bis(2-mercaptoethylthio)benzene,
1.2-bis(2-mercaptoethylthiomethyl)benzene,
1.3-bis(2-mercaptoGethylthiomethyl)benzene,
1.4-bis(2-mercaptoethylthiomethyl)benzene,
1.2.3-tris(2-mercaptoethylthio)benzene,
1.2.4-tris(2-mercaptoethylthio)benzene,
1.3.5-tris(2-mercaptoethylthio)benzene,
1.2.3,4-tetrakis(2-mercaptoethylthio)benzene,
1.2.3,5-tetrakis(2-mercaptoethylthio)benzene,
1,2,4,5-tetrakis(2-mercaptoethylthio)benzene,
3,4-thiophenedithiol,
dithiothreitol, 2,3-dimercapto-1-propanol, meso-2,3-dimercaptosuccinic acid and C1-C4 alcohol esters thereof.

10. Process according to any one of the preceding claims, characterized in that the thiol compound is chosen from cysteine, cysteamine, thioglycolic acid, (3-mercaptopropyl)triethoxysilane, dithiothreitol and pentaerythritol tetra(3-mercaptopropionate).

11. Process according to any one of the preceding claims, characterized in that the thiol applied to the skin is left on for a period ranging from 3 to 30 minutes to one hour, preferably ranging from 5 to 45 minutes.

12. Process according to any one of the preceding claims, characterized in that, after the step of applying the thiol to the skin, a step of rinsing with water, optionally as a mixture with a surfactant, is carried out.

13. Process according to the preceding claim, characterized in that, after the rinsing step, a step of removing the excess water at the surface of the treated skin is carried out.

14. Process according to any one of the preceding claims, characterized in that the composition containing the thiol and/or the composition containing the polysaccharide polymer grafted with (meth)acrylate groups is in the form of an O/W emulsion or an aqueous gel.

15. Process according to any one of the preceding claims, characterized in that the composition comprising the crosslinking thiol is an aqueous composition having a pH ranging from 5 to 10.5, preferably ranging from 6 to 9, and preferentially ranging from 7 to 8.5.

16. Process according to any one of Claims 7 to 15, characterized in that it comprises the following steps:
topical application to the skin of a thiol of formula (I), preferably for which n = 1, or of a composition comprising same, leaving it on for a period ranging from 1 minute to 1 hour;
optional performing of a step of rinsing with water or a mixture of water and surfactant;
optional performing of a step of removing the excess water at the surface of the skin;
then application to the treated skin of a composition comprising said polysaccharide grafted with (meth)acrylate groups.
17. Process according to any one of Claims 7 to 15, characterized in that it comprises the following steps:
topical application to the skin of a thiol polymer of formula (II) or of a composition comprising same, leaving it on for a period ranging from 1 minute to 1 hour;
optional performing of a step of rinsing with water or a mixture of water and surfactant;
optional performing of a step of removing the excess water at the surface of the skin;
then application to the treated skin of a composition comprising said polysaccharide grafted with (meth)acrylate groups.

18. Process according to any one of the preceding claims, characterized in that it is intended for attenuating wrinkles.
INTERNATIONAL SEARCH REPORT

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

A61K8/44 A61K8/46 A61Q19/08 A61K8/91

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

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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<td>FR 2 984 125 AI (OREAL [FR]) 21 June 2013 (2013-06-21) page 3, lines 7-11; claims 1,5</td>
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<td>A</td>
<td>US 5 254 331 A (MAUSNER JACK [US]) 19 October 1993 (1993-10-19) claim 6</td>
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Further documents are listed in the continuation of Box C.

See patent family annex.

* Special categories of cited documents:
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Date of the actual completion of the international search: 3 November 2015

Date of mailing of the international search report: 10/11/2015

Name and mailing address of the ISA:
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Fax: (+31-70) 340-3018

Authorized officer: Skulj, Primoz

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### DOCUMENTS CONSIDERED TO BE RELEVANT

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<td>FR 2 969 489 Al (SI LAB SA [FR]) 29 June 2012 (2012-06-29) pages 1,21,22; example 1</td>
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<td>Y</td>
<td>J P H10 265360 A (KA0 CORP) 6 October 1998 (1998-10-06) abstract</td>
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