Title: HAIR CONDITIONING COMPOSITIONS

Abstract

Disclosed is a hair conditioning composition comprising by weight: (1) at least about 3 % of a high melting point compound having a melting point of at least about 25 °C; (2) an emulsifying agent selected from the group consisting of amines, betaines, nonionic compounds, and mixtures thereof; (3) a quaternary compound; and (4) an aqueous carrier, wherein the composition shows a DSC profile having substantially no peaks larger than about 3 mJ/mg from about 40 °C to about 65 °C.
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HAIR CONDITIONING COMPOSITIONS

TECHNICAL FIELD

The present invention relates to hair conditioning compositions having a layered gel structure. The present invention further relates to a method of making hair conditioning compositions having a layered gel structure.

BACKGROUND

Human hair becomes soiled due to its contact with the surrounding environment and from sebum secreted from the scalp. The soiling of the hair causes it to have a dirty or greasy feel, and an unattractive appearance. The soiling of the hair necessitates shampooing with regularity.

Shampooing cleans the hair by removing excess soil and sebum. However, shampooing can leave the hair in a wet, tangled, and generally unmanageable state. Once the hair dries, it is often left in a dry, rough, lusterless, or frizzy condition due to removal of the hair's natural oils and other natural conditioning and moisturizing components. The hair can further be left with increased levels of static upon drying which can interfere with combing and result in a condition commonly referred to as "fly-away hair", or contribute to an undesirable phenomena of "split ends", particularly for long hair.

A variety of approaches have been developed to alleviate these after-shampoo problems. These approaches range from post-shampoo application of hair conditioner such as leave-on and rinse-off products, to hair conditioning shampoos which attempt to both cleanse and condition the hair from a single product. Although some consumers prefer the ease and convenience of a shampoo which includes conditioners, a substantial proportion of consumers prefer the more conventional conditioner formulations which are applied to the hair as a separate step from shampooing, usually subsequent to shampooing. Conditioning formulation can be in the form of rinse-off products or leave-on products, and can be in the form of an emulsion, cream, gel, spray, or mousse.
Such consumers who prefer the conventional conditioner formulations value the relatively higher conditioning effect, or convenience of changing the amount of conditioning depending on the condition of hair or portion of hair.

Hair conditioning compositions have conventionally been based on the combination of a cationic surfactant, which is generally a quaternary ammonium compound, in combination with various conditioning agents such as polymers, silicone conditioning agents, hydrocarbon and other organic oils, and high melting point compounds such as fatty alcohols. It is known that the combination of a cationic surfactant and a fatty alcohol generally provides a thick, creamy texture which is favorable to some consumers. However, when used at increased levels, fatty alcohols may crystallize and isolate from the matrix of the conditioning composition. Consequently, the increased level of fatty alcohols may not completely contribute toward providing conditioning benefits. Certain phase structures for the combination of quaternary ammonium compounds and fatty alcohol compounds have been suggested in the art such as in Japanese Kokai Patent Publication (A) S61-286311. Yet, these compositions are not capable of delivering satisfactory conditioning benefit both when the hair is wet and also after it has dried.

Based on the foregoing, there remains a desire to provide hair conditioning compositions containing an increased level of high melting point compounds wherein the increased level of high melting point compounds can contribute effectively toward providing conditioning benefits. There is also a desire to provide hair conditioning compositions which provide hair conditioning compositions which can provide improved conditioning benefits such as smoothness, softness, and ease of combing, both when the hair is wet and also after it has dried. There is further a desire to provide such hair conditioning compositions by a convenient method.

None of the existing art provides all of the advantages and benefits of the present invention.

**SUMMARY**

The present invention is directed to a hair conditioning composition comprising by weight:

(1) at least about 3% of a high melting point compound having a melting point of at least about 25°C;
(2) an emulsifying agent selected from the group consisting of amines, betaines, nonionic compounds, and mixtures thereof;

(3) a quaternary compound; and

(4) an aqueous carrier;

wherein the composition shows a DSC profile having substantially no peaks larger than about 3mJ/mg from about 40°C to about 65°C.

The present invention is also directed to a suitable method of making the hair conditioning composition.

These and other features, aspects, and advantages of the present invention will become evident to those skilled in the art from a reading of the present disclosure.

BRIEF DESCRIPTION OF THE DRAWINGS

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 of preferred embodiments taken in conjunction with the accompanying drawings, in which Fig. 1 is a profile chart obtained by DSC (differential scanning calorimetry) measurement of a preferred embodiment composition of the present invention.

DETAILED DESCRIPTION

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

All cited references are incorporated herein by reference in their entireties. Citation of any reference is not an admission regarding any determination as to its availability as prior art to the claimed invention.

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.
The aspects and embodiments of the present invention set forth in this document have many advantages. For example, the hair conditioning compositions of the present invention provide improved conditioning benefits such as smoothness, softness, and ease of combing, both when the hair is wet and also after it has dried. The hair conditioning compositions of the present invention are suitable for product forms to leave on the hair, or rinse off from the hair.

**LAYERED GEL STRUCTURE**

The hair conditioning compositions herein are those which have a layered gel structure, the layered gel structure made by a high melting point compound and a quaternary compound. The existence of a layered gel structure can be detected by differential scanning calorimetry (hereinafter referred to as "DSC") measurement of the composition. A profile chart obtained by DSC measurement describes chemical and physical changes of the scanned sample that involve an enthalpy change or energy gradient when the temperature of the sample is fluctuated. As such, the phase behavior and interaction among components of hair conditioning compositions of the present invention can be understood by their DSC profiles. DSC measurement of compositions of the present invention can be conducted by any suitable instrument available. For example, DSC measurement can be suitably conducted by Seiko DSC 6000 instrument available from Seiko Instruments Inc. In a typical measurement procedure, a sample is prepared by sealing an appropriate amount of the composition into a container made for DSC measurement and sealed. The weight of the sample is recorded. A blank sample i.e; an unsealed sample of the same container is also prepared. The sample and blank sample are placed inside the instrument, and run under a measurement condition of from about -50°C to about 130°C at a heating rate of from about 1°C/minute to about 10°C/minute. The area of the peaks as identified are calculated and divided by the weight of the sample to obtain the enthalpy change represented by unit, mJ/mg.

When the compositions comprising the essential components of the present invention form a layered gel structure, the DSC profile shows substantially no peaks larger than about 3 mJ/mg from about 40°C to about 65°C. The position of the peaks are identified by the peak top position. Fig. 1 is a profile chart obtained by such DSC measurement of 12.04mg of the composition of Example 1 as specified later herein. The DSC profile of this
composition shows the only peak having a peak top temperature of 69.1°C, which peak is 7.9mJ/mg. The DSC profile of this composition further shows no peaks larger than 3mJ/mg from 40°C to 65°C. It is believed that a composition formed predominantly with a layered gel structure shows a relatively stable phase behavior during the temperature range of from about 40°C to about 65°C.

A layered gel structure can be distinguished from spherical crystalline phase structures. By definition, spherical crystalline phase structures include, for example, phases encompassing solid crystals at random, the M-phase structure as defined in pages 83 to 84 of “Physicochemistry of Cetyl Alcohol” issued by Fragrance Journal Ltd. 1992, and onion-like spherical layers of liquid crystals as taught in Japanese Kokai Patent Publication (A) S61-286311.

As taught in the references cited above, spherical crystalline phase structures encompass either crystals or lamellar liquid crystals. Such crystals or lamellar liquid crystals are believed to be made solely by a high melting point compound, or by a combination of a high melting point compound and a quaternary compound. It is believed that the DSC profile of a composition formed predominantly with spherical crystalline phase structures shows alteration of phase, i.e; non-stable phase behaviour due to the crystals and/or liquid crystals during the temperature range of from about 40°C to about 65°C.

The difference of a layered gel structure and spherical crystalline phase structures can also be identified by the cyro scanning electron micrographs (hereinafter referred to as “SEM”) of the compositions. A layered gel structure shows flexible layers, the layers being linear, curved, or waved, but not spherical. In contrast, the spherical crystalline phase structures either do not show any systematic patterns, or show onion-like spherical layers.

The hair conditioning compositions of the present invention which have a layered gel structure are believed to provide improved conditioning benefits over the same composition which do not have a layered gel structure. Without being bound by theory, it is believed that the solid crystals and/or liquid crystals of high melting point compounds contained in spherical crystalline phase structures cannot be effectively spread onto and deposited on the surface of the hair. Consequently, the high melting point compounds incorporated in spherical crystalline phase structures contribute less than those incorporated in a layered gel structure with regard to providing conditioning benefit to the hair.
HIGH MELTING POINT COMPOUNDS

The hair conditioning composition of the present invention comprises by weight at least about 3%, preferably from about 3% to about 10%, more preferably from about 4.5% to about 8% of a high melting point compound. The high melting point compound herein has a melting point of at least about 25°C and is selected from the group consisting of fatty alcohols, fatty acids, fatty alchol derivatives, fatty acid derivatives, hydrocarbons, steroids, and mixtures thereof. The high melting point compound, together with the quaternary compound, make the layered gel structure.

Without being bound by theory, it is believed that these high melting point compounds cover the hair surface and reduce friction, thereby resulting in providing smooth feel on the hair and ease of combing. 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 required carbon atoms may have a melting point of less than about 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.

The fatty alcohols useful herein are those having from about 14 to about 30 carbon atoms, preferably from about 16 to about 22 carbon atoms. These fatty alcohols can be straight or branched chain alcohols and can be saturated or unsaturated. Nonlimiting examples of fatty alcohols include, cetyl alcohol, stearyl alcohol, behenyl alcohol, and mixtures thereof.

The fatty acids useful herein are those having from about 10 to about 30 carbon atoms, preferably from about 12 to about 22 carbon atoms, and more preferably from about 16 to about 22 carbon atoms. These fatty acids can be straight or branched chain acids and can be saturated or unsaturated. Also included are diacids, triacids, and other multiple acids which meet the requirements herein. Also included herein are salts of these fatty acids.
Nonlimiting examples of fatty acids include lauric acid, palmitic acid, stearic acid, behenic acid, sebacic acid, and mixtures thereof.

The fatty alcohol derivatives and fatty acid derivatives useful herein include alkyl ethers of fatty alcohols, alkoxylated fatty alcohols, alkyl ethers of alkoxylated fatty alcohols, esters of fatty alcohols, fatty acid esters of compounds having esterifiable hydroxy groups, hydroxy-substituted fatty acids, and mixtures thereof. Nonlimiting examples of fatty alcohol derivatives and fatty acid derivatives include materials such as methyl stearyl ether; the ceteth series of compounds such as ceteth-1 through ceteth-45, which are ethylene glycol ethers of cetyl alcohol, wherein the numeric designation indicates the number of ethylene glycol moieties present; the steareth series of compounds such as steareth-1 through 10, which are ethylene glycol ethers of steareth alcohol, wherein the numeric designation indicates the number of ethylene glycol moieties present; ceteareth 1 through ceteareth-10, which are the ethylene glycol ethers of ceteareth alcohol, i.e. a mixture of fatty alcohols containing predominantly cetyl and stearyl alcohol, wherein the numeric designation indicates the number of ethylene glycol moieties present; C₁₋₃₀ alkyl ethers of the ceteth, steareth, and ceteareth compounds just described; polyoxyethylene ethers of behenyl alcohol; ethyl stearate, cetyl stearate, cetyl palmitate, stearyl stearate, myristyl myristate, polyoxyethylene cetyl ether stearate, polyoxyethylene stearyl ether stearate, polyoxyethylene lauryl ether stearate, ethyleneglycol monostearate, polyoxyethylene monostearate, polyoxyethylene distearate, propyleneglycol monostearate, propyleneglycol distearate, trimethylolpropane distearate, sorbitan stearate, polyglyceryl stearate, glyceryl monostearate, glyceryl distearate, glyceryl tristearate, and mixtures thereof.

Hydrocarbons useful herein include compounds having at least about 20 carbons.

Steroids useful herein include compounds such as cholesterol.

High melting point compounds of a single compound of high purity are preferred. Single compounds of pure fatty alcohols selected from the group of pure cetyl alcohol, stearyl alcohol, and behenyl alcohol are highly preferred. By "pure" herein, what is meant is that the compound has a purity of at least about 90%, preferably at least about 95%. These single compounds of high purity provide good rinsability from the hair when the consumer rinses off the composition.
Commercially available high melting point compounds useful herein include: cetyl alcohol, stearyl alcohol, and behenyl alcohol having tradenames KONOL series available from Shin Nihon Rika (Osaka, Japan), and NAA series available from NOF (Tokyo, Japan); pure behenyl alcohol having tradename 1-DOCASANOL available from WAKO (Osaka, Japan), various fatty acids having tradenames NEO-FAT available from Akzo (Chicago Illinois, USA), HYSTRENRE available from Witco Corp. (Dublin Ohio, USA), and DERMA available from Vevy (Genova, Italy); and cholesterol having tradename NIKKOL AGUASOME LA available from Nikko.

EMULSIFYING AGENT

The hair conditioning composition of the present invention comprises an emulsifying agent selected from the group consisting of amines, betaines, nonionic compounds, and mixtures thereof. The emulsifying agent herein help provide a layered gel structure to the composition. The emulsifying agent is comprised at a level of preferably from about 0.5% to about 5%, more preferably from about 1% to about 3% by weight of the composition.

Amines

Amines are suitable as emulsifying agents. 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, stearamidoethylidihyamine, stearamidoethyldimethylamine, palmitamidopropylidihyamine, palmitamidoethyldimethylamine, behenamidopropylidihyamine, behenamidoethylidihyamine, arachidamidopropylidihyamine, arachidamidoethylidihyamine, arachidamidoethyldimethylamine, diethylaminoethylstearamide. Also useful are dimethylstearamine, dimethylsoyamine, soyamine, myristylamine, tridecylamine, ethylestearylamine, N-tallowpropane diamine, ethoxylated (with 5 moles of ethylene oxide) stearylamine, dihydroxyethylstearylamine, and arachidylbehenylamine. 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 l-
glutamic acid, lactic acid, hydrochloric acid, malic acid, succinic acid, acetic acid, fumaric acid, tartaric acid, citric acid, \(\ell\)-glutamic acid, maleic acid, and mixtures thereof; more preferably \(\ell\)-glutamic acid, lactic acid, citric acid. The amines herein are preferably 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, more preferably from about 1 : 0.4 to about 1 : 1.

Betaines

Betaines are suitable as emulsifying agents. Betaines useful herein may have some surfactant properties, but are generally too low to provide good cleaning properties.

Betaines useful herein are those having the following two formulae:

\[
\begin{align*}
R^69 & \quad \text{O} \quad R^{68} \\
R^{67} & \quad \text{C} \quad \text{N} \quad \text{(CH}_2\text{)}_{x} \quad \text{Y} \\
R^66 & \quad \text{N} \quad \text{Y} \quad R^{65}
\end{align*}
\]

wherein: \(R^{65}\) is COO- or CH(OH)CH\(_2\)SO\(_3\)-, preferably COO-; \(R^{66}\) and \(R^{67}\), independently, are hydrogen, alkyl of 1 to about 4 carbons, CH\(_2\)COO\(^-\), CH\(_2\)CH\(_2\)OH, CH\(_2\)CH\(_2\)OCH\(_2\)CH\(_2\)COO\(^-\), or (CH\(_2\)CH\(_2\)O\(_x\))H \(x\) is an integer from 1 to about 25, preferably methyl or ethyl; \(R^{68}\) is hydrogen or alkyl of 1 to about 4 carbons, preferably hydrogen; \(R^{69}\) is a straight or branched, saturated or unsaturated alkyl of about 16 to about 30 carbon atoms, preferably a straight saturated or unsaturated alkyl of about 16 to about 22 carbon atoms; \(Y\) is an alkyl of 1 to about 4 carbons, preferably methyl; \(m\) is an integer from 1 to about 7, preferably from 1 to about 4; \(n\) is 1 or 0; and \(\text{Y}^+\) is hydrogen or an alkali metal, alkaline earth metal, or ammonium; and

\[
\begin{align*}
\left(\frac{R^{58}}{R^{57}}\right)^x \\
R^{57} & \quad \text{Y} \quad \text{CH}_{2} \quad R^{59} \quad Z
\end{align*}
\]

wherein \(R^{57}\) is a saturated or unsaturated alkyl, alkenyl, or hydroxy alkyl of from about 16 to about 30 carbon atoms, preferably a saturated or unsaturated alkyl of about 16 to about 22 carbon atoms; \(Y\) is nitrogen, phosphorus or sulfur atom; \(R^{58}\) is an alkyl or monohydroxyalkyl group containing 1 to about 4 carbon atoms; \(p\) is 1 when \(Y\) is a sulfur atom, and 2 when \(Y\) is a nitrogen or phosphorus atom; \(R^{59}\) is an alkylene or hydroxyalkylene of from 1 to about 4 carbon atoms; \(Z\) is a
carboxylate, sulfonate, sulfate, phosphonate, or phosphate; and is as previously defined.

Examples of betaines useful herein include: alkylbetaines such as cetyltrimethylcarboxymethylbetaine, stearyldimethylcarboxymethylbetaine, isostearyldimethylcarboxymethylbetaine, behenyltrimethylcarboxymethylbetaine, oleyldimethylcarboxymethylbetaine, stearyl-bis-(2-hydroxypropyl) carboxymethylbetaine, oleyldimethyl-\(\gamma\)-carboxypropylbetaine, and stearylidi hydroxyethylbetaine; amido betaines such as cetylaminodimethylcarboxymethyl betaine, isostearamidopropyl betaine, isostearylamidodimethylcarboxymethyl betaine, and stearylaminodimethylcarboxypropyl betaine; amidosulfobetaines such as stearylaminodimethylsulfopropylbetaine; sulfobetaines such as stearylidi methylsulfopropylbetaine; sultaines such as stearylidi methylpropylsultaine; and amidosultaines. Commercially available material highly suitable for use herein include stearyl betaine with tradename Rikabion A-700 available from Shin Nihon Rika, oleyl dimethyl betaine with tradename Rikabion A-300 available from Shin Nihon Rika, and stearyl dihydroxyethyl betaine with tradename Anon AB 202 available from Nihon Oil & Fats.

20 Nonionic Compounds

Nonionic compounds are suitable as emulsifying agents. Nonionic compounds useful herein include those compounds produced by condensation of alkylene oxide groups, hydrophilic in nature, with an organic hydrophobic compound, which may be aliphatic or alkyl aromatic in nature. Although nonionic compounds herein may have some surfactant properties, they are generally too low to provide good cleaning properties.

Preferred nonlimiting examples of nonionic compounds herein include the following:

(1) polyethylene oxide condensates of alkyl phenols, e.g., the condensation products of alkyl phenols having an alkyl group containing from about 16 to about 30 carbon atoms in either a straight chain or branched chain configuration, with ethylene oxide, the said ethylene oxide being present in amounts equal to from about 2 to about 60 moles of ethylene oxide per mole of alkyl phenol;
(2) those derived from the condensation of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylene diamine products;

(3) condensation products of aliphatic alcohols having from about 16 to about 30 carbon atoms, in either straight chain or branched chain configurations, with ethylene oxide, e.g., a stearyl alcohol ethylene oxide condensate having from about 2 to about 30 moles of ethylene oxide per mole of stearyl alcohol;

(4) long chain tertiary amine oxides of the formula \([R^{70}\rightarrow R^{71}R^{72}N \rightarrow O]\) where \(R^{70}\) contains an alkyl, alkenyl or monohydroxy alkyl radical of from about 16 to about 30 carbon atoms, from 0 to about 10 ethylene oxide moieties, and from 0 to about 1 glyceryl moiety, and \(R^{71}\) and \(R^{72}\) contain from about 1 to about 3 carbon atoms and from 0 to about 1 hydroxy group, e.g., methyl, ethyl, propyl, hydroxyethyl, or hydroxypropyl radicals;

(5) long chain tertiary phosphine oxides of the formula \([R^{73}R^{74}\rightarrow R^{75}P \rightarrow O]\) where \(R^{73}\) contains an alkyl, alkenyl or monohydroxyalkyl radical ranging from about 16 to about 30 carbon atoms in chain length, from 0 to about 10 ethylene oxide moieties and from 0 to 1 glyceryl moieties and \(R^{74}\) and \(R^{75}\) are each alkyl or monohydroxyalkyl groups containing from about 1 to about 3 carbon atoms;

(6) long chain dialkyl sulfoxides containing one short chain alkyl or hydroxy alkyl radical of from 1 to about 3 carbon atoms (usually methyl) and one long hydrophobic chain which include alkyl, alkenyl, hydroxy alkyl, or keto alkyl radicals containing from about 16 to about 30 carbon atoms, from 0 to about 10 ethylene oxide moieties and from 0 to 1 glyceryl moieties;

(7) alkyl polysaccharide (APS) surfactants (e.g. alkyl polyglycosides), examples of which are described in U.S. Patent 4,565,647, which discloses APS surfactants having a hydrophobic group with about 8 to about 30 carbon atoms and a polysaccharide (e.g., polyglycoside) as the hydrophilic group; optionally, there can be a polyalkylene-oxide group joining the hydrophobic and hydrophilic moieties; and the alkyl group (i.e., the hydrophobic moiety) can be saturated or unsaturated, branched or unbranched, and unsubstituted or substituted (e.g., with hydroxy or cyclic rings); a preferred material is alkyl polyglucoside which is commercially available from Henkel, ICI Americas, and Seppic; and

(8) polyoxymethylene alkyl ethers such as those of the formula \(R^{76}O(CH_2CH_2)_xH\) and polyethylene glycol (PEG) glyceryl fatty esters, such as those of the formula \(R^{76}(O)OCH_2CH(OH)CH_2(OCH_2CH_2)_xOH\), wherein \(x\) is from
1 to about 200, preferably from about 20 to about 100, and \( R^{76} \) is an alkyl having from about 16 to about 30 carbon atoms.

**QUATERNARY COMPOUND**

The hair conditioning composition of the present invention comprises a quaternary compound. The quaternary compound, together with the high melting point compound, make the layered gel structure. The quaternary compound is comprised at a level of preferably from about 0.5% to about 5%, more preferably from about 1% to about 3% by weight of the composition.

Among the quaternary compounds useful herein are those corresponding to the general formula (I):

\[
\begin{array}{c}
\text{R}^{101} \\
\text{R}^{102} \\
\text{N} \\ \\
\text{R}^{103} \\
\text{X} \\
\text{R}^{104}
\end{array}
\]

wherein at least one of \( R^{101}, R^{102}, R^{103} \) and \( R^{104} \) is selected from an aliphatic group of from 8 to 30 carbon atoms or an aromatic, alkoxy, polyoxalkylene, alkylamido, hydroxyalkyl, aryl or alkylaryl group having up to about 22 carbon atoms, the remainder of \( R^{101}, R^{102}, R^{103} \) and \( R^{104} \) are independently selected from an aliphatic group of from 1 to about 22 carbon atoms or an aromatic, alkoxy, polyoxalkylene, alkylamido, hydroxyalkyl, aryl or alkylaryl group having up to about 22 carbon atoms; and \( X \) 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 aliphatic groups can contain, in addition to carbon and hydrogen atoms, ether linkages, and other groups such as amino groups. The longer chain aliphatic groups, e.g., those of about 12 carbons, or higher, can be saturated or unsaturated. Preferred is when \( R^{101}, R^{102}, R^{103} \) and \( R^{104} \) are independently selected from \( \text{C}_1 \) to about \( \text{C}_{22} \) alkyl. Nonlimiting examples of quaternary compounds useful in the present invention include the materials having the following CTFA designations: quaternium-8, quaternium-14, quaternium-18, quaternium-18 methosulfate, quaternium-24, and mixtures thereof.

Among the quaternary compounds of general formula (I), preferred are those containing in the molecule at least one alkyl chain having at least 16 carbons. Nonlimiting examples of such preferred quaternary compounds include: behenyl trimethyl ammonium chloride available, for example, with tradename INCROQUAT TMC-80 from Croda and ECONOL TM22 from Sanyo...
Kasei; cetyl trimethyl ammonium chloride available, for example, with tradename CA-2350 from Nikko Chemicals, hydrogenated tallow alkyl trimethyl ammonium chloride, dialkyl (14-18) dimethyl ammonium chloride, ditallow alkyl dimethyl ammonium chloride, dihydrogenated tallow alkyl dimethyl ammonium chloride, distearyl dimethyl ammonium chloride, dicetyl dimethyl ammonium chloride, di(beheny/lanarachidyl) dimethyl ammonium chloride, dibehenyl dimethyl ammonium chloride, stearyl dimethyl benzyl ammonium chloride, stearyl propylene glycol phosphate dimethyl ammonium chloride, stearyl amido propyl dimethyl benzyl ammonium chloride, stearyl amido propyl dimethyl (myristylacetate) ammonium chloride, and N-(stearyl colamino formyl methy) pyridinium chloride.

Also preferred as quaternary compounds are hydrophilically substituted cationic surfactants in which at least one of the substituents contain one or more aromatic, ether, ester, amido, or amino moieties present as substituents or as linkages in the radical chain, wherein at least one of the $R^{101}$-$R^{104}$ radicals contain one or more hydrophilic moieties selected from alkoxy (preferably C$_1$-C$_3$ alkoxy), polyoxyalkylene (preferably C$_1$-C$_3$ polyoxyalkylene), alkylamido, hydroxylalkyl, alkylester, and combinations thereof. Preferably, the hydrophilically substituted cationic surfactant contains from 2 to about 10 nonionic hydrophilic moieties located within the above stated ranges. Preferred hydrophilically substituted cationic surfactants include those of the formula (II) through (VIII) below:

$$
\begin{align*}
\text{CH}_3(\text{CH}_2)_n^1 \text{CH}_2 \quad &\quad N^+((\text{CH}_2\text{CH}_2\text{O})_{m^1}^1\text{H}) \quad X^- \\
&\quad (\text{CH}_2\text{CH}_2\text{O})_{m^2}^1 \text{H} \\
\end{align*}
$$

(II)

wherein $n^1$ is from 8 to about 28, $m^1+m^2$ is from 2 to about 40, $Z^1$ is a short chain alkyl, preferably a C$_1$-C$_3$ alkyl, more preferably methyl, or $(\text{CH}_2\text{CH}_2\text{O})_{m^3}^1\text{H}$ wherein $m^1+m^2+m^3$ is up to 60, and $X$ is a salt forming anion as defined above;

$$
\begin{align*}
\text{R}^{106} \quad &\quad R^{108} \\
R^{105} N^+((\text{CH}_2)_n^2 \quad N^+ R^{109} \quad 2X^- \\
&\quad R^{107} \quad R^{110} \\
\end{align*}
$$

(III)

wherein $n^2$ is 1 to 5, one or more of $R^{105}$, $R^{106}$, and $R^{107}$ are independently an C$_1$-C$_30$ alkyl, the remainder are CH$_2$CH$_2$OH, one or two of $R^{108}$, $R^{109}$, and $R^{110}$ are
independently an C₁⁻C₃₀ alkyl, and remainder are CH₂CH₂OH, and X is a salt forming anion as mentioned above;

\[
\begin{array}{c}
\text{IV} \\
R\text{—N}^+\text{—(CH₂)ₙ}_³\text{—N}^+\text{—(CH₂)ₜ}_⁴\text{—C—R}^{112} \\
\text{X}^-
\end{array}
\]

\[
\begin{array}{c}
\text{V} \\
R\text{—O—(CH₂)ₙ}_³\text{—N}^+\text{—(CH₂)ₜ}_⁴\text{—O—C—R}^{112} \\
\text{X}^-
\end{array}
\]

wherein, independently for formulae (IV) and (V), Z² is an alkyl, preferably C₁⁻C₃ alkyl, more preferably methyl, and Z³ is a short chain hydroxyalkyl, preferably hydroxymethyl or hydroxyethyl, n³ and n⁴ independently are integers from 2 to 4, inclusive, preferably from 2 to 3, inclusive, more preferably from 2, R⁹ and R¹², independently, are substituted or unsubstituted hydrocarbys, C₁₂⁻C₂₀ alkyl or alkenyl, and X is a salt forming anion as defined above;

\[
\begin{array}{c}
\text{VI} \\
R\text{—N}^+\text{—(CH₂CHO)}_{m⁵}H \\
\text{X}^-
\end{array}
\]

wherein R¹¹ is a hydrocarbyl, preferably a C₁⁻C₃ alkyl, more preferably methyl, Z⁴ and Z⁵ are, independently, short chain hydrocarbys, preferably C₂⁻C₄ alkyl or alkenyl, more preferably ethyl, m⁵ is from 2 to about 40, preferably from about 7 to about 30, and X is a salt forming anion as defined above;

\[
\begin{array}{c}
\text{VII} \\
R\text{—OH} \\
\text{X}^-
\end{array}
\]

wherein R¹¹ and R¹₅, independently, are C₁⁻C₃ alkyl, preferably methyl, Z⁵ is a C₁₂⁻C₂₂ hydrocarbyl, alkyl carboxy or alkylamido, and A is a protein, preferably a collagen, keratin, milk protein, silk, soy protein, wheat protein, or hydrolyzed forms thereof; and X is a salt forming anion as defined above;

\[
\begin{array}{c}
\text{VIII} \\
\text{X}^-
\end{array}
\]
wherein \( n^5 \) is 2 or 3, \( R^{16} \) and \( R^{17} \), independently are C\(_1\)-C\(_3\) hydrocarbys preferably methyl, and X is a salt forming anion as defined above. Nonlimiting examples of hydrophilically substituted cationic surfactants useful in the present invention include the materials having the following CTFA designations: quaternium-16, quaternium-26, quaternium-27, quaternium-30, quaternium-33, quaternium-43, quaternium-52, quaternium-53, quaternium-56, quaternium-60, quaternium-61, quaternium-62, quaternium-70, quaternium-71, quaternium-72, quaternium-75, quaternium-76 hydrolyzed collagen, quaternium-77, quaternium-78, quaternium-79 hydrolyzed collagen, quaternium-79 hydrolyzed keratin, quaternium-79 hydrolyzed milk protein, quaternium-79 hydrolyzed silk, quaternium-79 hydrolyzed soy protein, and quaternium-79 hydrolyzed wheat protein, quaternium-80, quaternium-81, quaternium-82, quaternium-83, quaternium-84, and mixtures thereof.

Highly preferred hydrophilically substituted cationic surfactants include dialkylamidio ethyl hydroxyethylmonium salt, dialkylamidoethyl dimonium salt, dialkyloyl ethyl hydroxyethylmonium salt, dialkyloyl ethylidimonium salt, and mixtures thereof; for example, commercially available under the following tradenames; VARISOFT 110, VARISOFT 222, VARIQUAT K1215 and VARIQUAT 638 from Witco Chemical, MACKPRO KLP, MACKPRO WLW, MACKPRO MLP, MACKPRO NSP, MACKPRO NLW, MACKPRO WWP, MACKPRO NLP, MACKPRO SLP from McIntyre, ETHOQUAD 18/25, ETHOQUAD O/12PG, ETHOQUAD C/25, ETHOQUAD S/25, and ETHODOUQUAD from Akzo, DEHYQUAT SP from Henkel, and ATLAS G265 from ICI Americas.

**AQUEOUS CARRIER**

The compositions of the present invention comprise an aqueous carrier wherein water is contained at a level of at least about 70% by weight of the composition. The level and species of the carrier are selected according to the compatibility with other components, and other desired characteristic of the product.

Carriers useful in the present invention include water and water solutions of lower alkyl alcohols and polyhydric alcohols. Lower alkyl alcohols useful herein are monohydric alcohols having 1 to 6 carbons, more preferably ethanol and isopropanol. The polyhydric alcohols useful herein include propylene glycol, hexylene glycol, glycerin, and propane diol.
Preferably, the aqueous carrier is substantially water. Deionized water is preferably used. Water from natural sources including mineral cations can also be used, depending on the desired characteristic of the product. The compositions of the present invention comprise at least about 70%, preferably at least about 80% water.

HIGH MOLECULAR WEIGHT ESTER OIL

The compositions of the present invention may further comprise a high molecular weight ester oil selected from the group consisting of pentaerythritol ester oils, trimethylol ester oils, poly α-olefin oils, citrate ester oils, glyceryl ester oils, and mixtures thereof. The high molecular weight ester oils useful herein are those which are water-insoluble, and are in liquid form at 25°C. As used herein, the term “water-insoluble” means the compound is substantially not soluble in water at 25°C; when the compound is mixed with water at a concentration by weight of above 1.0%, preferably at above 0.5%, the compound is temporarily dispersed to form an unstable colloid in water, then is quickly separated from water into two phases.

The high molecular weight ester oil herein provides moisturized feel, smooth feel, and manageability control to the hair when the hair is dried, yet not leave the hair feeling greasy. Thus, with the addition of the high molecular weight ester oil, obtained is a composition that can provide particularly suitable conditioning benefits both when the hair is wet and also after it has dried. The high molecular weight ester oil may be comprised at a level of preferably from about 0.2% to about 10%, more preferably from about 0.5% to about 5% by weight of the composition.

Pentaerythritol ester oils useful herein are those of the following formula having a molecular weight of at least 800:

\[
\begin{align*}
&\text{CH}_2\text{O} - \text{C} - \text{R}^2 \\
&\text{R}^1\text{C} - \text{OCH}_2 - \text{C} - \text{CH}_2\text{O} - \text{C} - \text{R}^3 \\
&\text{CH}_2\text{O} - \text{C} - \text{R}^4
\end{align*}
\]

wherein R¹, R², R³, and R⁴, independently, are branched, straight, saturated, or unsaturated alkyl, aryl, and alkylaryl groups having from 1 to about 30 carbons. Preferably, R¹, R², R³, and R⁴, independently, are branched, straight, saturated, or unsaturated alkyl groups having from about 8 to about 22 carbons. More
preferably, \( R^1, R^2, R^3 \) and \( R^4 \) are defined so that the molecular weight of the compound is from about 800 to about 1200.

Trimethylol ester oils useful herein are those of the following formula having a molecular weight of at least 800:

\[
\begin{align*}
R^{11} & \quad \text{CH}_2O - C - R^{12} \\
R^{11} & \quad \text{CH}_2 - \text{CH}_2O - C - R^{13} \\
\text{CH}_2O & \quad \text{C} - R^{14}
\end{align*}
\]

wherein \( R^{11} \) is an alkyl group having from 1 to about 30 carbons, and \( R^{12}, R^{13}, \) and \( R^{14} \), independently, are branched, straight, saturated, or unsaturated alkyl, aryl, and alkylarylated groups having from 1 to about 30 carbons. Preferably, \( R^{11} \) is ethyl and \( R^{12}, R^{13}, \) and \( R^{14} \), independently, are branched, straight, saturated, or unsaturated alkyl groups having from 8 to about 22 carbons. More preferably, \( R^{11}, R^{12}, R^{13} \) and \( R^{14} \) are defined so that the molecular weight of the compound is from about 800 to about 1200.

Poly \( \alpha \)-olefin oils useful herein are those derived from 1-alkene monomers having from about 6 to about 16 carbons, preferably from about 6 to about 12 carbons atoms. Nonlimiting examples of 1-alkene monomers useful for preparing the poly \( \alpha \)-olefin oils include 1-hexene, 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, branched isomers such as 4-methyl-1-pentene, and mixtures thereof. Preferred 1-alkene monomers useful for preparing the poly \( \alpha \)-olefin oils are 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, and mixtures thereof. Poly \( \alpha \)-olefin oils useful herein further have a viscosity of from about 1 to about 35,000 cst, a molecular weight of from about 200 to about 60,000, and a polydispersity of no more than about 3.

Poly \( \alpha \)-olefin oils having a molecular weight of at least about 800 are useful herein. Such high molecular weight poly \( \alpha \)-olefin oils are believed to provide long lasting moisturized feel to the hair. Poly \( \alpha \)-olefin oils having a molecular weight of less than about 800 are useful herein. Such low molecular weight poly \( \alpha \)-olefin oils are believed to provide a smooth, light, clean feel to the hair.

Citrate ester oils useful herein are those having a molecular weight of at least about 500 having the following formula:
wherein \( R^{21} \) is OH or \( CH_3COO \), and \( R^{22}, R^{23}, \) and \( R^{24} \), independently, are branched, straight, saturated, or unsaturated alkyl, aryl, and alkylaryl groups having from 1 to about 30 carbons. Preferably, \( R^{21} \) is OH, and \( R^{22}, R^{23}, \) and \( R^{24} \), independently, are branched, straight, saturated, or unsaturated alkyl, aryl, and alkylaryl groups having from 8 to about 22 carbons. More preferably, \( R^{21}, R^{22}, R^{23}, \) and \( R^{24} \) are defined so that the molecular weight of the compound is at least about 800.

Glyceryl ester oils useful herein are those having a molecular weight of at least about 500 and having the following formula:

wherein \( R^{41}, R^{42}, \) and \( R^{43} \), independently, are branched, straight, saturated, or unsaturated alkyl, aryl, and alkylaryl groups having from 1 to about 30 carbons. Preferably, \( R^{41}, R^{42}, \) and \( R^{43} \), independently, are branched, straight, saturated, or unsaturated alkyl, aryl, and alkylaryl groups having from 8 to about 22 carbons. More preferably, \( R^{41}, R^{42}, \) and \( R^{43} \) are defined so that the molecular weight of the compound is at least about 800.

Particularly preferable high molecular weight ester oils are pentaester oils and trimethylol ester oils.

Particularly useful pentaerythritol ester oils and trimethylol ester oils herein include pentaerythritol tetraisostearate, pentaerythritol tetraoleate, trimethylolpropane triisostearate, trimethylolpropane trioleate, and mixtures thereof. Such compounds are available from Kokyo Alcohol with tradenames KAKPTI, KAKTTI, and Shin-nihon Rika with tradenames PTO, ENUJERUBU TP3SO.

Particularly useful poly \( \alpha \)-olefin oils herein include polydecenes with tradename PURESYN 6 having a molecular weight of about 500 and PURESYN
100 having a molecular weight of over 3000 available from Mobil Chemical Co.

Particularly useful citrate ester oils herein include trisocetyl citrate with tradename CITMOL 316 available from Bernel, triisostearyl citrate with tradename PELEMOL TISC available from Phoenix, and trioctyldodecyl citrate with tradename CITMOL 320 available from Bernel.

Particularly useful glyceryl ester oils herein include triisostearin with tradename SUN ESPOL G-318 available from Taiyo Kagaku, triolein with tradename CITHROL GTO available from Croda Surfactants Ltd., trilinolein with tradename EFADERMA-F available from Vevey, or tradename EFA-GLYCERIDES from Brooks.

**ADDITIONAL CONDITIONING AGENTS**

The compositions of the present invention may further comprise by weight from about 0.01% to about 20.0%, preferably from about 1.0% to about 15.0%, and more preferably from about 2.0% to about 10.0%, of additional conditioning agents. Suitable additional conditioning agents useful herein include additional oily compounds, cationic polymers, silicone compounds, and nonionic polymers.

**Additional Oily Compound**

Additional oily compounds useful herein include fatty alcohols and their derivatives, fatty acids and their derivatives, and hydrocarbons. The additional oily compounds useful herein may be volatile or nonvolatile, and have a melting point of not more than about 25°C. Without being bound by theory, it is believed that, the additional oily compounds may penetrate into the hair to modify the hydroxy bonds of the hair, thereby resulting in providing softness and flexibility to the hair. The additional oily compounds of this section are to be distinguished from the high melting point compounds described above. Nonlimiting examples of the additional oily compounds are found in International Cosmetic Ingredient Dictionary, Fifth Edition, 1993, and CTFA Cosmetic Ingredient Handbook, Second Edition, 1992.

The fatty alcohols useful herein include those having from about 10 to about 30 carbon atoms, preferably from about 12 to about 22 carbon atoms, and more preferably from about 16 to about 22 carbon atoms. These fatty alcohols can be straight or branched chain alcohols and can be saturated or unsaturated alcohols, preferably unsaturated alcohols. Nonlimiting examples of these compounds include oleyl alcohol, palmitoleic alcohol, isostearyl alcohol, isocetyl alcohol, undecanol, octyl dodecanol, octyl decanol, octyl alcohol, caprylic alcohol,
decyl alcohol and lauryl alcohol.

The fatty acids useful herein include those having from about 10 to about 30 carbon atoms, preferably from about 12 to about 22 carbon atoms, and more preferably from about 16 to about 22 carbon atoms. These fatty acids can be straight or branched chain acids and can be saturated or unsaturated. Suitable fatty acids include, for example, oleic acid, linoleic acid, isostearic acid, linolenic acid, ethyl linolenic acid, ethyl linolenic acid, arachidonic acid, and ricinolic acid.

The fatty acid derivatives and fatty alcohol derivatives are defined herein to include, for example, esters of fatty alcohols, alkoxyloated fatty alcohols, alkyl ethers of fatty alcohols, alkyl ethers of alkoxyloated fatty alcohols, and bulky ester oils such as pentaerythritol ester oils, trimethylol ester oils, citrate ester oils, glycercyl ester oils, and mixtures thereof. Nonlimiting examples of fatty acid derivatives and fatty alcohol derivatives include, for example, methyl linoleate, ethyl linoleate, isopropyl linoleate, isodecyl oleate, isopropyl oleate, ethyl oleate, octydodecyl oleate, oleyl oleate, decyl oleate, butyl oleate, methyl oleate, octydodecyl stearate, octydodecyl isostearate, octyl isopelargonate, octyl pelargonate, hexyl isostearate, isopropyl isostearate, isodecyl isononoate, isopropyl isostearate, ethyl isostearate, methyl isostearate and Olenth-2. Bulky ester oils such as pentaerythritol ester oils, trimethylol ester oils, citrate ester oils and glycercyl ester oils useful herein are those which have a molecular weight of less than about 800, preferably less than about 500.

The hydrocarbons useful herein include straight chain, cyclic, and branched chain hydrocarbons which can be either saturated or unsaturated, so long as they have a melting point of not more than about 25°C. These hydrocarbons have from about 12 to about 40 carbon atoms, preferably from about 12 to about 30 carbon atoms, and preferably from about 12 to about 22 carbon atoms. Also encompassed herein are polymeric hydrocarbons of alkenyl monomers, such as polymers of C2-8 alkenyl monomers. These polymers can be straight or branched chain polymers. The straight chain polymers will typically be relatively short in length, having a total number of carbon atoms as described above. The branched chain polymers can have substantially higher chain lengths. The number average molecular weight of such materials can vary widely, but will typically be up to about 500, preferably from about 200 to about 400, and more preferably from about 300 to about 350. Also useful herein are
the various grades of mineral oils. Mineral oils are liquid mixtures of hydrocarbons that are obtained from petroleum. Specific examples of suitable hydrocarbon materials include paraffin oil, mineral oil, dodecane, isododecane, hexadecane, isohexadecane, eicosene, isoeicosene, tridecane, tetradecane, polybutene, polyisobutene, and mixtures thereof. Preferred for use herein are hydrocarbons selected from the group consisting of mineral oil, poly α-olefin oils such as isododecane, isohexadecane, polybutene, polyisobutene, and mixtures thereof.

Commercially available fatty alcohols and their derivatives useful herein include: oleyl alcohol with tradename UNJECOL 90BHR available from Shin Nihon Rika, various liquid esters with tradenames SCHERCEMOL series available from Scher, and hexyl isostearate with a tradename HIS and isopropryl isostearate having a tradename ZPIS available from Kokyu Alcohol. Commercially available bulky ester oils useful herein include: trimethylolpropane tricaprylate/tricaprate with tradename MOBIL ESTER P43 from Mobil Chemical Co. Commercially available hydrocarbons useful herein include isododecane, isohexadecane, and isoeicosene with tradenames PERMETHYL 99A, PERMETHYL 101A, and PERMETHYL 1082, available from Presperse (South Plainfield New Jersey, USA), a copolymer of isobutene and normal butene with tradenames INDOPOL H-100 available from Amoco Chemicals (Chicago Illinois, USA), mineral oil with tradename BENOL available from Witco, isoparaffin with tradename ISOPAR from Exxon Chemical Co. (Houston Texas, USA), and polydecene with tradename PURESYN 6 from Mobil Chemical Co.

**Cationic Polymers**

The hair conditioning compositions of the present invention may contain one or more cationic polymers. As used herein, the term "polymer" shall include materials whether made by polymerization of one type of monomer or made by two (i.e., copolymers) or more types of monomers. Preferably, the cationic polymer is a water-soluble cationic polymer. By "water soluble" cationic polymer, what is meant is a polymer which is sufficiently soluble in water to form a substantially clear solution to the naked eye at a concentration of 0.1% in water (distilled or equivalent) at 25°C. The preferred polymer will be sufficiently soluble to form a substantially clear solution at 0.5% concentration, more preferably at 1.0% concentration.

The cationic polymers hereof will generally have a weight average
molecular weight which is at least about 5,000, typically at least about 10,000, and is less than about 10 million. Preferably, the molecular weight is from about 100,000 to about 2 million. The cationic polymers will generally have cationic nitrogen-containing moieties such as quaternary ammonium or cationic amino moieties, and mixtures thereof.

The cationic charge density is preferably at least about 0.1 meq/gram, more preferably at least about 1.5 meq/gram, even more preferably at least about 1.1 meq/gram, still more preferably at least about 1.2 meq/gram. Cationic charge density of the cationic polymer can be determined according to the Kjeldahl Method. Those skilled in the art will recognize that the charge density of amino-containing polymers may vary depending upon pH and the isoelectric point of the amino groups. The charge density should be within the above limits at the pH of intended use.

Any anionic counterions can be utilized for the cationic polymers so long as the water solubility criteria is met. Suitable counterions include halides (e.g., Cl, Br, I, or F, preferably Cl, Br, or I), sulfate, and methylsulfate. Others can also be used, as this list is not exclusive.

The cationic nitrogen-containing moiety will be present generally as a substituent, on a fraction of the total monomer units of the cationic hair conditioning polymers. Thus, the cationic polymer can comprise copolymers, terpolymers, etc. of quaternary ammonium or cationic amine-substituted monomer units and other non-cationic units referred to herein as spacer monomer units. Such polymers are known in the art, and a variety can be found in the CTFA Cosmetic Ingredient Dictionary, 3rd edition, edited by Estrin, Crosley, and Haynes, (The Cosmetic, Tolley, and Fragrance Association, Inc., Washington, D.C., 1982).

Suitable cationic polymers include, for example, copolymers of vinyl monomers having cationic amine or quaternary ammonium functionalities with water soluble spacer monomers such as acrylamide, methacrylamide, alkyl and dialkyl acrylamides, alkyl and dialkyl methacrylamides, alkyl acrylate, alkyl methacrylate, vinyl caprolactone, and vinyl pyrrolidone. The alkyl and dialkyl substituted monomers preferably have C1 - C3 alkyl groups, more preferably C1 - C3 alkyl groups. Other suitable spacer monomers include vinyl esters, vinyl alcohol (made by hydrolysis of polyvinyl acetate), maleic anhydride, propylene glycol, and ethylene glycol.
The cationic amines can be primary, secondary, or tertiary amines, depending upon the particular species and the pH of the composition. In general, secondary and tertiary amines, especially tertiary amines, are preferred.

Amine-substituted vinyl monomers can be polymerized in the amine form, and then optionally can be converted to ammonium by a quaternization reaction. Amines can also be similarly quaternized subsequent to formation of the polymer. For example, tertiary amine functionalities can be quaternized by reaction with a salt of the formula $R^{118}X$ wherein $R^{118}$ is a short chain alkyl, preferably a C$_1$ - C$_7$ alkyl, more preferably a C$_1$ - C$_3$ alkyl, and X is a salt forming anion as defined above.

Suitable cationic amino and quaternary ammonium monomers include, for example, vinyl compounds substituted with dialkylaminoalkyl acrylate, dialkylaminoalkyl methacrylate, monoalkylaminoalkyl acrylate, monoalkylaminoalkyl methacrylate, trialkyl methacryloxyalkyl ammonium salt, trialkyl acryloxyalkyl ammonium salt, dialkyl quaternary ammonium salts, and vinyl quaternary ammonium monomers having cyclic cationic nitrogen-containing rings such as pyridinium, imidazolium, and quaternized pyrrolidone, e.g., alkyl vinyl imidazolium, alkyl vinyl pyridinium, alkyl vinyl pyrrolidone salts. The alkyl portions of these monomers are preferably lower alkyls such as the C$_1$ - C$_5$ alkyls, more preferably C$_1$ and C$_2$ alkyls. Suitable amine-substituted vinyl monomers for use herein include dialkylaminoalkyl acrylate, dialkylaminoalkyl methacrylate, dialkylaminoalkyl acrylamide, and dialkylaminoalkyl methacrylamide, wherein the alkyl groups are preferably C$_1$ - C$_7$ hydrocarbys, more preferably C$_1$ - C$_3$ alkyls.

The cationic polymers herewith can comprise mixtures of monomer units derived from amine- and/or quaternary ammonium-substituted monomer and/or compatible spacer monomers.

Suitable cationic hair conditioning polymers include, for example: copolymers of 1-vinyl-2-pyrrolidone and 1-vinyl-3-methylimidazolium salt (e.g., chloride salt) (referred to in the industry by the Cosmetic, Toiletry, and Fragrance Association, "CTFA", as Polyquaternium-16), such as those commercially available from BASF Wyandotte Corp. (Parsippany, NJ, USA) under the LUVIQUAT tradename (e.g., LUVIQUAT FC 370); copolymers of 1-vinyl-2-pyrrolidone and dimethylaminoethyl methacrylate (referred to in the industry by CTFA as Polyquaternium-11) such as those commercially available from Gaf Corporation (Wayne, NJ, USA) under the GAFQUAT tradename (e.g., GAFQUAT...
755N); cationic diallyl quaternary ammonium-containing polymers, including, for example, dimethylidiallylammonium chloride homopolymer and copolymers of acrylamide and dimethylidiallylammonium chloride, referred to in the industry (CTFA) as Polyquaternium 6 and Polyquaternium 7, respectively; and mineral acid salts of amino-alkyl esters of homo- and co-polymers of unsaturated carboxylic acids having from 3 to 5 carbon atoms, as described in U.S. Patent 4,009,256.

Other suitable cationic polymers are amphoteric terpolymers consisting of acrylic acid methacrylamidopropyl trimethylammonium chloride and methyl acrylate, having a structure as shown below referred to in the industry (CTFA) as Polyquaternium 47. An example of a suitable commercial material is MERQUAT 2001®, wherein the ratio of n⁶:n⁷:n⁸ is 45:45:10 supplied by Calgon Corp.

Other cationic polymers that can be used include polysaccharide polymers, such as cationic cellulose derivatives and cationic starch derivatives.

Cationic polysaccharide polymer materials suitable for use herein include those of the formula:

\[
Z^-\overset{\text{R}^{120}}{\text{O}}(\overset{\text{R}^{119}}{\text{N}}=\overset{\text{R}^{122}}{\text{R}})\overset{\text{R}^{121}}{X^-}
\]

wherein: Z⁻ is an anhydroglucose residual group, such as a starch or cellulose anhydroglucose residual, R¹¹⁹ is an alkylene oxyalkylene, polyoxyalkylene, or hydroxyalkylene group, or combination thereof, R¹²⁰, R¹²¹, and R¹²² independently are alkyl, aryl, alkylaryl, arylalkyl, alkoxylkyl, or alkoxyaryl groups, each group containing up to about 18 carbon atoms, and the total number of carbon atoms for each cationic moiety (i.e., the sum of carbon atoms in R¹²⁰, R¹²¹ and R¹²²)
preferably being about 20 or less, and X is as previously described.

Cationic cellulose is available from Amerchol Corp. (Edison, NJ, USA) in their Polymer JR® and LR® series of polymers, as salts of hydroxyethyl cellulose reacted with trimethyl ammonium substituted epoxide, referred to in the industry (CTFA) as Polyquaternium 10. Another type of cationic cellulose includes the polymeric quaternary ammonium salts of hydroxyethyl cellulose reacted with lauryl dimethyl ammonium-substituted epoxide, referred to in the industry (CTFA) as Polyquaternium 24. These materials are available from Amerchol Corp. (Edison, NJ, USA) under the tradename Polymer LM-200®.

Other cationic polymers that can be used include cationic guar gum derivatives, such as guar hydroxypropyltrimonium chloride commercially available from Celanese Corp. in their Jaguar R series. Other materials include quaternary nitrogen-containing cellulose ethers (as described in U.S. Patent 3,962,418, and copolymers of etherified cellulose and starch (as described in U.S. Patent 3,958,581.

Particularly useful cationic polymers herein include Polyquaternium-7, Polyquaternium-10, Polyquaternium-24, Polyquaternium-39, Polyquaternium-47, and mixtures thereof.

Silicone Compounds

The compositions of the present invention may contain a silicone compound. The silicone compounds useful herein include volatile soluble or insoluble, or nonvolatile soluble or insoluble silicone conditioning agents. By soluble what is meant is that the silicone compound is miscible with the carrier of the composition so as to form part of the same phase. By insoluble what is meant is that the silicone forms a separate, discontinuous phase from the carrier, such as in the form of an emulsion or a suspension of droplets of the silicone. The silicone compounds herein may be made by any suitable method known in the art, including emulsion polymerization. The silicone compounds may further be incorporated in the present composition in the form of an emulsion, wherein the emulsion is made my mechanical mixing, or in the stage of synthesis through emulsion polymerization, with or without the aid of a surfactant selected from anionic surfactants, nonionic surfactants, cationic surfactants, and mixtures thereof.

The silicone compounds for use herein will preferably have a viscosity of from about 1,000 to about 2,000,000 centistokes at 25°C, more preferably from
about 10,000 to about 1,800,000, and even more preferably from about 100,000 to about 1,500,000. The viscosity can be measured by means of a glass capillary viscometer as set forth in Dow Corning Corporate Test Method CTM0004, July 20, 1970. Silicone compound of high molecular weight may be made by emulsion polymerization. Suitable silicone fluids include polyalkyl siloxanes, polyaryl siloxanes, polyalkylaryl siloxanes, polyether siloxane copolymers, and mixtures thereof. Other nonvolatile silicone compounds having hair conditioning properties can also be used.

The silicone compound is preferably included in the composition at a level by weight from about 0.01% to about 20%, more preferably from about 0.05% to about 10%.

The silicone compounds herein also include polyalkyl or polyaryl siloxanes with the following structure (I)

\[
\begin{array}{c}
Z^8 \quad \text{Si} \quad \text{O} \quad \text{Si} \quad \text{O} \\
R_{123} \quad R_{123} \quad R_{123}
\end{array}
\]

wherein R\textsuperscript{123} is alkyl or aryl, and x is an integer from about 7 to about 8,000. Z\textsuperscript{8} represents groups which block the ends of the silicone chains. The alkyl or aryl groups substituted on the siloxane chain (R\textsuperscript{123}) or at the ends of the siloxane chains Z\textsuperscript{8} 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. Suitable Z\textsuperscript{8} groups include hydroxy, methyl, methoxy, ethoxy, propoxy, and aryloxy. The two R\textsuperscript{123} groups on the silicon atom may represent the same group or different groups. Preferably, the two R\textsuperscript{123} groups represent the same group. Suitable R\textsuperscript{123} groups include methyl, ethyl, propyl, phenyl, methylphenyl and phenylmethyl. The preferred silicone compounds are polydimethylsiloxane, polydiethylsiloxane, and polymethylphenylsiloxane. Polydimethylsiloxane, which is also known as dimethicone, is especially preferred. The polyalkylsiloxanes that can be used include, for example, polydimethylsiloxanes. These silicone compounds are available, for example, from the General Electric Company in their Viscasil\textsuperscript{®} and SF 96 series, and from Dow Corning in their Dow Corning 200 series.
Polyalkylaryl siloxane fluids can also be used and include, for example, polymethylphenylsiloxanes. These siloxanes are available, for example, from the General Electric Company as SF 1075 methyl phenyl fluid or from Dow Corning as 556 Cosmetic Grade Fluid.

Especially preferred, for enhancing the shine characteristics of hair, are highly arylated silicone compounds, such as highly phenylated polyethyl silicone having refractive index of about 1.46 or higher, especially about 1.52 or higher. When these high refractive index silicone compounds are used, they should be mixed with a spreading agent, such as a surfactant or a silicone resin, as described below to decrease the surface tension and enhance the film forming ability of the material.

The silicone compounds that can be used include, for example, a polypropylene oxide modified polydimethylsiloxane although ethylene oxide or mixtures of ethylene oxide and propylene oxide can also be used. The ethylene oxide and polypropylene oxide level should be sufficiently low so as not to interfere with the dispersibility characteristics of the silicone. These material are also known as dimethicone copolyls.

Other silicone compounds include amino substituted materials. Suitable alkylamino substituted silicone compounds include those represented by the following structure (II)

![Chemical Structure](image)

wherein $R^{124}$ is H, CH₃ or OH, $p^1$, $p^2$, $q^1$ and $q^2$ are integers which depend on the molecular weight, the average molecular weight being approximately between 5,000 and 10,000. This polymer is also known as "amodimethicone".

Suitable amino substituted silicone fluids include those represented by the formula (III)

$$(R^{125})_a G_{3+a} - Si - (OSiG)_{2-p^3} - (OSiG_b (R^{126})_{2-a})_{p^4} - O - SiG_{2-a} (R^{125})_a$$

(III)

in which G is chosen from the group consisting of hydrogen, phenyl, OH, C₁-C₈ alkyl and preferably methyl; a denotes 0 or an integer from 1 to 3, and preferably
equals 0; b denotes 0 or 1 and preferably equals 1; the sum p^3+p^4 is a number from 1 to 2,000 and preferably from 50 to 150, p^3 being able to denote a number from 0 to 1,999 and preferably from 49 to 149 and p^4 being able to denote an integer from 1 to 2,000 and preferably from 1 to 10; R^{129} is a monovalent radical of formula C_{93}H_{220}L in which q^{3} is an integer from 2 to 8 and L is chosen from the groups

\[ -N(R^{126})CH_{2}-CH_{2}-N(R^{126})_{2} \]

\[ -N(R^{126})_{2} \]
\[ -N(R^{126})_{3}X' \]
\[ -N(R^{126})CH_{2}-CH_{2}-NR^{126}H_{2}X' \]

in which R^{126} is chosen from the group consisting of hydrogen, phenyl, benzyl, a saturated hydrocarbon radical, preferably an alkyl radical containing from 1 to 20 carbon atoms, and X' denotes a halide ion.

An especially preferred amino substituted silicone corresponding to formula (III) is the polymer known as "trimethylsilylamodimethicone" wherein R^{124} is CH_{3}.

Other amino substituted silicone polymers which can be used are represented by the formula (V):

\[ \text{(V)} \]

where R^{128} denotes a monovalent hydrocarbon radical having from 1 to 18 carbon atoms, preferably an alkyl or alkenyl radical such as methyl; R^{129} denotes a hydrocarbon radical, preferably a C_{1}-C_{18} alkylene radical or a C_{1}-C_{18}, and more preferably C_{1}-C_{8}, alkyleneoxy radical; Q' is a halide ion, preferably chloride; p^5 denotes an average statistical value from 2 to 20, preferably from 2 to 8; p^6 denotes an average statistical value from 20 to 200, and preferably from 20 to 50. A preferred polymer of this class is available from Union Carbide under the name "UCAR SILICONE ALE 56."

References disclosing suitable nonvolatile dispersed silicone compounds include U.S. Patent No. 2,826,551, to Geen; U.S. Patent No. 3,964,500, to

Another nonvolatile dispersed silicone that can be especially useful is 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 centistokes. 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. Silicone gums are described by Petrarch, and others including U.S. Patent No. 4,152,416, to Spitzer et al., issued May 1, 1979 and Noll, Walter, Chemistry and Technology of Silicones, New York: Academic Press 1968. Also describing silicone gums are General Electric Silicone Rubber Product Data Sheets SE 30, SE 33, SE 54 and SE 76. The "silicone gums" will typically have a mass molecular weight in excess of about 200,000, generally between about 200,000 and about 1,000,000. Specific examples include polydimethylsiloxane, poly(dimethylsiloxane methylvinylsiloxane) copolymer, poly(dimethylsiloxane diphenylsiloxane methylvinylsiloxane) copolymer and mixtures thereof.

Also useful are silicone resins, which are highly crosslinked polymeric siloxane systems. The crosslinking is introduced through the incorporation of tri-functional and tetra-functional silanes with mono-functional or di-functional, or both, silanes during manufacture of the silicone resin. As is well understood in the art, the degree of crosslinking that is required in order to result in a silicone resin will vary according to the specific silane units incorporated into the silicone resin. In general, silicone materials which have a sufficient level of trifunctional and tetrafunctional siloxane monomer units, and hence, a sufficient level of crosslinking, such that they dry down to a rigid, or hard, film are considered to be silicone resins. The ratio of oxygen atoms to silicon atoms is indicative of the level of crosslinking in a particular silicone material. Silicone materials which have at least about 1.1 oxygen atoms per silicon atom will generally be silicone resins herein. Preferably, the ratio of oxygen:silicon atoms is at least about 1.2:1.0. Silanes used in the manufacture of silicone resins include monomethyl-, dimethyl-, trimethyl-, monophenyl-, diphenyl-, methylphenyl-, monovinyl-, and methylvinylchlorosilanes, and tetrachlorosilane, with the methyl substituted
silanes being most commonly utilized. Preferred resins are offered by General Electric as GE SS4230 and SS4267. Commercially available silicone resins will generally be supplied in a dissolved form in a low viscosity volatile or nonvolatile silicone fluid. The silicone resins for use herein should be supplied and incorporated into the present compositions in such dissolved form, as will be readily apparent to those skilled in the art. Without being bound by theory, it is believed that the silicone resins can enhance deposition of other silicone compounds on the hair and can enhance the glossiness of hair with high refractive index volumes.

Other useful silicone resins are silicone resin powders such as the material given the CTFA designation polymethylsilsequioxane, which is commercially available as Tospearl™ from Toshiba Silicones.


Silicone materials and silicone resins in particular, can conveniently be identified according to a shorthand nomenclature system well known to those skilled in the art as the "MDTQ" nomenclature. Under this system, the silicone is described according to the presence of various siloxane monomer units which make up the silicone. Briefly, the symbol M denotes the mono-functional unit \((\text{CH}_3)_3\text{SiO}_{0.5}\); D denotes the difunctional unit \((\text{CH}_3)_2\text{SiO}\); T denotes the trifunctional unit \((\text{CH}_3)\text{SiO}_{1.5}\); and Q denotes the quadri- or tetra-functional unit \(\text{SiO}_2\). Primes of the unit symbols, e.g., \(\text{M'}\), \(\text{D'}\), \(\text{T'}\), and \(\text{Q'}\) denote substituents other than methyl, and must be specifically defined for each occurrence. Typical alternate substituents include groups such as vinyl, phenyl, amino, hydroxyl, etc.

The molar ratios of the various units, either in terms of subscripts to the symbols indicating the total number of each type of unit in the silicone, or an average thereof, or as specifically indicated ratios in combination with molecular weight, complete the description of the silicone material under the MDTQ system.

Higher relative molar amounts of \(\text{T}, \text{Q}, \text{T'}\) and/or \(\text{Q'}\) to \(\text{D}, \text{D'}, \text{M}\) and/or or \(\text{M'}\) in a silicone resin is indicative of higher levels of crosslinking. As discussed before, however, the overall level of crosslinking can also be indicated by the oxygen to silicon ratio.

The silicone resins for use herein which are preferred are MQ, MT, MTQ, MQ and MDTQ resins. Thus, the preferred silicone substituent is methyl.
Especially preferred are MQ resins wherein the M:Q ratio is from about 0.5:1.0 to about 1.5:1.0 and the average molecular weight of the resin is from about 1000 to about 10,000.

Commercially available silicone compounds which are useful herein include Dimethicone with tradename D-130, cetyl Dimethicone with tradename DC2502, stearyl Dimethicone with tradename DC2503, emulsified polydimethyl siloxanes with tradenames DC1664 and DC1784, and alkyl grafted copolymer silicone emulsion with tradename DC2-2845; all available from Dow Corning Corporation, and emulsion polymerized Dimethiconol available from Toshiba Silicone as described in GB application 2,303,857.

Nonionic Polymer

Nonionic polymers useful herein include cellulose derivatives, hydrophobically modified cellulose derivatives, ethylene oxide polymers, and ethylene oxide/propylene oxide based polymers. Suitable nonionic polymers are cellulose derivatives including methylcellulose with tradename BENECCEL, hydroxyethyl cellulose with tradename NATROSOL, hydroxypropyl cellulose with tradename KLUCEL, cetyl hydroxyethyl cellulose with tradename POLYSURF 67, all supplied by Hercules. Other suitable nonionic polymers are ethylene oxide and/or propylene oxide based polymers with tradenames CARBOWAX PEGs, POLYOX WASRs, and UCON FLUIDS, all supplied by Amerchol.

Polyalkylene Glycol

The polyalkylene glycols are characterized by the general formula:

\[ \text{H(OCH}_2\text{CH}_2\text{)}_{x3}\text{-OH} \]

\[ R^{201} \]

wherein R\(^{201}\) is selected from the group consisting of H, methyl, and mixtures thereof. When R\(^{201}\) is H, these materials are polymers of ethylene oxide, which are also known as polyethylene oxides, polyoxyethylenes, and polyethylene glycols. When R\(^{201}\) is methyl, these materials are polymers of propylene oxide, which are also known as polypropylene oxides, polyoxypropylenes, and polypropylene glycols. When R\(^{201}\) is methyl, it is also understood that various positional isomers of the resulting polymers can exist.

In the above structure, x3 has an average value of from about 1500 to about 25,000, preferably from about 2500 to about 20,000, and more preferably from about 3500 to about 15,000.
Other useful polymers include the polypropylene glycols and mixed polyethylene/polypropylene glycols.

Polyethylene glycol polymers useful herein are PEG-2M wherein \( R^{201} \) equals H and \( x3 \) has an average value of about 2,000 (PEG-2M is also known as Polyox WSR® N-10, which is available from Union Carbide and as PEG-2,000); PEG-5M wherein \( R^{201} \) equals H and \( x3 \) has an average value of about 5,000 (PEG-5M is also known as Polyox WSR® N-35 and Polyox WSR® N-80, both available from Union Carbide and as PEG-5,000 and Polyethylene Glycol 300,000); PEG-7M wherein \( R^{201} \) equals H and \( x3 \) has an average value of about 7,000 (PEG-7M is also known as Polyox WSR® N-750 available from Union Carbide); PEG-9M wherein \( R^{201} \) equals H and \( x3 \) has an average value of about 9,000 (PEG 9-M is also known as Polyox WSR® N-3333 available from Union Carbide); and PEG-14 M wherein \( R^{201} \) equals H and \( x3 \) has an average value of about 14,000 (PEG-14M is also known as Polyox WSR® N-3000 available from Union Carbide).

**OTHER ADDITIONAL COMPONENTS**

The compositions of the present invention may include other additional components, which may be selected by the artisan according to the desired characteristics of the final product and which are suitable for rendering the compositions more cosmetically or aesthetically acceptable or to provide them with additional usage benefits. Such other additional components generally are used individually at levels from about 0.001% to about 10.0%, preferably from about 0.01% to about 5.0% by weight of the composition.

A wide variety of other additional ingredients can be formulated into the present compositions. These include: other conditioning agents such as hydrolysed collagen with tradename Peptein 2000 available from Hormel, vitamin E with tradename Emix-d available from Eisai, panthenol available from Roche, panthenyl ethyl ether available from Roche, hydrolysed keratin, proteins, plant extracts, and nutrients; hair-fixative polymers such as amphoteric fixative polymers, cationic fixative polymers, anionic fixative polymers, nonionic fixative polymers, and silicone grafted copolymers; preservatives such as benzyl alcohol, methyl paraben, propyl paraben and imidazolidinyl urea; pH adjusting agents, such as citric acid, sodium citrate, succinic acid, phosphoric acid, sodium hydroxide, sodium carbonate; salts, in general, such as potassium acetate and sodium chloride; coloring agents, such as any of the FD&C or D&C dyes; hair
oxidizing (bleaching) agents, such as hydrogen peroxide, perborate and per sulfate salts; hair reducing agents such as the thioglycolates; perfumes; and sequestering agents, such as disodium ethylenediamine tetra-acetate; ultraviolet and infrared screening and absorbing agents such as octyl salicylate, antidandruff agents such as zinc pyridinethione; and optical brighteners, for example polystyrilstibenes, triazinstibenes, hydroxycoumarins, aminocoumarins, triazoles, pyrazolines, oxazoles, pyrenes, porphyrins, imidazoles, and mixtures thereof.

METHOD OF MAKING

The hair conditioning composition of the present invention can be made by any means which provide the composition with a layered gel structure, and thereby the DSC profile of the composition shows substantially no peaks larger than about 3 mJ/mg from about 40°C to about 65°C. A suitable method of making the present invention comprises the steps of:

1. forming a first mixture comprising the high melting point compound, the emulsifying agent, and the aqueous carrier at a first temperature of at least about 75°C;
2. cooling the first mixture by at least 5°C to a second temperature of from about 50°C to about 75°C; and
3. adding the quaternary compound to the product of step (2) while maintaining the second temperature.

Forming a First Mixture

The first step comprises forming a first mixture comprising the high melting point compound, the emulsifying agent, and water at a first temperature of at least about 75°C. The first mixture is made homogeneous by a suitable means such as stirring. Certain compounds in the hair conditioning composition are not contained in the first mixture. Compounds not contained are the quaternary compound, and, if present, volatile and heat-sensitive compounds. Any other compounds of the present composition are typically included in the first mixture. The first temperature for making the first mixture is at least about 75°C, preferably from about 75°C to about 85°C.

Cooling the First Mixture

The second step comprises cooling the first mixture by at least 5°C to a second temperature of from about 50°C to about 75°C. The cooling can be done by any suitable means, for example by heat exchangers, or jacket cooling
instruments. The second temperature is from about 50°C to about 75°C, preferably from about 55°C to about 65°C, more preferably from about 55°C to about 60°C. The second temperature is higher than the melting point of the high melting point compound.

Typically, the second temperature is no more than 5°C higher, preferably from about 2°C to 5°C higher than the thickening temperature of the first mixture. The thickening temperature is a point in which the rheology of a composition significantly changes, i.e., the first mixture becomes dramatically and significantly viscous. Such phenomena are well recognized by the artisan for compositions which contain high melting point compounds.

Adding the Quaternary Compound

The third step comprises adding the quaternary compound to the product of the second step while maintaining the second temperature. Such addition of the quaternary compound is typically done under stirring. Without being bound by theory, it is believed that, by adding the quaternary compound at the second temperature, the phase of the composition is transformed to a layered gel structure. Certain compounds which are not contained in the first mixture such as volatile and heat-sensitive compounds can be included at the third step, or after the product of the third step is cooled to room temperature.

EXAMPLES

The following examples further describe and demonstrate embodiments within the scope of the present invention. The examples are given solely for the purpose of illustration and are not to be construed as limitations of the present invention, as many variations thereof are possible without departing from the spirit and scope of the invention. Ingredients are identified by chemical or CTFA name, or otherwise defined below.

The compositions of the present invention are suitable for rinse-off products and leave-on products, and are particularly useful for making products in the form of emulsion, cream, gel, spray, or mousse.

Examples 1 through 6 are hair conditioning compositions of the present invention which are particularly useful for rinse-off use.

<table>
<thead>
<tr>
<th>Components</th>
<th>Ex. 1</th>
<th>Ex. 2</th>
<th>Ex. 3</th>
<th>Ex. 4</th>
<th>Ex. 5</th>
<th>Ex. 6</th>
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<td>Ex. 6</td>
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Temperatures used in Process

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<th>Ex. 3</th>
<th>Ex. 4</th>
<th>Ex. 5</th>
<th>Ex. 6</th>
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* q.s. to 100%
Definitions of Components

*1 Cetyl Alcohol: Konol series obtained by Shin-Nihon Rika.
*2 Stearyl Alcohol: Konol series obtained by Shin-Nihon Rika.
*3 Behenyl Alcohol: 1-Docosanol (97%) obtained by Wako.
*4 Stearamidopropyl Dimethylamine: Amidoamine MPS obtained by Nikko.
*5 ε-Glutamic Acid: ε-Glutamic acid (cosmetic grade) obtained by Ajinomoto.
*7 Dihydrogenated Tallowamidoethyl Hydroxyethylmonium Methosulfate: Varisoft 110 obtained by Witco.
*8 Hydroxyethyl Cellulose: Available from Aqualon.
*9 Polyoxyethylene glycol: WSR N-10 obtained Amerchol.
*10 Polyquaternium-10: UCARE Polymer LR 400 obtained by Amerchol.
*11 Polyquaternium-7: Merquat S obtained by Calgon.
*12 Pentaerythritol Tetraisostearate: KAK PTI obtained by Kokyu alcohol.
*14 Trimethylolpropene Trioleate: Enujerubu TP3SO obtained by Shin-Nihon RiKa.
*15 Trimethylolpropene Triisostearate: KAK TTI obtained by Kokyu alcohol.
*16 Silicone Blend: SE76 obtained by G.E.
*17 Silicone Emulsion: X65-4829 obtained by Tosil/GE.
*18 Hydrolyzed Collagen: Peptein 2000 obtained by Hormel.
*19 Vitamin E: Emix-d obtained by Eisai.
*20 Panthenol: Available from Roche.
*21 Panthenyl Ethyl Ether: Available from Roche.
*22 Citric Acid: Anhydrous Citric acid obtained by Haarman & Reimer.

Method of Preparation

The compositions of Examples 1 through 6 as shown above are prepared as follows: If included in the composition, polymeric materials such as hydroxyethyl cellulose, polyoxyethylene glycol, Polyquaternium-10, and Polyquaternium-7 are dispersed in water at room temperature to make a polymer solution. High melting point compounds, emulsifying agents, and the polymer solution, if present, are mixed and heated up to the first temperature. The mixture thus obtained is cooled down to the second temperature, and the quaternary compound is added. The final mixture thus obtained is cooled below 55°C, and the remaining components are added with agitation, and further
cooled down to about 30°C.

A triblender and/or mill can be used in each step, if necessary to disperse the materials.

Method of DSC Measurement

DSC measurement of the compositions of Examples 1 through 6 as shown above can be conducted by the following method.

A conditioner sample is prepared by sealing 10mg to 15mg of the composition into a simple sealing container available from Seiko and sealed. The weight of the conditioner sample is recorded. A blank sample (unsealed simple sealing container) is also prepared. The conditioner sample and blank sample are placed inside a Seiko DSC 6000 instrument available from Seiko Instruments Inc. The DSC measurements are run under a measurement condition of from about -50°C to about 130°C at a heating rate of 2°C/minute.

Fig. 1 is a profile chart obtained by such DSC measurement of 12.04mg of the composition of Example 1. The DSC profile of this composition shows the only peak having a peak top temperature of 69.1°C, which peak is calculated as 7.9mJ/mg. The DSC profile of this composition further shows no peaks larger than 3mJ/mg from 40°C to 65°C.

The embodiments disclosed and represented by the previous examples have many advantages. For example, they can provide improved conditioning benefits such as smoothness, softness, and ease of combing, both when the hair is wet and also after it has dried.

It is understood that the examples and embodiments described herein are for illustrative purposes only and that various modifications or changes in light thereof will be suggested to one skilled in the art without departing from its spirit and scope.
WHAT IS CLAIMED IS:

1. A hair conditioning composition comprising by weight:
   (1) at least about 3% of a high melting point compound having a melting point
       of at least about 25°C;
   (2) an emulsifying agent selected from the group consisting of amines, betaines, nonionic compounds, and mixtures thereof;
   (3) a quaternary compound; and
   (4) an aqueous carrier;
   wherein the composition shows a DSC profile having substantially no peaks
   larger than about 3mJ/mg from about 40°C to about 65°C.

2. The hair conditioning composition according to Claim 1 wherein the
   emulsifying agent is selected from amines.

3. The hair conditioning composition according to Claim 2 wherein the
   amines are tertiary amido amines having an alkyl group of from about 12 to about
   22 carbons.

4. The hair conditioning composition according to Claim 3 further comprising
   an acid selected from the group consisting of \( \ell \)-glutamic acid, lactic acid, hydrochloric acid, malic acid, succinic acid, acetic acid, fumaric acid, \( \ell \)-glutamic acid hydrochloride, tartaric acid, citric acid, and mixtures thereof; wherein the
   molar ratio of the tertiary amido amine to the acid is from about 1 : 0.3 to about 1
   : 2.

5. The hair conditioning composition according to Claim 1 wherein the
   emulsifying agent is selected from betaines.

6. The hair conditioning composition according to Claim 2 or 5 wherein the
   quaternary compound is a hydrophilically substituted cationic surfactant selected
   from the group consisting of dialkylamido ethyl hydroxyethylmonium salt,
   dialkylamido ethyl dimonium salt, dialkoyl ethyl hydroxyethylmonium salt, dialkoyl
   ethyldimonium salt, and mixtures thereof.
7. The hair conditioning composition according to Claim 2 or 5 wherein the high melting point compound is selected from cetyl alcohol, stearyl alcohol, behenyl alcohol, and mixtures thereof.

8. The hair conditioning composition according to any of the claims above further comprising a high molecular weight ester oil being water-insoluble, and in liquid form at 25°C, the high molecular weight ester oil selected from the group consisting of:

(a) pentaerythritol ester oils of the following formula having a molecular weight of at least about 800:

```
\[ \begin{array}{c}
\text{O} \\
\text{R}^1\text{C} \text{OCH}_2\text{C} \text{CH}_2\text{O} \text{O} \\
\text{O} \\
\text{CH}_2\text{O} \text{C} \text{R}^4 \\
\text{CH}_2\text{O} \text{C} \text{R}^2 \\
\text{R}^3\end{array} \]
```

wherein R1, R2, R3, and R4, independently, are branched, straight, saturated, or unsaturated alkyl, aryl, and alkylaryl groups having from 1 to about 30 carbons;

(b) trimethylol ester oils of the following formula having a molecular weight of at least about 800:

```
\[ \begin{array}{c}
\text{O} \\
\text{R}^{12} \\
\text{R}^{13} \\
\text{R}^{14} \end{array} \]
```

wherein R11 is an alkyl group having from 1 to about 30 carbons, and R12, R13, and R14, independently, are branched, straight, saturated, or unsaturated alkyl, aryl, and alkylaryl groups having from 1 to about 30 carbons;

(c) poly α-olefin oils derived from 1-alkene monomers having from about 6 to about 16 carbons, the poly α-olefin oils having a viscosity of from about 1 to about 35,000 cst, a molecular weight of from about 200 to about 60,000, and a polydispersity of no more than about 3;

(d) citrate ester oils of the following formula being water-insoluble,
having a molecular weight of at least about 500:

\[
\begin{align*}
\text{O} & \text{O} \\
\text{C-O-R}^{22} & \\
\text{R}^{21} & \\
\text{C-O-R}^{23} & \\
\text{C-O-R}^{24} & \\
\text{CH}_2 & \\
\end{align*}
\]

wherein R21 is OH or CH₃COO, and R22, R23, and R24, independently, are branched, straight, saturated, or unsaturated alkyl, aryl, and alkylaryl groups having from 1 to about 30 carbons; glyceryl ester oils being water-insoluble, having a molecular weight of at least about 500, and in liquid form at 25°C and having the following formula:

\[
\begin{align*}
\text{O} & \\
\text{CH}_2 & \\
\text{C-O-R}^{41} & \\
\text{O} & \\
\text{HC-O-C-O} & \\
\text{O} & \\
\text{CH}_2 & \\
\text{C-O-R}^{43} & \\
\end{align*}
\]

wherein R⁴¹, R⁴², and R⁴³, independently, are branched, straight, saturated, or unsaturated alkyl, aryl, and alkylaryl groups having from 1 to about 30 carbons; and mixtures thereof.

9. The hair conditioning composition according to Claim 8 wherein the high molecular weight ester oil is selected from the group consisting of pentaerythritol ester oils, trimethylol ester oils, and mixtures thereof.

10. The hair conditioning composition according to Claim 4 comprising by weight:

(1) from about 4.5% to about 10% of the high melting point compound;
(2) from about 0.5% to about 5% of the tertiary amido amine;
(3) the acid in an amount so that the molar ratio of the tertiary amido amine to the acid is from about 1 : 0.4 to about 1 : 1;
(4) from about 0.5% to about 5% the quaternary compound selected from the group consisting of dialkylamido ethyl hydroxyethylmonium salt, dialkylamido ethyl dimonium salt, dialkoyl ethyl hydroxyethylmonium salt,
dialkoyl ethyldimonium salt, and mixtures thereof.

11. The hair conditioning composition according to Claim 5 comprising by weight:
   (1) from about 4.5% to about 10% of the high melting point compound;
   (2) from about 0.5% to about 5% of the betaine; and
   (3) from about 0.5% to about 5% of the quaternary compound selected from
        the group consisting of dialkylamido ethyl hydroxyethylmonium salt,
        dialkylamido ethyl dimonium salt, dialkoyl ethyl hydroxyethylmonium salt,
        dialkoyl ethyldimonium salt, and mixtures thereof.

12. A method of making the hair conditioning composition according to Claims
    1, 2, or 5 comprising the steps of:
    (1) forming a first mixture comprising the high melting point compound, the
        emulsifying agent, and the aqueous carrier at a first temperature of at
        least about 75°C;
    (2) cooling the first mixture by at least 5°C to a second temperature of from
        about 50°C to about 75°C; and
    (3) adding the quaternary compound to the product of step (2) while
        maintaining the second temperature.

13. The method of Claim 11 wherein the second temperature is no more than
    5°C higher than the thickening temperature of the product of the first
    mixture.
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6  A61K7/50  A61K7/06

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)
IPC 6  A61K

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

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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<td>WO 98 31340 A (THE PROCTER &amp; GAMBLE CO.) 23 July 1998 see the whole document</td>
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<td>X</td>
<td>EP 0 761 206 A (L'OREAL) 12 March 1997 see the whole document</td>
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<td>EP 0 155 015 A (SHIONOGI &amp; CO., LTD) 18 September 1985 see the whole document</td>
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X Further documents are listed in the continuation of box C.  X Patent family members are listed in annex.

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Date of the actual completion of the international search

12 April 1999

Date of mailing of the international search report

22/04/1999

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Glikman, J-F

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