



Office de la Propriété
Intellectuelle
du Canada

Un organisme
d'Industrie Canada

Canadian
Intellectual Property
Office

An agency of
Industry Canada

CA 2304574 C 2002/11/26

(11)(21) **2 304 574**

(12) **BREVET CANADIEN
CANADIAN PATENT**

(13) **C**

(86) Date de dépôt PCT/PCT Filing Date: 1998/09/30
(87) Date publication PCT/PCT Publication Date: 1999/04/15
(45) Date de délivrance/Issue Date: 2002/11/26
(85) Entrée phase nationale/National Entry: 2000/03/22
(86) N° demande PCT/PCT Application No.: EP 1998/006242
(87) N° publication PCT/PCT Publication No.: 1999/017719
(30) Priorité/Priority: 1997/10/03 (08/943609) US

(51) Cl.Int.⁷/Int.Cl.⁷ A61K 7/06
(72) Inventeurs/Inventors:
CRUDELE, JOANNE, US;
BHATT, DARSHNA, US;
KAMIS, KIMBERLY, US;
MILCZAREK, PAWEL, US
(73) Propriétaire/Owner:
UNILEVER PLC, GB
(74) Agent: BERESKIN & PARR

(54) Titre : TENUE DU CHEVEU INDUITE PAR LA CHALEUR ET OBTENUE A PARTIR DE COMPOSITIONS APRES-SHAMPOOING SANS RINCAGE CONTENANT DU SILICONE
(54) Title: HEAT-MEDIATED CONDITIONING FROM LEAVE-ON HAIR CARE COMPOSITIONS CONTAINING SILICONE

(57) **Abrégé/Abstract:**

In brief, the present invention is directed to a method for conditioning hair which comprises: (a) applying to hair a leave-on composition comprising: (1) a nonvolatile, silicone conditioning agent; (2) a resin; and (3) a carrier; (b) applying heat via a heating appliance to the composition treated hair to dry or style the hair and wherein a reduction in the bending modulus caused by the silicone conditioning agent is at least 1.00 %, even when offset by an increase in bending modulus caused by the presence of a resin, and wherein the method of the invention results in the deposition on the hair of at least 30 microgram silicone/1g of hair.



**PCT**WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : A61K 7/06	A1	(11) International Publication Number: WO 99/17719 (43) International Publication Date: 15 April 1999 (15.04.99)
(21) International Application Number: PCT/EP98/06242 (22) International Filing Date: 30 September 1998 (30.09.98) (30) Priority Data: 08/943,609 3 October 1997 (03.10.97) US (71) Applicant (for AU BB CA CY GB GD GH GM IE IL KE LC LK LS MN MW NZ SD SG SL SZ TT UG ZW only): UNILEVER PLC [GB/GB]; Unilever House, Blackfriars, London EC4P 4BQ (GB). (71) Applicant (for all designated States except AU BB CA CY GB GD GH GM IE IL KE LC LK LS MN MW NZ SD SG SL SZ TT UG ZW): UNILEVER N.V. [NL/NL]; Weena 455, NL-3013 AL Rotterdam (NL). (72) Inventors: CRUDELE, Joanne; Helene Curtis, Inc., 3100 East Golf Road, Rolling Meadows, Chicago, IL 60008 (US). BHATT, Darshna; Helene Curtis, Inc., 3100 East Golf Road, Rolling Meadows, Chicago, IL 60008 (US). KAMIS, Kimberley; Helene Curtis, Inc., 3100 East Golf Road, Rolling Meadows, Chicago, IL 60008 (US). MILCZAREK, Pawel; Helene Curtis, Inc., 3100 East Golf Road, Rolling Meadows, Chicago, IL 60008 (US).		(74) Agent: GRIFFITHS, Helen, Sarah; Unilever plc, Patent Dept., Colworth House, Sharnbrook, Bedford MK44 1LQ (GB). (81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: HEAT-MEDIATED CONDITIONING FROM LEAVE-ON HAIR CARE COMPOSITIONS CONTAINING SILICONE (57) Abstract In brief, the present invention is directed to a method for conditioning hair which comprises: (a) applying to hair a leave-on composition comprising: (1) a nonvolatile, silicone conditioning agent; (2) a resin; and (3) a carrier; (b) applying heat via a heating appliance to the composition treated hair to dry or style the hair and wherein a reduction in the bending modulus caused by the silicone conditioning agent is at least 1.00 %, even when offset by an increase in bending modulus caused by the presence of a resin, and wherein the method of the invention results in the deposition on the hair of at least 30 microgram silicone/1g of hair.		

- 1 -

HEAT-MEDIATED CONDITIONING FROM LEAVE-ON HAIR CARE
COMPOSITIONS CONTAINING SILICONE

5

BACKGROUND OF INVENTION AND PRIOR ART

Hair setting is basically the process of shaping wet hair by the steps of stretching and forming the hair during blow
10 drying or by curling the hair, fixing the hair in place after it has been dried and then curling or straightening the hair to give the finishing touches to provide the desired hairstyle.

15 However, heating the hair often damages the hair. Therefore, it would be highly desirable to develop heat mediated methods for conditioning the hair while styling the hair, which do not result in such damage. It would also be desirable to develop compositions which could be used in
20 such methods.

An inherent problem encountered in hair setting is the natural tendency of the hair to return to its natural shape. For example, the set hair returns to its natural
25 shape almost immediately if moistened or exposed to high humidity.

Investigators have sought to delay the combined action of natural forces and moisture that causes the hair to
30 return to its original state by applying solutions

- 2 -

containing naturally-occurring or synthetic polymers after the hair is shaped into a desired configuration. When applied to the shaped hair from aqueous or aqueous/alcoholic solutions (setting lotions), the polymers
5 leave a film on the hair, after drying, to help maintain the hair in the previously shaped configuration. The polymeric film promotes cohesion and gives stability to the hair set. The principal objective of a setting lotion and/or styling aid is to cover the hair with an invisible polymeric
10 film that will give the styled hair a degree of rigidity and protect the hair style against wind and humidity.

The general principles of hair setting are thoroughly discussed by C. Zviak, in The Science of Hair Care,
15 Marcel Dekker, pp. 149-181 (1986). Zviak reviews both the polymers used in hair setting products/styling aids and the formulation principles used to produce a hair set product that provides such beneficial hair set
properties as improved hairstyle hold, easy application
20 and combing, quick drying and non-stickiness, good hair body and bounce, increased hair volume and gloss, and hydrophobicity. It is evident that in the formulation of any end-use hair-styling product, some of these benefits may be sacrificed to some degree to achieve a competing
25 benefit.

There is sufficient evidence both from both consumer and clinical testing that the use of heat styling appliances is damaging to human hair. For consumers that heat style their
30 hair the primary concern is to use a leave-on product that

- 3 -

can protect and improve the condition of their hair while providing preferred setting characteristics.

The claimed invention not only provides good hair setting
5 characteristics and protective benefits, but in addition, uses heat to mediate increased conditioning and softness dependent on the delivery and deposition of conditioning agent between certain known levels.

10 SUMMARY OF THE INVENTION

The invention is the use of silicone based conditioning agents in leave-on hair care compositions to elicit a heat -
mediated reduction in bending modulus, or softening, or
15 conditioning to hair, as compared to air dried, treated hair. The heat required to elicit the effect would be the heat of a blow dryer or styling appliance, ranging from 200° to 400°F measured at the point of origin of the appliance.

20

In brief, the present invention is directed to a method for thermal conditioning hair which comprises:

- 25 (a) applying to hair a leave-on composition comprising:
- (1) a nonvolatile, silicone conditioning agent;
 - (2) a resin; and
 - (3) a carrier;

- 4 -

(b) applying heat via a heating appliance to the composition treated hair to dry or style the hair and wherein a reduction in the bending modulus caused by the silicone agent is at least 1.00%, and wherein the method
5 of the invention results in the deposition on the hair of at least 30 micrograms silicone/ 1 gram of hair.

- 5 -

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

As used herein nonvolatile, silicone conditioning agent means any silicone having a boiling point of 200°C or
5 greater, typically this would include silicones within a broad range of molecular weight, and having viscosities of between 5 centistokes to 1 million centistokes.

As used herein % means weight percent unless otherwise
10 indicated.

As used herein hair serum is a silicone hair treatment.

Heat activation is defined as some change that is mediated
15 by use of the composition of the invention with heat, from styling appliances such as a blow dryer, curling iron, hot curlers, hot brush, hot comb, hot rollers, crimper, or hair dryer. From internal testing of various appliances this average temperature can range on the "hot" setting to be
20 200° to 400°F.

Any non-volatile, silicone conditioning agent which will deposit silicone on hair may be used in the compositions and methods of the present invention. Silicone agents in the
25 compositions of the present invention include dimethicone, dimethiconol, phenyl trimethicone, dimethicone copolyols, amino functional silicones, organically modified silicone resins such as stearyl siloxysilicate and lauric siloxysilicate, silicone gums, silicone elastomers, and

- 6 -

cross-linked siloxane polymers which may be either linear or branched.

Silicone conditioning agents are responsible for a heat-induced reduction in bending modulus or softening of the hair. The preferred non-volatile, silicone conditioning agents are dimethicone, dimethiconol, phenyl trimethicone, and dimethicone copolyol which are added to compositions of the present invention in amounts sufficient to provide good feel and hold characteristics.

10

Preferred silicones include linear and branched polydimethylsiloxanes, of the following general formula: $(CH_3)_3SiO--[Si(CH_3)_2O]_n--Si(CH_3)_3$, wherein n is from 7 to 15,000, preferably from 7 to 9,000. Silicones useful in compositions of the present invention are available from a variety of commercial sources, including General Electric Company and Dow Corning. In addition to the linear and branched polydimethylsiloxanes, the polydimethylsiloxanes can be organically modified to include amine, hydroxyl, alkyl, alkyl aryl, ethoxylated, and propoxylated functionalities.

In accordance with one important embodiment, the composition of the present invention also includes from 0.001% to 10%, particularly 0.01% to 10%, and preferably from 0.01% to 5.0%, by weight of a non-volatile silicone compound or other conditioning agent(s), preferably a water-insoluble, emulsifiable conditioning agent. Any nonvolatile silicone containing agent will work

- 7 -

in the present invention provided that the silicone agent deposits sufficient silicone onto the hair.

Deposition of silicone onto the hair may be quantitated by extraction of silicone from hair treated with the

5 composition followed by spectroscopic analysis for the element silicon. Comparison against a standard (i.e a solution of the silicone of known concentration) then gives an amount of silicone which may be converted into micrograms of silicone/ gram of hair.

10

Using compositions and methods of the invention, the nonvolatile, silicone conditioning agent was present in the compositions at an active range of 0.1 to 2.0%, depositing on hair in the range of 30microgram/g to 1200microgram/g
15 hair. In these just above mentioned compositions, the nonvolatile, silicone conditioning agents were as follows:

Dimethiconol containing silicone emulsions such as,
dimethiconol and dimethiconol/silsesquioxane copolymer (and)
20 sodium C14-16 olefin sulfonate (and) trideceth -12;

Dimethicone copolyol;

and Phenyl Trimethicone.

The resins which can be employed in the compositions and
25 methods of the invention are as follows: A Polyquaternium - 11 such as Gafquat 734 or Gafquat 755N; a hydrophilic Polyether Urethane such as Polyurethane Resin 142-89; a Polyquaternium -4 such as Celquat L-200 or Celquat H-100; a

- 8 -

Polyvinylpyrrolidone such as PVP K-30; a
PVP/Dimethylaminoethyl methacrylate copolymer such as
Copolymer 845; a VA/Crotonate/Vinyl Neodecanoate Copolymer
such as Resyn 28-2930; an

- 5 Octylacrylamide/Acrylates/Butylaminoethyl Methacrylate such
as Amphomer; and a PVP/VA Copolymer such as PVP/VA E-635.

Other resins include Gantrez 425, 335, and 215 (Ester of
PVM/MA Copolymer);

- 10 Gantrez XL-80 (PVM/MA Decadiene Crosspolymer); LoVocryl
(Octylacrylamide/Acrylates/Butylaminoethyl Methacrylate
Copolymer); Luvimer (Acrylates Copolymer); PVP K-60, K-90,
K-120 (PVP); PVP/VA 335, 535, 735, 630 (PVP/VA Copolymers);
Resyn 28-2913 (VA/Crotonates/Vinyl Neodecanoate Copolymer);
15 and Ultrahold (Acrylate/Acrylamide Copolymer).

Shaping of the hair is best accomplished by first
applying the composition to hair while wet, shaping
the hair while drying with a heat appliance, and then if
20 needed, physically shaping the hair with a hot styling
appliance. The heat softens the resin; thereby, allowing it
to spread along the hair shaft. After removing the hot
styling appliance, the resin hardens, maintaining the
hair in the desired style. In addition, heat interacts
25 with the silicone conditioning agent resulting in reduction
in bending modulus; thereby, allowing the hair softer
characteristics.

The composition also can include a suspending agent in an
30 amount of 0.001% to 10%, by total weight of the

- 9 -

composition. The particular suspending agent is not critical and can be selected from any materials known to suspend water-insoluble liquids in leave-on compositions. Suitable suspending agents are for example, distearyl
5 amate (distearyl phthalamic acid); fatty acid alkanolamides; esters of polyols and sugars; polyethyleneglycols; the ethoxylated or propoxylated alkylphenols; ethoxylated or propoxylated fatty alcohols; and the condensation
10 products of ethylene oxide with long chain amides. These suspending agents, as well as numerous others not cited herein, are well known in the art and are fully described in the literature, such as McCUTCHEON'S DETERGENTS AND
EMULSIFIERS, 1989 Annual, published by McCutcheon Division, MC Publishing Co.

15

A nonionic alkanolamide also is optionally included in an amount of 0.001% to 5% by weight in the leave-on compositions to provide exceptionally stable
emulsification of water-insoluble conditioning agents
20 and to aid in thickening and foam stability.

Suitable alkanolamides include, but are not limited to, those known in the art of hair care formulations, such as cocamide monoethanolamide (MEA), cocamide diethanolamide
25 (DEA), soyamide DEA, lauramide DEA, oleamide monoisopropylamide (MIPA), stearamide MEA, myristamide MEA, lauramide MEA, capramide DEA, ricinoleamide DEA, myristamide DEA, stearamide DEA, oleylamide DEA, tallowamide DEA, lauramide MIPA, tallowamide MEA,
30 isostearamide DEA, isostearamide MEA and combinations

- 10 -

thereof. Other suitable suspending agents are disclosed in Oh et al. U.S. Pat. No. 4,704,272 Grote et al. U.S. Pat. No. 4,741,855; and Bolich, Jr. et al. U. S. Pat. No. 4,788,006, which patents are hereby incorporated by
5 reference.

Other useful suspending and thickening agents can be used instead of the alkanolamides such as sodium alginate; guar gum; xanthan gum; gum arabic; cellulose
10 derivatives, such as carbomer, methylcellulose, hydroxybutylcellulose, hydroxyethylcellulose, hydroxypropylcellulose and carboxymethylcellulose; and various synthetic polymeric thickeners, such as the polyacrylic acid derivatives.

15 Emulsion stabilizers also may be used in compositions of the invention. Useful examples include, such compounds as polyethylene glycol, silicone copolyols, polyvinyl alcohol, sorbitan monostearate, oleth-2, sorbitan
20 monolaurate, and nonionic block copolymers of ethylene oxide and propylene oxide such as those marketed by BASF Wyandotte under the name PLURONICS(r). When present, such stabilizers comprise from 0.05% to 1%, preferably from 0.1% to 0.8%, by weight of the composition.

25 The propellant gas included in the aerosol forms of the compositions of the present invention can be any liquefiable gas conventionally used for aerosol containers. Examples of materials that are suitable for use as
30 propellants are trichlorofluoromethane, hydrofluorocarbon,

- 11 -

dichlorodifluoromethane, dichlorotetrafluoroethane, monochlorodifluoromethane, trichlorotrifluoroethane, dimethyl ether, propane, n-butane and isobutane, used singly or admixed. Water-soluble gases such as dimethyl
5 ether, carbon dioxide, and/or nitrous oxide also can be used to obtain aerosols having reduced flammability. Water-immiscible, liquified, hydrocarbon and halogenated hydrocarbon gases such as propane, butane, hydrofluorocarbon, and chlorofluorocarbons can be used
10 advantageously to deliver the contents of the aerosol container without the dramatic pressure drops associated with other immiscible gases. Here there is no concern for the head space to be left inside the aerosol container, because the liquified gas will sit on top of the aqueous
15 formulation and the pressure inside the container is always the vapor pressure of saturated hydrocarbon vapor. Other insoluble, compressed gases such as nitrogen, helium and fully-fluorinated oxetanes and oxepanes also are useful to deliver the compositions from aerosol
20 containers.

Other means of delivery of the above-described leave-on, styling aid compositions include, pump sprayers, all forms of bag-in-can devices, in situ carbon dioxide
25 generator systems, compressors, and the like. The amount of the propellant gas is governed by normal factors well known in the aerosol art. For mousses, the level of propellant is generally from 3% to 30%, preferably from 5% to 15% of the total composition. For hairsprays, the level of
30 propellant is generally from 10% to 40%, preferably from

- 12 -

15% to 35% of the total composition. If a propellant such as dimethyl ether utilizes a vapor pressure suppressant (e.g., trichlorethane or dichloromethane), for weight percentage calculations, the amount of suppressant
5 is included as part of the propellant.

Other common cosmetic additives can be incorporated with the essential ingredients of the present invention, as long as the basic properties of the composition are not
10 adversely affected. These additives include, but are not limited to, commonly used fragrances, dyes, opacifiers, pearlescing agents, foam stabilizers, preservatives, water softening agents, acids, bases, sequestering agents, buffers, proteins, amino acids, and the
15 like; and will usually be present in weight percentages of less than 1% each, and 2% to 5% in total.

The composition vehicle, or carrier, is predominantly water or organic solvents which can be added to the
20 composition in order to solubilize compounds that are not sufficiently soluble in water. Suitable solvents include the lower alcohols like most preferred ethanol and isopropanol; polyols like glycerol; glycols or glycol ethers, like 2-butoxyethanol, ethylene glycol, ethylene
25 glycol monoethyl ether, propylene glycol and diethylene glycol monomethyl ether; and mixtures thereof. These solvents can be present in the composition of the present invention in an amount from 1% to 95% by weight.

- 13 -

The compositions can be thickened, for example, with sodium alginate, gum arabic, cellulose derivatives such as carbomer, methylcellulose, hydroxyethylcellulose, hydroxypropylmethylcellulose and carboxymethyl-cellulose, and various polymeric thickeners, such as acrylic acid derivatives. It is also possible to use inorganic thickeners such as bentonite. These thickeners are preferably present in the amount from 0.1% to 10% by weight and, in particular, from 0.5% to 3% by weight, relative to the total weight of the composition.

The compositions also can include anionic, amphoteric or nonionic surfactants. Representative nonionic surfactants include polyols and sugars; the polyethoxylated and/or polypropoxylated alkylphenols; the polyhydroxylated polyethers of fatty alcohols; and the condensation products of ethylene oxide with long chain mercaptans or long chain amides. Similarly, representative anionic surfactants include alkali metal salts, ammonium salts or salts of amines or amino alcohols of fatty acids such as oleic acid; of the sulfates of fatty alcohols, principally C₁₂, -C₁₄ and C₁₆ fatty alcohols; of the sulfates of polyethoxylated fatty alcohols; the alkylbenzenesulfonates, such as those wherein the alkyl moiety has 12 to 22 carbon atoms; or the alkylarylpolyether sulfates and monoglyceride sulfates. All these nonionic and anionic surfactants, as well as numerous others not cited here, are well known in the art and are fully described in the literature.

- 14 -

The optional alcohols employed in the compositions of the invention are an aliphatic straight or branched chain monohydric alcohol having 2 to 4 carbon atoms.

Isopropanol and especially ethanol are preferred. The
5 concentration of the alcohol in the composition can be 0-95%, as low as 0%, preferably 0-80%, more preferably 0-75%.

FORMULATION EXAMPLES

10

As shown in the data below, silicone conditioning agents, contained within the formulations of the invention and depositing silicone within certain ranges, are responsible for the heat-mediated reduction in bending modulus, or hair
15 softening, or conditioning. These formulations listed in Table I are made by methods known in the art.

Table I. Leave-On Composition Formulas

20

Formula A: Mousse

FORMULA	INGREDIENTS	WEIGHT %	BENDING MODULUS RESULT
	water, deionized	q.s.*	Approximate Reduction of 28.00%
	polyquaternium 11	8.09600000	
	dimethiconol,	1.84000000	

- 15 -

dimethiconol/silsesqu i-oxane copolymer		
preservative	0.09936000	
SD alcohol 40-B (190 proof)	7.63600000	
nonoxynol-9	0.49680000	
fragrance	0.13800000	
butane or isobutane	8.00000000	
phytantriol	0.025	

- 16 -

Formula B: Leave-On Conditioner

FORMULA B INGREDIENTS	WEIGHT %	BENDING MODULUS RESULT
water, soft	q.s. *	Approximate Reduction of 16.00%
dl-panthenol	0.8000000	
PEG-2 oleammonium chloride & propylene glycol	1.0000000	
cetrimonium chloride	1.5000000	
propylene glycol, USP	0.5000000	
preservative	0.3000000	
nonoxynol-10	0.2500000	
fragrance	0.3000000	
phytantriol	0.0250000	
sodium dihydrogen phosphate, granular	0.2000000	
phosphoric acid, 85%	0.0500000	
dimethicone, silica	0.0100000	

- 17 -

Formula C: Non-Aerosol Hair Spray

FORMULA C INGREDIENTS	WEIGHT %	BENDING MODULUS RESULT
SD alcohol 40-B (190 proof)	81.5487000	Approximate Reduction of 40.00%
aminomethyl propanol	0.5770000	
octylacrylamide/acryl ates/butylaminoethyl methacrylate	3.0000000	
PVP/VA copolymer	1.0000000	
dimethicone copolyol	0.1000000	
fragrance	0.3000000	
phytantriol	0.0250000	
water, soft	q.s.*	

- 18 -

Formula D: Aerosol Hair Spray

FORMULA D INGREDIENTS	WEIGHT %	BENDING MODULUS RESULT
SD alcohol 40-B (200 proof)	q.s.	Approximate Reduction of 13.00%.
aminomethyl propanol	0.5062500	
octylacrylamide/acrylates/butylaminoethyl methacrylate	2.2500000	
dimethicone copolyol	0.0750000	
VA/crotonates/vinyl neodecanoate copolymer	1.5000000	
phenyl trimethicone	0.2625000	
PPG-12-PEG-50-lanolin	0.1875000	
fragrance	0.2625000	
hydrofluorocarbon 152-A, butane	25.0000000	
phytantiol	0.025	

* q.s. - quantity sufficient for total weight % to be equal to 100%.

- 19 -

TESTING METHODSQuantitation of Silicone Deposited on Treated Tresses

5 A one gram sampling of a tress that has been treated with the test composition is extracted with two 50 ml aliquots of chloroform using sonication to aid the extraction. The extracts are combined and evaporated to dryness. The residue is dissolved in 10 ml of chloroform.

10

This solution is analyzed by aspiration into an Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES) using a solution of known concentration of the silicone as the one point standard. This instrument is an elemental analyzer,
15 so the element, silicon, is being quantitated. The amount of silicone in the extract can be calculated using the known silicon fraction in the silicone.

20 Dynamic mechanical testing of bending modulus

Dynamic mechanical testing of the force or modulus to bend a bundle of hair fibers characterizes the stiffness of the hair array, i.e., its resistance to a controlled normal force
25 imposed on the array in the vertical direction. If the modulus increases with treatment the array is stiffer. If the modulus decreases with treatment the array is less stiff; softer; fibers have reduced interfiber friction.

- 20 -

The measurement of bending modulus is not unique to analysis of the physical properties of hair, but reported works had been exclusively devoted to the properties of single hair fiber (see Robbins, Clarence R., Chemical and Physical Behavior of Hair, Third edition. Springer-Verlag, New York. 1993 herein incorporated by reference) and therefore never addressed the characteristics of multiple fibers. In addition, the bending modulus was calculated from the deflection of a single fiber in a static not dynamic mode as used in this test method and reported in the literature for other materials (Lee, T.H., Boey, F.Y., and Loh, N.L.. Characterization of Fibre-Reinforced PPS Composite By Dynamic Mechanical Analysis: Effect of Aspect Ratio and Static Stress. *Composites Science and Technology* 49 (1993) 217-223.)

15

Instruments are commercially available to measure the mechanical properties of a variety of materials, hair included. The Perkin Elmer DMA 7 Dynamic Mechanical Analyzer, used at Helene Curtis R&D, is equipped to perform three point bending modulus, and was used for thermal studies of bending modulus of treated hair. The use of a hair bundle or array allows evaluation of multiple fiber changes and/or fiber interaction in contrast to single fiber effect.

25 Two hundred fifty fibers of the same length are selected from a regular brown hair tress. The fibers are wetted and aligned on a flat surface to form a ribbon-like swatch. single drop of water proof adhesive is placed at five spots on the swatch.

- 21 -

The distance between each junction is about 1 inch. When dry, four bundles are cut from one swatch.

Eight hair bundles are treated with composition per treatment group. The weight of each hair bundle is measured prior to the test in order to assure that the amount of composition applied remains at a constant proportion to the mass of hair of 1:10 for shampoos and 3:5 with respect to conditioners. For rinse-off products such as shampoos and conditioners, the desired amount of product is applied with a micropipette to the wet hair, worked in for 30 seconds and rinsed out in warm water for 30 seconds. All samples are air dried in the instrument at 72F and a controlled humidity of 30%. To heat the sample in the testing chamber the DMA furnace is engaged to 200° F, and the sample is heated for approximately 7 minutes.

The results of testing are presented in Table I with the formulas. Hair arrays treated with the formulations of the invention: mousse, leave-on conditioner, aerosol and nonaerosol hair sprays exhibit a statistically significant reduction in bending modulus following heat treatment. Measurement of the storage bending modulus of untreated, air dried hair vs. heated hair reveals that untreated hair will exhibit an increase in bending modulus of approximately +8.00%, probably due to water loss. Hair arrays treated with a mousse formulated without silicone exhibit nearly the exact opposite change in modulus (24.00% increase) compared to the same mousse formulated with silicone (formula A in Table I) which produced a 28.00% reduction in modulus with

- 22 -

heat. All decreases in bending modulus listed in Table I are statistically significant at >95% confidence level using a t-test to compare the means.

CLAIMS

1. A method for thermal conditioning hair which comprises:
 - (a) applying to hair a leave-on composition comprising:
 - (1) a non-volatile, silicone conditioning agent;
 - (2) a resin; and
 - (3) a carrier;
 - (b) applying heat via a heating appliance to the composition treated hair to dry or style the hair, wherein the temperature of the heating appliance during the heating step is from 200°F to 400°F at the point of origin of the appliance and wherein a reduction in the bending modulus caused by the silicone styling agent is at least 1.00%.
2. A method according to claim 1, wherein the silicone conditioning agent is non-volatile having a boiling point greater than 200°C, typically having a wide range of molecular weights, and having viscosities ranging from 5 centistokes to 1 million centistokes.
3. A method according to claim 1, wherein the nonvolatile, silicone conditioning agent is selected from the group consisting of linear and branched polydimethylsiloxanes, of the following general formulas: $(\text{CH}_3)_3\text{SiO}(\text{Si}(\text{CH}_3)_2)_n\text{SiCH}_3$ wherein n is from 7 to 15,000; and further comprising polydimethylsiloxanes which are organically modified to include amine, hydroxyl, alkyl, alkylaryl, ethoxylated and propoxylated functionalities.
4. A method according to claim 1, wherein the nonvolatile, silicone conditioning agent is selected from the group consisting of: Dimethiconol and Dimethiconol containing silicone emulsions such as, Dimethiconol and

Dimethiconol/Silsesquioxane Copolymer and Sodium C14-16 Olefin Sulfonate; Dimethicone Copolyol; and Phenyl Trimethicone.

5. A method according to claim 1, wherein the nonvolatile silicone conditioning agent is an emulsion.
6. A method according to claim 1, wherein the nonvolatile, silicone conditioning agent is a defoamer.
7. A method according to claim 1, wherein the composition is a mousse, nonaerosol spray, aerosol spray, leave-on conditioner, gel or leave-on lotion.
8. A method according to claim 1, wherein the styling resin is selected from the group consisting of: A Polyquaternium –11 such as Gafquat 734 or Gafquat 755N; a hydrophilic Polyether Urethan such as Polyurethane Resin 142-89; a Polyquaternium –4 such as Celquat L-200 or Celquat H-100; a Polyvinylpyrrolidone such as PVP K-30; a PVP/Dimethylaminoethyl methacrylate copolymer such as Copolymer 845; a VA/Crotonate/Vinyl Neodecanoate Copolymer such as resyn 28-2930; an Octylacrylamide/Acrylates/Butylaminoethyl Methacrylate such as amphomer; and a PVP/VA Copolymer such as PVP/VA E-635.
9. A method according to claim 1, wherein the heating appliance is a blow-dryer, curling iron, hot comb, hot brush, hot curlers, hot rollers, crimper, or hair dryer.
10. A method according to claim 1, wherein the hair being styled has an ornament in it.
11. A method according to claim 1, wherein the hair being styled is in a hairpiece, extension, or wig.
12. A method for thermal conditioning hair which comprises:

(a) applying to hair a leave-on composition comprising:

- (1) a non-volatile silicone conditioning agent;
- (2) a resin; and
- (3) a carrier;

(b) applying heat via a heating appliance to the composition treated hair to dry or style the hair, wherein the temperature of the heating appliance during the heating step is from 200°F to 400°F at the point of origin of the appliance and wherein the method of the invention results in the deposition on the hair of at least 30 microgram silicone/ 1g of hair.

13. A method according to claim 12, wherein the silicone conditioning agent is non-volatile, having a boiling point greater than 200°C, typically having a wide range of molecular weights, and having viscosities ranging from 5 centistokes to 1 million centistokes.

14. A method according to claim 12, wherein the nonvolatile, silicone conditioning agent is selected from the group consisting of linear and branched polydimethylsiloxanes, of the following general formulas: $(CH_3)_3SiO(Si(CH_3)_2)_nSiCH_3$ wherein n is from 7 to 15,000; and further comprising polydimethylsiloxanes which are organically modified to include amine, hydroxyl, alkyl, alkylaryl, ethoxylated and propoxylated functionalities.

15. A method according to claim 12, wherein the silicone conditioning agent is in an emulsion.

16. A method according to claim 1, wherein the nonvolatile, silicone conditioning agent is a defoamer.

17. A method according to claim 12, wherein the composition is a mousse, nonaerosol spray, aerosol spray, leave-on conditioner, gel or leave-on lotion.

18. A method according to claim 12, wherein the styling resin is selected from the group consisting of: A Polyquaternium –11 such as Gafquat 734 of Gafquat 755N; a hydrophilic Polyether Urethane such as Polyurethane Resin 142-89; a Polyquaternium –4 such as Celquat L-200 or Celquat H-100; a Polyvinylpyrrolidone such as PVP K-30; a PVP/Dimethylaminoethyl methacrylate copolymer such as Copolymer 845; a VA/Crotonate/Vinyl Neodecanoate Copolymer such as Resyn 28-2930; an Octylacrylamide/Acrylates/Butylaminoethyl Methacrylate such as amphomer; and a PVP/VA Copolymer such as PVP/VA E-635.

19. A method according to claim 12, wherein the heating appliance is a blow-dryer, curling iron, hot comb, hot brush, hot curlers, hot rollers, crimper, or hair dryer.

20. A method according to claim 12, wherein the hair being styled has an ornament in it.

21. A method according to claim 12, wherein the hair being styled is in a hairpiece, extension, or wig.

22. A method for thermal conditioning of hair which comprises:

(a) applying to hair a leave-on composition comprising:

- (1) a nonvolatile, silicone conditioning agent;
- (2) a styling resin; and
- (3) a carrier;

(b) applying heat via a heating appliance to the composition treated hair to dry or style the hair, wherein the temperature of the heating appliance during the heating step is from 200°F to 400°F at the point of origin of the appliance and wherein a reduction in the bending modulus caused by the

silicone styling agent is at least 1.00%, even when offset by an increase in bending modulus caused by the presence of a styling resin, and wherein the method of the invention results in the deposition on the hair of at least 30 microgram silicone/ 1g of hair.

23. A method for thermal conditioning hair according to claim 1 wherein the reduction in the bending modulus caused by the silicone agent is at least 13.00% - 40.00%.

24. A method for thermal conditioning hair according to claim 1 wherein the amount of silicone deposited on the hair is at least 30 microgram silicone/ 1g of hair.

25. A method for thermal conditioning of hair which comprises:

(a) applying to hair a leave-on composition comprising:

(1) a nonvolatile, silicone conditioning agent;

(2) a carrier;

(b) applying heat via a heating appliance to the composition treated hair to dry or style the hair, wherein the temperature of the heating appliance during the heating step is from 200°F to 400°F at the point of origin of the appliance and wherein a reduction in the bending modulus caused by the silicone conditioning agent is at least 1.00%, even when offset by an increase in bending modulus caused by the presence of a styling resin, and wherein the method of the invention results in the deposition on the hair of at least 30 microgram silicone/ 1g of hair.

26. A method according to claim 25, wherein the leave-on composition is a leave-on conditioner spray.

27. The use of a silicone conditioning agent to elicit a heat-mediated reduction in bending modulus, or softening, or conditioning to hair, as compared to air-dried, treated hair, in a method for thermal conditioning hair which comprises:

(a) applying to hair a leave-on composition comprising:

- (1) a non-volatile, silicone conditioning agent;
- (2) a resin; and
- (3) a carrier;

(b) applying heat via a heating appliance to the composition treated hair to dry or style the hair, wherein the temperature of the heating appliance during the heating step is from 200°F to 400°F at the point of origin of the appliance and wherein a reduction in the bending modulus caused by the silicone conditioning agent is at least 1.00%.

28. Use according to claim 27, wherein the silicone conditioning agent is non-volatile having a boiling point greater than 200°C, typically having a wide range of molecular weights, and having viscosities ranging from 5 centistokes to 1 million centistokes.

29. Use according to claim 27, wherein the nonvolatile, silicone conditioning agent is selected from the group consisting of linear and branched polydimethylsiloxanes, of the following general formulas: $(\text{CH}_3)_3\text{SiO}(\text{Si}(\text{CH}_3)_2)_n\text{SiCH}_3$ wherein n is from 7 to 15,000; and further comprising polydimethylsiloxanes which are organically modified to include amine, hydroxyl, alkyl, alkylaryl, ethoxylated and propoxylated functionalities.

30. Use according to claim 27, wherein the nonvolatile, silicone conditioning agent is selected from the group consisting of: Dimethiconol and

Dimethiconol containing silicone emulsions such as, Dimethiconol and Dimethiconol/Silsesquioxane Copolymer and Sodium C14-16 Olefin Sulfonate; Dimethicone Copolyol; and Phenyl Trimethicone.

31. Use according to claim 27, wherein the nonvolatile silicone conditioning agent is an emulsion.

32. Use according to claim 27, wherein the nonvolatile, silicone conditioning agent is a defoamer.

33. Use according to claim 27, wherein the composition is a mousse, nonaerosol spray, aerosol spray, leave-on conditioner, gel or leave-on lotion.

34. Use according to claim 27, wherein the styling resin is selected from the group consisting of: A Polyquaternium -11 such as Gafquat 734 of Gafquat 755N; a hydrophilic Polyether Urethan such as Polyurethane Resin142-89; a Polyvinylpyrrolidone such as PVP K-30; a PVP/Dimethylaminoethyl methacrylate copolymer such as Copolymer 845; a VA/Crotonate/Vinyl Neodecanoate Copolymer such as resyn 28-2930; an Octylacrylamide/Acrylates/Butylaminoethyl Methacrylate such as amphomer; and a PVP/VA Copolymer such as PVP/VA E-635.

35. Use according to claim 27, wherein the heating appliance is a blow-dryer, curling iron, hot comb, hot brush, hot curlers, hot roller, crimper, or hair dryer.

36. Use according to claim 27, wherein the hair being styled has an ornament in it.

37. Use according to claim 27, wherein the hair being styled is in a hairpiece, extension, or wig.

38. The use of a silicone conditioning agent to elicit a heat-mediated reduction in bending modulus, or softening or conditioning to hair, as compared to air-dried, treated hair in a method for thermal conditioning hair which comprises:

(a) applying to hair a leave-on composition comprising:

- (1) a non-volatile silicone conditioning agent;
- (2) a resin; and
- (3) a carrier;

(b) applying heat via a heating appliance to the composition treated hair to dry or style the hair wherein the temperature of the heating appliance during the heating step is from 200°F to 400°F at the point of origin of the appliance and wherein the method of the invention results in the deposition on the hair of at least 30 microgram silicone/ 1g of hair.

39. Use according to claim 38, wherein the silicone conditioning agent is non-volatile, having a boiling point greater than 200°C, typically having a wide range of molecular weights, and having viscosities ranging from 5 centistokes to 1 million centistokes.

40. Use according to claim 38, wherein the nonvolatile, silicone conditioning agent is selected from the group consisting of linear and branched polydimethylsiloxanes, of the following general formulas: $(CH_3)_3SiO(Si(CH_3)_2)_nSiCH_3$ wherein n is from 7 to 15,000; and further comprising polydimethylsiloxanes which are organically modified to include amine, hydroxyl, alkyl, alkylaryl, ethoxylated and propoxylated functionalities.

41. Use according to claim 38, wherein the silicone conditioning agent is in an emulsion.

42. Use according to claim 27, wherein the nonvolatile, silicone conditioning agent is a defoamer.
43. Use according to claim 38, wherein the composition is a mousse, nonaerosol spray, aerosol spray, leave-on conditioner, gel or leave-on lotion.
44. Use according to claim 38, wherein the styling resin is selected from the group consisting of: A Polyquaternium –11 such as Gafquat 734 of Gafquat 755N; a hydrophilic Polyether Urethane such as Polyurethane Resin 142-89; a Polyquaternium –4 such as Celquat L-200 or Celquat H-100; a Polyvinylpyrrolidone such as PVP K-30; a PVP/Dimethylaminoethyl methacrylate copolymer such as Copolymer 845; a VA/Crotonate/Vinyl Neodecanoate Copolymer such as Resyn 28-2930; an Octylacrylamide/Acrylates/Butylaminoethyl Methacrylate such as amphomer; and a PVP/VA Copolymer such as PVP/VA E-635.
45. Use according to claim 38, wherein the heating appliance is a blow-dryer, curling iron, hot comb, hot brush, hot curlers, hot rollers, crimper, or hair dryer.
46. Use according to claim 38, wherein the hair being styled has an ornament in it.
47. Use according to claim 38, wherein the hair being styled is in a hairpiece, extension, or wig.
48. The use of a silicone conditioning agent to elicit a heat-mediated reduction in bending modulus, or softening or conditioning to hair as, compared to air-dried, treated hair, in a method for thermal conditioning of hair which comprises:
- (a) applying to hair a leave-on composition comprising:

- (1) a nonvolatile, silicone conditioning agent;
- (2) a styling resin; and
- (3) a carrier;

(b) applying heat via a heating appliance to the composition treated hair to dry or style the hair wherein the temperature of the heating appliance during the heating step is from 200°F to 400°F at the point of origin of the appliance and wherein a reduction in the bending modulus caused by the silicone conditioning agent is at least 1.00%, even when offset by an increase in bending modulus caused by the presence of a styling resin, and wherein the method of the invention results in the deposition on the hair of at least 30 microgram silicone/ 1g of hair.

49. Use according to claim 27 wherein the reduction in the bending modulus caused by the silicone conditioning agent is at least 13.00% - 40.00%

50. Use according to claim 27 wherein the amount of silicone deposited on the hair is at least 30 microgram silicone/ 1g of hair.

51. The use of a silicone conditioning agent to elicit a heat-mediated reduction in bending modulus, or softening or conditioning to hair, as compared to air-dried treated hair, in a method for thermal conditioning of hair which comprises:

- (a) applying to hair a leave-on composition comprising:
 - (1) a nonvolatile, silicone conditioning agent;
 - (2) a carrier;

(b) applying heat via a heating appliance to the composition treated hair to dry or style the hair wherein the temperature of the heating appliance

during the heating step is from 200°F to 400°F at the point of origin of the appliance and wherein a reduction in the bending modulus caused by the silicone conditioning agent is at least 1.00%, even when offset by an increase in bending modulus caused by the presence of a styling resin, and wherein the method of the invention results in the deposition on the hair of at least 30 microgram silicone/ 1g of hair.

52. Use according to claim 51, wherein the leave-on composition is a leave-on conditioner spray.