

(19) United States

(12) Patent Application Publication (10) Pub. No.: US 2016/0271049 A1

Schulze zur Wiesche et al.

Sep. 22, 2016 (43) Pub. Date:

(54) HAIR TREATMENT COMPOSITION WITH SUBSTITUTED SILICONE(S)

- (71) Applicant: Henkel AG & Co. KGaA, Duesseldorf
- Inventors: Erik Schulze zur Wiesche, Hamburg (DE); Rene Krohn, Norderstedt (DE)
- Assignee: Henkel AG & Co. KGaA, Duesseldorf (DE)
- Appl. No.: 15/169,086
- (22) Filed: May 31, 2016

Related U.S. Application Data

- Continuation of application No. PCT/EP2014/ (63)074232, filed on Nov. 11, 2014.
- (30)Foreign Application Priority Data

Dec. 5, 2013 (DE) 10 2013 224 993.4

Publication Classification

(51) Int. Cl.

A61K 8/898 (2006.01)A61Q 5/00 (2006.01)A61K 8/41 (2006.01)

(52) U.S. Cl.

CPC A61K 8/898 (2013.01); A61K 8/41 (2013.01); A61Q 5/002 (2013.01); A61Q 5/004 (2013.01); A61K 2800/594 (2013.01)

(57)**ABSTRACT**

A hair treatment composition includes, based on the weight of the composition, 0.1 to 20 wt. % at least one silicone which has groupings of the formula (I) as defined herein; 0.1 to 20 wt. % at least one copolymer which has monomer units of the formulas (V) and (VI) as defined herein; and 0.1 to 10 wt. % (RS)-2-cyano-3,3-diphenylacrylic acid-2-ethylhexyl ester. The hair treatment composition has an improved protection effect against UV radiation and imparts better combability, shine, elasticity, brittleness, and maximum tear resistance to hair.

HAIR TREATMENT COMPOSITION WITH SUBSTITUTED SILICONE(S)

FIELD OF THE INVENTION

[0001] The present invention generally relates to hair treatment compositions including specially substituted silicone(s) and also to the use of these compositions to clean and/or care for hair.

BACKGROUND OF THE INVENTION

[0002] Care products for keratin fibers influence the natural structure and the properties of the hair. Following treatments of this type, the wet and dry combability of the hair, the hold, and the volume of the hair, for example, can be optimized, or the hair can be protected against increased splitting. It has therefore long been usual to subject the hair to a special post-treatment. Here, the hair is treated with special active substances, for example quaternary ammonium salts or special polymers, usually in the form of a rinse. As a result of this treatment, depending on the formulation, the combability, the hold, and the volume of the hair are improved, and the splitting rate is reduced.

[0003] By way of example, due to the intensive use of tanning salons or extensive physical leisure activities, the structure of hair is more heavily compromised in a lasting manner as a result of UV light. This damage manifests itself on the hair for example in the form of a loss of elasticity. It is therefore not surprising that the proportion of consumers with sensitive, brittle and irritated skin having poor elasticity and also with hair that is of poorer quality in terms of combability, shine, elasticity, brittleness and maximum tear resistance is significantly increasing.

[0004] A further problem lies in colored hair. If the dyes formed or used directly during the course of the coloring have considerably different fastness properties (for example UV stability, perspiration fastness, washing fastness, etc.), this may result over time in a noticeable and therefore undesirable color change. This phenomenon occurs in a more pronounced manner when the hairstyle, hair or hair zones has/have different degrees of damage. One example is long hair, in which case the hair ends exposed over a long time to all possible environmental influences are generally damaged much more heavily than the relatively freshly grown hair zones.

[0005] There is thus a need to provide care products that include a high protective effect against the fading of natural or dyed hair color and against damage to the hair structure as a result of UV radiation.

[0006] It has therefore long been conventional, both in skin and hair cosmetics, to incorporate UV filters into the compositions. According to European law, UV filters are defined in terms of their purpose. They are therefore "substances, which are intended exclusively or primarily to protect the skin against specific UV radiation by absorption, reflection or scattering of specific UV radiation". This definition is attributed to all UV filters, regardless of whether they are organic or inorganic, so-called chemical or physical, natural or artificial UV filters. Only the UV filters that are

listed in the Cosmetics Regulation may be used. Since the individual substances generally do not offer protection across the entire UV spectrum, a number of substances are usually combined. In addition, synergistic effects usually result from the combination of UV filters.

[0007] Whereas the formulation of UV protection in skincare products is widely elaborated, less complex systems are used in hair care products for "dead" hair material. In addition, the amounts in which filter substances can be incorporated are also usually smaller, partly due to formulation reasons and partly due to cost reasons. So as to nevertheless provide effective UV protection, it is desirable to improve the protective effect of known and economical UV filters and to provide the corresponding compositions additionally with positive effects with respect to combability, shine, elasticity, brittleness, and maximum tear resistance of the hair treated therewith.

[0008] Furthermore, other desirable features and characteristics of the present invention will become apparent from the subsequent detailed description of the invention and the appended claims, taken in conjunction with this background of the invention.

BRIEF SUMMARY OF THE INVENTION

[0009] A hair treatment composition includes—in each case based on the weight of the hair treatment composition—0.1 to 20 wt. % at least one silicone, which has groupings of formula (I)

*—
$$\begin{bmatrix} \text{CH}_3 \\ \\ \\ \text{Si} \\ \\ \text{O} \\ \end{bmatrix}_{\pi} *,$$
(I)

in which n represents values from 1 to 1000 and A represents a grouping

$$*$$
 CO
 A
 R
 R
 R

in which R1 represents —H or — $\mathrm{CH_3}$ and R represents a straight-chain or branched alkyl group having 8 to 24 C atoms and a represents an integer from 1 to 20; 0.1 to 20 wt. % at least one copolymer, which has monomer units of formulas (V) and (VI)

$$* \underbrace{ \begin{pmatrix} R^2 \\ Q \\ N \end{pmatrix}_q }_{X} *,$$

in which R2 represents —H or — $\mathrm{CH_3}$ and X represents —H, an alkali metal cation, or a straight-chain or branched alkyl group having 1 to 24 C atoms; and 0.1 to 10 wt. % (RS)-2-cyano-3,3 -diphenylacrylic acid-2-ethylhexylester.

[0010] Silicones which have groupings of formula (I)

$$* - \underbrace{ \begin{array}{c} \text{CH}_3 \\ \text{Si} - \text{O} \xrightarrow{1}_n *, \end{array} }_{\text{A}}$$
(I)

in which n represents values from 1 to 1000 and A represents a grouping

$$*$$
 $($
 R_1
 $($
 R_1

in which R1 represents —H or — CH_3 and R represents a straight-chain or branched alkyl group having 8 to 24 C atoms and a represents an integer from 1 to 20, are used for reducing damage to the hair structure caused by external influences, in particular by UV radiation.

DETAILED DESCRIPTION OF THE INVENTION

[0011] The following detailed description of the invention is merely exemplary in nature and is not intended to limit the invention or the application and uses of the invention. Furthermore, there is no intention to be bound by any theory presented in the preceding background of the invention or the following detailed description of the invention.

[0012] It has now been found that octocrylene-containing compositions can be significantly improved in respect to the above-mentioned series of tasks when certain acrylate polymers and substituted silicones are used.

[0013] A first subject matter of the present invention is a hair treatment composition that includes—in each case based on the weight of the hair treatment composition—

[0014] a) 0.1 to 20 wt. % at least one silicone, which has groupings of formula (I)

$$* - \underbrace{ \begin{array}{c} \text{CH}_3 \\ \text{Si} - \text{O} \xrightarrow{\text{J}_n} *, \\ \text{A} & \\ \text{N} & \\ \text{A} & \\ \end{array} }_{\text{A}}$$

[0015] in which

[0016] n represents values from 1 to 1000 and

[0017] A represents a grouping

$$*$$
 R_1
 R_1

[0018] in which R1 represents —H or —CH3 and R represents a straight-chain or branched alkyl group having 8 to 24 C atoms and a represents an integer from 1 to 20;

[0019] b) 0.1 to 20 wt. % at least one copolymer, which has monomer units of formulas (V) and (VI)

[0020] in which R2 represents —H or —CH₃ and X represents —H, an alkali metal cation, or a straight-chain or branched alkyl group having 1 to 24 C atoms:

[0021] c) 0.1 to 10 wt. % (RS)-2-cyano-3,3-dipheny-lacrylic acid-2-ethylhexylester.

[0022] Hair treatment compositions in the sense of the present invention are, for example, hair shampoos, hair conditioners, conditioning shampoos, hairsprays, hair rinses, hair treatments, hair packs, hair tonics, permanent wave fixing solutions, coloring shampoos, coloring compositions, hair fixers, hair setting compositions, hair styling preparations, blow-dry lotions, foam fixers, hair gels, hair waxes, or combinations thereof. In view of the fact that men often avoid the application of a number of different compositions and/or a number of application steps, compositions according to the invention are preferably compositions according to the invention are therefore shampoos, conditioning compositions or hair tonics.

[0023] The compositions of the invention provide the keratin fibers treated therewith with improved properties, which are maintained even under intensive UV irradiation (for example lightness, softness, detangling ability, natural feeling, and airy hairstyle, brightness), and in addition the effects are persistent and lasting. In particular, these effects are resistant to many shampoos.

[0024] The compositions according to the invention include, as first essential ingredient, 0.1 to 20 wt. % at least one silicone, which comprises groupings of formula (I), In formula (I) n represents values from 1 to 1000, wherein preferred values are 1 to 40, preferably 1 to 30, more preferably 1 to 20, and in particular the values 2, 3, 4, 5, 6, 7, 8, 9 or 10.

[0025] In formula (I) A represents a grouping

$$*$$
 R_1
 R_1

in which R1 represents —H or — $\rm CH_3$ and R represents a straight-chain or branched alkyl group having 8 to 24 C atoms and a represents an integer from 1 to 20.

[0026] Particularly preferably R1=—H.

[0027] Particularly good UV protection is attained when the group R represents

[0029]
$$-\text{CH}(\text{CH}_2\text{CH}_3)-(\text{CH}_2)_5$$
.

[0030] In accordance with the invention, particularly preferred hair treatment compositions are characterized in that they include 0.1 to 20 wt. %, preferably 0.25 to 15 wt. %, more preferably 0.5 to 10 wt. %, even more preferably 0.75

to 7.5 wt. %, and in particular 1 to 5 wt. % at least one silicone, which comprises groupings of formula (Ia)

in which R is selected from

and a represents an integer from 1 to 20.

[0033] The silicones used in accordance with the invention can consist completely of groupings of formula (I) or (Ia), wherein $-CH_3$, $-O-CH_3$ or -OH are preferred as end groups.

[0034] However, it is preferable for the silicones used in accordance with the invention to include further groupings, in particular those of formula

[0035] Co silicones formed from units of the above-mentioned formula and units of formula (I) or (Ia) can also have —CH₃, —O—CH₃ or —OH as end groups. The units can be present in such Co silicones in blocks or randomly distributed.

[0036] Particularly preferred hair treatment compositions according to the invention are characterized in that they include 0.1 to 20 wt. %, preferably 0.25 to 15 wt. %, more preferably 0.5 to 10 wt. %, even more preferably 0.75 to 7.5 wt. %, and in particular 1 to 5 wt. % at least one silicone of formula (II):

[0037] in which

[0038] A represents a grouping

$$* \overbrace{ \qquad \qquad }^{O} \overbrace{ \qquad \qquad }_{R,}$$

[0039] in which R1 represents —H or —CH₃ and R represents a straight-chain or branched alkyl group having 8 to 24 C atoms and a represents an integer from 1 to 20;

[0044] Particularly good UV protection is attained when the group R represents

[0045]
$$-(CH_2)_k$$
— CH_3 with k=7, 8, 9, 10, 11, 12, 13, 14, 15, 16 or 17

[0046]
$$-\text{CH}(\text{CH}_2\text{CH}_3)-(\text{CH}_2)_5$$
.

[0047] Further preferred hair treatment compositions according to the invention are therefore characterized in that they include 0.1 to 20 wt. %, preferably 0.25 to 15 wt. %, more preferably 0.5 to 10 wt. %, even more preferably 0.75 to 7.5 wt. %, and in particular 1 to 5 wt. % at least one silicone of formula (III):

[0040] Q represents —OH or —CH₃ or —OCH₃;

[0041] the indices k, n, m, o, p and q represent integers from 0 to 1000, provided that n+p>0 and k+m+o+q>0 wherein the units with the indices k, n, m, o, p, q can be

present in the molecule as a block or randomly distributed. [0042] In the case of the silicones of formula (II) as well, A represents a grouping

$$*$$
 $($
 R_1
 $($
 $)_a$
 R_s

in which R1 represents —H or —CH₃ and R represents a straight-chain or branched alkyl group having 8 to 24 C atoms and a represents an integer from 1 to 20;

[0043] Particularly preferably R1=H.

in which

[0048] R is selected from

[0049] (CH₂)_k—CH₃ with k=7, 8, 9, 10, 11, 12, 13, 14, 15, 16 or 17

[0050] $-\text{CH}(\text{CH}_2\text{CH}_3)-(\text{CH}_2)_5$

[0051] a represents an integer from 1 to 20;

[0052] Q represents —OH or —CH $_3$ or —OCH $_3$;

[0053] the indices k, n, m, o, p and q represent integers from 0 to 1000, provided that n+p>0 and k+m+o+q>0 wherein the units with the indices k, n, m, o, p, q can be present in the molecule as a block or randomly distributed.

[0054] The index a most preferably represents the number 9, and R is a straight-chain alkyl group having 13 carbon atoms. Particularly preferred hair treatment compositions are therefore characterized in that they include 0.1 to 20 wt. %, preferably 0.25 to 15 wt. %, more preferably 0.5 to 10 wt. %, even more preferably 0.75 to 7.5 wt. %, and in particular 1 to 5 wt. % at least one silicone of formula (IV):

[0055] in which

[0056] R represents — $(CH_2)_{12}$ — CH_3 and Q represents —OH or — OCH_3 ;

[0057] Q represents —OH or —CH₃ or —OCH₃;

[0058] the indices k, n, m, o, p and q represent integers from 0 to 1000, provided that n+p>0 and k+m+o+q>0

wherein the units with the indices k, n, m, o, p, q can be present in the molecule as a block or randomly distributed.

[0059] In formulas (II), (III), and (IV), Q represents —OH or —CH₃ or —OCH₃. In all three formulas the two Q must not be identical, rather the termination at one end can be different from that at the other end, wherein the following combinations are preferred:

"left" end group Q	"right end group"
OH CH ₃ OCH ₃ OH CH ₃ OCH ₃ OH CH ₃ OCH ₃	—ОН —ОН —ОН —СН ₃ —СН ₃ —ОСН ₃ —ОСН ₃ —ОСН ₃

[0060] The two groupings at each of the chain ends are particularly preferably identical, and Q particularly preferably represents —OH or —OCH $_3$. The silicones of formulas (IIa), (IIIb), (IIIb), (IVa) and (IVb) are particularly preferred embodiments:

$$\begin{array}{c} \text{CH}_{3} & \text{CH}_{3} \\ \text{HO} - \overset{\cdot}{\text{Si}} + O - \overset{\cdot}{\text{Si}} \overset{\cdot}{\text{J}_{k}} + O - \overset{\cdot}{\text{Si}} - O \overset{\cdot}{\text{J}_{m}} + \overset{\cdot}{\text{Si}} - O \overset{\cdot}{\text{J}_{m}} + \overset{\cdot}{\text{Si}} - O \overset{\cdot}{\text{J}_{0}} + O - \overset{\cdot}{\text{Si}} - O \overset{\cdot}{\text{J}_{q}} \overset{\cdot}{\text{Si}} - O \overset{\cdot}{\text{J}_{q}} & \overset{\cdot}{\text{CH}_{3}} \\ \text{CH}_{3} & \text{CH}_{3} & \text{CH}_{3} & \text{CH}_{3} & \text{CH}_{3} & \text{CH}_{3} \\ \text{CH}_{3} & \text{CH}_{3} & \text{CH}_{3} & \text{CH}_{3} & \text{CH}_{3} & \text{CH}_{3} \\ \text{CH}_{3} & \text{CH}_{3} & \text{CH}_{3} & \text{CH}_{3} & \text{CH}_{3} & \text{CH}_{3} \\ \text{CH}_{3} & \text{CH}_{3} & \text{CH}_{3} & \text{CH}_{3} & \text{CH}_{3} \\ \text{CH}_{3} & \text{CH}_{3} & \text{CH}_{3} & \text{CH}_{3} & \text{CH}_{3} \\ \text{CH}_{3} & \text{CH}_{3} & \text{CH}_{3} & \text{CH}_{3} & \text{CH}_{3} \\ \text{CH}_{3} & \text{CH}_{3} & \text{CH}_{3} & \text{CH}_{3} & \text{CH}_{3} \\ \text{CH}_{3} & \text{CH}_{3} & \text{CH}_{3} & \text{CH}_{3} & \text{CH}_{3} \\ \text{CH}_{3} & \text{CH}_{3} & \text{CH}_{3} & \text{CH}_{3} & \text{CH}_{3} \\ \text{CH}_{3} & \text{CH}_{3} & \text{CH}_{3} & \text{CH}_{3} & \text{CH}_{3} \\ \text{CH}_{3} & \text{CH}_{3} & \text{CH}_{3} & \text{CH}_{3} & \text{CH}_{3} \\ \text{CH}_{3} & \text{CH}_{3} & \text{CH}_{3} & \text{CH}_{3} \\ \text{CH}_{3} & \text{CH}_{3} & \text{CH}_{3} & \text{CH}_{$$

-continued -continued (IIIa)

$$\begin{array}{c} \text{CH}_3 \quad \text{CH}_4 \quad \text{CH}_5 \quad$$

[0061] The mean molecular weights of the silicones a) included in the compositions according to the invention is preferably from 2,000 to 300,000 and even more preferably from 5,000 to 200,000, in particular 10,000 to 150,000 Dalton. Hair treatment compositions in which the weight-average molar mass of the silicone of formula (IV) included

therein lies in the range from 10,000 to 150,000 gmol⁻¹, preferably in the range from 50,000 to 130,000 gmol⁻¹, are preferred.

[0062] The mean molecular weights of amino-substituted silicones can be measured for example by gel permeation chromatography (GPC) at room temperature in polystyrene.

Styragel columns μ can be selected as columns, THF can be selected as eluent, and a flow rate of 1 ml/min can be selected. The detection is performed preferably by means of refractometry and UV meters.

[0063] As a further constituent, the compositions according to the invention include 0.1 to 20 wt. % at least one copolymer, which has monomer units of formulas (V) and

in which R2 represents —H or —CH₂ and X represents —H, an alkali metal cation, or a straight-chain or branched alkyl group having 1 to 24 C atoms.

[0064] The copolymers can consist only of monomers of formulas (V) and (VI), but can additionally also include further monomer building blocks. In view of the protection against damage to the hair structure, it has proven to be preferable when at least 50 wt. %, preferably at least 60 wt. %, more preferably at least 70 wt. %, even more preferably at least 80 wt. %, particularly preferably at least 90 wt. %, and in particular at least 99 wt. % of the copolymers consist of monomers of the formulas (V) and (VI).

[0065] The monomer to be allocated to the structural unit (V) is styrene; the structural unit (VI) can be derived from acrylic acid (R2=-H, X=-H), methacrylic acid (R2=-CH₃, X=—H), salts thereof (X=Na+, K+, etc.) and/or esters thereof (X=alkyl). The copolymers can include a single type of monomer unit (VI) or a plurality of different monomer units (VI, VI', VI", etc.). An example for the first embodiment would be copolymers of styrene and acrylic acid, and an example for the second embodiment would be copolymers of styrene, acrylic acid and methacrylate.

[0066] Among the copolymers that include exclusively monomer units of formulas (V) and (VI), the following copolymers are preferred:

[0067] copolymers of styrene and acrylic acid [0068] copolymers of styrene and methacrylic acid [0069] copolymers of styrene and sodium acrylate

copolymers of styrene and sodium methacrylate [0070]

[0071] copolymers of styrene and potassium acrylate [0072] copolymers of styrene and potassium methacrylate

[0073]copolymers of styrene and methyl acrylate [0074]

copolymers of styrene and methyl methacrylate copolymers of styrene and ethyl acrylate [0075]

copolymers of styrene and ethyl methacrylate [0076] copolymers of styrene and propyl acrylate [0077]

[0078]copolymers of styrene and propyl methacrylate [0079] copolymers of styrene and isopropyl acrylate

[0080] copolymers of styrene and isopropyl methacrylate

[0081] copolymers of styrene and acrylic acid (n-butyl)

[0082] copolymers of styrene and methacrylic acid (n-butyl) ester

[0083] copolymers of styrene and acrylic acid and methacrylic acid

[0084] copolymers of styrene and acrylic acid and sodium acrylate

[0085] copolymers of styrene and acrylic acid and sodium methacrylate

[0086] copolymers of styrene and acrylic acid and methyl acrylate

[0087] copolymers of styrene and acrylic acid and methyl methacrylate

[0088] copolymers of styrene and acrylic acid and ethyl acrylate

[0089] copolymers of styrene and acrylic acid and ethyl methacrylate

[0090] copolymers of styrene and acrylic acid ester and acrylic acid (n-butyl) ester

[0091] copolymers of styrene and acrylic acid and methacrylic acid (n-butyl) ester

[0092] copolymers of styrene and methacrylic acid and sodium acrylate

[0093] copolymers of styrene and methacrylic acid and sodium methacrylate

[0094] copolymers of styrene and methacrylic acid and methyl acrylate

[0095] copolymers of styrene and methacrylic acid and ethyl methacrylate

[0096] copolymers of styrene and methacrylic acid and ethyl acrylate

[0097] copolymers of styrene and methacrylic acid and ethyl methacrylate

[0098] copolymers of styrene and methacrylic acid ester and acrylic acid (n-butyl) ester

[0099] copolymers of styrene and methacrylic acid and methacrylic acid (n-butyl) ester

[0100] copolymers of styrene and acrylic acid and methacrylic acid and sodium acrylate

[0101] copolymers of styrene and acrylic acid and methacrylic acid and sodium methacrylate

[0102] copolymers of styrene and acrylic acid and methacrylic acid and methyl acrylate

[0103] copolymers of styrene and acrylic acid and methacrylic acid and methyl methacrylate

[0104] copolymers of styrene and acrylic acid and methacrylic acid and ethyl acrylate

[0105] copolymers of styrene and acrylic acid and methacrylic acid and ethyl methacrylate

[0106] copolymers of styrene and acrylic acid and methacrylic acid and acrylic acid (n-butyl) ester

[0107] copolymers of styrene and acrylic acid and methacrylic acid and methacrylic acid (n-butyl) ester).

[0108] Particularly preferred hair treatment compositions are therefore characterized in that they include 0.5 to 17.5 wt. %, preferably 1 to 15 wt. %, more preferably 1.5 to 12.5, particularly preferably 2 to 10, and in particular 3 to 8 wt. % at least one copolymer, which has monomer units of the formulas (V) and (VIa)

$$(VIa)$$

$$O O X^+$$

in which X represents H+ or Na+.

[0109] As further constituent, the compositions according to the invention include 0.1 to 10 wt. % (RS)-2-cyano-3,3-diphenylacrylic acid-2-ethylhexylester. Particularly preferred hair treatment compositions according to the invention are characterized in that they include 0.25 to 9 wt. %, preferably 0.5 to 8 wt. %, more preferably 0.75 to 7 wt. %, particularly preferably 1 to 6 wt. %, and in particular 2.5 to 5 wt. % (RS)-2-cyano-3,3-diphenylacrylic acid-2-ethyl-hexylester.

[0110] It has been found to be preferable when ingredients a), b) and c) are used in certain ratios by weight to one another. In this way, the UV protection is optimally intensified. Hair treatment compositions that are preferred in accordance with the invention are characterized in that the ratio by weight of ingredients b) to a) lies in the range from 1:50 to 50:1, preferably in the range from 1:10 to 25:1, more preferably in the range from 1:1 to 5:1, particularly preferably in the range from 1.5:1 to 4:1, and in particular in the range from 1.75:1 to 2.5:1.

[0111] More preferred hair treatment compositions according to the invention are characterized in that the ratio by weight of ingredients a) to c) lies in the range from 1:50 to 50:1, preferably in the range from 1:10 to 25:1, more preferably in the range from 1:5 to 5:1, particularly preferably in the range from 1.5:1 to 4:1, and in particular in the range from 1.1:1 to 1:1.1.

[0112] Depending on their intended purpose, the compositions according to the invention include further essential ingredients. Cleaning or caring compositions, such as shampoos or conditioners, include at least one surfactant, wherein surface-active substances are referred to as surfactants or emulsifiers depending on the field of application and are selected from anionic, cationic, zwitterionic, ampholytic, and non-ionic surfactants and emulsifiers.

[0113] Hair treatment compositions that are preferred in accordance with the invention are characterized in that they include—based on the weight of said hair treatment compositions—0.5 to 70 wt. %, preferably 1 to 60 wt. %, and in particular 5 to 25 wt. % anionic and/or non-ionic and/or cationic and/or amphoteric surfactant(s).

[0114] All anionic surface-active substances suitable for use on the human body are suitable as anionic surfactants and emulsifiers for the compositions according to the invention. These are characterized by an anionic group conveying water solubility, such as a carboxylate, sulfate, sulfonate or phosphate group and a lipophilic alkyl group having approximately 8 to 30 C atoms. In addition, glycol or

polygycol ether groups, ester, ether and amide groups, and hydroxyl groups can be included in the molecule.

[0115] Surface-active compounds that carry at least one quaternary ammonium group and at least one —COO⁽⁻⁾ or —SO₃⁽⁻⁾ group in the molecule are designated as zwitterionic surfactants and molecules. Particularly suitable zwitterionic surfactants and emulsifiers are the so-called betaines, such as N-alkyl-N,N-dimethyl ammonium glycinates, for example coco-alkyl dimethyl ammonium glycinates, for example coco-acyl aminopropyl dimethyl ammonium glycinate, and 2-alkyl-3-carboxymethyl-3-hydroxyethyl-imidazolines, each having 8 to 18 C atoms in the alkyl or acyl group, as well as coco-acyl aminoethyl hydroxyl ethyl carboxymethyl glycinate. A preferred zwitterionic surfactant is the fatty acid amide derivative known under the INCI name cocamidopropyl betaine.

[0116] Surface-active compounds that carry at least one quaternary ammonium group and at least one —COO⁽⁻⁾ or —SO₃⁽⁻⁾ group in the molecule are designated as zwitterionic surfactants and molecules. Particularly suitable zwitterionic surfactants and emulsifiers are the so-called betaines, such as N-alkyl-N,N-dimethyl ammonium glycinates, for example coco-alkyl dimethyl ammonium glycinates, for example coco-acyl aminopropyl dimethyl ammonium glycinate, and 2-alkyl-3-carboxymethyl-3-hydroxyethyl-imidazolines, each having 8 to 18 C atoms in the alkyl or acyl group, as well as coco-acyl aminoethyl hydroxyl ethyl carboxymethyl glycinate. A preferred zwitterionic surfactant is the fatty acide amide derivative known under the INCI name cocamidopropyl betaine.

[0117] Ampholytic surfactants and emulsifiers are understood to be surface-active compounds which, in addition to a $\rm C_{8^-}C_{24}$ alkyl or acyl group, also include at least one free amino group and at least one —COOH or —SO_3H group and are capable of forming inner salts. Examples of suitable ampholytic surfactants are N-alkyl glycines, N-alkylamino-propionic acids, N-alkyl aminobutyric acids, N-alkylamino-dipropionic acids, N-hydroxyethyl-N-alkylamido propyl glycines, N-alkyltaurines N-alkylsarcosines, 2-alkylamino-propionic acids and alkyl aminoacetic acids each having approximately 8 to 24 C atoms in the alkyl group. Particularly preferred ampholytic surfactants are N-coco-alkyl aminopropionate, coco-acyl aminoethyl aminopropionate and $\rm C_{12^-}C_{18}$ acyl sarcosine.

[0118] Cationic surfactants of the quaternary ammonium compound, esterquat and amidoamine type can be used in accordance with the invention. Preferred quaternary ammonium compounds are ammonium halides, in particular chlorides and bromides, such as alkyl trimethylammonium chlodialkyldimethylammonium chlorides trialkylmethylammonium chlorides. The long alkyl chains of these surfactants preferably have 10 to 18 carbon atoms, such as in cetyltrimethylammonium chloride, stearyltrimethylammonium chloride, distearyldimethylammonium chloride, lauryldimethylammonium chloride, lauryldimethylbenzylammonium chloride, and tricetylmethylammonium chloride. Other preferred cationic surfactants are imidazolium compounds known under the INCI names quaternium-27 and quaternium-83.

[0119] As a further ingredient, the compositions according to the invention can particularly preferably include one or more amino acids. Amino acids that can be used particularly

preferably in accordance with the invention originate from the group glycine, alanine, valine, leucine, isoleucine, phenylalanine, tyrosine, tryptophan, proline, aspartic acid, glutamic acid, asparagine, glutamine, serine, threonine, cysteine, methionine, lysine, arginine, histidine, B-alanine, 4-aminobutyric acid (GABA), betaine, L-cystine (L-Cyss), L-carnitine, L-citrulline, L-theanine, 3',4-dihydroxy-L-phenylalanine (L-Dopa), 5' hydroxy-L-tryptophan, L-homocysteine, S-methyl-L-methionine, S-allyl-L-cysteine sulfoxide (L-Alliin), L-trans-4-hydroxyproline, L-5-oxoproline (L-pyroglutamic acid), L-phosphoserine, creatine, 3-methyl-L-histidine, and L-ornithine, wherein both the individual amino acids as well as mixtures can be used.

[0120] Preferred compositions according to the invention include one or more amino acids in narrower quantity ranges. Here, cosmetic compositions that are preferred in accordance with the invention are characterized in that they include as care substance—based on the weight of said compositions—0.01 to 5 wt. %, preferably 0.02 to 2.5 wt. %, particularly preferably 0.05 to 1.5 wt. %, more preferably 0.075 to 1 wt. %, and in particular 0.1 to 0.25 wt. % amino acid(s), preferably from the group of glycine and/or alanine and/or valine and/or lysine and/or leucine and/or threonine.

[0121] The silicones used in accordance with the invention comprising structural units of formula (I) can of course be used together with other conventional silicones.

[0122] Preferred compositions according to the invention are characterized in that they include at least one additional silicone.

[0123] Preferred silicones that can be used in accordance with the invention have viscosities at 20° C. from 0.2 to $2 \text{ mm}^2\text{s}^{-1}$, wherein silicones with viscosities from 0.5 to $1 \text{ mm}^2\text{s}^{-1}$ are particularly preferred.

[0124] Particularly preferred compositions according to the invention include one or more amino-functional silicones.

[0125] Preferred compositions according to the invention are characterized in that they include an amino-functional silicone of formula (Si-II)

$$\begin{array}{lll} {\rm Ra'}_a {\rm G}_{3-a} - {\rm Si}({\rm OSiG}_2)_n - ({\rm OSiG}_b {\rm R'}_{2-b})_m - {\rm O} - {\rm SiG}_{3-} \\ & {}_a - {\rm R'}_a \end{array}$$

in which:

[0127] a represents a number between 0 and 3, in particular 0;

[0128] b represents a number between 0 and 1, in particular 1,

[0129] m and n are numbers of which the sum (m+n) is between 1 and 2000, preferably between 50 and 150, wherein n preferably assumes values from 0 to 1999 and in particular from 49 to 149, and m preferably assumes values from 1 to 2000, in particular from 1 to 10.

[0130] R' is a monovalent group selected from

[0131] -Q-N(R")—CH₂—CH₂—N(R")₂

[0132] -Q-N(R")₂

[0133] $-Q-N^+(R'')_3A^-$

[0134] $-Q-N^+H(R'')_2A^-$

[0135] -Q-N⁺H₂(R")A⁻
[0136] -Q-N(R")—CH₂—CH₂—N⁺R"H₂A,
wherein each Q represents a chemical bond, —CH₂—,
—CH₂—CH₂—, —CH₂CH₂CH₂—, —C(CH₃)₂—,
—CH₂CH₂CH₂CH₂—, —CH₂(C(CH₃)₂—, —CH(CH₃)
CH₂CH₂—, R" represents the same or different groups from the group —H, phenyl, benzyl, —CH₂—CH(CH₃)Ph, C₁₋₂₀
alkyl groups, preferably —CH₃, —CH₂CH₂H₃,
—CH₂CH₂CH₃, —CH(CH₃)₂, —CH₂CH₂CH₂H₃,
—CH₂CH(CH₃)₂, —CH(CH₃)CH₂CH₃, —C(CH₃)₃, and A represents an anion, preferably selected from chloride, bromide, iodide or methosulfate.

[0137] Particularly preferred compositions according to the invention are characterized in that they include at least one amino-functional silicone of formula (Si-IIa)

$$(CH_3)_3Si \longrightarrow [O \longrightarrow Si(CH_3)_2]_n[OSi(CH_3)]_m \longrightarrow OSi(CH_3)_3\\ |\\ CH_2CH(CH_3)CH_2NH(CH_2)_2NH_2,$$

in which m and n are numbers of which the sum (m+n) is between 1 and 2000, preferably between 50 and 150, wherein n preferably assumes values from 0 to 1999 and in particular from 49 to 149, and m preferably assumes values from 1 to 2000, in particular from 1 to 10.

[0138] These silicones are referred to in accordance with the INCI declaration as trimethylsilylamidodimethicones.

[0139] Compositions according to the invention that include an amino-functional silicone of formula (Si-IIb)

$$\begin{array}{c} R \longrightarrow [Si(CH_3)_2 \longrightarrow O]_{n1}[Si(R) \longrightarrow O]_m \longrightarrow [Si(CH_3)_2]_{n2} - R, \\ | \\ (CH_2)_3 NH(CH_2)_2 NH_2 \end{array} \tag{Si-IIb}$$

in which R represents —OH, —O—CH₃ or a —CH₃ group and m, n1 and n2 are numbers of which the sum (m+n1+n2) is between 1 and 2000, preferably between 50 and 150, wherein the sum (n1+n2) preferably assumes values from 0 to 1999 and in particular from 49 to 149, and m preferably assumes values from 1 to 2000, in particular from 1 to 10, are particularly preferred.

[0140] These silicones are referred to in accordance with the INCI declaration as amidodimethicones.

[0141] Regardless of which amino-functional silicones are used, compositions according to the invention which include an amino-functional silicone of which the amine number is above 0.25 meq/g, preferably above 0.3 meq/g and in particular above 0.4 meq/g are preferred. The amine number stands here for milliequivalents of amine per gram of amino-functional silicone. It can be determined by titration and expressed in the unit mg KOH/g.

[0142] Compositions that are preferred in accordance with the example are characterized in that they include, based on their weight, 0.01 to 10 wt. %, preferably 0.1 to 8 wt. %, particularly preferably 0.25 to 7.5 wt. %, and in particular 0.5 to 5 wt. % amino-functional silicone(s).

[0143] The silicones described above have a backbone, which is composed of —Si—O—Si units. Of course, these Si—O—Si units can also be interrupted by carbon chains.

Corresponding molecules are accessible by chain extension reactions and are preferably used in the form of silicone-inwater emulsions.

[0144] Compositions that are likewise preferred in accordance with the invention are characterized in that they include at least one silicone of formula Si-IV

in which R represents the same or different groups from the group —H, phenyl, benzyl, — CH_2 — $CH(CH_3)Ph$, C_{1-20} alkyl groups, preferably — CH_3 , — CH_2CH_3 , — $CH_2CH_2CH_3$, — $CH(CH_3)_2$, — $CH_2CH_2CH_2H_3$, — $CH_2CH_2CH_3$, — $CH(CH_3)CH_2CH_3$, — $C(CH_3)_3$, x and y represent a number from 0 to 200, preferably from 0 to 10, more preferably from 0 to 7, and in particular 0, 1, 2, 3, 4, 5 or 6, and n represents a number from 0 to 10, preferably from 1 to 8, and in particular for 2, 3, 4, 5 or 6.

[0145] The silicones are preferably water-soluble. Compositions that are preferred in accordance with the invention are characterized in that they include at least one water-soluble silicone.

[0146] It has been found that certain proteolipids enhance the effect of the combination according to the invention even further and improve the prevention of damage to the hair structure by UV radiation even further. As a further ingredient, the compositions according to the invention can include at least one proteolipid of formula (P-1)

$$R'' - X - R'' \tag{P-1},$$

in which

[0147] R' represents a straight-chain or branched, saturated or unsaturated hydrocarbon having 11 to 24 carbon atoms,

[0148] R" is a protein, a peptide or a protein hydrolyzate.

[0149] X represents
$$-C(O)O$$
— or $-N^+(R^{III}_2)R^{IV}$ — or $-N(R^{III})R^{IV}$ — or $-C(O)-N(R^V)R^{VI}$ —,

[0150] R^{III} is $O(CH_2)_x$ — CH_3 with x=0-22, and

[0151]
$$R^{IV}$$
 is —CH₂—CH(OH)—CH₂— or —(CH₂)
 $_x$ — with x=0-22;

[0152] R^V and R^V , independently of one another, represent —H or —(CH₂)_x—CH₃ with x=0-22;

provided that R" represents keratin or a keratin hydrolyzate when X represents —C(O)O—.

[0153] The proteolipids are preferably used within certain amounts in the compositions according to the invention. Preferred cosmetic compositions according to the invention include—based on their weight—0.01 to 10 wt. %, preferably 0.02 to 5 wt. %, particularly preferably 0.05 to 2.5 wt. %, more preferably 0.1 to 1 wt. %, and in particular 0.15 to 0.5 wt. % proteolipid(s).

[0154] The group R" in formula (P-l) represents a peptide or a protein or a protein hydrolyzate. If X = C(O)O, R" is selected from the group of keratin or keratin hydrolyzate.

 $\begin{tabular}{ll} \begin{tabular}{ll} \beg$

wherein the amino group can be present in free or protonated form and the carboxy groups can be present in free or deprotonated form.

[0156] In this, as in all formulas below, the bracketed hydrogen atom of the amino group as well as the bracketed hydroxyl group of the acid function means that the relevant groups may be present as such (it is then an oligopeptide with the relevant number of amino acids as shown (in the above formula 3)), or that the amino acid sequence is present in an oligopeptide which comprises further amino acids—depending on where the further amino acid(s) is/are bonded, the bracketed constituents of the above-mentioned formula are replaced by the further amino acid group(s).

[0157] Oligopeptides within the meaning of the present application are condensation products of amino acids linked in an acid amide-like manner by peptide bonds, comprising at least 3 and at most 25 amino acids,

[0158] In hair treatment compositions that are preferred in accordance with the invention corresponding to the above described embodiment the oligopeptide (=the group R") comprises 5 to 15 amino acids, preferably 6 to 13 amino acids, particularly preferably 7 to 12 amino acids, and in particular 8, 9 or 10 amino acids.

[0159] Depending on whether further amino acids are bonded to the sequence Glu-Glu-Glu and depending on the nature of these amino acids, as well as in dependence of the selection of the groups R' and, as appropriate, R^{III} and R^{IV} , the molar mass of the proteolipid included in the compositions according to the invention can vary. Cosmetic compositions that are preferred in accordance with the invention are characterized in that the proteolipid has a molar mass from 1000 to 30,000 Da, preferably from 1250 to 25,000 Da, particularly preferably 1500 to 20,000 Da and in particular from 2000 to 15,000 Da.

[0160] Oligopeptides which not only consist of the three glutamic acids, but have other amino acids bonded to this sequence are preferably used as group R". These further amino acids are preferably selected from specific amino acids, whereas certain other representatives are less preferred in accordance with the invention.

[0161] It is thus preferred if the group R" of the proteolipids used in the compositions according to the invention does not include methionine. It is further preferred if the group R" of proteolipids used in the compositions according to the invention does not include cysteine and/or cystine.

[0162] It is more preferred when the group R" of proteolipids used in the compositions according to the invention does not include aspartic acid and/or asparagine. It is more

preferred if the group R" of proteolipids used in the compositions according to the invention does not include serine and/or threonine.

[0163] By contrast, it is preferred if the group R" of proteolipids used in the compositions according to the invention includes tyrosine. It is more preferred if the group R" of proteolipids used in the compositions according to the invention includes leucine. It is more preferred if the group R" of proteolipids used in the compositions according to the invention includes isoleucine. It is more preferred if the group R" of proteolipids used in the compositions according to the invention includes arginine. It is more preferred if the group R" of proteolipids used in the compositions according to the invention includes valine.

[0164] Oligopeptides that are particularly preferred as the group R" and amino acid sequences included in the preferred oligopeptides will be described below:

[0165] A particularly preferred oligopeptide additionally includes tyrosine, which is preferably bonded via its acid function to the Glu-Glu-Glu-sequence. Cosmetic compositions that are preferred in accordance with the invention are therefore characterized in that the oligopeptide included as group R" in the proteolipids of formula (I) has at least one amino acid sequence Tyr-Glu-Glu, wherein the amino group can be present in free or protonated form and the carboxy groups can be present in free or deprotonated form.

[0166] A further particularly preferred oligopeptide additionally includes isoleucine, which is preferably bonded via its amino function to the Glu-Glu-Sequence. Cosmetic compositions that are preferred in accordance with the invention are therefore characterized in that the oligopeptide included as group R" in the proteolipids of formula (I) has at least one amino acid sequence Glu-Glu-Glu-Ile, wherein the amino group can be present in free or protonated form and the carboxy groups can be present in free or deprotonated form.

[0167] Oligopeptides which have both of the aforementioned amino acids (tyrosine and isoleucine) are preferred in accordance with the invention. Hair treatment compositions according to the invention that are particularly preferred here are those in which the oligopeptide included as group R" in the proteolipids of formula (I) has at least one amino acid sequence Tyr-Glu-Glu-Glu-Ile, wherein the amino group can be present in free or protonated form and the carboxy groups can be present in free or deprotonated form.

[0168] More preferred oligopeptides additionally include arginine, which is preferably bonded to isoleucine. Cosmetic compositions that are preferred in accordance with the invention are therefore characterized in that the oligopeptide included as group R" in the proteolipids of formula (I) has least one amino acid sequence Tyr Glu-Glu-Glu-Ile-Arg, wherein the amino groups can be present in free or protonated form and the carboxy groups can be present in free or deprotonated form.

[0169] Even more preferred oligopeptides additionally include valine, which is preferably bonded to the arginine. Cosmetic compositions that are more preferred in accordance with the invention are therefore characterized in that the oligopeptide included as group R" in the proteolipids of formula (I) has at least an amino acid sequence Tyr-Glu-Glu-Glu-Ile-Arg-Val, wherein the amino groups can be present in free or protonated form and the carboxy groups can be present in free or deprotonated form.

[0170] Even more preferred oligopeptides additionally include leucine, which is preferably bonded to valine. Cosmetic compositions that are more preferred in accordance with the invention are characterized in that the oligopeptide included as group R" in the proteolipids of formula (I) has at least one amino acid sequence Tyr-Glu-Glu-Glu-Ile-Arg-Val-Leu, wherein the amino groups can be present in free or protonated form and the carboxy groups can be present in free or deprotonated form.

[0171] Particularly preferred oligopeptides additionally include leucine, which is preferably bonded to the tyrosine. Cosmetic compositions that are more preferred in accordance with the invention are characterized in that the oligopeptide included as group R" in the proteolipids of formula (I) has at least one amino acid sequence Leu-Tyr-Glu-Glu-Glu-Ile-Arg-Val-Leu, wherein the amino groups can be present in free or protonated form and the carboxy groups can be present in free or deprotonated form.

[0172] In summary, cosmetic compositions that are preferred in accordance with the invention are in particular those which include at least one proteolipid of formula (I), in which R" has at least one amino acid sequence Leu-Tyr-Glu-Glu-Glu-Ile-Arg-Val-Leu, wherein the amino groups can be present in free or protonated form and the carboxy groups can be present in free or deprotonated form.

[0173] As already mentioned, R" is selected from the group of keratin or keratin hydrolyzate, when X=—C(O)

[0174] In all other cases, the group R" in formula (P-I) can represent a peptide or a protein or a protein hydrolyzate, wherein protein hydrolyzates are preferred. Protein hydrolyzates are product mixtures obtained by acid-, base- or enzyme-catalyzed degradation of proteins. Protein hydrolyzates of both plant and animal origin can be used in accordance with the invention.

[0175] Animal protein hydrolyzates are, for example, elastin, collagen, keratin, silk and milk protein hydrolyzates, which can also be present in the form of salts. Such products are marketed for example under the trade names Dehylan® (Cognis), Promois® (Interorgana) Collapuron® (Cognis), Nutrilan® (Cognis), Gelita-Sol® (German gelatin factories Stoess & Co), Lexein® (Inolex) and Kerasol® (Croda).

[0176] The use of protein hydrolyzates of plant origin, for example soy, almond, rice, pea, potato and wheat protein hydrolyzates, is preferred in accordance with the invention. Such products are obtainable, for example, under the trade names Gluadin® (Cognis), DiaMin® (Diamalt), Lexenin® (Inolex) and Crotein® (Croda).

[0177] Regardless of the choice of X in formula (P-I), the group R" is preferably selected from keratin or keratin hydrolyzates. Preferred cosmetic compositions according to the invention are characterized in that they include at least one proteolipid of formula (P-I), in which R" represents keratin or a keratin hydrolyzate.

[0178] In particular, preferred cosmetic compositions according to the invention are those which include at least one proteolipid of formula (P-I), in which R^{III} means —CH₃ and R^{IV} represents —(CH₂)_x— with x=0, 1, 2, 3, 4, 5, 6, 7 or 8.

[0179] Furthermore, particularly preferred cosmetic compositions according to the invention are characterized in that they include at least one proteolipid of formula (I), in which X is $-N^+(CH_3)_2-CH_2-CH(OH)-CH_2$ —and R' represents $-(CH_2)_{1,7}-CH_3$.

[0180] Cosmetic compositions according to the invention that are more preferred are likewise characterized in that they include at least one proteolipid of formula (P-I), in which X represents —C(O)—O— and R' represents —(CH₂)_{1.7}—CH₃.

[0181] It has proven to be advantageous if protein hydrolyzates are used in addition to the proteolipids. These protein hydrolyzates intensify the effect of the proteolipids and are in turn intensified in terms of their own effects. The protein hydrolyzates have been described in greater detail above as the group R".

[0182] To summarize, preferred cosmetic compositions according to the invention are those which additionally—based on their weight—include 0.01 to 10 wt. %, preferably 0.05 to 7 wt. %, particularly preferably 0.1 to 5 wt. %, more preferably 0.25 to 2.5 wt. %, and in particular 0.5 to 2.0 wt. % protein hydrolyzate(s), preferably keratin hydrolyzate(s).

[0183] For aesthetic reasons "clear" products are often preferred by consumers. Cosmetic compositions that are preferred in accordance with the invention are therefore characterized in that they are transparent or translucent.

[0184] The term 'transparent' or 'translucent' is understood within the scope of the present invention to mean a composition that has an NTU value of less than 100. The NTU value (Nephelometric Turbidity Unit; NTU) is a unit used in water treatment for turbidity measurements in liquids. It is the unit of the turbidity of a liquid measured using a calibrated nephelometer.

[0185] A further subject matter of the present invention is the use of silicones that have groupings of formula (I)

*—
$$O$$
— Si — O $\frac{1}{1}$,

in which

[0186] n represents values from 1 to 1000,

[0187] A represents a grouping

$$*$$
 R_1
 R_1
 R_2
 R_3

[0188] in which R1 represents —H or —CH₃ and R represents a straight-chain or branched alkyl group having 8 to 24 C atoms and a represents an integer from 1 to 20,

for reducing damage to the hair structure caused by external influences, in particular by UV radiation.

[0189] The silicones are preferably used in accordance with the invention in combination with at least one copolymer having monomer units of formulas (V) and (VI)

in which R2 represents —H or — CH_3 and X represents —H, an alkali metal cation or for a straight-chain or branched alkyl group having 1 to 24 C atoms.

[0190] That described in respect of the compositions according to the invention also applies, mutatis mutandis, to further preferred embodiments of the uses according to the invention.

[0191] While at least one exemplary embodiment has been presented in the foregoing detailed description of the invention, it should be appreciated that a vast number of variations exist. It should also be appreciated that the exemplary embodiment or exemplary embodiments are only examples, and are not intended to limit the scope, applicability, or configuration of the invention in any way. Rather, the foregoing detailed description will provide those skilled in the art with a convenient road map for implementing an exemplary embodiment of the invention, it being understood that various changes may be made in the function and arrangement of elements described in an exemplary embodiment without departing from the scope of the invention as set forth in the appended claims and their legal equivalents.

What is claimed is:

- 1. A hair treatment composition, including—in each case based on the weight of the hair treatment composition
 - a) 0.1 to 20 wt. % at least one silicone, which has groupings of formula (I)

in which
n represents values from 1 to 1000 and
A represents a grouping

$$*$$
 R_1
 R_2
 R_3

wherein R1 represents —H or —CH₃ and R represents a straight-chain or branched alkyl group having 8 to 24 C atoms and a represents an integer from 1 to 20;

b) 0.1 to 20 wt. % at least one copolymer, which has monomer units of formulas (V) and (VI)

$$^{*} \bigvee_{p} _{*}$$

 $* + O \longrightarrow_{\operatorname{Si}} O \xrightarrow{\operatorname{In}} *$ $R \longrightarrow_{\operatorname{N}} N \longrightarrow_{\operatorname{A}} R,$ $R \longrightarrow_{\operatorname{N}} N \longrightarrow_{\operatorname{A}} R,$ $R \longrightarrow_{\operatorname{N}} N \longrightarrow_{\operatorname{A}} R,$ $R \longrightarrow_{\operatorname{N}} N \longrightarrow_{\operatorname{A}} R,$

in which R is selected from

 $-(CH_2)_k$ — CH_3 with k=7, 8, 9, 10, 11, 12, 13, 14, 15, 16 or 17, and

--CH(CH₂CH₃)--(CH₂)₅

and a represents an integer from 1 to 20.

3. The hair treatment composition according to claim 1, including 0.1 to 20 wt. % the at least one silicone, which is represented by formula (II):

$$Q \xrightarrow{\text{CH}_3} \xrightarrow{\text{CH}$$

-continued

wherein R2 represents —H or —CH₃ and X represents —H, an alkali metal cation, or a straight-chain or branched alkyl group having 1 to 24 C atoms; and

- c) 0.1 to 10 wt. % (RS)-2-cyano-3,3-diphenylacrylic acid-2-ethylhexylester.
- 2. The hair treatment composition according to claim 1, including 0.1 to 20 wt. % the at least one silicone, which includes groupings of formula (Ia)

in which

A represents a grouping

$$*$$
 R_1
 R_2
 R_3

wherein R1 represents —H or —CH₃ and R represents a straight-chain or branched alkyl group having 8 to 24 C atoms and a represents an integer from 1 to 20;

Q represents —OH or —CH₃ or —OCH₃; and

the indices k, n, m, o, p and q represent integers from 0 to 1000, provided that n+p>0 and k+m+o+q>0,

wherein the units with the indices k, n, m, o, p, q can be present in the molecule as a block or randomly distributed

4. The hair treatment composition according to claim 1, including 0.1 to 20 wt. % the at least one silicone, which is represented by formula (III):

$$Q \xrightarrow{\text{CH}_3} \xrightarrow{\text{CH}$$

in which

R is selected from

 $-(CH₂)_k$ -CH₃ with k=7, 8, 9, 10, 11, 12, 13, 14, 15, 16 or 17, and

--CH(CH₂CH₃)--(CH₂)₅

a represents an integer from 1 to 20;

Q represents —OH or —CH₃ or —OCH₃;

the indices k, n, m, o, p and q represent integers from 0 to 1000, provided that n+p>0 and k+m+o+q>0

wherein the units with the indices k, n, m, o, p, q can be present in the molecule as a block or randomly distributed.

5. The hair treatment composition according to claim 1, including 0.1 to 20 wt. % the at least one silicone, which is represented by formula (IV):

-continued

"left" end group Q	"right end group"
—ОСН ₃ —ОН —СН ₃ —ОСН ₃ —ОН —СН ₃ —ОН	$-$ OH $-$ CH $_3$ $-$ CH $_3$ $-$ CH $_3$ $-$ OCH $_3$ $-$ OCH $_3$ $-$ OCH $_3$.

7. The hair treatment composition according to claim 4, wherein the two Q in formula (III) are selected from the following combinations:

in which

R represents — $(CH_2)_{12}$ — CH_3 and Q represents —OH or —OCH $_3$:

Q represents —OH or —CH₃ or —OCH₃;

the indices k, n, m, o, p and q represent integers from 0 to 1000, provided that n+p>0 and k+m+o+q>0

wherein the units with the indices k, n, m, o, p, q can be present in the molecule as a block or randomly distributed.

6. The hair treatment composition according to claim **3**, wherein the two Q in formula (II) are selected from the following combinations:

"left" end group Q	"right end group"
—ОН	—ОН
—СН ₃	—ОН

"left" end group Q	"right end group"
—ОН	—ОН
—CH ₃	—ОН
—OCH ₃	—ОН
—ОН	—СН ₃
—СН ₃	—CH ₃
—OCH ₃	—CH ₃
—ОН	—OCH ₃
—СН ₃	—OCH ₃
—OCH ₃	—OCH ₃ .

8. The hair treatment composition according to claim **5**, wherein the two Q in formula (IV) are selected from the following combinations:

"left" end group Q	"right end group"
—ОН —СН ₃ —ОСН ₃ —ОН	—ОН —ОН —ОН
—ОН —СН ₃ —ОСН ₃ —ОН	—СН ₃ —СН ₃ —СН ₃ —ОСН ₃

-continued

"left" end group Q	"right end group"
—СН ₃	—ОСН ₃
—ОСН ₃	—ОСН ₃ .

9. The hair treatment composition according to claim 1, wherein the at least one silicone(s) is/are selected from silicone(s) of formulas (IIa), (IIb), (IIIa), (IIIb), (IVa) and (IVb):

$$\begin{array}{c} \text{CH}_3 & \text{CH}_3 & \text{CH}_3 & \text{CH}_3 & \text{CH}_3 & \text{CH}_3 & \text{CH}_3 \\ \text{N} & \text{CH}_3 & \text{CH}_3 & \text{CH}_3 & \text{CH}_3 & \text{CH}_3 \\ \text{CH}_3 & \text{CH}_3 & \text{CH}_3 & \text{CH}_3 & \text{CH}_3 \\ \text{CH}_3 & \text{CH}_3 & \text{CH}_3 & \text{CH}_3 & \text{CH}_3 \\ \text{CH}_3 & \text{CH}_3 & \text{CH}_3 & \text{CH}_3 & \text{CH}_3 \\ \text{CH}_3 & \text{CH}_3 & \text{CH}_3 & \text{CH}_3 \\ \text{CH}_3 & \text{CH}_3 & \text{CH}_3 & \text{CH}_3 \\ \end{array}$$

-continued (IIIb)
$$H_{3}C = O = S_{1} + O$$

10. The hair treatment composition according to claim 1, wherein at least 50 wt. % consist of monomers of the formulas (V) and (VI).

11. The hair treatment composition according to claim 1, wherein the copolymer(s) is/are selected from the group consisting of:

copolymers of styrene and acrylic acid copolymers of styrene and methacrylic acid copolymers of styrene and sodium acrylate copolymers of styrene and sodium methacrylate copolymers of styrene and potassium acrylate copolymers of styrene and potassium methacrylate copolymers of styrene and methyl acrylate copolymers of styrene and methyl methacrylate copolymers of styrene and ethyl acrylate copolymers of styrene and ethyl acrylate copolymers of styrene and ethyl methacrylate copolymers of styrene and propyl acrylate copolymers of styrene and propyl methacrylate copolymers of styrene and isopropyl acrylate copolymers of styrene and isopropyl methacrylate copolymers of styrene and isopropyl methacrylate copolymers of styrene and acrylic acid (n-butyl) ester

copolymers of styrene and methacrylic acid (n-butyl)

copolymers of styrene and acrylic acid and methacrylic acid

copolymers of styrene and acrylic acid and sodium acrylate

copolymers of styrene and acrylic acid and sodium methacrylate

copolymers of styrene and acrylic acid and methyl acry-

copolymers of styrene and acrylic acid and methyl methacrylate

copolymers of styrene and acrylic acid and ethyl acrylate copolymers of styrene and acrylic acid and ethyl methacrylate

copolymers of styrene and acrylic acid ester and acrylic acid (n-butyl) ester

copolymers of styrene and acrylic acid and methacrylic acid (n-butyl) ester

copolymers of styrene and methacrylic acid and sodium acrylate

copolymers of styrene and methacrylic acid and sodium methacrylate

copolymers of styrene and methacrylic acid and methyl acrylate

copolymers of styrene and methacrylic acid and ethyl methacrylate

copolymers of styrene and methacrylic acid and ethyl acrylate

copolymers of styrene and methacrylic acid and ethyl methacrylate

copolymers of styrene and methacrylic acid ester and acrylic acid (n-butyl) ester

copolymers of styrene and methacrylic acid and methacrylic acid (n-butyl) ester

copolymers of styrene and acrylic acid and methacrylic acid and sodium acrylate

copolymers of styrene and acrylic acid and methacrylic acid and sodium methacrylate

copolymers of styrene and acrylic acid and methacrylic acid and methyl acrylate

copolymers of styrene and acrylic acid and methacrylic acid and methyl methacrylate

copolymers of styrene and acrylic acid and methacrylic acid and ethyl acrylate

copolymers of styrene and acrylic acid and methacrylic acid and ethyl methacrylate

copolymers of styrene and acrylic acid and methacrylic acid and acrylic acid (n-butyl) ester and

copolymers of styrene and acrylic acid and methacrylic acid and methacrylic acid (n-butyl) ester).

12. The hair treatment composition according to claim 1, wherein the composition includes 0.5 to 17.5 wt. % at least one copolymer, which has monomer units of the formulas (V) and (VIa)

$$(V)$$

$$(VIa)$$

$$X^{+}$$

in which X represents H⁺ or Na⁺.

13. The hair treatment composition according to claim 1, further including 0.25 to 9 wt. % (RS)-2-cyano-3,3-diphenylacrylic acid-2-ethylhexylester.

14. The hair treatment composition according to claim 1, wherein a ratio by weight of ingredients b) to a) lies in the range from 1:50 to 50:1.

15. The hair treatment composition according to claim 1, wherein a ratio by weight of ingredients a) to c) lies in the range from 1:50 to 50:1.

16. A method for reducing damage to the hair structure caused by external influences, in particular by UV radiation, including applying to the hair silicones which have groupings of formula (1)

*-
$$+$$
O- Si -O- $\frac{CH_3}{N}$ *,

A- $\frac{N}{N}$ A

in which

n represents values from 1 to 1000 and

A represents a grouping

$$*$$
 R_1
 R_1

wherein R1 represents -H or —CH3 and R represents a straight-chain or branched alkyl group having 8 to 24 C atoms and a represents an integer from 1 to 20.

* * * * *