Novel amphoteric polysaccharide compounds containing sulfonate function(s), composition comprising them and cosmetic use thereof

(54) Title: NOVEL AMPHOTERIC POLYSACCHARIDE COMPOUNDS CONTAINING SULFONATE FUNCTION(S), COMPOSITION COMPRISSING THEM AND COSMETIC USE THEREOF

(57) Abstract: The invention relates to novel amphoteric polysaccharide compounds containing sulfonate function(s) corresponding to the formula (I) in which P represents a polysaccharide chain; X, Y and Z each represent a linear or branched, saturated or unsaturated, optionally hydroxylated C₁₋₁₂ divalent hydrocarbon-based group optionally comprising at least one ether and/or amine function in the hydrocarbon-based chain, or a group -Si(R)₂₋₃-O-Si(R)₂₋₃-A--; r is 0 or 1; An represents an anionic group chosen from formula (II) CAT represents a quaternary ammonium group or a cationic polymer chain obtained by grafting and polymerization of ethylenic monomers bearing a quaternary ammonium function, Sulfo represents a sulfonic or sulfonate group; and n, m and p are such that the total degree of substitution of the polysaccharide does not exceed 2. The invention also relates to compositions comprising them and to their use in cosmetics.

\[
\text{An} \xrightarrow{-X-O} \xrightarrow{n} P \xrightarrow{\text{O}} \xrightarrow{\text{Y}} \xrightarrow{\text{CAT}} \xrightarrow{\text{m}} \text{O} \xrightarrow{\text{I}} \xrightarrow{\text{Z}} \xrightarrow{\text{Sulfo}} \xrightarrow{\text{p}} \text{C-O-V}, \text{P-O-V}, \text{O-V}
\]
Novel amphoteric polysaccharide compounds containing sulfonate function(s), composition comprising them and cosmetic use thereof

The present invention relates to novel amphoteric polysaccharide compounds containing sulfonate function(s), to their use in cosmetics and to compositions comprising them.

In the cosmetics field, it is especially sought to improve the cosmetic properties of keratin materials, such as the hair and the skin, and more particularly sensitized hair, i.e. hair that has become damaged or embrittled, especially due to the chemical action of atmospheric agents and/or of hair treatments such as permanent-waving, dyeing or bleaching.

With this aim, it is common practice to use complementary cosmetic agents known as conditioning agents, for example cationic polymers or silicones, which are intended mainly to repair or limit the harmful or undesirable effects induced by the various treatments or attacking factors to which hair fibres are more or less repeatedly subjected. These conditioning agents also improve the cosmetic behaviour of natural hair.

Other conditioning agents, such as the amphoteric polysaccharides described in documents US 4 803 071, US 4 464 523, WO 90/03779 and FR 2 883 599 may be used in cosmetic hair compositions. However, these polysaccharides are not very efficient as regards conditioning and remanence.

The Applicant has found that, after several uses, the hair becomes laden and lacks lightness.

The Applicant has thus found, surprisingly and unexpectedly, novel amphoteric polysaccharide compounds containing sulfate function(s), which, when used in cosmetics, make it possible to overcome the drawbacks described above and to obtain excellent cosmetic properties such as an excellent conditioning and protecting effect on the hair, good disentangling of the hair, good hold and good discipline of the hairstyle. In addition, the use of these amphoteric
polysaccharide compounds containing sulfonate function(s) leads to good remanence of these properties, even after washing the hair several times, without observing an excessive deposit that would lead to laden, non-malleable and non-supple hair.

These conditioning agents also give the skin cosmetic properties such as good moisturization.

One subject of the present invention is thus novel amphoteric polysaccharide compounds containing sulfonate function(s) as described below.

A second subject of the invention consists of a use of such a polysaccharide compound in cosmetics and especially for the cosmetic treatment of keratin materials, such as caring for and protecting the hair, hairstyling, permanent-waving, relaxing, dyeing or bleaching the hair, or alternatively cleansing and care of the skin, or makeup of the skin, the lips or the nails.

A subject of the invention is also a cosmetic composition comprising at least one polysaccharide compound according to the invention, in a cosmetically acceptable medium.

Other subjects, characteristics, aspects and advantages of the invention will emerge even more clearly on reading the description and the various examples that follow.

The amphoteric polysaccharide compounds containing sulfonate function(s) according to the invention bear, as substituents other than the sulfonate functions, at least one anionic group and at least one cationic group, the said groups being linked to the polysaccharide chain via the oxygen atoms of the saccharide units.

The amphoteric polysaccharide compounds containing sulfonate function(s) according to the invention may be represented by formula (I) below:
\[(\text{An}-\text{X}-\text{O})_n P \left(\text{O}-\text{Y}+\text{CAT}\right)_m \left(\begin{array}{c}
\text{O} \\
\text{Z} \\
\text{Sulfo}_p
\end{array}\right)\]

(1)

in which:

the oxygen atoms belong to one or more saccharide units of P,
P represents a polysaccharide chain,
X, Y and Z represent, independently of each other:
- a linear or branched, saturated or unsaturated, optionally hydroxylated divalent C\(_1\)-C\(_{12}\) hydrocarbon-based group optionally comprising at least one ether and/or amine function in the hydrocarbon-based chain, or
- a group

\[
\begin{array}{c}
\text{Si} \\
\text{R}
\end{array}
\begin{array}{c}
\text{O} \\
\text{Si}
\end{array}
\begin{array}{c}
\text{A} \\
\text{R}_q
\end{array}
\]

the silicon atom being attached to the oxygen atom in the group An-X-O-\, CAT-(Y)_n-O- or Sulfo-Z-O-,
in which each R, which may be identical or different, represents R\(_1\) or -OR\(_1\),
R\(_1\) represents a linear or branched, saturated or unsaturated, optionally hydroxylated C\(_1\)-C\(_8\) and preferably C\(_1\)-C\(_4\) monovalent hydrocarbon-based group optionally comprising at least one ether and/or amine function in the hydrocarbon-based chain, q represents an integer ranging from 0 to 10 and preferably from 0 to 5, q = 0 being particularly preferred, and
A represents a linear or branched, saturated or unsaturated, optionally hydroxylated C\(_1\)-C\(_{12}\) divalent
hydrocarbon-based group optionally comprising at least one ether and/or amine function in the hydrocarbon-based chain,

\( r \) is equal to 0 or 1, \( r \) being 0 when CAT represents a cationic polymer chain obtained by grafting and polymerization of ethylenic monomers bearing an ammonium group,

An represents an anionic group chosen from:

\[
\begin{align*}
\text{O} & \quad \text{O} \\
\text{C} & \quad \text{O} \\
\text{V} & \quad \text{P} \\
\text{O} & \quad \text{O} \\
\text{V} &
\end{align*}
\]

with \( V \) representing a hydrogen atom or an alkali metal or alkaline-earth metal, for example a sodium or potassium atom,

CAT represents:

an ammonium group

\[
\begin{align*}
\text{R}_2 \\
\text{N}^+ \quad \text{R}_3 \\
\text{Q}^- \\
\text{R}_4
\end{align*}
\]

in which \( R_2, R_3 \) and \( R_4 \) represent, independently of each other, a hydrogen atom or a linear or branched, saturated or unsaturated, optionally hydroxylated \( C_1-C_{22} \) and preferably \( C_1-C_{18} \) monovalent hydrocarbon-based group optionally comprising at least one ether and/or amine function in the hydrocarbon-based chain, and \( Q^- \) represents a mineral or organic anion, for example a halogen atom such as a chlorine or bromine atom, the chlorine atom being particularly preferred, or an acetate, a citrate, a lactate, an oleate or a behenate, or

- a cationic polymer chain obtained by grafting and
polymerization of ethylenic monomers bearing an ammonium group, for example of formula:

\[
\begin{array}{c}
\text{R}_5 \\
\text{N}^+ \text{R}_6 \\
\text{R}_7
\end{array}
\]

in which \(R_5\), \(R_6\) and \(R_7\) represent, independently of each other, a hydrogen atom, a linear or branched \(C_1-C_{22}\) and preferably \(C_1-C_{18}\) alkyl group, or a linear or branched \(C_{22}-C_{22}\) and preferably \(C_2-C_{18}\) alkenyl group,

Sulfo represents a sulfonic or sulfonate group, such as \(-\text{SO}_3\text{V, V}\)

having the same meaning as above,

\(n\) is such that the degree of substitution of the polysaccharide compound with an anionic group \(-\text{CO}_2\text{V and/or }-\text{PO}_3\text{V}_2\ (\text{DS}(-)_1)\), is within the range from 0.01 to 1.5 and preferably from 0.05 to 1,

\(m\) is such that the degree of substitution of the polysaccharide compound with a cationic group (\(\text{DS}(+)\)) is within the range from 0.01 to 1.5 and preferably from 0.05 to 1,

\(p\) is such that the degree of substitution of the polysaccharide compound with a sulfonic or sulfonate group (\(\text{DS}(-)_2\)) is within the range from 0.01 to 1.5 and preferably from 0.02 to 1,

the total degree of substitution of the polysaccharide compound not exceeding 3, and it is preferably within the range from 0.05 to 2.5.

The term “degree of substitution \(\text{DS}(-)_1\) of the amphoteric polysaccharide compounds” according to the invention means the ratio of the number of hydroxyl groups substituted with an anionic group \(-\text{CO}_2\text{V and/or }-\text{PO}_3\text{V}_2\) in the repeating unit to the number of elementary monosaccharides constituting the unit.

The term “degree of substitution \(\text{DS}(-)_2\) of the amphoteric polysaccharide compounds” according to the invention means the ratio
of the number of hydroxyl groups substituted with a sulfonic or sulfonate group in the repeating unit to the number of elementary monosaccharides constituting the unit.

The term “degree of substitution DS(+) of the amphoteric polysaccharide compounds” according to the invention means the ratio of the number of hydroxyl groups substituted with a cationic group in the repeating unit to the number of elementary monosaccharides constituting the unit.

The polysaccharide chain represented by P is preferably a cellulose, a starch, an inulin, a guar gum, a xanthan gum, a pullulan, an agar-agar, a sodium, potassium or ammonium alginate, a carrageenan, a dextran, a fucellaran, a gellan gum, a gum arabic, a gum tragacanth, a hyaluronic acid, a konjac mannan, a lignin sulfonate, a carob gum, a partially N-acetylated chitin, a pectin, a polydextrose, a rhamson gum or a welan gum.

More preferably, the polysaccharide chain is a cellulose, a carboxymethylcellulose, a hydroxyethylcellulose, a hydroxypropylcellulose, a hydroxypropylmethylcellulose, a methylcellulose, a starch, a starch acetate, a hydroxyethyl starch, a hydroxypropyl starch, an inulin, a guar gum, a carboxymethylguar gum, a carboxymethylhydroxypropylguar gum, a hydroxyethylguar gum, a hydroxypropylguar gum or a xanthan gum.

The polysaccharide chain containing sulfonate function(s) preferably has a weight-average molecular mass within the range from 500 to 15,000,000 and better still from 1000 to 10,000,000.

Examples of linear or branched, saturated or unsaturated C₁-C₁₂ and preferably C₁-C₈ divalent hydrocarbon-based groups X, Y, Z or A that may especially be mentioned include linear or branched C₁-C₈ alkylene groups, such as methylene, ethylene, n-propylene, isopropylene, n-butylene, tert-butylene, hexylene or octylene; linear or branched C₂-C₈ alkylene groups, such as vinylene, allylene, crotonylene, butenylene, isobutenylene, tert-butenylene, hexenylene or octenylene. These groups may also bear at least one hydroxyl substituent and/or may comprise at least one ether and/or amine function in the alkylene or
alkylene chain.

Examples of linear or branched, saturated or unsaturated C<sub>1</sub>-C<sub>8</sub> and preferably C<sub>1</sub>-C<sub>4</sub> monovalent hydrocarbon-based groups R<sub>1</sub> that may especially be mentioned include linear or branched C<sub>1</sub>-C<sub>4</sub> alkyl groups, such as methyl, ethyl, n-propyl, isopropyl, n-butyl or tert-butyl; linear or branched C<sub>2</sub>-C<sub>4</sub> alkenyl groups, such as vinyl, allyl, crotonyl, butenyl, isobutenyl or tert-butenyl; the said groups possibly bearing at least one hydroxyl substituent and possibly comprising at least one ether and/or amine function in the alkyl or alkenyl chain.

Examples of R<sub>2</sub> to R<sub>7</sub> that may especially be mentioned include linear or branched C<sub>1</sub>-C<sub>4</sub> alkyl groups, such as methyl, ethyl, n-propyl, isopropyl, n-butyl or tert-butyl groups, and linear or branched C<sub>12</sub>-C<sub>18</sub> alkyl groups, such as lauryl, myristyl, cetyl or stearyl groups. Examples of linear or branched C<sub>2</sub>-C<sub>18</sub> and preferably C<sub>2</sub>-C<sub>6</sub> alkenyl groups that may especially be mentioned include vinyl, allyl, crotonyl and butenyl groups.

The amphoteric polyanionic compounds that are most particularly preferred in the invention are those corresponding to formula (I) in which:

P represents a cellulose, a carboxymethylcellulose, a hydroxyethylcellulose, a hydroxypropylcellulose, a hydroxypropylmethylcellulose, a methylcellulose, a starch, a starch acetate, a hydroxyethyl starch, a hydroxypropyl starch, an inulin, a guar gum, a carboxymethylguar gum, a carboxymethylhydroxypropylguar gum, a hydroxyethylguar gum, a hydroxypropylguar gum or a xanthan gum,

X, Y and Z represent, independently of each other, a linear or branched C<sub>1</sub>-C<sub>8</sub> alkyene group, such as methylene, ethylene, n-propylene, isopropylene, n-butylene, tert-butylene, hexylene or octylene; or a linear or branched C<sub>2</sub>-C<sub>8</sub> alkenylene group, such as vinylene, allylene, crotonylene, butenylene, isobutenylene, tert-butenylene, hexenylene or octenylene, or...
in which each R, which may be identical or different, represents R₁ or OR₁,
R₁ represents a linear or branched C₁-C₄ alkyl group, such as methyl, ethyl, n-propyl, isopropyl, n-butyl or tert-butyl; or a linear or branched C₂-C₄ alkenyl group, such as vinyl, allyl, crotonyl, butenyl, isobutenyl or tert-butenyl;
q represents an integer ranging from 0 to 5,
A represents a linear or branched C₁-C₈ alkenylene group, such as methylene, ethylene, n-propylene, isopropylene, n-butylene, tert-butylene, hexylene or octylene; or a linear or branched C₂-C₈ alkenylene group, such as vinylene, allylene, crotonylene, butenylene, isobutenylene, tert-butenylene, hexenylene or octenylene,
r, An, CAT, Sulfo, m, n and p have the same meanings as those above, and
R₂ to R₇ represent a hydrogen atom, a C₁₋₄ alkyl group such as methyl, ethyl, n-propyl, isopropyl, n-butyl, or tert-butyl, or a C₁₂₋₁₈ alkyl group such as lauryl, myristyl, cetyl or stearyl, or a linear or branched C₂₋₆ alkenyl group such as vinyl, allyl, crotonyl or butenyl.

The amphoteric polysaccharide compounds containing sulfonate function(s) as described above may be used in cosmetics, as conditioning agents, and especially for the cosmetic treatment of keratin materials, such as caring for and protecting the hair, hold and discipline of the hairstyle, but also for cleansing and caring for the skin and for making up the skin, the lips and the nails.

A subject of the present invention is also a cosmetic composition comprising, in a cosmetically acceptable medium, at least one amphoteric polysaccharide compound containing sulfonate function(s) according to the invention, preferably in an amount ranging from 0.01% to 50% by weight and better still from 0.03% to 25% by weight relative to the total weight of the composition.
The term “cosmetically acceptable medium” means a medium that is compatible with any keratin material, such as the skin, the hair, the nails, the eyelashes, the eyebrows and the lips and any other area of body or facial skin.

The cosmetically acceptable medium may consist solely of water or of a mixture of water and of a cosmetically acceptable solvent such as a C₁-C₄ lower alcohol, such as ethanol, isopropanol, tert-butanol or n-butanol; alkylene polyols, for instance propylene glycol; polyol ethers; and mixtures thereof.

The composition according to the invention may also comprise one or more standard additives that are well known in the art, such as anionic, cationic, nonionic, amphoteric or zwitterionic surfactants, anionic, cationic, nonionic, amphoteric or zwitterionic polymers, thickeners, nacreous agents, opacifiers, UV-screening agents, fragrances, mineral, plant and/or synthetic oils, fatty acid esters, dyes, volatile or non-volatile, organomodified or non-organomodified, cyclic or acyclic, branched or unbranched silicones, mineral or organic, natural or synthetic particles, preserving agents and pH stabilizers.

A person skilled in the art will take care to select the optional additives and the amount thereof such that they do not harm the properties of the compositions of the present invention.

These additives are generally present in the composition according to the invention in an amount ranging from 0 to 20% by weight relative to the total weight of the composition.

The cosmetic compositions in accordance with the invention may be in the form of a mousse, a gel, a spray or a lacquer and may be used in rinse-out or leave-in application.

The compositions in accordance with the invention may be used as hair products, especially rinse-out or leave-in products, and in particular for washing, caring for and/or conditioning the hair, holding the hairstyle, and shaping, dyeing, bleaching, permanently reshaping or relaxing the hair.

The compositions of the invention may also be used as care or hygiene products such as protective, treating or care creams for the face,
the hands or the body, protective or care body milks, gels or mousses for
caring for or cleansing the skin, or alternatively as products for making
up or for removing makeup from the skin, the lips, the nails and the
eyelashes.

The examples presented below are given as illustrations of the
present patent application.

EXAMPLES

Example 1

The sulfonation and then quaternization of a sodium salt of
carboxymethylcellulose is performed.

Sulfonation

57 g of sodium salt of carboxymethylcellulose with a DS of 0.6-
0.95, sold by the company Fluka, are dispersed with vigorous stirring in
200 ml of anhydrous 1,4-dioxane.

1.2 g (50 mmol) of sodium hydride are added portionwise. The
mixture is refluxed (99-100°C) for 2 hours.

The mixture is allowed to cool until the temperature is 80°C, and
6.1 g (50 mmol) of 1,3-propanesultone predissolved in 50 ml of
anhydrous dioxane are then rapidly introduced. The mixture is refluxed
for a further 5 hours.

After cooling to room temperature, a beige-coloured powder is
collected by filtration, and reslurried 3 times in dioxane and dried under
vacuum at 50°C. 59.3 g of product are obtained.

Quaternization

All of the sulfonated product is dispersed in 500 ml of
acetonitrile and 0.5 ml of 50% sodium hydroxide solution.

9.7 g of aqueous 78% 2,3-epoxypropyltrimethylammonium
chloride solution (50 mmol) are then introduced.

The mixture is heated at 50°C for 5 hours. After cooling to room
temperature, a light-brown powder is collected by filtration and reslurried twice in 200 ml of acetonitrile: the acetonitrile penetrates the gum and allows certain impurities to be extracted, which are then removed by suction-filtering the gum, this operation being repeated twice. The product is dried under vacuum at 50°C.

Example 2: Shampoo

A shampoo was prepared using the following ingredients, the amounts of which are given as weight percentages of active material relative to the total weight of the composition:

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium lauryl ether sulfate (Texapon N702 from Cognis)</td>
<td>12.5%</td>
</tr>
<tr>
<td>Cocoyletaïne (Dehyton AB 30 from Goldschmidt)</td>
<td>2.5%</td>
</tr>
<tr>
<td>Dimethicone (DC200 Fluid from Dow Corning)</td>
<td>2.0%</td>
</tr>
<tr>
<td>Compound of Example 1</td>
<td>0.5%</td>
</tr>
<tr>
<td>Cocamide monoisopropanolamine</td>
<td>0.4%</td>
</tr>
<tr>
<td>Carbomer</td>
<td>0.2%</td>
</tr>
<tr>
<td>Preserving agent</td>
<td>qs</td>
</tr>
<tr>
<td>Fragrance</td>
<td>qs</td>
</tr>
<tr>
<td>Citric acid/sodium hydroxide</td>
<td>qs</td>
</tr>
<tr>
<td>pH 6.5</td>
<td></td>
</tr>
<tr>
<td>Water</td>
<td>qs</td>
</tr>
<tr>
<td>Total</td>
<td>100%</td>
</tr>
</tbody>
</table>

Example 3: Conditioner

A conditioner was prepared using the following ingredients, the amounts of which are given as weight percentages of active material relative to the total weight of the composition:
Behenyltrimethylammonium chloride (Genamin KDMP from Clariant) | 1.2%
PEG/PPG Dimethicone (Abil B8851 from Goldschmidt) | 0.5%
Cyclopentasiloxane (Dow Corning 245 Fluid) | 15.0%
Compound of Example 1 | 1.0%
Propylene glycol | 2.5%
Preserving agent | qs
Fragrance | qs
Citric acid/sodium hydroxide | qs | pH 6.5
Water | qs | 100

Examples 4-6

Dye compositions were prepared using the following ingredients, the amounts of which are given as weight percentages of active material relative to the total weight of the composition:

<table>
<thead>
<tr>
<th></th>
<th>Ex. 4</th>
<th>Ex. 5</th>
<th>Ex. 6</th>
</tr>
</thead>
<tbody>
<tr>
<td>para-Phenylenediamine</td>
<td>0.24</td>
<td>0.24</td>
<td>0.24</td>
</tr>
<tr>
<td>para-Aminophenol</td>
<td>0.44</td>
<td>0.44</td>
<td>0.44</td>
</tr>
<tr>
<td>2-Aminophenol</td>
<td>0.028</td>
<td>0.028</td>
<td>0.028</td>
</tr>
<tr>
<td>1,3-Dihydroxybenzene</td>
<td>0.192</td>
<td>0.192</td>
<td>0.192</td>
</tr>
<tr>
<td>3-Aminophenol</td>
<td>0.019</td>
<td>0.019</td>
<td>0.019</td>
</tr>
<tr>
<td>5-N-(β-Hydroxyethyl)amino-2-methylphenol</td>
<td>0.021</td>
<td>0.021</td>
<td>0.021</td>
</tr>
<tr>
<td>1,3-Dihydroxy-2-methylbenzene</td>
<td>0.055</td>
<td>0.055</td>
<td>0.055</td>
</tr>
<tr>
<td>Anhydrous sodium metasilicate</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Monoethanolamine</td>
<td>5.45</td>
<td>5.45</td>
<td>5.45</td>
</tr>
<tr>
<td>Reducing agent, antioxidant, sequestering agent, fragrance</td>
<td>qs</td>
<td>qs</td>
<td>qs</td>
</tr>
<tr>
<td>Propylene glycol</td>
<td>10</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Crosslinked acrylic acid polymer</td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
</tr>
<tr>
<td>Compound of Example 1</td>
<td>Ex. 4</td>
<td>Ex. 5</td>
<td>Ex. 6</td>
</tr>
<tr>
<td>---------------------------------------------------------</td>
<td>-------</td>
<td>-------</td>
<td>-------</td>
</tr>
<tr>
<td>Cationic polymer: hexadimethrine chloride (CTFA name)</td>
<td>1.5</td>
<td>1.5</td>
<td>2.8</td>
</tr>
<tr>
<td>Mexomer PO sold by the company Chimex</td>
<td>3</td>
<td>3</td>
<td>-</td>
</tr>
<tr>
<td>Powdered sodium lauryl sulfate</td>
<td>3</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Lauryl alcohol oxyethylenated with 12 mol of ethylene oxide</td>
<td>-</td>
<td>7.5</td>
<td>7.5</td>
</tr>
<tr>
<td>Oleocetyl alcohol oxyethylenated with 30 mol of ethylene oxide</td>
<td>-</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Decyl alcohol oxyethylenated with 3 mol of ethylene oxide</td>
<td>10</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Decyl alcohol oxyethylenated with 5 mol of ethylene oxide</td>
<td>8</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Lauric acid</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
</tr>
<tr>
<td>50/50 cetylstearyl alcohol</td>
<td>11.5</td>
<td>11.5</td>
<td>11.5</td>
</tr>
<tr>
<td>Nacreous agent: hydrophobic fumed silica</td>
<td>1.2</td>
<td>1.2</td>
<td>1.2</td>
</tr>
<tr>
<td>Nacreous agent: glyceryl monostearate</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Demineralized water</td>
<td>qs</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>

At the time of use, each dye composition described above was mixed weight-for-weight with a 20-volumes hydrogen peroxide solution (6% by weight).

The mixtures thus prepared were applied for 30 minutes to locks of natural or permanent-waved grey hair containing 90% white hairs. The locks were then rinsed, washed with a standard shampoo, rinsed again and then dried.

The hair was dyed in a golden-blond shade for each of the Examples 4 to 6.
Example 7

Another dye composition was prepared using the following ingredients, the amounts of which are given as weight percentages of active material relative to the total weight of the composition:

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mixture of C18 to C24 linear alcohols (C18/C20/C22/C24: 7/57/30/6 - alcohol content &gt; 95%)</td>
<td>3</td>
</tr>
<tr>
<td>Oxyethylenated stearyl alcohol (2 mol of ethylene oxide)</td>
<td>4.5</td>
</tr>
<tr>
<td>Oxyethylenated stearyl alcohol (21 mol of ethylene oxide)</td>
<td>1.75</td>
</tr>
<tr>
<td>Oleic acid</td>
<td>2.6</td>
</tr>
<tr>
<td>Cationic polyurethane obtained by condensation of 1,3-bis-(isocyanatomethylcyclohexane), N,N-dimethylethanamine quaternized with bromododecane, N,N-dimethylethanamine and polyoxyethylene of molecular weight 10 000</td>
<td>0.2</td>
</tr>
<tr>
<td>Crosslinked poly(acrylic acid) (product sold under the name Carbopol 980 by the company Noveon)</td>
<td>0.4</td>
</tr>
<tr>
<td>Hydroxypropylmethylcellulose</td>
<td>0.2</td>
</tr>
<tr>
<td>Coconut acid monoisopropanolamide</td>
<td>3</td>
</tr>
<tr>
<td>Merquat 100 as an aqueous 40% solution</td>
<td>1.6</td>
</tr>
<tr>
<td>Compound of Example 1</td>
<td>2</td>
</tr>
<tr>
<td>Sodium metabisulfite</td>
<td>0.71</td>
</tr>
<tr>
<td>EDTA (ethylenediaminetetraacetic acid)</td>
<td>0.2</td>
</tr>
<tr>
<td>tert-Butylhydroquinone</td>
<td>0.3</td>
</tr>
<tr>
<td>1,4-Diaminobenzene</td>
<td>0.2</td>
</tr>
<tr>
<td>para-Aminophenol</td>
<td>1.2</td>
</tr>
<tr>
<td>1,3-Dihydroxybenzene</td>
<td>0.1</td>
</tr>
<tr>
<td>1-Hydroxy-3-aminobenzene</td>
<td>0.2</td>
</tr>
<tr>
<td>1-Methyl-2-hydroxy-4-β-hydroxyethylaminobenzene</td>
<td>0.8</td>
</tr>
<tr>
<td>Monoethanolamine</td>
<td>1</td>
</tr>
<tr>
<td>Aqueous ammonia containing 20% NH₃</td>
<td>11</td>
</tr>
<tr>
<td>Fragrance</td>
<td>qs</td>
</tr>
<tr>
<td>Demineralized water</td>
<td>100</td>
</tr>
</tbody>
</table>

This composition is mixed at the time of use with an oxidizing
composition in emulsion form containing as oxidizing agent 7.5% hydrogen peroxide, in a proportion of 1 part by weight of dye composition per 1.5 parts by weight of oxidizing composition. The mixture obtained is applied to locks of natural hair containing 90% white hairs, and is left to act for 30 minutes. After rinsing, washing with shampoo and drying, hair dyed in a strong coppery-red light-chestnut shade is obtained.

Example 8

The following compositions were prepared, the percentages indicated being weight percentages relative to the total weight of the composition:

**Oxidizing composition:**

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fatty alcohol</td>
<td>2.3</td>
</tr>
<tr>
<td>Oxyethylenated fatty alcohol</td>
<td>0.6</td>
</tr>
<tr>
<td>Fatty amide</td>
<td>0.9</td>
</tr>
<tr>
<td>Glycerol</td>
<td>0.5</td>
</tr>
<tr>
<td>Hydrogen peroxide</td>
<td>7.5</td>
</tr>
<tr>
<td>Fragrance</td>
<td>qs</td>
</tr>
<tr>
<td>Demineralized water</td>
<td></td>
</tr>
</tbody>
</table>

**Dye composition:**

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mixture of C18 to C24 linear alcohols [C18/C20/C22/C24, 7/58/30/6, alcohol content &gt; 95%] (Nafol 20-22)</td>
<td>3%</td>
</tr>
<tr>
<td>Mixture of C18 to C24 linear alcohols [C18/C20/C22/C24, 7/58/30/6, alcohol content &gt; 95%] in oxyethylenated form (30 mol of ethylene oxide) (Nafolox 20-22)</td>
<td>1.35%</td>
</tr>
<tr>
<td>Ingredient</td>
<td>Concentration</td>
</tr>
<tr>
<td>---------------------------------------------------------------------------</td>
<td>---------------</td>
</tr>
<tr>
<td>Oxyethylenated stearyl alcohol (2 mol of ethylene oxide)</td>
<td>4%</td>
</tr>
<tr>
<td>Oxyethylenated stearyl alcohol (21 mol of ethylene oxide)</td>
<td>2%</td>
</tr>
<tr>
<td>Oleic acid</td>
<td>2.6%</td>
</tr>
<tr>
<td>Glycol distearate</td>
<td>2%</td>
</tr>
<tr>
<td>Propylene glycol</td>
<td>5%</td>
</tr>
<tr>
<td>Coconut acid monoisopropanolamide</td>
<td>2%</td>
</tr>
<tr>
<td>Aculyn 44 sold by the company Rohm &amp; Haas</td>
<td>1.4% AM*</td>
</tr>
<tr>
<td>Crosslinked poly(acrylic acid)</td>
<td>0.6%</td>
</tr>
<tr>
<td>Compound of Example 1</td>
<td>3% AM*</td>
</tr>
<tr>
<td>Merquat 100 sold by the company Calgon</td>
<td>0.4% AM*</td>
</tr>
<tr>
<td>Reducing agents</td>
<td>0.7%</td>
</tr>
<tr>
<td>Sequestrering agents</td>
<td>0.2%</td>
</tr>
<tr>
<td>1,3-Dihydroxybenzene (resorcinol)</td>
<td>0.6%</td>
</tr>
<tr>
<td>1,4-Diaminobenzene</td>
<td>0.5%</td>
</tr>
<tr>
<td>1-Hydroxy-3-aminobenzene</td>
<td>0.1%</td>
</tr>
<tr>
<td>1-Hydroxy-2-aminobenzene</td>
<td>0.05%</td>
</tr>
<tr>
<td>1-Hydroxy-4-aminobenzene</td>
<td>0.09%</td>
</tr>
<tr>
<td>6-Hydroxybenzomorpholine</td>
<td>0.017%</td>
</tr>
<tr>
<td>1-β-Hydroxyethylxyloxy-2,4-diaminobenzene dihydrochloride</td>
<td>0.039%</td>
</tr>
<tr>
<td>Propylene glycol monobutyl ether</td>
<td>2.5%</td>
</tr>
<tr>
<td>Pure monoethanolamine</td>
<td>1.06%</td>
</tr>
<tr>
<td>Aqueous ammonia (containing 20.5% ammonia)</td>
<td>11.1%</td>
</tr>
<tr>
<td>Water</td>
<td>qs</td>
</tr>
<tr>
<td>AM* = Active Material</td>
<td></td>
</tr>
</tbody>
</table>

The dye composition was mixed, at the time of use, in a plastic bowl and for 2 minutes, with the oxidizing composition given above, in a proportion of 1 part of dye composition per 1.5 parts of oxidizing composition.

The mixture obtained was applied to locks of natural hair containing 90% white hairs, and was left to act for 30 minutes.
The locks were then rinsed with water, washed with shampoo, rinsed again with water and then dried and disentangled.

The hair was then dyed in a strong light-chestnut shade.

Example 9

Another dye composition was prepared using the following ingredients, the amounts of which are given as weight percentages of active material relative to the total weight of the composition:

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oleocetyl alcohol oxyethylenated with 30 mol of ethylene oxide (nCA=17 - HLB=16.5)</td>
<td>7%</td>
</tr>
<tr>
<td>Lauryl alcohol (C12-C14/55-45%) oxyethylenated with 12 mol of ethylene oxide (nCA=12.5 - HLB=14)</td>
<td>8%</td>
</tr>
<tr>
<td>Cetylstearyl alcohol (C16/C18-50/50)(nCB=17- HLB=1)</td>
<td>5%</td>
</tr>
<tr>
<td>Decyl alcohol (C10-C12-C14/85-8.5-6.5) oxyethylenated with 3.5 mol of ethylene oxide, sold under the name Mergital BL 309 by the company Henkel (nCB=10.4 - HLB=8.5)</td>
<td>22%</td>
</tr>
<tr>
<td>Copolymer of diallyldimethylammonium chloride and of acrylic acid, sold under the name Merquat 280 by the company Calgon, containing 35% AM</td>
<td>3% AM</td>
</tr>
<tr>
<td>Compound of Example 1</td>
<td>1%</td>
</tr>
<tr>
<td>Crosslinked poly(acrylic acid) sold under the name Carbopol 934 (MW 3 000 000) by the company Goodrich</td>
<td>0.4%</td>
</tr>
<tr>
<td>Propylene glycol</td>
<td>8%</td>
</tr>
<tr>
<td>Monoethanolamine</td>
<td>8.3 %</td>
</tr>
<tr>
<td>Hydroquinone</td>
<td>0.1 %</td>
</tr>
<tr>
<td>1-Phenyl-3-methyl-5-pyrazolone</td>
<td>0.1 %</td>
</tr>
<tr>
<td>Aqueous sodium bisulfite solution containing 35% AM</td>
<td>1.3 %</td>
</tr>
<tr>
<td>para-Phenylenediamine</td>
<td>0.5 %</td>
</tr>
<tr>
<td>m-Dihydroxybenzene</td>
<td>0.4 %</td>
</tr>
<tr>
<td>Fragrance, sequestering agent</td>
<td>qs</td>
</tr>
<tr>
<td>Eau</td>
<td>qs</td>
</tr>
<tr>
<td>pH = 11.0</td>
<td>100%</td>
</tr>
</tbody>
</table>

AM: Active Material
CLAIMS

1. Amphoteric polysaccharide compound containing sulfonate function(s) corresponding to formula (I):

\[
\left(\text{An}-\text{X}-\text{O}\right)_{n}\text{P}\left(\text{O}-\text{Y}\right)_{m}\text{CAT}
\]

in which:

- the oxygen atoms belong to one or more saccharide units of P,
- P represents a polysaccharide chain,
- X, Y and Z represent, independently of each other:
  - a linear or branched, saturated or unsaturated, optionally hydroxylated divalent C₁₋₁₂ hydrocarbon-based group optionally comprising at least one ether and/or amine function in the hydrocarbon-based chain, or
  - a group

\[
\begin{array}{c}
\text{Si} \\
\text{R} \\
\text{Si} \\
\text{O} \\
\text{R} \\
\text{A} \\
\end{array}
\]

the silicon atom being attached to the oxygen atom in the group An-X-O-, CAT-(Y)ₙ-O- or Sulfo-Z-O-, in which each R, which may be identical or different, represents R₁ or -OR₁,

R₁ represents a linear or branched, saturated or unsaturated, optionally hydroxylated C₁₋₈ monovalent hydrocarbon-based group optionally comprising at least
one ether and/or amine function in the hydrocarbon-based chain,
q represents an integer ranging from 0 to 10, and
A represents a linear or branched, saturated or unsaturated, optionally hydroxylated C₁₋C₁₂ divalent hydrocarbon-based group optionally comprising at least one ether and/or amine function in the hydrocarbon-based chain,
r is equal to 0 or 1, r being 0 when CAT represents a cationic polymer chain obtained by grafting and polymerization of ethylenic monomers bearing an ammonium group,
An represents an anionic group chosen from:
\[ \begin{align*}
\text{O} & \quad \text{O} \\
\text{C} & \quad \text{P} \\
\text{O} & \quad \text{O} \\
\text{V} & \quad \text{V}
\end{align*} \]
with V representing a hydrogen atom or an alkali metal or alkaline-earth metal,
CAT represents:
- an ammonium group
\[ \begin{align*}
\text{R}_2 & \\
\text{N}^+ & \\
\text{R}_3 & \\
\text{Q}^- & \\
\text{R}_4
\end{align*} \]
in which R₂, R₃ and R₄ represent, independently of each other, a hydrogen atom or a linear or branched, saturated or unsaturated, optionally hydroxylated C₁₋C₂₂ monovalent hydrocarbon-based group optionally comprising at least one ether and/or amine function in the hydrocarbon-based chain, and Q⁻ represents a mineral or organic anion, or
- a cationic polymer chain obtained by grafting and polymerization of ethylenic monomers bearing an ammonium group,
Sulfo

represents a sulfonic or sulfonate group,

is such that the degree of substitution of the polysaccharide
compound with an anionic group \(-\text{CO}_2\text{V}\) and/or \(-\text{PO}_3\text{V}_2\), is
within the range from 0.01 to 1.5,

is such that the degree of substitution of the polysaccharide
compound with a cationic group is within the range from 0.01
to 1.5,

is such that the degree of substitution of the polysaccharide
compound with a sulfonic or sulfonate group is within the
range from 0.01 to 1.5,

the total degree of substitution of the polysaccharide compound not
exceeding 3.

2. Amphoteric polysaccharide compound according to Claim 1,
characterized in that P represents a cellulose, a starch, an inulin, a guar
gum, a xanthan gum, a pullulan, an agar-agar, a sodium, potassium or
ammonium alginate, a carrageenan, a dextran, a furcellaran, a gellan
gum, a gum arabic, a gum tragacanth, a hyaluronic acid, a konjac
manna, a lignin sulfonate, a carob gum, a partially N-acetylated chitin,
a pectin, a polydextrose, a rhaman gum or a welan gum.

3. Amphoteric polysaccharide compound according to Claim 2,
characterized in that P represents a cellulose, a carboxymethylcellulose,
a hydroxyethylcellulose, a hydroxypropylcellulose, a hydroxypropyl-
methylcellulose, a methylcellulose, a starch, a starch acetate, a hydroxy-
ethyl starch, a hydroxypropyl starch, an inulin, a guar gum, a carboxy-
methylguar gum, a carboxymethylhydroxypropylguar gum, a hydroxy-
ethylguar gum, a hydroxypropylguar gum or a xanthan gum.

4. Amphoteric polysaccharide compound according to any one
of the preceding claims, characterized in that the \(\text{C}_1-\text{C}_{12}\) divalent
hydrocarbon-based group X, Y, Z or A is chosen from linear or branched
\(\text{C}_1-\text{C}_8\) alkylene groups and linear or branched \(\text{C}_2-\text{C}_8\) alkenylene groups,
on optionally bearing at least one hydroxyl group and/or optionally
comprising at least one ether and/or amine function in the alkylene or
alkenylene chain.

5. Amphoteric polysaccharide compound according to Claim 4,
characterized in that the C\textsubscript{1}-C\textsubscript{12} divalent hydrocarbon-based group is
chosen from methylene, ethylene, n-propylene, isopropylene, n-butylene, tert-butylene, hexylene, octylene, vinylene, allylene, crotonylene, butenylene, isobutenylene, tert-butenylene, hexenylene and
octenylene groups.

6. Amphoteric polysaccharide compound according to any one of the preceding claims, characterized in that R\textsubscript{1} represents a linear or branched C\textsubscript{1}-C\textsubscript{4} alkyl group or a linear or branched C\textsubscript{2}-C\textsubscript{4} alkenyl group.

7. Amphoteric polysaccharide compound according to Claim 6, characterized in that R\textsubscript{1} is chosen from methyl, ethyl, n-propyl, isopropyl, n-butyl, tert-butyl, vinyl, allyl, crotonyl, butenyl, isobutenyl and tert-butenyl groups.

8. Amphoteric polysaccharide compound according to any one of the preceding claims, characterized in that Q represents a halogen atom, an acetate, a citrate, a lactate, an olate or a behenate.

9. Amphoteric polysaccharide compound according to any one of the preceding claims, characterized in that R\textsubscript{2}, R\textsubscript{3} and R\textsubscript{4} represent, independently of each other, a hydrogen atom, a linear or branched C\textsubscript{1}-C\textsubscript{4} alkyl group, a linear or branched C\textsubscript{12}-C\textsubscript{18} alkyl group or a linear or branched C\textsubscript{2}-C\textsubscript{6} alkenyl group.

10. Amphoteric polysaccharide compound according to Claim 9, characterized in that R\textsubscript{2}, R\textsubscript{3} and R\textsubscript{4} represent, independently of each other, a hydrogen atom or a methyl, ethyl, n-propyl, isopropyl, n-butyl, tert-butyl, lauryl, myristyl, cetyl, stearyl, vinyl, allyl, crotonyl or butenyl group.

11. Amphoteric polysaccharide compound according to any one of the preceding claims, characterized in that the ethylenic monomers bearing an ammonium group correspond to the formula:

\[
\begin{align*}
\text{N}^+ & \quad \text{R}_5 \\
\text{R}_6 & \quad \text{R}_7 \\
\end{align*}
\]

in which R\textsubscript{5}, R\textsubscript{6} and R\textsubscript{7} represents, independently of each other, a hydrogen atom, a linear or branched C\textsubscript{1}-C\textsubscript{22} alkyl group or a linear or branched C\textsubscript{2}-C\textsubscript{22} alkenyl group.
12. Amphoteric polysaccharide compound according to Claim 11, characterized in that R₅, R₆ and R₇ represent, independently of each other, a hydrogen atom, a linear or branched C₁-C₄ alkyl group, a linear or branched C₁₂-C₁₈ alkyl group or a linear or branched C₂-C₆ alkenyl group.

13. Amphoteric polysaccharide compound according to Claim 12, characterized in that R₅, R₆ and R₇ represent, independently of each other, a hydrogen atom or a methyl, ethyl, n-propyl, isopropyl, n-butyl, tert-butyl, lauryl, myristyl, cetyl, stearyl, vinyl, allyl, crotonyl or butenyl group.

14. Use of at least one amphoteric polysaccharide compound containing sulfonate function(s) according to any one of the preceding claims, in cosmetics, as a conditioning agent.

15. Use according to Claim 14, for the cosmetic treatment of keratin materials.

16. Use according to Claim 15, for caring for and protecting the hair.

17. Use according to Claim 15, for cleansing and caring for the skin.

18. Use according to Claim 15, for making up the skin, the lips and the nails.

19. Cosmetic composition comprising, in a cosmically acceptable medium, at least one amphoteric polysaccharide compound containing sulfonate function(s) according to any one of Claims 1 to 13.

20. Cosmetic composition according to Claim 19, characterized in that it comprises the said amphoteric polysaccharide compound containing sulfonate function(s) in an amount ranging from 0.01% to 50% by weight relative to the total weight of the composition.

21. Cosmetic composition according to Claim 20, characterized in that it comprises the said amphoteric polysaccharide compound containing sulfonate function(s) in an amount ranging from 0.03% to 25% by weight relative to the total weight of the composition.

22. Cosmetic composition according to any one of Claims 19 to 21, characterized in that the cosmically acceptable medium comprises
water or a mixture of water and of at least one organic solvent.

23. Cosmetic composition according to Claim 22, characterized in that the organic solvent is chosen from C₁-C₄ lower alcohols, alkylene polyols, polyol ethers, and mixtures thereof.

24. Cosmetic composition according to any one of Claims 19 to 23, characterized in that it comprises at least one additive chosen from anionic, cationic, nonionic, amphoteric or zwitterionic surfactants, anionic, cationic, nonionic, amphoteric or zwitterionic polymers, thickeners, nacreous agents, opacifiers, UV-screening agents, fragrances, mineral, plant and/or synthetic oils, fatty acid esters, dyes, volatile or non-volatile, organomodified or non-organomodified, cyclic or acyclic, branched or unbranched silicones, mineral or organic, natural or synthetic particles, preserving agents and pH stabilizers.