



(43) International Publication Date  
13 November 2014 (13.11.2014)

W I P O | P C T

(10) International Publication Number  
**WO 2014/182766 A1**

(51) International Patent Classification:

**A61K 8/34** (2006.01) **A61K 8/49** (2006.01)  
**A61K 8/41** (2006.01) **A61Q 5/12** (2006.01)

(21) International Application Number:

PCT/US20 14/037068

(22) International Filing Date:

7 May 2014 (07.05.2014)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

61/821,459 9 May 2013 (09.05.2013) US

(71) Applicant: **THE PROCTER & GAMBLE COMPANY**  
[US/US]; One Procter & Gamble Plaza, Cincinnati, Ohio  
45202 (US).

(72) Inventors: **MARSH, Jennifer, Mary**; One Procter &  
Gamble Plaza, Cincinnati, Ohio 45202 (US). **KELLY, Ca-**  
**sey, Patrick**; One Procter & Gamble Company, Cincinnati,  
Ohio 45202 (US).

(74) Agent: **GUFFEY, Timothy B.**; c/o THE PROCTER &  
GAMBLE COMPANY, Global Patent Services, 299 East  
6th Street, Sycamore Building, 4th Floor, Cincinnati, Ohio  
45202 (US).

(81) Designated States (unless otherwise indicated, for every  
kind of national protection available): AE, AG, AL, AM,

AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY,  
BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM,  
DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT,  
HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR,  
KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME,  
MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ,  
OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA,  
SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM,  
TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM,  
ZW.

(84) Designated States (unless otherwise indicated, for every  
kind of regional protection available): ARIPO (BW, GH,  
GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ,  
UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ,  
TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK,  
EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV,  
MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM,  
TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW,  
KM, ML, MR, NE, SN, TD, TG).

Published:

- with international search report (Art. 21(3))
- before the expiration of the time limit for amending the  
claims and to be republished in the event of receipt of  
amendments (Rule 48.2(h))

(54) Title: HAIR CARE CONDITIONING COMPOSITION COMPRISING HISTIDINE

(57) Abstract: Use of a histidine compound for removing minerals from hair. Use of a hair care composition having from about 0.025% to about 0.25% by weight of the composition of a histidine compound. The hair care composition further includes a gel matrix phase. The gel matrix has from about 0.1% to about 20% of one or more high melting point fatty compounds, from about 0.1% to about 10% of a cationic surfactant system, and at least about 20% of an aqueous carrier, by weight of said hair care composition.



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## HAIR CARE CONDITIONING COMPOSITION COMPRISING HISTIDINE

### FIELD OF THE INVENTION

The present invention relates to a hair care composition that removes minerals from the hair during use.

### BACKGROUND OF THE INVENTION

Many water sources that are used by consumers for personal care contain elevated levels of calcium and magnesium salts, as well as undesirable levels of redox metals (e.g., copper and/or iron) salts. As such, using chelants to sequester trace redox metals often proves to be ineffective because most chelants also competitively bind calcium and/or magnesium.

It has been found that even trace quantities of these minerals can deposit on the hair surface and in between the cuticle layers of hair. This deposition of minerals on hair is especially problematic because transition metal ions, such as copper and iron, can facilitate reduction-oxidation (redox) reactions during hair coloring treatments and during UV exposure. These reactions generate reactive oxygen species (ROS), which in turn can cause damage to the hair. In addition, they can interfere with the oxidative color formation chemistry and lead to reduced color uptake for hair colorant users.

It has also been found that traditional chelating agents such as EDDS, can result in stability problems for conditioners containing cationic surfactants.

Accordingly, there is a need for hair care compositions that can inhibit minerals depositing on keratinous tissue, as well as facilitate the removal of minerals already deposited thereon. Additionally, there is a need for chelating agents which can facilitate removal of minerals deposited on the hair without interfering with the hair care formulation in which the chelating agent is included.

### SUMMARY OF THE INVENTION

The use of histidine for removing minerals from the hair. Additionally, the use of histidine in a conditioner composition to condition and remove minerals from the hair.

### DETAILED DESCRIPTION OF THE INVENTION

While the specification concludes with claims particularly pointing out and distinctly claiming the invention, it is believed that the present invention will be better understood from the following description.

Herein, "comprising" means that other steps and other ingredients which do not affect the end result can be added. This term encompasses the terms "consisting of" and "consisting essentially of".

All percentages, parts and ratios are based upon the total weight of the compositions of the present invention, unless otherwise specified. All such weights as they pertain to listed ingredients are based on the active level and, therefore, do not include carriers or by-products that may be included in commercially available materials.

Herein, "mixtures" is meant to include a simple combination of materials and any compounds that may result from their combination.

The term "molecular weight" or "M.Wt." as used herein refers to the weight average molecular weight unless otherwise stated.

### **Hair Care Composition**

The hair composition described herein is a conditioning hair care composition that delivers consumer desired conditioning in addition to inhibiting the deposition of minerals (i.e. from the water used to rinse) on the hair.

It has been found that a chelant having a high Stability Constant for Copper ( $K_{CuL}$ ) in combination with a low Stability Constant for Calcium ( $K_{CaL}$ ) will demonstrate a sufficient level of selective affinity for these redox metals and thus inhibit the deposition of the minerals onto hair. Chelants having this selective affinity may also reduce the quantities of redox metals already deposited. Suitable chelants for high affinity for transition metals such as copper and iron generally have at least one negative charge such as amino carboxylates or amino phosphonates. However, chelants with a negative charge, for example EDDS, can interfere with the stability of the product and specifically form a precipitate with the cationic surfactants which ultimately can lead to difficulties maintaining the desired viscosity of the conditioner, making it runny and not acceptable for use. In addition the higher charged anionic materials increase ionic strength of the system which can lead to phase separation. Specifically, the longer chain cationic surfactants (C22) will form a turbid solution when these anionic chelants are added, even at low levels. (See Fig. 1) Thus there is a need to identify a chelant that can inhibit the deposition of minerals in hair but not interfere with the stability of the conditioner and its wet conditioning performance and deliver superior conditioning performance.

#### **A. HISTIDINE**

It has been found that histidine compounds have the high stability constant for copper and low stability constant for calcium that is desired for efficient inhibition of deposition of minerals and can be formulated up to a level of 0.25% in conditioners to give a stable product

with no negative impact on conditioning performance. Histidine compounds can be either zwitterionic or uncharged at the pH of a typical hair conditioning composition (pH 4-6) and thus have limited interaction with the cationic surfactants. This enables the formulation of a stable conditioner with histidine at a level of from about 0.025% to about 0.25%, from about 0.05 to about 0.25%, from about 0.08 to about 0.15, and/or from about 0.10 to about 0.15. Histidine is included at levels sufficient to deliver adequate copper removal performance without interfering with conditioning performance.

The Stability Constant of a metal chelant interaction is defined as:

$$K_{ML} = \frac{[ML]}{[M][L]}$$

where:

[ML] = concentration of metal ligand complex at equilibrium  
 [M] = concentration of free metal ion  
 [L] = concentration of free ligand in a fully deprotonated form  
 $K_{ML}$  = stability constant for the metal chelant complex.

All concentrations are expressed in mol/dm<sup>3</sup>. Stability constants are conveniently expressed as logarithms.

Histidine compounds means compounds according to the general formula (I) below wherein each X is independently selected from substituted or unsubstituted, saturated or unsaturated carbon, preferably unsubstituted and saturated carbon.

n is 0-10, preferably 0-2, more preferably 0

R1 is selected from hydrogen, alkyl, aryl, arylalkyl or alkaryl, preferably hydrogen or alkyl, more preferably hydrogen

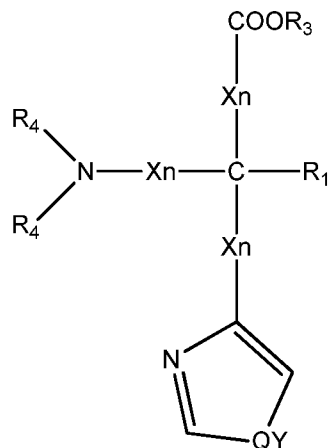
Y is a heteroatom, preferably nitrogen

Q is selected from nil, hydrogen, aryl or alkyl, preferably hydrogen

R3 is selected from hydrogen, alkyl, aryl, arylalkyl or alkaryl, preferably hydrogen or alkyl, more preferably hydrogen

R4 is independently selected from hydrogen and alkyl, preferably hydrogen

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Suitable histidine compounds for use herein include histidine and ester derivatives of histidine. Histidine compounds contain a chiral center and are present in the D- and L- form. For present compositions either form is acceptable as is a mixture of the D- and L-forms.

A person skilled in the art could manufacture histidine compounds using standard techniques. See, for example, *Organic Chemistry, Fifth Edition, TW Graham Soloman, John Wiley & Son Inc (1992) p 1092-1136*

## B. CATIONIC SURFACTANT SYSTEM

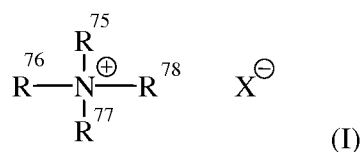
The composition of the present invention comprises a cationic surfactant system. The cationic surfactant system can be one cationic surfactant or a mixture of two or more cationic surfactants. The cationic surfactant system can be selected from: mono-long alkyl quaternized ammonium salt; a combination of mono-long alkyl quaternized ammonium salt and di-long alkyl quaternized ammonium salt; mono-long alkyl amidoamine salt; a combination of mono-long alkyl amidoamine salt and di-long alkyl quaternized ammonium salt, a combination of mono-long alkyl amidoamine salt and mono-long alkyl quaternized ammonium salt.

The cationic surfactant system can be included in the composition at a level by weight of from about 0.1% to about 10%, from about 0.5% to about 8%, from about 0.8 % to about 5%, and from about 1.0% to about 4%.

### Mono-long alkyl quaternized ammonium salt

The monoalkyl quaternized ammonium salt cationic surfactants useful herein are those having one long alkyl chain which has from 12 to 30 carbon atoms, from 16 to 24 carbon atoms, and in one embodiment at C18-22 alkyl group. The remaining groups attached to nitrogen are independently selected from an alkyl group of from 1 to about 4 carbon atoms or an alkoxy, polyoxyalkylene, alkylamido, hydroxyalkyl, aryl or alkylaryl group having up to about 4 carbon atoms.

Mono-long alkyl quaternized ammonium salts useful herein are those having the formula (I):



wherein one of  $\text{R}^{75}$ ,  $\text{R}^{76}$ ,  $\text{R}^{77}$  and  $\text{R}^{78}$  is selected from an alkyl group of from 12 to 30 carbon atoms or an aromatic, alkoxy, polyoxyalkylene, alkylamido, hydroxyalkyl, aryl or alkylaryl group having up to about 30 carbon atoms; the remainder of  $\text{R}^{75}$ ,  $\text{R}^{76}$ ,  $\text{R}^{77}$  and  $\text{R}^{78}$  are independently selected from an alkyl group of from 1 to about 4 carbon atoms or an alkoxy, polyoxyalkylene, alkylamido, hydroxyalkyl, aryl or alkylaryl group having up to about 4 carbon atoms; and  $\text{X}^-$  is a salt-forming anion such as those selected from halogen, (e.g. chloride, bromide), acetate, citrate, lactate, glycolate, phosphate, nitrate, sulfonate, sulfate, alkylsulfate, and alkyl sulfonate radicals. The alkyl groups can contain, in addition to carbon and hydrogen atoms, ether and/or ester linkages, and other groups such as amino groups. The longer chain alkyl groups, e.g., those of about 12 carbons, or higher, can be saturated or unsaturated. One of  $\text{R}^{75}$ ,  $\text{R}^{76}$ ,  $\text{R}^{77}$  and  $\text{R}^{78}$  can be selected from an alkyl group of from 12 to 30 carbon atoms, from 16 to 24 carbon atoms, from 18 to 22 carbon atoms, an/or 22 carbon atoms; the remainder of  $\text{R}^{75}$ ,  $\text{R}^{76}$ ,  $\text{R}^{77}$  and  $\text{R}^{78}$  are independently selected from  $\text{CH}_3$ ,  $\text{C}_2\text{H}_5$ ,  $\text{C}_2\text{H}_4\text{OH}$ , and mixtures thereof; and  $\text{X}$  is selected from the group consisting of  $\text{Cl}$ ,  $\text{Br}$ ,  $\text{CH}_3\text{OSO}_3$ ,  $\text{C}_2\text{H}_5\text{OSO}_3$ , and mixtures thereof.

Nonlimiting examples of such mono-long alkyl quaternized ammonium salt cationic surfactants include: behenyl trimethyl ammonium salt; stearyl trimethyl ammonium salt; cetyl trimethyl ammonium salt; and hydrogenated tallow alkyl trimethyl ammonium salt.

#### **M0110-I0112 alkyl amidoamine salt**

Mono-long alkyl amines are also suitable as cationic surfactants. Primary, secondary, and tertiary fatty amines are useful. Particularly useful are tertiary amido amines having an alkyl group of from about 12 to about 22 carbons. Exemplary tertiary amido amines include: stearamidopropyldimethylamine, stearamidopropyldiethylamine, stearamidoethyldiethylamine, stearamidoethyldimethylamine, palmitamidopropyldimethylamine, palmitamidopropyldiethylamine, palmitamidoethyldiethylamine, palmitamidoethyldimethylamine, behenamidopropyldimethylamine, behenamidopropyldiethylamine, behenamidoethyldiethylamine, behenamidoethyldimethylamine, arachidamidopropyldimethylamine, arachidamidopropyldiethylamine, arachidamidoethyldiethylamine, arachidamidoethyldimethylamine, diethylaminoethylstearamide. Useful amines in the present invention are disclosed in U.S. Patent 4,275,055, Nachtigal, et al. These amines can also be used in combination with acids such as  $\alpha$ -glutamic acid, lactic acid, hydrochloric acid, malic acid, succinic acid, acetic acid, fumaric acid, tartaric acid, citric acid,  $\ell$ -

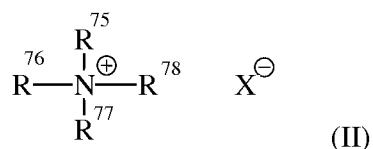
glutamic hydrochloride, maleic acid, and mixtures thereof; in one embodiment  $\alpha$ -glutamic acid, lactic acid, and/or citric acid. The amines herein can be partially neutralized with any of the acids at a molar ratio of the amine to the acid of from about 1 : 0.3 to about 1 : 2, and/or from about 1 : 0.4 to about 1 : 1.

### **Di-long alkyl quaternized ammonium salt**

Di-long alkyl quaternized ammonium salt can be combined with a mono-long alkyl quaternized ammonium salt or mono-long alkyl amidoamine salt. It is believed that such combination can provide easy-to rinse feel, compared to single use of a monoalkyl quaternized ammonium salt or mono-long alkyl amidoamine salt. In such combination with a mono-long alkyl quaternized ammonium salt or mono-long alkyl amidoamine salt, the di-long alkyl quaternized ammonium salts are used at a level such that the wt% of the dialkyl quaternized ammonium salt in the cationic surfactant system is in the range of from about 10% to about 50%, and/or from about 30% to about 45%.

The dialkyl quaternized ammonium salt cationic surfactants useful herein are those having two long alkyl chains having 12-30 carbon atoms, and/or 16-24 carbon atoms, and/or 18-22 carbon atoms. The remaining groups attached to nitrogen are independently selected from an alkyl group of from 1 to about 4 carbon atoms or an alkoxy, polyoxyalkylene, alkylamido, hydroxyalkyl, aryl or alkylaryl group having up to about 4 carbon atoms.

Di-long alkyl quaternized ammonium salts useful herein are those having the formula (II):



wherein two of  $\text{R}^{75}$ ,  $\text{R}^{76}$ ,  $\text{R}^{77}$  and  $\text{R}^{78}$  is selected from an alkyl group of from 12 to 30 carbon atoms or an aromatic, alkoxy, polyoxyalkylene, alkylamido, hydroxyalkyl, aryl or alkylaryl group having up to about 30 carbon atoms; the remainder of  $\text{R}^{75}$ ,  $\text{R}^{76}$ ,  $\text{R}^{77}$  and  $\text{R}^{78}$  are independently selected from an alkyl group of from 1 to about 4 carbon atoms or an alkoxy, polyoxyalkylene, alkylamido, hydroxyalkyl, aryl or alkylaryl group having up to about 4 carbon atoms; and  $\text{X}^-$  is a salt-forming anion such as those selected from halogen, (e.g. chloride, bromide), acetate, citrate, lactate, glycolate, phosphate, nitrate, sulfonate, sulfate, alkylsulfate, and alkyl sulfonate radicals. The alkyl groups can contain, in addition to carbon and hydrogen atoms, ether and/or ester linkages, and other groups such as amino groups. The longer chain alkyl groups, e.g., those of about 12 carbons, or higher, can be saturated or unsaturated. One of  $\text{R}^{75}$ ,  $\text{R}^{76}$ ,  $\text{R}^{77}$  and  $\text{R}^{78}$  can be selected from an alkyl group of from 12 to 30 carbon atoms, from 16 to 24 carbon atoms, from 18 to 22 carbon atoms, and/or 22 carbon atoms; the remainder of  $\text{R}^{75}$ ,

R<sup>76</sup>, R<sup>77</sup> and R<sup>78</sup> are independently selected from CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, C<sub>2</sub>H<sub>4</sub>OH, and mixtures thereof; and X is selected from the group consisting of Cl, Br, CH<sub>3</sub>OSO<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>OSO<sub>3</sub>, and mixtures thereof.

Such dialkyl quaternized ammonium salt cationic surfactants include, for example, dialkyl (14-18) dimethyl ammonium chloride, ditallow alkyl dimethyl ammonium chloride, dihydrogenated tallow alkyl dimethyl ammonium chloride, distearyl dimethyl ammonium chloride, and dicetyl dimethyl ammonium chloride. Such dialkyl quaternized ammonium salt cationic surfactants also include, for example, asymmetric dialkyl quaternized ammonium salt cationic surfactants.

### **C. HIGH MELTING POINT FATTY COMPOUND**

The high melting point fatty compound useful herein have a melting point of 25°C or higher, and is selected from the group consisting of fatty alcohols, fatty acids, fatty alcohol derivatives, fatty acid derivatives, and mixtures thereof. It is understood by the artisan that the compounds disclosed in this section of the specification can in some instances fall into more than one classification, e.g., some fatty alcohol derivatives can also be classified as fatty acid derivatives. However, a given classification is not intended to be a limitation on that particular compound, but is done so for convenience of classification and nomenclature. Further, it is understood by the artisan that, depending on the number and position of double bonds, and length and position of the branches, certain compounds having certain carbon atoms may have a melting point of less than 25°C. Such compounds of low melting point are not intended to be included in this section. Nonlimiting examples of the high melting point compounds are found in International Cosmetic Ingredient Dictionary, Fifth Edition, 1993, and CTFA Cosmetic Ingredient Handbook, Second Edition, 1992.

Among a variety of high melting point fatty compounds, fatty alcohols are suitable for use in the composition of the present invention. The fatty alcohols useful herein are those having from about 14 to about 30 carbon atoms, from about 16 to about 22 carbon atoms. These fatty alcohols are saturated and can be straight or branched chain alcohols. Suitable fatty alcohols include, for example, cetyl alcohol, stearyl alcohol, behenyl alcohol, and mixtures thereof.

High melting point fatty compounds of a single compound of high purity can be used. Single compounds of pure fatty alcohols selected from the group of pure cetyl alcohol, stearyl alcohol, and behenyl alcohol can also be used. By "pure" herein, what is meant is that the compound has a purity of at least about 90%, and/or at least about 95%. These single compounds of high purity provide good rinsability from the hair when the consumer rinses off the composition.

The high melting point fatty compound can be included in the composition at a level of from about 0.1% to about 20%, from about 1% to about 15%, and/or from about 1.5% to about 8% by



weight of the composition, in view of providing improved conditioning benefits such as slippery feel during the application to wet hair, softness and moisturized feel on dry hair.

#### **D. AQUEOUS CARRIER**

The gel matrix of the hair care composition of the present invention includes an aqueous carrier. Accordingly, the formulations of the present invention can be in the form of pourable liquids (under ambient conditions). Such compositions will therefore typically comprise an aqueous carrier, which is present at a level of from about 20 wt% to about 95 wt%, or from about 60 wt% to about 85 wt%. The aqueous carrier may comprise water, or a miscible mixture of water and organic solvent, and in one aspect may comprise water with minimal or no significant concentrations of organic solvent, except as otherwise incidentally incorporated into the composition as minor ingredients of other components.

The aqueous carrier useful in the present invention includes water and water solutions of lower alkyl alcohols and polyhydric alcohols. The lower alkyl alcohols useful herein are monohydric alcohols having 1 to 6 carbons, in one aspect, ethanol and isopropanol. The polyhydric alcohols useful herein include propylene glycol, hexylene glycol, glycerin, and propane diol.

According to embodiments of the present invention, the hair care compositions may have a pH in the range from about 2 to about 10, at 25°C. In one embodiment, the hair care composition has a pH in the range from about 2 to about 6, which may help to solubilize minerals and redox metals already deposited on the hair. Thus, the hair care composition can also be effective toward washing out the existing minerals and redox metals deposits, which can reduce cuticle distortion and thereby reduce cuticle chipping and damage.

#### **E. GEL MATRIX**

The composition of the present invention comprises a gel matrix. The gel matrix comprises a cationic surfactant, a high melting point fatty compound, and an aqueous carrier.

The gel matrix is suitable for providing various conditioning benefits such as slippery feel during the application to wet hair and softness and moisturized feel on dry hair. In view of providing the above gel matrix, the cationic surfactant and the high melting point fatty compound are contained at a level such that the weight ratio of the cationic surfactant to the high melting point fatty compound is in the range of, from about 1:1 to about 1:10, and/or from about 1:1 to about 1:6.

#### **F. Additional Components**

### 1. Silicone Conditioning Agent

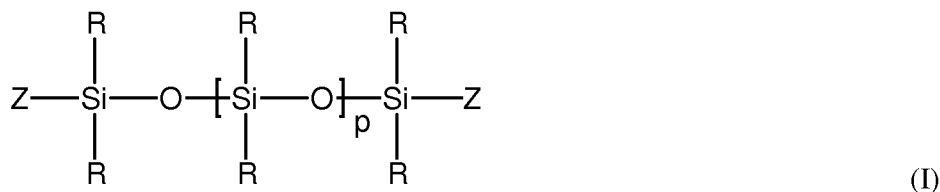
According to embodiments of the present invention, the hair care composition includes a silicone conditioning agent which comprises a silicone compound. The silicone compound may comprise volatile silicone, non-volatile silicones, or combinations thereof. In one aspect, non-volatile silicones are employed. If volatile silicones are present, it will typically be incidental to their use as a solvent or carrier for commercially available forms of non-volatile silicone materials ingredients, such as silicone gums and resins. The silicone compounds may comprise a silicone fluid conditioning agent and may also comprise other ingredients, such as a silicone resin to improve silicone fluid deposition efficiency or enhance glossiness of the hair. The concentration of the silicone compound in the conditioner composition typically ranges from about 0.01 wt% to about 10 wt%, from about 0.1 wt% to about 8 wt%, from about 0.1 wt% to about 5 wt%, or even from about 0.2 wt% to about 3 wt%, for example

Exemplary silicone compounds include (a) a first polysiloxane which is non-volatile, substantially free of amino groups, and has a viscosity of from about 100,000 **mmV**<sup>1</sup> to about 30,000,000 **mmV**<sup>1</sup>; (b) a second polysiloxane which is non-volatile, substantially free of amino groups, and has a viscosity of from about 5 **mmV**<sup>1</sup> to about 10,000 **mmV**<sup>1</sup>; (c) an aminosilicone having less than about 0.5 wt% nitrogen by weight of the aminosilicone; (d) a silicone copolymer emulsion with an internal phase viscosity of greater than about 100x10<sup>6</sup> **mmV**<sup>1</sup>, as measured at 25°C; (e) a silicone polymer containing quaternary groups; or (f) a grafted silicone polyol, wherein the silicone compounds (a) - (f) are disclosed in U.S. Patent Application Publication Nos. 2008/0292574, 2007/0041929, 2008/0292575, and 2007/0286837, each of which is incorporated by reference herein in its entirety.

#### a. First Polysiloxane

The hair care composition of the present invention may comprise a first polysiloxane. The first polysiloxane is non-volatile, and substantially free of amino groups. In the present invention, the first polysiloxanes being "substantially free of amino groups" means that the first polysiloxane contains 0 wt% of amino groups. The first polysiloxane has a viscosity of from about 100,000 **mmV**<sup>1</sup> to about 30,000,000 **mmV**<sup>1</sup> at 25°C. For example, the viscosity may range from about 300,000 **mmV** to about 25,000,000 **mmV**<sup>1</sup>, or from about 10,000,000 **mmV**<sup>1</sup> to about 20,000,000 **mmV**<sup>1</sup>. The first polysiloxane has a molecular weight from about 100,000 to about 1,000,000. For example, the molecular weight may range from about 130,000 to about 800,000, or from about 230,000 to about 600,000. According to one aspect, the first polysiloxane may be nonionic.

Exemplary first non-volatile polysiloxanes useful herein include those in accordance with the following the general formula (I):



wherein R is alkyl or aryl, and p is an integer from about 1,300 to about 15,000, such as from about 1,700 to about 11,000, or from about 3,000 to about 8,000. Z represents groups which block the ends of the silicone chains. The alkyl or aryl groups substituted on the siloxane chain (R) or at the ends of the siloxane chains Z can have any structure as long as the resulting silicone remains fluid at room temperature, is dispersible, is neither irritating, toxic nor otherwise harmful when applied to the hair, is compatible with the other components of the composition, is chemically stable under normal use and storage conditions, and is capable of being deposited on and conditions the hair. According to an embodiment, suitable Z groups include hydroxy, methyl, methoxy, ethoxy, propoxy, and aryloxy. The two R groups on each silicon atom may represent the same group or different groups. According to one embodiment, the two R groups may represent the same group. Suitable R groups include methyl, ethyl, propyl, phenyl, methylphenyl and phenylmethyl. Exemplary silicone compounds include polydimethylsiloxane, polydiethylsiloxane, and polymethylphenylsiloxane. According to one embodiment, polydimethylsiloxane is the first polysiloxane. Commercially available silicone compounds useful herein include, for example, those available from the General Electric Company in their TSF451 series, and those available from Dow Corning in their Dow Corning SH200 series.

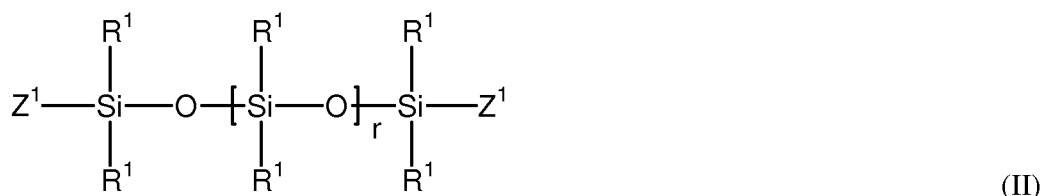
The silicone compounds that can be used herein also include a silicone gum. The term "silicone gum", as used herein, means a polyorganosiloxane material having a viscosity at 25°C of greater than or equal to 1,000,000 **mmV**<sup>1</sup>. It is recognized that the silicone gums described herein can also have some overlap with the above-disclosed silicone compounds. This overlap is not intended as a limitation on any of these materials. The "silicone gums" will typically have a mass molecular weight in excess of about 165,000, generally between about 165,000 and about 1,000,000. Specific examples include polydimethylsiloxane, poly(dimethylsiloxane methylvinylsiloxane) copolymer, poly(dimethylsiloxane diphenylsiloxane methylvinylsiloxane) copolymer and mixtures thereof. Commercially available silicone gums useful herein include, for example, TSE200A available from the General Electric Company.

#### b. Second Polysiloxane

The hair care composition of the present invention may comprise a second polysiloxane.

The second polysiloxane is non-volatile, and substantially free of amino groups. In the present invention, the second polysiloxane being "substantially free of amino groups" means that the second polysiloxane contains 0 wt% of amino groups. The second polysiloxane has a viscosity of from about 5  $\text{mmV}^1$  to about 10,000  $\text{mmV}^1$  at 25°C, such as from about 5  $\text{mmV}^1$  to about 5,000  $\text{mmV}^1$ , from about 10  $\text{mmV}^1$  to about 1,000  $\text{mmV}^1$ , or from about 20  $\text{mmV}^1$  to about 350  $\text{mmV}^1$ . The second polysiloxane has a molecular weight of from about 400 to about 65,000. For example, the molecular weight of the second polysiloxane may range from about 800 to about 50,000, from about 400 to about 30,000, or from about 400 to about 15,000. According to one aspect, the second polysiloxane may be nonionic. According to another aspect, the second polysiloxane may be a linear silicone.

Exemplary second non-volatile polysiloxanes useful herein include polyalkyl or polyaryl siloxanes in accordance with the following the general formula (II):



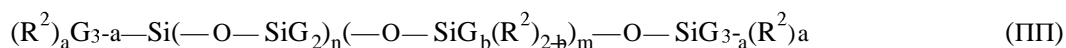
wherein  $\text{R}^1$  is alkyl or aryl, and  $r$  is an integer from about 7 to about 850, such as from about 7 to about 665, from about 7 to about 400, or from about 7 to about 200.  $\text{Z}^1$  represents groups which block the ends of the silicone chains. The alkyl or aryl groups substituted on the siloxane chain ( $\text{R}^1$ ) or at the ends of the siloxane chains  $\text{Z}^1$  can have any structure as long as the resulting silicone remains fluid at room temperature, is dispersible, is neither irritating, toxic nor otherwise harmful when applied to the hair, is compatible with the other components of the composition, is chemically stable under normal use and storage conditions, and is capable of being deposited on and conditions the hair. According to an embodiment, suitable  $\text{Z}^1$  groups include hydroxy, methyl, methoxy, ethoxy, propoxy, and aryloxy. The two  $\text{R}^1$  groups on each silicon atom may represent the same group or different groups. According to one embodiment, the two  $\text{R}^1$  groups may represent the same group. Suitable  $\text{R}^1$  groups include methyl, ethyl, propyl, phenyl, methylphenyl and phenylmethyl. Exemplary silicone compounds include polydimethylsiloxane, polydiethylsiloxane, and polymethylphenylsiloxane. According to one embodiment, polydimethylsiloxane is the second polysiloxane. Commercially available silicone compounds useful herein include, for example, those available from the General Electric Company in their TSF451 series, and those available from Dow Corning in their Dow Corning SH200 series.

#### c. Aminosilicone

The hair care composition of the present invention may comprise an amino silicone having less than about 0.5 wt% nitrogen by weight of the aminosilicone, such as less than about 0.2 wt%, or less than about 0.1 wt%, in view of friction reduction benefit. It has been surprisingly found that higher levels of nitrogen (amine functional groups) in the amino silicone tend to result in less friction reduction, and consequently less conditioning benefit from the aminosilicone. The aminosilicone useful herein may have at least one silicone block with greater than 200 siloxane units, in view of friction reduction benefit. The aminosilicones useful herein include, for example, quaternized aminosilicone and non-quaternized aminosilicone.

In one embodiment, the aminosilicones useful herein are water-insoluble. In the present invention, "water-insoluble aminosilicone" means that the aminosilicone has a solubility of 10g or less per 100g water at 25°C, in another embodiment 5g or less per 100g water at 25°C, and in another embodiment 1g or less per 100g water at 25°C. In the present invention, "water-insoluble aminosilicone" means that the aminosilicone is substantially free of copolyol groups. If copolyol groups are present, they are present at a level of less than 10 wt%, less than 1 wt%, or less than 0.1 wt% by weight of the aminosilicone.

According to one embodiment, aminosilicone useful herein are those which conform to the general formula (III):



wherein G is hydrogen, phenyl, hydroxy, or Ci-Cs alkyl, such as methyl; a is an integer having a value from 1 to 3, such as 1; b is an integer having a value from 0 to 2, such as 1; n is a number from 1 to 2,000, such as from 100 to 1,800, from 300 to 800, or from 500 to 600; m is an integer having a value from 0 to 1,999, such as from 0 to 10, or 0;  $R^2$  is a monovalent radical conforming to the general formula  $C_qH_{2q}L$ , wherein q is an integer having a value from 2 to 8 and L is selected from the following groups:  $-N(R^3)_2CH_2-CH_2-N(R^3)_2$ ;  $-N(R^3)_2$ ;  $-N^+(R^3)_3A^-$ ;  $-N(R^3)CH_2-CH_2-N^+R^3H_2A^-$ ; wherein  $R^3$  is hydrogen, phenyl, benzyl, or a saturated hydrocarbon radical, such as an alkyl radical from about  $C_1$  to about  $C_{20}$ ;  $A^-$  is a halide ion. According to an embodiment, L is  $-N(CH_3)_2$  or  $-NH_2$ . According to another embodiment, L is  $-NH_2$ .

The aminosilicone of the above formula is used at levels by weight of the composition of from about 0.1 wt% to about 5 wt%, alternatively from about 0.2 wt% to about 2 wt%, alternatively from about 0.2 wt% to about 1.0 wt%, and alternatively from about 0.3 wt% to about 0.8 wt%.

According to one embodiment, the aminosilicone may include those compounds

corresponding to formula (III) wherein  $m=0$ ;  $a=1$ ;  $q=3$ ;  $G=\text{methyl}$ ;  $n$  is from about 1400 to about 1700, such as about 1600; and  $L$  is  $-\text{N}(\text{CH}_3)_2$  or  $-\text{NH}_2$ , such as  $-\text{NH}_2$ . According to another embodiment, the aminosilicone may include those compounds corresponding to formula (III) wherein  $m=0$ ;  $a=1$ ;  $q=3$ ;  $G=\text{methyl}$ ;  $n$  is from about 400 to about 800, such as from about 500 to around 600; and  $L$  is  $-\text{N}(\text{CH}_3)_2$  or  $-\text{NH}_2$ , such as  $-\text{NH}_2$ . Accordingly, the aforementioned aminosilicones can be called terminal aminosilicones, as one or both ends of the silicone chain are terminated by nitrogen containing group. Such terminal aminosilicones may provide improved friction reduction compared to graft aminosilicones.

Another example of an aminosilicone useful herein includes, for example, quaternized aminosilicone having a tradename KF8020 available from Shinetsu.

The above aminosilicones, when incorporated into the hair care composition, can be mixed with solvent having a lower viscosity. Such solvents include, for example, polar or non-polar, volatile or non-volatile oils. Such oils include, for example, silicone oils, hydrocarbons, and esters. Among such a variety of solvents, exemplary solvents include those selected from the group consisting of non-polar, volatile hydrocarbons, volatile cyclic silicones, non-volatile linear silicones, and mixtures thereof. The non-volatile linear silicones useful herein are those having a viscosity of from about 1  $\text{mmV}^1$  to about 20,000  $\text{mmV}^1$ , such as from about 20  $\text{mmV}^1$  to about 10,000  $\text{mmV}^1$ , at 25°C. According to one embodiment, the solvents are non-polar, volatile hydrocarbons, especially non-polar, volatile isoparaffins, in view of reducing the viscosity of the aminosilicones and providing improved hair conditioning benefits such as reduced friction on dry hair. Such mixtures may have a viscosity of from about 1,000 mPa.s to about 100,000 mPa.s, and alternatively from about 5,000 mPa.s to about 50,000 mPa.s.

#### d. Silicone Copolymer Emulsion

The hair care composition of the present invention may comprise a silicone copolymer emulsion with an internal phase viscosity of greater than about  $100 \times 10^6 \text{ mmV}^1$ . The silicone copolymer emulsion may be present in an amount of from about 0.1 wt% to about 15 wt%, alternatively from about 0.3 wt% to about 10 wt%, and alternatively about 0.5 wt% to about 5 wt%, by weight of the composition, in view of providing clean feel.

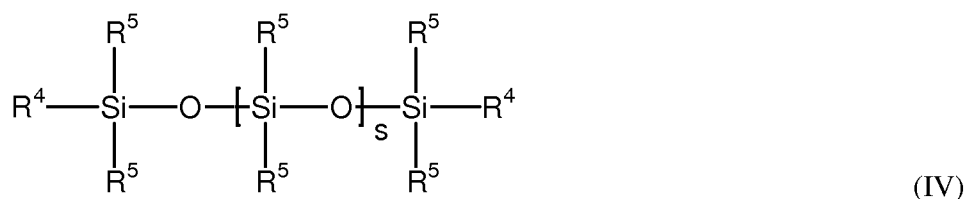
According to one embodiment, the silicone copolymer emulsion has a viscosity at 25°C of greater than about  $100 \times 10^6 \text{ mmV}^1$ , alternatively greater than about  $120 \times 10^6 \text{ mmV}^1$ , and alternatively greater than about  $150 \times 10^6 \text{ mmV}^1$ . According to another embodiment, the silicone copolymer emulsion has a viscosity at 25°C of less than about  $1000 \times 10^6 \text{ mmV}^1$ , alternatively less than about  $500 \times 10^6 \text{ mmV}^1$ , and alternatively less than about  $300 \times 10^6 \text{ mmV}^1$ . To measure the internal phase viscosity of the silicone copolymer emulsion, one may first break the polymer from the emulsion. By way of example, the following procedure can be used

to break the polymer from the emulsion: 1) add 10 grams of an emulsion sample to 15 milliliters of isopropyl alcohol; 2) mix well with a spatula; 3) decant the isopropyl alcohol; 4) add 10 milliliters of acetone and knead polymer with spatula; 5) decant the acetone; 6) place polymer in an aluminum container and flatten/dry with a paper towel; and 7) dry for two hours in an 80°C. The polymer can then be tested using any known rheometer, such as, for example, a CarriMed, Haake, or Monsanto rheometer, which operates in the dynamic shear mode. The internal phase viscosity values can be obtained by recording the dynamic viscosity ( $\eta'$ ) at a  $9.900 \times 10^{-3}$  Hz frequency point. According to one embodiment, the average particle size of the emulsions is less than about 1 micron, such as less than about 0.7 micron.

The silicone copolymer emulsions of the present invention may comprise a silicone copolymer, at least one surfactant, and water.

The silicone copolymer results from the addition reaction of the following two materials in the presence of a metal containing catalyst:

(i) a polysiloxane with reactive groups on both termini, represented by a general formula (IV):



wherein:

$\text{R}^4$  is a group capable of reacting by chain addition reaction such as, for example, a hydrogen atom, an aliphatic group with ethylenic unsaturation (i.e., vinyl, allyl, or hexenyl), a hydroxyl group, an alkoxyl group (i.e., methoxy, ethoxy, or propoxy), an acetoxyl group, or an amino or alkylamino group;

$\text{R}^5$  is alkyl, cycloalkyl, aryl, or alkylaryl and may include additional functional groups such as ethers, hydroxyls, amines, carboxyls, thiols esters, and sulfonates; in an embodiment,  $\text{R}^5$  is methyl. Optionally, a small mole percentage of the groups may be reactive groups as described above for  $\text{R}^5$ , to produce a polymer which is substantially linear but with a small amount of branching. In this case, the level of  $\text{R}^5$  groups equivalent to  $\text{R}^4$  groups may be less than about 10% on a mole percentage basis, such as less than about 2%;

$s$  is an integer having a value such that the polysiloxane of formula (IV) has a viscosity of from about 1 **raraV**<sup>1</sup> to about  $1 \times 10^6$  **mmV**<sup>1</sup>;

and,

(ii) at least one silicone compound or non-silicone compound comprising at least one or at most two groups capable of reacting with the  $R^4$  groups of the polysiloxane in formula (IV). According to one embodiment, the reactive group is an aliphatic group with ethylenic unsaturation.

The metal containing catalysts used in the above described reactions are often specific to the particular reaction. Such catalysts are known in the art. Generally, they are materials containing metals such as platinum, rhodium, tin, titanium, copper, lead, etc.

The mixture used to form the emulsion also may contain at least one surfactant. This can include non-ionic surfactants, cationic surfactants, anionic surfactants, alkylpolysaccharides, amphoteric surfactants, and the like. The above surfactants can be used individually or in combination.

An exemplary method of making the silicone copolymer emulsions described herein comprises the steps of 1) mixing materials (a) described above with material (b) described above, followed by mixing in an appropriate metal containing catalyst, such that material (b) is capable of reacting with material (a) in the presence of the metal containing catalyst; 2) further mixing in at least one surfactant and water; and 3) emulsifying the mixture. Methods of making such silicone copolymer emulsions are disclosed in U.S. Pat. No. 6,013,682; PCT Application No. WO 01/58986 A1; and European Patent Application No. EP0874017 A2.

A commercially available example of a silicone copolymer emulsion is an emulsion of about 60-70 wt% of divinyl dimethicone/dimethicone copolymer having an internal phase viscosity of minimum  $120 \times 10^6 \text{ mmV}^1$ , available from Dow Corning with a tradename HMW2220.

e. Silicone polymer containing quaternary groups

The hair care composition of the present invention may comprise a silicone polymer containing quaternary groups (i.e., a quaternized silicone polymer). The quaternized silicone polymer provides improved conditioning benefits such as smooth feel, reduced friction, prevention of hair damage. Especially, the quaternary group can have good affinity with damaged/colorant hairs. The quaternized silicone polymer is present in an amount of from about 0.1 wt% to about 15 wt%, based on the total weight of the hair conditioning composition. For example, according to an embodiment, the quaternized silicone polymer may be present in an amount from about 0.2 wt% to about 10 wt%, alternatively from about 0.3 wt% to about 5 wt%, and alternatively from about 0.5 wt% to about 4 wt%, by weight of the composition.

The quaternized silicone polymer of the present invention is comprised of at least one silicone block and at least one non-silicone block containing quaternary nitrogen groups, wherein the number of the non-silicone blocks is one greater than the number of the silicone



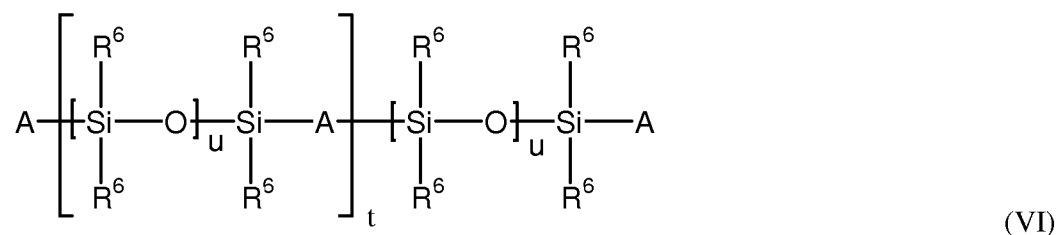
blocks. The silicone polymers correspond to the general structure (V):



wherein, B is a silicone block having greater than 200 siloxane units;  $A^1$  is an end group which may contain quaternary groups;  $A^2$  is a non-silicone blocks containing quaternary nitrogen groups; and m is an integer 0 or greater, with the proviso that if m=0 then the  $A^1$  group contains quaternary groups.

Structures corresponding to the general formula, for example, are disclosed in U.S. Pat. No. 4,833,225, in U.S. Patent Application Publication No. 2004/0138400, in U.S. Patent Application Publication No. 2004/0048996, and in U.S. Patent Application Publication No. 2008/0292575.

In one embodiment, the silicone polymers can be represented by the following structure (VI)



wherein, A is a group which contains at least one quaternary nitrogen group, and which is linked to the silicon atoms of the silicone block by a silicon-carbon bond, each A independently can be the same or different;  $R^6$  is an alkyl group of from about 1 to about 22 carbon atoms or an aryl group; each  $R^6$  independently can be the same or different; t is an integer having a value of from 0 or greater, for example t can be less than 20, or less than 10; and u is an integer greater than about 200, such as greater than about 250, or greater than about 300, and u may be less than about 700, or less than about 500. According to an embodiment,  $R^6$  is methyl.

#### f. Grafted Silicone Copolyol

The hair care composition of the present invention may comprise a grafted silicone copolyol in combination with the quaternized silicone polymer. It is believed that this grafted silicone copolyol can improve the spreadability of the quaternized silicone polymer by reducing the viscosity of the quaternized silicone polymer, and also can stabilize the quaternized silicone polymer in aqueous conditioner matrix. It is also believed that, by such improved spreadability, the hair care compositions of the present invention can provide better dry conditioning benefits

such as friction reduction and/or prevention of damage with reduced tacky feel. It has been surprisingly found that the combination of the quaternized silicone polymer, grafted silicone copolyol, and cationic surfactant system comprising di-alkyl quaternized ammonium salt cationic surfactants provides improved friction reduction benefit, compared to a similar combination. Such similar combinations are, for example, a combination in which the grafted silicone copolyol is replaced with end-capped silicone copolyol, and another combination in which the cationic surfactant system is substantially free of di-alkyl quaternized ammonium salt cationic surfactants.

The grafted silicone copolyol is contained in the composition at a level such that the weight % of the grafted silicone copolyol to its mixture with quaternized silicone copolymer is in the range of from about 1 wt% to about 50 wt%, alternatively from about 5 wt% to about 40 wt%, and alternatively from about 10 wt% to 30 wt%.

The grafted silicone copolyols useful herein are those having a silicone backbone such as dimethicone backbone and polyoxyalkylene substitutions such as polyethylene oxide and/or polypropylene oxide substitutions. The grafted silicone copolyols useful herein have a hydrophilic-lipophilic balance (HLB) value of from about 5 to about 17, such as from about 8 to about 17, or from about 8 to about 12. The grafted silicone copolyols having the same INCI name have a variety of the weight ratio, depending on the molecular weight of the silicone portion and the number of the polyethylene oxide and/or polypropylene oxide substitutions.

According to an embodiment, exemplary commercially available grafted dimethicone copolyols include, for example: those having a tradename Silsoft 430 having an HLB value of from about 9 to about 12 (INCI name "PEG/PPG-20/23 dimethicone") available from GE; those having a tradename Silsoft 475 having an HLB value of from about 13 to about 17 (INCI name "PEG-23/PPG-6 dimethicone"); those having a tradename Silsoft 880 having an HLB value of from about 13 to about 17 (INCI name "PEG-12 dimethicone"); those having a tradename Silsoft 440 having an HLB value of from about 9 to about 12 (INCI name "PEG-20/PPG-23 dimethicone"); those having a tradename DC5330 (INCI name "PEG-15/PPG-15 dimethicone") available from Dow Corning.

The above quaternized silicone polymer and the grafted silicone copolyol may be mixed and emulsified by a emulsifying surfactant, prior to incorporating them into a gel matrix formed by cationic surfactants and high melting point fatty compounds, as discussed below. It is believed that, this pre-mixture can improve behavior of the quaternized silicone polymer and the grafted silicone copolyol, for example, increase the stability and reduce the viscosity to form more homogenized formulation together with the other components. Such emulsifying surfactant can be used at a level of about 0.001 wt% to about 1.5 wt%, alternatively from about

0.005% to about 1.0%, and alternatively from about 0.01 wt% to about 0.5 wt%, based on the total weight of the hair conditioning composition. Such surfactants may be nonionic, and have an HLB value of from about 2 to about 15, such as from about 3 to about 14, or from about 3 to about 10. Commercially available examples of emulsifying surfactant include nonionic surfactants having an INCI name C12-C14 Pareth-3 and having an HLB value of about 8 supplied from NIKKO Chemicals Co., Ltd. with tradename NIKKOL BT-3.

According to one embodiment, the hair care composition comprises a combination of two or more silicone conditioning agents, along with an EDDS sequestering agent and a gel matrix.

In one embodiment, the hair care composition comprises a polyalkylsiloxane mixture comprising (i) a first polyalkylsiloxane which is non-volatile, substantially free of amino groups, and has a viscosity of from about 100,000  $\text{mmV}^1$  to about 30,000,000  $\text{mmV}^1$ , and (ii) a second polyalkylsiloxane which is non-volatile, substantially free of amino groups, and has a viscosity of from about 5  $\text{mmV}^1$  to about 10,000  $\text{mmV}^1$ ; an aminosilicone having less than about 0.5 wt% nitrogen by weight of the aminosilicone; and a silicone copolymer emulsion with an internal phase viscosity of greater than about  $100 \times 10^6 \text{ mmV}^1$ , as measured at 25°C. For example, in another embodiment, the hair care composition comprises from about 0.5 wt% to about 10 wt% of a polyalkylsiloxane mixture comprising (i) a first polyalkylsiloxane which is non-volatile, substantially free of amino groups, and has a viscosity of from about 100,000  $\text{mmV}^1$  to about 30,000,000  $\text{mm}^2\text{s}^{-1}$ , and (ii) a second polyalkylsiloxane which is non-volatile, substantially free of amino groups, and has a viscosity of from about 5  $\text{mmV}^1$  to about 10,000  $\text{mmV}^1$ ; from about 0.1 wt% to about 5 wt% of an aminosilicone having less than about 0.5 wt% nitrogen by weight of the aminosilicone; and from about 0.1 wt% to about 5 wt% of a silicone copolymer emulsion with an internal phase viscosity of greater than about  $100 \times 10^6 \text{ mmV}^1$ , as measured at 25°C.

In another embodiment, the hair care composition comprises a silicone polymer containing quaternary groups wherein said silicone polymer comprises silicone blocks with greater than about 200 siloxane units; and a grafted silicone copolyol. For example, in another embodiment, the hair care composition comprises from about 0.1 wt% to about 15 wt% of a silicone polymer containing quaternary groups wherein said silicone polymer comprises silicone blocks with greater than about 200 siloxane units; and a grafted silicone copolyol at a level such that the weight % of the grafted silicone copolyol in its mixture with the quaternized silicone polymer is in the range of from about 1 wt% to about 50 wt%.

In yet another embodiment, the hair care composition comprises an aminosilicone having a viscosity of from about 1,000 centistokes to about 1,000,000 centistokes, and less than about

0.5% nitrogen by weight of the aminosilicone; and (2) a silicone copolymer emulsion with an internal phase viscosity of greater than about  $120 \times 10^6$  centistokes, as measured at 25°C.

## 2. Other Conditioning Agents

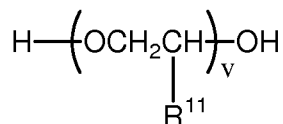
Also suitable for use in the hair care compositions herein are the conditioning agents described by the Procter & Gamble Company in U.S. Pat. Nos. 5,674,478, and 5,750,122. Also suitable for use herein are those conditioning agents described in U.S. Pat. Nos. 4,529,586, 4,507,280, 4,663,158, 4,197,865, 4,217, 914, 4,381,919, and 4,422, 853.

### a. Organic Conditioning Oils

The hair care compositions of the present invention may also further comprise an organic conditioning oil. According to embodiments of the present invention, the hair care composition may comprise from about 0.05 wt% to about 3 wt%, from about 0.08 wt% to about 1.5 wt%, or even from about 0.1 wt% to about 1 wt%, of at least one organic conditioning oil as the conditioning agent, in combination with other conditioning agents, such as the silicones (described herein). Suitable conditioning oils include hydrocarbon oils, polyolefins, and fatty esters. Suitable hydrocarbon oils include, but are not limited to, hydrocarbon oils having at least about 10 carbon atoms, such as cyclic hydrocarbons, straight chain aliphatic hydrocarbons (saturated or unsaturated), and branched chain aliphatic hydrocarbons (saturated or unsaturated), including polymers and mixtures thereof. Straight chain hydrocarbon oils are typically from about C12 to about C19. Branched chain hydrocarbon oils, including hydrocarbon polymers, typically will contain more than 19 carbon atoms. Suitable polyolefins include liquid polyolefins, liquid poly- $\alpha$ -olefins, or even hydrogenated liquid poly- $\alpha$ -olefins. Polyolefins for use herein may be prepared by polymerization of C4 to about C14 or even C6 to about C12. Suitable fatty esters include, but are not limited to, fatty esters having at least 10 carbon atoms. These fatty esters include esters with hydrocarbyl chains derived from fatty acids or alcohols (e.g. mono-esters, polyhydric alcohol esters, and di- and tri-carboxylic acid esters). The hydrocarbyl radicals of the fatty esters hereof may include or have covalently bonded thereto other compatible functionalities, such as amides and alkoxy moieties (e.g., ethoxy or ether linkages, etc.).

## 3. Nonionic Polymers

The hair care composition of the present invention may also further comprise a nonionic polymer. According to an embodiment, the conditioning agent for use in the hair care composition of the present invention may include a polyalkylene glycol polymer. For example, polyalkylene glycols having a molecular weight of more than about 1000 are useful herein. Useful are those having the following general formula (VIII):



(VIII)

wherein R<sup>11</sup> is selected from the group consisting of H, methyl, and mixtures thereof; and v is the number of ethoxy units. The polyalkylene glycols, such as polyethylene glycols, can be included in the hair care compositions of the present invention at a level of from about 0.001 wt% to about 10 wt%. In an embodiment, the polyethylene glycol is present in an amount up to about 5 wt% based on the weight of the composition. Polyethylene glycol polymers useful herein are PEG-2M (also known as Polyox WSR<sup>®</sup> N-10, which is available from Union Carbide and as PEG-2,000); PEG-5M (also known as Polyox WSR<sup>®</sup> N-35 and Polyox WSR<sup>®</sup> N-80, available from Union Carbide and as PEG-5,000 and Polyethylene Glycol 300,000); PEG-7M (also known as Polyox WSR<sup>®</sup> N-750 available from Union Carbide); PEG-9M (also known as Polyox WSR<sup>®</sup> N-3333 available from Union Carbide); and PEG-14 M (also known as Polyox WSR<sup>®</sup> N-3000 available from Union Carbide).

#### 4. Suspending Agent

The hair care compositions of the present invention may further comprise a suspending agent at concentrations effective for suspending water-insoluble material in dispersed form in the compositions or for modifying the viscosity of the composition. Such concentrations range from about 0.1 wt% to about 10 wt%, or even from about 0.3 wt% to about 5.0 wt%.

Suspending agents useful herein include anionic polymers and nonionic polymers. Useful herein are vinyl polymers such as cross linked acrylic acid polymers with the CTFA name Carbomer, cellulose derivatives and modified cellulose polymers such as methyl cellulose, ethyl cellulose, hydroxyethyl cellulose, hydroxypropyl methyl cellulose, nitro cellulose, sodium cellulose sulfate, sodium carboxymethyl cellulose, crystalline cellulose, cellulose powder, polyvinylpyrrolidone, polyvinyl alcohol, guar gum, hydroxypropyl guar gum, xanthan gum, arabia gum, tragacanth, galactan, carob gum, guar gum, karaya gum, carrageenan, pectin, agar, quince seed (Cydonia oblonga Mill), starch (rice, corn, potato, wheat), algae colloids (algae extract), microbiological polymers such as dextran, succinoglucan, pullulan, starch-based polymers such as carboxymethyl starch, methylhydroxypropyl starch, alginic acid-based polymers such as sodium alginate, alginic acid propylene glycol esters, acrylate polymers such as sodium polyacrylate, polyethylacrylate, polyacrylamide, polyethyleneimine, and inorganic water soluble material such as bentonite, aluminum magnesium silicate, laponite, hectonite, and anhydrous silicic acid.

Commercially available viscosity modifiers highly useful herein include Carbomers with trade names Carbopol<sup>®</sup> 934, Carbopol<sup>®</sup> 940, Carbopol<sup>®</sup> 950, Carbopol<sup>®</sup> 980, and Carbopol<sup>®</sup> 981,

all available from B. F. Goodrich Company, acrylates/steareth-20 methacrylate copolymer with trade name ACRY SOL™ 22 available from Rohm and Hass, nonoxynyl hydroxyethylcellulose with trade name Amercell™ POLYMER HM-1500 available from Amerchol, methylcellulose with trade name BENECEL®, hydroxyethyl cellulose with trade name NATROSOL®, hydroxypropyl cellulose with trade name KLUCEL®, cetyl hydroxyethyl cellulose with trade name POLYSURF® 67, all supplied by Hercules, ethylene oxide and/or propylene oxide based polymers with trade names CARBOWAX® PEGs, POLYOX WASRs, and UCON® FLUIDS, all supplied by Amerchol.

Other optional suspending agents include crystalline suspending agents which can be categorized as acyl derivatives, long chain amine oxides, and mixtures thereof. These suspending agents are described in U.S. Pat. No. 4,741,855.

These suspending agents include ethylene glycol esters of fatty acids in one aspect having from about 16 to about 22 carbon atoms. In one aspect, useful suspending agents include ethylene glycol stearates, both mono and distearate, but in one aspect, the distearate containing less than about 7% of the mono stearate. Other suitable suspending agents include alkanol amides of fatty acids, having from about 16 to about 22 carbon atoms, or even about 16 to 18 carbon atoms, examples of which include stearic monoethanolamide, stearic diethanolamide, stearic monoisopropanolamide and stearic monoethanolamide stearate. Other long chain acyl derivatives include long chain esters of long chain fatty acids (e.g., stearyl stearate, cetyl palmitate, etc.); long chain esters of long chain alkanol amides (e.g., stearamide diethanolamide distearate, stearamide monoethanolamide stearate); and glyceryl esters (e.g., glyceryl distearate, trihydroxystearin, tribehenin) a commercial example of which is Thixin® R available from Rheox, Inc. Long chain acyl derivatives, ethylene glycol esters of long chain carboxylic acids, long chain amine oxides, and alkanol amides of long chain carboxylic acids in addition to the materials listed above may be used as suspending agents.

Other long chain acyl derivatives suitable for use as suspending agents include N,N-dihydrocarbyl amido benzoic acid and soluble salts thereof (e.g., Na, K), particularly N,N-di(hydrogenated) CI6, CI8 and tallow amido benzoic acid species of this family, which are commercially available from Stepan Company (Northfield, Ill., USA).

Examples of suitable long chain amine oxides for use as suspending agents include alkyl dimethyl amine oxides, e.g., stearyl dimethyl amine oxide.

Other suitable suspending agents include primary amines having a fatty alkyl moiety having at least about 16 carbon atoms, examples of which include palmitamine or stearamine, and secondary amines having two fatty alkyl moieties each having at least about 12 carbon atoms, examples of which include dipalmitoylamine or di(hydrogenated tallow)amine. Still

other suitable suspending agents include di(hydrogenated tallow)phthalic acid amide, and crosslinked maleic anhydride-methyl vinyl ether copolymer.

## 5. Benefit Agents

In an embodiment, the hair care composition further comprises one or more additional benefit agents. The benefit agents comprise a material selected from the group consisting of anti-dandruff agents, vitamins, lipid soluble vitamins, chelants, perfumes, brighteners, enzymes, sensates, attractants, anti-bacterial agents, dyes, pigments, bleaches, and mixtures thereof.

In one aspect said benefit agent may comprise an anti-dandruff agent. Such anti-dandruff particulate should be physically and chemically compatible with the components of the composition, and should not otherwise unduly impair product stability, aesthetics or performance.

According to an embodiment, the hair care composition comprises an anti-dandruff active, which may be an anti-dandruff active particulate. In an embodiment, the anti-dandruff active is selected from the group consisting of: pyridinethione salts; azoles, such as ketoconazole, econazole, and elubiol; selenium sulphide; particulate sulfur; keratolytic agents such as salicylic acid; and mixtures thereof. In an embodiment, the anti-dandruff particulate is a pyridinethione salt.

Pyridinethione particulates are suitable particulate anti-dandruff actives. In an embodiment, the anti-dandruff active is a 1-hydroxy-2-pyridinethione salt and is in particulate form. In an embodiment, the concentration of pyridinethione anti-dandruff particulate ranges from about 0.01 wt% to about 5 wt%, or from about 0.1 wt% to about 3 wt%, or from about 0.1 wt% to about 2 wt%. In an embodiment, the pyridinethione salts are those formed from heavy metals such as zinc, tin, cadmium, magnesium, aluminium and zirconium, generally zinc, typically the zinc salt of 1-hydroxy-2-pyridinethione (known as "zinc pyridinethione" or "ZPT"), commonly 1-hydroxy-2-pyridinethione salts in platelet particle form. In an embodiment, the 1-hydroxy-2-pyridinethione salts in platelet particle form have an average particle size of up to about 20 microns, or up to about 5 microns, or up to about 2.5 microns. Salts formed from other cations, such as sodium, may also be suitable. Pyridinethione anti-dandruff actives are described, for example, in U.S. Pat. No. 2,809,971; U.S. Pat. No. 3,236,733; U.S. Pat. No. 3,753,196; U.S. Pat. No. 3,761,418; U.S. Pat. No. 4,345,080; U.S. Pat. No. 4,323,683; U.S. Pat. No. 4,379,753; and U.S. Pat. No. 4,470,982.

In an embodiment, in addition to the anti-dandruff active selected from polyvalent metal salts of pyrrhione, the composition further comprises one or more anti-fungal and/or anti-microbial actives. In an embodiment, the anti-microbial active is selected from the group consisting of: coal tar, sulfur, fcharcoal, whitfield' s ointment, castellani' s paint, aluminum

chloride, gentian violet, octopirox (picrotone olamine), ciclopirox olamine, undecylenic acid and its metal salts, potassium permanganate, selenium sulphide, sodium thiosulfate, propylene glycol, oil of bitter orange, urea preparations, griseofulvin, 8-hydroxyquinoline ciloquinol, thiobendazole, thiocarbamates, haloprogin, polyenes, hydroxypyridone, morpholine, benzylamine, allylamines (such as terbinafine), tea tree oil, clove leaf oil, coriander, palmarosa, berberine, thyme red, cinnamon oil, cinnamic aldehyde, citronellic acid, hinokitol, ichthyol pale, Sensiva SC-50, Elestab HP-100, azelaic acid, lyticase, iodopropynyl butylcarbamate (IPBC), isothiazalinones such as octyl isothiazalinone, and azoles, and mixtures thereof. In an embodiment, the anti-microbial is selected from the group consisting of: itraconazole, ketoconazole, selenium sulphide, coal tar, and mixtures thereof.

In an embodiment, the azole anti-microbials is an imidazole selected from the group consisting of: benzimidazole, benzothiazole, bifonazole, butaconazole nitrate, climbazole, clotrimazole, croconazole, eberconazole, econazole, elubiol, fenticonazole, fluconazole, flutimazole, isoconazole, ketoconazole, lanoconazole, metronidazole, miconazole, neticonazole, omoconazole, oxiconazole nitrate, sertaconazole, sulconazole nitrate, tioconazole, thiazole, and mixtures thereof, or the azole anti-microbials is a triazole selected from the group consisting of: terconazole, itraconazole, and mixtures thereof. When present in the hair care composition, the azole anti-microbial active can be included in an amount of from about 0.01 wt% to about 5 wt%, or from about 0.1 wt% to about 3 wt%, or from about 0.3 wt% to about 2 wt%. In an embodiment, the azole anti-microbial active is ketoconazole. In an embodiment, the sole anti-microbial active is ketoconazole.

Embodiments of the hair care composition may also comprise a combination of anti-microbial actives. In an embodiment, the combination of anti-microbial active is selected from the group of combinations consisting of: octopirox and zinc pyrithione, pine tar and sulfur, salicylic acid and zinc pyrithione, salicylic acid and elubiol, zinc pyrithione and elubiol, zinc pyrithione and climbazole, octopirox and climbazole, salicylic acid and octopirox, and mixtures thereof.

In an embodiment, the composition comprises an effective amount of a zinc-containing layered material. In an embodiment, the composition comprises from about 0.001 wt% to about 10 wt%, or from about 0.01 wt% to about 7 wt%, or from about 0.1 wt% to about 5 wt% of a zinc-containing layered material, by total weight of the composition.

Zinc-containing layered materials may be those with crystal growth primarily occurring in two dimensions. It is conventional to describe layer structures as not only those in which all the atoms are incorporated in well-defined layers, but also those in which there are ions or molecules between the layers, called gallery ions (A.F. Wells "Structural Inorganic Chemistry"



Clarendon Press, 1975). Zinc-containing layered materials (ZLMs) may have zinc incorporated in the layers and/or be components of the gallery ions. The following classes of ZLMs represent relatively common examples of the general category and are not intended to be limiting as to the broader scope of materials which fit this definition.

Many ZLMs occur naturally as minerals. In an embodiment, the ZLM is selected from the group consisting of: hydrozincite (zinc carbonate hydroxide), aurichalcite (zinc copper carbonate hydroxide), rosasite (copper zinc carbonate hydroxide), and mixtures thereof. Related minerals that are zinc-containing may also be included in the composition. Natural ZLMs can also occur wherein anionic layer species such as clay-type minerals (e.g., phyllosilicates) contain ion-exchanged zinc gallery ions. All of these natural materials can also be obtained synthetically or formed *in situ* in a composition or during a production process.

Another common class of ZLMs, which are often, but not always, synthetic, is layered double hydroxides. In an embodiment, the ZLM is a layered double hydroxide conforming to the formula  $[M^{2+}_x M^{3+}_{3-x} (OH)_2]^{x+} A^{m-}_{x/m} \cdot nH_2O$  wherein some or all of the divalent ions ( $M^{2+}$ ) are zinc ions (Crepaldi, EL, Pava, PC, Tronto, J, Valim, JB *J. Colloid Interfac. Sci.* 2002, 248, 429-42).

Yet another class of ZLMs can be prepared called hydroxy double salts (Morioka, H., Tagaya, H., Karasu, M, Kadokawa, J, Chiba, K *Inorg. Chem.* 1999, 38, 4211-6). In an embodiment, the ZLM is a hydroxy double salt conforming to the formula  $[M^{2+}_{1-x} M^{2+}_{1+x} (OH)_3]^{(1-y)+} A^{n-}_{(1=3y)/n} \cdot nH_2O$  where the two metal ions ( $M^{2+}$ ) may be the same or different. If they are the same and represented by zinc, the formula simplifies to  $[Zn_{1-x} (OH)_2]^{2x+} 2x A^{-} \cdot nH_2O$ . This latter formula represents (where  $x=0.4$ ) materials such as zinc hydroxychloride and zinc hydroxynitrate. In an embodiment, the ZLM is zinc hydroxychloride and/or zinc hydroxynitrate. These are related to hydrozincite as well wherein a divalent anion replaces the monovalent anion. These materials can also be formed *in situ* in a composition or in or during a production process.

In embodiments having a zinc-containing layered material and a pyrrhione or polyvalent metal salt of pyrrhione, the ratio of zinc-containing layered material to pyrrhione or a polyvalent metal salt of pyrrhione is from about 5:100 to about 10:1, or from about 2:10 to about 5:1, or from about 1:2 to about 3:1.

The on-scalp deposition of the anti-dandruff active is at least about 1 microgram/cm<sup>2</sup>. The on-scalp deposition of the anti-dandruff active is important in view of ensuring that the anti-dandruff active reaches the scalp where it is able to perform its function. In an embodiment, the deposition of the anti-dandruff active on the scalp is at least about 1.5 microgram/cm<sup>2</sup>, or at least about 2.5 microgram/cm<sup>2</sup>, or at least about 3 microgram/cm<sup>2</sup>, or at least about 4 microgram/cm<sup>2</sup>, or at least about 6 microgram/cm<sup>2</sup>, or at least about 7 microgram/cm<sup>2</sup>, or at least about 8

microgram/cm<sup>2</sup>, or at least about 8 microgram/cm<sup>2</sup>, or at least about 10 microgram/cm<sup>2</sup>. The on-scalp deposition of the anti-dandruff active is measured by having the hair of individuals washed with a composition comprising an anti-dandruff active, for example a composition pursuant to the present invention, by trained a cosmetician according to a conventional washing protocol. The hair is then parted on an area of the scalp to allow an open-ended glass cylinder to be held on the surface while an aliquot of an extraction solution is added and agitated prior to recovery and analytical determination of anti-dandruff active content by conventional methodology, such as HPLC.

## TEST METHODS

It is understood that the test methods that are disclosed in the Test Methods Section of the present application should be used to determine the respective values of the parameters of Applicants' invention as such invention is described and claimed herein.

### A. Viscosity Measurements

A Brookfield viscometer is equipped with a CPE-41 cone and cup assembly. Water bath of cup are set to 30 °C. Gap is set according to the manufacturer's instruction manual. 2.0mL of sample is placed in the center of the cup and a shear rate of 0.3 RPM is set. Viscosity measurement was taken after 210 seconds.

## EXAMPLES

The following examples illustrate the present invention. The exemplified compositions can be prepared by conventional formulation and mixing techniques. It will be appreciated that other modifications of the present invention within the skill of those in the hair care formulation art can be undertaken without departing from the spirit and scope of this invention. All parts, percentages, and ratios herein are by weight unless otherwise specified. Some components may come from suppliers as dilute solutions. The amount stated reflects the weight percent of the active material, unless otherwise specified.

The following are non-limiting examples of hair care compositions encompassed by embodiments of the present invention.

Components	Ex.1	Ex.2	Ex.3	Ex. 4	Ex. 5
Behenyl trimethyl ammonium chloride	-	-	2.5	-	-
Behenyl trimethyl ammonium methosulfate	2.3	2.6	-	2.6	2.3
Dicetyl dimethyl ammonium chloride	-	-	-	-	-
Steramidopropyl Dimethylamine	-	-	-	-	-
Cetyl alcohol	1.5	1.0	1.0	1.0	1.5
Stearyl alcohol	3.7	2.4	2.3	2.4	3.7
Aminosilicone *	0.5	0.5	0.5	0.5	0.5
Histidine	0.1	0.05	0.2	0.1	0.05
N,N'Ethylene Diamine Disuccinic Acid					
Preservatives	0.56	0.56	0.9	0.9	0.56
Perfume	0.5	0.5	0.5	0.5	0.5
Panthenol	-	-	0.05	-	-
Panthenyl ethyl ether	-	-	0.03	-	-
Deionized Water	q.s. to 100%				
Method of preparation	I				

Components	Ex. 6
Behenyl trimethyl ammonium methosulfate	2.0
Steramidopropyl Dimethylamine	
Cetyl alcohol	1.4
Stearyl alcohol	3.4
Aminosilicone *	2.0
Histidine	0.1
N,N'Ethylene Diamine Disuccinic Acid	
Preservatives	0.9
Perfume	0.5
Deionized Water	q.s. to 100%
Method of preparation	II

### Comparative Examples

Components	Comp. Ex. 1	Comp. Ex. 2	Comp. Ex. 3
Behenyl trimethyl ammonium chloride	-	-	-
Behenyl trimethyl ammonium methosulfate	1.43	3.1	-
Dicetyl dimethyl ammonium chloride	0.50	-	-
Steramidopropyl Dimethylamine	-	-	2.6
Cetyl alcohol	0.93	1.0	1.8
Stearyl alcohol	2.3	2.5	3.0
Aminosilicone *	0.75	-	-
Histidine	-	-	-
N,N'Ethylene Diamine Disuccinic Acid	0.2	0.2	0.2
Preservatives	0.56	0.56	-
Perfume	0.5	-	-
Panthenol	-	-	-
Panthenyl ethyl ether	-	-	-
Deionized Water	q.s. to 100%		
Method of preparation	I	II	I

#### Definitions of Components

\* Aminosilicone: Terminal aminosilicone which is available from GE having a viscosity of about 10,000mPa<sup>s</sup>, and having following formula:



wherein G is methyl; a is an integer of 1; n is a number from 400 to about 600;  $\mathbf{R}_1$  is a monovalent radical conforming to the general formula  $\text{C}_q\text{H}_{2q}\text{L}$ , wherein q is an integer of 3 and L is  $\text{--NH}_2$ .

#### Method of Preparation

The conditioning compositions of "Ex. 1" through "Ex. 6" or Comparative Ex. "1" through "3" as shown above can be prepared by any conventional method well known in the art. They are suitably made by one of the following Methods I or II as shown below.

#### Method I

Cationic surfactants and high melting point fatty compounds are added to water with agitation, and heated to about 80°C. The mixture is cooled down to about 55°C and gel matrix is formed. Silicones, perfumes and preservatives are added to the gel matrix with agitation. Then,

if included polymers are added with agitation at about 30°C. Then, if included, other components are added with agitation.

#### Method II

Cationic surfactants and high melting point fatty compounds are mixed and heated to from about 66°C to about 85°C to form an oil phase. Separately, water is heated to from about 20°C to about 48°C to form an aqueous phase. In Becomix® direct injection rotor-stator homogenizer, the oil phase is injected and it takes 0.2 second or less for the oils phase to reach to a high shear field having an energy density of from  $1.0 \times 10^5$  J/m<sup>3</sup> to  $1.0 \times 10^7$  J/m<sup>3</sup> where the aqueous phase is already present. A gel matrix is formed at a temperature of above 50°C to about 60°C. Silicones and preservatives are added to the gel matrix with agitation. Then, if included, polymers are added with agitation at about 32°C. Then, if included, other components such as perfumes are added with agitation. Then the composition is cooled down to room temperature.

The hair care compositions are generally prepared by conventional methods such as those known in the art of making the compositions. Such methods typically involve mixing of the ingredients in one or more steps to a relatively uniform state, with or without heating, cooling, application of vacuum, and the like. The compositions are prepared such as to optimize stability (physical stability, chemical stability, photostability) and/or delivery of the active materials. The hair care composition may be in a single phase or a single product, or the hair care composition may be in a separate phases or separate products. If two products are used, the products may be used together, at the same time or sequentially. Sequential use may occur in a short period of time, such as immediately after the use of one product, or it may occur over a period of hours or days.

#### Stability/Viscosity Data

To demonstrate the stability of histidine in a hair conditioning composition, the histidine level in Example 1 was varied from 0% up to 0.25% and the viscosity was measured. The viscosity remains stable with -histidine at a level of 0.10% and 0.25%, as demonstrated by the viscosity measurements included in Table 1.

Table 1

% Histidine Added	Ex. 1 Viscosity in cP at ~30C
0.00	5772
0.10	5444
0.25	5608

The dimensions and values disclosed herein are not to be understood as being strictly limited to the exact numerical values recited. Instead, unless otherwise specified, each such dimension is intended to mean both the recited value and a functionally equivalent range surrounding that value. For example, a dimension disclosed as "40 mm" is intended to mean "about 40 mm."

Every document cited herein, including any cross referenced or related patent or application, is hereby incorporated herein by reference in its entirety unless expressly excluded or otherwise limited. The citation of any document is not an admission that it is prior art with respect to any invention disclosed or claimed herein or that it alone, or in any combination with any other reference or references, teaches, suggests, or discloses any such invention. Further, to the extent that any meaning or definition of a term in this document conflicts with any meaning or definition of the same term in a document incorporated by reference, the meaning or definition assigned to that term in this document shall govern.

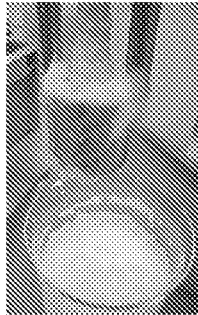
While particular embodiments of the present invention have been illustrated and described, it would be obvious to those skilled in the art that various other changes and modifications can be made without departing from the spirit and scope of the invention. It is therefore intended to cover in the appended claims all such changes and modifications that are within the scope of this invention.

## CLAIMS

What is claimed is:

1. Use of a histidine compound for removing minerals from hair.
2. Use of a composition comprising from 0.025% to 0.25% by weight of the composition of a histidine compound for removing minerals from hair and for conditioning hair.
3. Use according to claim 2, wherein the composition further comprises a gel matrix comprising:
  - i. from 0.1% to 20% of one or more high melting point fatty compounds, by weight of said hair care composition;
  - ii. from 0.1% to 10% a cationic surfactant system of , by weight of said hair care composition; and
  - iii. at least 20% of an aqueous carrier, by weight of said hair care composition.
4. Use according to any of claim 2 or 3, wherein the composition comprises from 0.05% to 0.25% of the histidine compound, by weight of the composition.
5. Use according to any of claims 2 to 4, wherein the composition comprises from 0.08% to 0.15% of the histidine, by weight of the composition.
6. Use according to any of claims 2 to 5, wherein the composition comprises from 0.10% to 0.15% of the histidine, by weight of the composition.
7. Use according to any of claims 2 to 6, wherein the composition further comprises one or more additional conditioning agents.
8. Use according to claim 7, wherein the one or more additional conditioning agents is a silicone.
9. Use according to any of claims 2 to 8, wherein the composition further comprises one or more additional benefit agents.
10. Use according to claim 9, wherein the one or more additional benefit agents is selected from the group consisting of anti-dandruff agents, vitamins, chelants, perfumes, brighteners, enzymes, sensates, attractants, anti-bacterial agents, dyes, pigments, bleaches, and mixtures thereof.

FIGURE 1

Conditioner Chassis	EDDS level	Observation
Comparative Ex. 1	0.2%	Phase separation
Comparative Ex. 2	0.2%	 <p>Solid bits were observed upon addition (Phase separation)</p>
Comparative Ex. 3	0.2%	Viscosity increased by 60Pa at shear stress 950



## INTERNATIONAL SEARCH REPORT

International application No

PCT/US2014/037068

A. CLASSIFICATION OF SUBJECT MATTER  
 INV. A61K8/34 A61K8/41 A61K8/49 A61Q5/12  
 ADD.

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

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

A61K A61Q

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

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

EPO-Internal , WPI Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5 635 167 A (SAID HAYEL [US] ET AL) 3 June 1997 (1997-06-03) claim 1 page 4, line 64 - page 5, line 51 -----	1-10
Y	US 5 158 684 A (MOULTON ROGER D [US] ET AL) 27 October 1992 (1992-10-27) column 3, line 47 - line 54 tables I, II column 6, line 47 - line 62 -----	1-10
Y	FR 2 853 531 A1 (SEPHYTAL [FR]) 15 October 2004 (2004-10-15) example 1 ----- -/- .	1-10



Further documents are listed in the continuation of Box C.



See patent family annex.

\* Special categories of cited documents :

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

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

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

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

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

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

Date of the actual completion of the international search

20 October 2014

Date of mailing of the international search report

28/10/2014

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2  
 NL - 2280 HV Rijswijk  
 Tel. (+31-70) 340-2040,  
 Fax: (+31-70) 340-3016

Authorized officer

Bri and, Benoit

## INTERNATIONAL SEARCH REPORT

International application No

PCT/US2014/037068

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	wo 00/51555 AI (PROCTER & GAMBLE [US] ; TOOLE EDEL 0 [GB] ; SCHOFIELD STEPHEN ROBERT [GB] 8 September 2000 (2000-09-08) page 2, line 4 - line 10 example III -----	1-10
A	wo 93/11737 AI (VITACHLOR CORP [US] ) 24 June 1993 (1993-06-24) claims 1, 3 -----	1-10

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Information on patent family members

International application No

PCT/US2014/037068

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