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(54) Title: HAIR SPRAY COMPOSITIONS WITH IONIC STYLING POLYMER		
(57) Abstract <p>Liquid hair styling composition useful for spray application to hair which comprises: (a) an ionic hair styling polymer having a weight average molecular weight of at least about 300,000; (b) a liquid vehicle selected from the group consisting of water, C₁-C₆ monohydric alcohols, and mixtures thereof; (c) an effective amount of an ionic strength modifier system for reducing viscosity of the composition, said system consisting essentially of a mixture of non-surface active cations and anions, wherein said cations and anions are at least partially soluble in said liquid carrier; said composition having a pH of about 10 or less. In yet another aspect of this invention, provided are reduced volatile organic solvent hair spray compositions having improved hair feel comprising silicone-containing hair setting polymer, an effective amount of an ionic strength modifier system for reducing viscosity of the compositions, as described above, and a liquid vehicle which comprises a mixture of water with one or more C₁-C₆ monohydric alcohols, wherein said composition comprises at least about 10 %, by weight, water.</p>		

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HAIR SPRAY COMPOSITIONS WITH IONIC STYLING POLYMER

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TECHNICAL FIELD

10 The present invention relates to hair spray compositions which comprise a high molecular weight hair styling polymer. More particularly, this invention relates to hair spray compositions containing high molecular weight hair styling polymer and having improved sprayability.

BACKGROUND OF THE INVENTION

15 The desire to have the hair retain a particular shape is widely held. A common methodology for accomplishing this is applying hair styling, or hair "setting" compositions to the hair, typically to damp or dry hair. These compositions provide temporary setting benefits, and should be removable by water and/or
20 by shampooing. The materials used in the compositions to provide the setting benefits are generally applied in the form of mousses, gels, lotions or sprays.

High levels of style retention, or hold, are typically expected from hair styling compositions applied as a spray. Style
25 retention is typically achieved by the use of resins, such as AMPHOMER, supplied by National Starch, and GANTREZ SP 225, supplied by GAF. As used in commercially sold hair spray products, these resins generally have a weight average molecular weight of from about 40,000 to about 150,000. When such resins are incor-
30 porated into pump and aerosol hair sprays, they can provide a combination of suitable style retention and good sprayability. "Sprayability" refers to the spray quality and pattern. Good sprayability for hair spray formulations is characterized by a wide spray pattern without a wet, drippy center, and by suf-
35 ficiently small droplet size to provide a fine mist.

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It remains desirable, however, to provide hair spray compositions that have improved hold and style retention performance. One technique for providing improved style retention for liquid hair spray compositions would be to utilize higher molecular weight hair styling resin. Alternately, this could reduce the amount of resin needed to provide a particular level of style retention. High molecular weight hair styling polymers, when utilized commercially, have typically been formulated as gels, lotions, or other non-spray compositions. Unfortunately, high molecular weight resins in liquid hair spray formulations tend to suffer from poor sprayability. More specifically, such formulations tend to have spray quality characterized by reduced spray pattern diameter, increased incidence of wet, drippy centers, and a tendency toward larger droplet size or streaming upon spraying, as opposed to a fine mist. This can result in overly heavy concentrations of hair spray in regions of the hair, causing the hair to be too stiff in those regions, whereas other areas may have too little hair spray applied and, consequently, have poor style retention and hold.

Thus, it is an object of this invention to provide liquid hair spray compositions utilizing high molecular weight styling resins that can provide improved style retention and retain good sprayability characteristics.

Recently, it has been found that certain polymers having silicone macromer portions can provide good style retention benefits to the hair while also providing improved hair feel. In other words, such silicone macromer-containing polymers can impart a tactile sense of softness and conditioning to the hair relative to conventional, non-silicone-containing resins. Silicone macromer-containing hair styling polymers and formulations containing them are disclosed, for example, in EPO Application 90307528.1, published as EPO Application 0 408 311 A2 on January 11, 1991, Hayama, et al., U.S. Patent 5,061,481, issued October 29, 1991, Suzuki et al., U.S. Patent 5,106,609, Bolich et al., issued April 21, 1992, U.S. Patent 5,100,658, Bolich et al.,

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issued March 31, 1992, U.S. Patent 5,100,657, Ansher-Jackson, et al., issued March 31, 1992, U.S. Patent 5,104,646, Bolich et al., issued April 14, 1992, U.S. Serial No. 07/758,319*, Bolich et al., filed August 27, 1991, and U.S. Serial No. 07/758,320*, Torgerson et al., filed August 27, 1991, all of which are incorporated by reference herein.

Whereas these silicone macromer-containing hair styling polymers can provide good overall hair styling performance with a desirable hair conditioning effect, they are preferably used in hair spray at relatively high molecular weights, compared to most commercial products (although they can also be used at more conventional hair spray resin molecular weights (eg., about 50,000 to about 150,000 weight average molecular weight). Furthermore, they are difficult to formulate into a hair spray composition with good sprayability characteristics.

Therefore, it is another object of this invention to provide liquid hair spray compositions containing high molecular weight silicone-containing hair styling polymers which have improved spray characteristics.

It is also desirable to formulate hairspray compositions with reduced levels of volatile organic solvents, e.g., ethanol, propanol, etc. One way to do this is to increase the amount of water present in the composition at the expense of the volatile organic solvent. Unfortunately, this tends to adversely affect hairspray performance, especially drying time upon application, spray quality, and hair feel. This is particularly a problem for reduced volatile organic solvent compositions utilizing silicone macromer-containing hair setting resins. It is especially difficult to obtain good spray quality and hair feel from high water content compositions.

It is yet another object of this invention to obtain improved hairspray compositions containing silicone macromer-containing hair setting resins having reduced volatile organic solvents.

These and other objects as may be apparent to one skilled in the art can be obtained by the invention hereof, which is described in the description which follows. Unless otherwise indicated (*equivalent to EP 0412704 and 0412707, published 13 February 1991)

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licated, all percentages and ratios herein are by weight.

SUMMARY OF THE INVENTION

5 The present invention provides improved sprayability hair spray compositions with high molecular weight hair styling polymers that can provide excellent hair styling/hold benefits upon spray application to the hair.

10 According to the present invention, sprayability of high molecular weight polymers can be improved through the use of ionic strength modifier systems consisting essentially of mixtures of non-surface active anions and cations. It is an essential aspect of the invention that the hair styling polymer also be of an ionic character.

15 More specifically, the present invention relates to a liquid hair styling composition useful for spray application to hair which comprises:

- 20 (a) an ionic hair styling polymer having a weight average molecular weight of at least about 300,000;
- (b) a liquid vehicle selected from the group consisting of water, C₁-C₆, preferably C₂-C₄, monohydric alcohols, and mixtures thereof;
- 25 (c) an effective amount of an ionic strength modifier system for reducing viscosity of the composition, said system consisting essentially of a mixture of non-surface active cations and anions, wherein said cations and anions are at least partially soluble in said liquid carrier;

said composition having a pH of about 10 or less.

30 In one aspect of the invention, the high molecular weight hair styling polymer can be any of the conventional classes of hair styling or hair setting polymers in the art, i.e., polymers free of silicone portions.

35 In another aspect of the invention, the high molecular weight polymer is a silicone macromer-containing hair setting polymer that can provide hair styling and hold benefits while also providing improved softness to the hair relative to non-silicone-containing polymers. In yet another aspect of this

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invention, provided are reduced volatile organic solvent hairspray compositions having improved hair feel comprising silicone-containing hair setting polymer, an effective amount of an ionic strength modifier system for reducing viscosity of the compositions, as described above, and a liquid vehicle which comprises a mixture of water with one or more C₁-C₆, preferably C₂-C₄, monohydric alcohols, wherein said composition comprises at least about 10%, by weight, water.

DETAILED DESCRIPTION OF THE INVENTION

The essential as well as various optional components are described below.

Hair Styling Polymer

The compositions of the present invention contain an effective amount of a high molecular weight hair styling polymer to impart styling benefits upon application to hair. As used herein, "hair styling polymer" means any polymer, natural or synthetic, that can provide hair setting benefits. Polymers of this type are well known in the art. Generally, the level of hair styling polymer used will be at least about 0.1%, by weight, of the composition. Typically, it will be present at a level of from about 0.1% to about 15%, preferably from about 0.5% to about 8%.

The hair styling polymers hereof also are of ionic character. As used herein, "ionic hair styling polymer", or the term "ionic character" in reference to hair styling polymers or monomers of which such hair styling polymers are comprised, means hair styling polymers that are anionic, cationic, amphoteric, zwitterionic, or otherwise can exist in the liquid vehicle of the hair styling composition in dissociated form.

Any type of ionic hair styling polymer which is soluble or dispersible in the liquid carrier can be used in the present invention. A wide variety of such types of hair styling polymers are known in the art.

The ionic hair styling polymers hereof can be homopolymers, copolymers, terpolymers, etc. As used herein, the term "polymer" shall encompass all of such types of polymeric materials.

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As an essential aspect, the polymers hereof must comprise monomers of an ionic character. For convenience in describing the polymers hereof, monomeric units present in the polymers may be referred to as the monomers from which they can be derived. The ionic monomers can be derived from polymerizable ionic starting monomers, or from polymerizable nonionic monomers which are modified subsequent to polymerization to be of ionic character. Also included are corresponding salts, acids and bases of the monomers exemplified.

10 Examples of anionic monomers include:

(i) unsaturated carboxylic acid monomers such as acrylic acid, methacrylic acid, maleic acid, maleic acid half ester, itaconic acid, fumaric acid, and crotonic acid;

15 (ii) half esters of an unsaturated polybasic acid anhydride such as succinic anhydride, phthalic anhydride or the like reacted with a hydroxyl group-containing acrylate and/or methacrylate such as hydroxyethyl acrylate and, hydroxyethyl methacrylate, hydroxypropyl acrylate and the like;

20 (iii) monomers having a sulfonic acid group such as styrene-sulfonic acid, sulfoethyl acrylate and methacrylate, and the like; and

(iv) monomers having a phosphoric acid group such as acid phosphoxyethyl acrylate and methacrylate, 3-chloro-2-acid phosphoxypropyl acrylate and methacrylate, and the like.

25 Examples of the cationic monomers include:

(i) monomers derived from acrylic acid or methacrylic acid, which is referred to hereinafter collectively as (meth)acrylic acid, and a quaternarized epihalohydrin product of a trialkylamine having 1 to 5 carbon atoms in the alkyl such as (meth)acryloxypropyltrimethylammonium chloride and (meth)acryloxypropyltriethylammonium bromide;

30 (ii) amine derivatives of (meth)acrylic acid or amine derivatives of (meth)acrylamide derived from (meth)acrylic acid or (meth)acrylamide and a dialkylalkanolamine having C₁-C₄ alkyl groups such as dimethylaminoethyl (meth)acrylate, diethylaminoethyl (meth)acrylate, dimethylaminopropyl (meth)acrylate, or

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dimethylaminopropyl (meth)acrylamide; and

(iii) derivatives of the products of the group (ii) above by
(1) neutralization with an acid such as hydrochloric acid, or
lactic acid, (2) modification with a halogenated alkyl, such as
5 methyl chloride, ethyl chloride, methyl bromide, or ethyl iodide,
(3) modification with a halogenated fatty acid ester such as ethyl
monochloroacetate, or methyl monochloropropionate, and (4)
modification with a dialkyl sulfate such as dimethyl sulfate, or
diethyl sulfate.

10 Furthermore, the cationic unsaturated monomers include amine
derivatives of allyl compounds such as diallyldimethylammonium
chloride and the like.

These cationic unsaturated monomers can be polymerized in
cationic form, or as an alternative they can be polymerized in the
15 form of their precursors, which are then modified to be cationic,
for example, by a quaternizing agent (e.g. ethyl monochloro-
acetate, dimethyl sulfate, etc.).

Examples of the amphoteric monomers include zwitterionized
derivatives of the aforementioned amine derivatives of (meth)-
20 acrylic acids or the amine derivatives of (meth)acrylamide such as
dimethylaminoethyl (meth)acrylate, dimethylaminopropyl(meth)acryl-
amide by a halogenated fatty acid salt such as potassium mono-
chloroacetate, sodium monobromopropionate, aminomethylpropanol
salt of monochloroacetic acid, triethanolamine salts of mono-
25 chloroacetic acid and the like; and amine derivatives of (meth)-
acrylic acid or (meth)acrylamide, as discussed above, modified
with propanesultone.

These amphoteric monomers, like the aforementioned cationic
monomers, can be polymerized in amphoteric form or, as an alterna-
30 tive, they can also be polymerized in the form of their pre-
cursors, which are then converted into the amphoteric state.

Preferred ionic monomers include acrylic acid, methacrylic
acid, dimethylaminoethyl methacrylate, quaternized dimethyl-
aminoethyl methacrylate, maleic acid, maleic anhydride half
35 esters, crotonic acid, itaconic acid, diallyldimethyl ammonium
chloride, polar vinyl heterocyclics such as vinyl imidazole, vinyl

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pyridine, styrene sulfonate, and mixtures thereof. Especially preferred ionic monomers include acrylic acid, dimethylaminoethyl methacrylate, quaternized dimethylaminoethyl methacrylate, and mixtures thereof.

5 Salts of acid and amine monomers listed above can also be used, e.g., sodium, potassium, or other alkali or alkaline earth metal salts.

The polymers hereof should contain at least about 1%, by weight, ionic monomer, preferably at least about 2%, more preferably at least about 5%.

10 The hair styling polymers hereof can also contain nonionic monomers including, both high polarity monomers and low polarity monomers.

The ionic polymers hereof will generally comprise from about 15 1% to 100% ionic monomers and from 0% to about 99% nonionic monomers, preferably from about 2% to about 75% ionic monomers and from about 25% to about 98% nonionic monomers, more preferably from about 5% to about 50% ionic monomers and from about 50% to about 95% nonionic monomers.

20 Representative examples of low polarity nonionic monomers are acrylic or methacrylic acid esters of C₁-C₂₄ alcohols, such as methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-methyl-1-propanol, 1-pentanol, 2-pentanol, 3-pentanol, 2-methyl-1-butanol, 1-methyl-1-butanol, 3-methyl-1-butanol, 1-methyl-1-pentanol, 25 2-methyl-1-pentanol, 3-methyl-1-pentanol, t-butanol, cyclohexanol, 2-ethyl-1-butanol, 3-heptanol, benzyl alcohol, 2-octanol, 6-methyl-1-heptanol, 2-ethyl-1-hexanol, 3,5-dimethyl-1-hexanol, 3,5,5-trimethyl-1-hexanol, 1-decanol, 1-dodecanol, 1-hexadecanol, 1-octadecanol, and the like, the alcohols having from about 1-24 30 carbon atoms with the average number of carbon atoms preferably being from about 4-18, more preferably from about 4-12; styrene; chlorostyrene; vinyl esters such as vinyl acetate; vinyl chloride; vinylidene chloride; acrylonitrile; alpha-methylstyrene; t-butylstyrene; butadiene; cyclohexadiene; ethylene; propylene; vinyl 35 toluene; alkoxyalkyl (meth)acrylate, such as methoxy ethyl (meth)acrylate, butoxyethyl (meth)acrylate; and mixtures thereof. Other

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nonionic monomers include acrylate and methacrylate derivatives such as allyl acrylate and methacrylate, cyclohexyl acrylate and methacrylate, and methacrylate, oleyl acrylate and methacrylate, benzyl acrylate and methacrylate, tetrahydrofurfuryl acrylate and methacrylate, ethylene glycol di-acrylate and -methacrylate, 1,3-butylene glycol di-acrylate and -methacrylate, diacetonacrylamide, isobornyl (meth)acrylate, and the like.

Preferred nonionic monomers include n-butyl methacrylate, isobutyl methacrylate, 2-ethylhexyl methacrylate, methyl methacrylate, t-butylacrylate, t-butylmethacrylate, and mixtures thereof.

Representative polar nonionic monomers include acrylamide, N,N-dimethylacrylamide, methacrylamide, N-t-butyl acrylamide, methacrylonitrile, acrylamide, acrylate alcohols (e.g. C₂-C₆ acrylate alcohols such as hydroxyethyl acrylate and hydroxypropyl acrylate), methacrylate, and hydroxypropyl methacrylate, vinyl pyrrolidone, vinyl ethers, such as methyl vinyl ether, acyl lactones, vinyl pyridine, allyl alcohols, vinyl alcohols and vinyl caprolactam.

Examples of anionic hair spray polymers are copolymers of vinyl acetate and crotonic acid, terpolymers of vinyl acetate, crotonic acid and a vinyl ester of an alpha-branched saturated aliphatic monocarboxylic acid such as vinyl neodecanoate; and copolymers of methyl vinyl ether and maleic anhydride (molar ratio about 1:1) wherein such copolymers are 50% esterified with a saturated aliphatic alcohol containing from 1 to 4 carbon atoms such as ethanol or butanol; and acrylic copolymers and terpolymers containing acrylic acid or methacrylic acid as the anionic radical containing moiety such as copolymers with methacrylic acid, butyl acrylate, ethyl methacrylate, etc. Another example of an acrylic polymer which can be employed in the compositions of the present invention is a polymer of tertiary-butyl acrylamide, acrylic acid, and ethyl acrylate.

An example of an amphoteric polymer which can be used in the present invention is Octylacrylamide/Acrylates/Butylaminoethyl Methacrylate Copolymer, described generally in U.S. Pat. No.

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4,192,861 as being a polymer of N-tert-octyl acrylamide, methyl methacrylate, hydroxypropyl methacrylate, acrylic acid and t-butyl aminoethyl methacrylate, of appropriate molecular weight for purposes hereof.

5 Examples of cationic hair spray polymers are copolymers of amino-functional acrylate monomers such as lower alkylamino alkyl acrylate or methacrylate monomers such as dimethyl aminoethyl-methacrylate with compatible monomers such as N-vinylpyrrolidone or alkyl methacrylates such as methyl methacrylate and ethyl
10 methacrylate and alkyl acrylates such as methyl acrylate and butyl acrylate. Cationic polymers containing N-vinylpyrrolidone are commercially available from GAF Corp.

 Still other organic, ionic hair styling polymers include carboxymethyl cellulose, copolymers of PVA and crotonic acid,
15 copolymers of PVA and maleic anhydride, sodium polystyrene sulfonate, PVP/ethylmethacrylate/methacrylic acid terpolymer, vinyl acetate/crotonic acid/vinyl neodecanoate copolymer, octylacrylamide/acrylates copolymer, monoethyl ester of poly(methyl vinyl ether-maleic acid), and octylacrylamide/acrylate/butylaminoethyl
20 methacrylate copolymers. Mixtures of polymers may also be used.

Silicone-Containing Hair Styling Polymers

 Preferred ionic hair styling polymers are silicone-containing polymers. Ionic silicone macromer-containing polymers are described, for example, in EPO Application 90307528.1,
25 published as EPO Application 0 408 311 A2 on January 11, 1991, Hayama, et al., U.S. Patent 5,061,481, issued October 29, 1991, Suzuki et al., U.S. Patent 5,106,609, Bolich et al., issued April 21, 1992, U.S. Patent 5,100,658, Bolich et al., issued March 31, 1992, U.S. Patent 5,100,657, Ansher-Jackson, et al., issued March
30 31, 1992, U.S. Patent 5,104,646, Bolich et al., issued April 14, 1992, U.S. Serial No. 07/758,319,* Bolich et al, filed August 27, 1991, and U.S. Serial No. 07/758,320,* Torgerson et al., filed August 27, 1991, all of which are incorporated by reference herein.

35 Examples of useful polymers and how they are made are also (*equivalent to EP 0412704 and 0412707, published 13 February 1991)

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described in detail in U.S. Patent 4,693,935, Mazurek, issued September 15, 1987, U.S. Patent 4,728,571, Clemens et al., issued March 1, 1988, both of which are incorporated herein by reference.

5 Preferred ionic silicone macromer-containing polymers comprise an organic polymeric backbone, preferably a vinyl backbone, having a Tg above about -20°C (more preferably above about 20°C) and, grafted to the backbone, a siloxane macromer having a weight average molecular weight of preferably at least about 500 preferably from about 1,000 to about 100,000, more preferably from 10 about 2,000 to about 50,000, most preferably about 5,000 to about 20,000. In addition to the graft copolymers described above, silicone-containing polymers also include block copolymers preferably containing up to about 50% (more preferably from about 10% to about 40%) by weight of one or more siloxane blocks and one or more non-silicone blocks (such as acrylates or vinyls). 15

The silicone macromer-containing polymers preferred for use herein are such that when formulated into the finished hair care composition, and dried, the polymer phase separates into a discontinuous phase which includes the silicone portion and a continuous phase which includes the organic portion. 20

The silicone macromer-containing ionic hair styling polymers generally comprise nonionic silicone-containing monomers together with ionic monomers as described above, and can also contain non-silicone-containing nonionic monomers, also described above. 25 The silicone-containing monomers also can be ionically charged and, as such, contribute, in part or in whole, to the overall charge density of the polymer.

The silicone-containing hair styling polymers hereof will generally comprise about 0.01% to about 50% of silicone-containing monomer, preferably from about 0.5% to about 40%, more preferably from about 2% to about 25%. 30

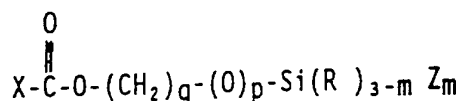
The silicone-containing monomer will generally have the formula:

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$$X(Y)_nSi(R)_{3-m}Z_m$$

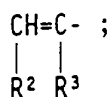
wherein X is a vinyl group copolymerizable with the other monomers

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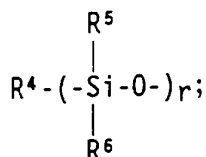
of the polymer; Y is a divalent linking group; R is a hydrogen, lower alkyl (eg. C₁-C₄), aryl, alkaryl, alkylamino, or alkoxy; Z is a monovalent siloxane polymeric moiety having a number average molecular weight of at least about 500, and is pendant from the organic polymeric backbone; n is 0 or 1; and m is an integer from 1 to 3. Of course, Z should be essentially unreactive under polymerization conditions. The silicone-containing monomer preferably has a weight average molecular weight of at least about 500, preferably from about 1,000 to about 100,000, more preferably from about 2,000 to about 50,000, most preferably from about 5,000 to about 20,000. Preferably, it is of the formula:



wherein m is 1, 2 or 3 (preferably m = 1); p is 0 or 1; q is an integer from 2 to 6; X is



R² is hydrogen or -COOH (preferably R² is hydrogen); R³ is hydrogen, methyl or -CH₂COOH (preferably R³ is methyl); Z is



R³, R⁴, R⁵, R⁶ independently are alkyl, alkoxy, alkylamino, aryl, alkaryl, hydrogen, or hydroxyl (preferably alkyl, more preferably methyl); and r is an integer of at least about 10, preferably from about 5 to about 1500 (more preferably r is from about 75 to about 700, most preferably from about 100 to about 250. Particularly preferred are monomers when p=0 and q=3.

The silicone-containing monomers of the ionic polymers hereof can be polymerized in a silicone-containing monomer form. Alternatively, they can be polymerized in the form of their non-silicone containing precursor, and a silicone group can then be added. For example, carboxylate-containing monomers, such as acrylic

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acid, can be polymerized and then reacted with a silicone-containing compound with a terminal epoxy group. The result will, in general, be a silicone-containing monomer in the polymer having an equivalent structure to the formula $X(Y)_nSi(R)_{3-m}Z_m$, described above, and is intended to be encompassed herein.

5 The preferred silicone-containing polymers useful in the present invention generally comprise from 0% to about 98% (preferably from about 5% to about 98%, more preferably from about 50% to about 90%) of nonionic monomer, from 1% to about 98% (preferably from about 15% to about 80%) of ionic monomer, with from about 10 0.1% to about 50% (preferably from about 0.5% to about 40%, most preferably from about 2% to about 25%) of the monomers being silicone-containing monomer. The combination of the non-silicone-containing monomers preferably is from about 50% to about 99% (more preferably about 60% to about 99%, most preferably from about 15 75% to about 95%) of the polymer.

Exemplary silicone-containing polymers for use in the present invention include the following:

- 20 (i) acrylic acid/n-butylmethacrylate/polydimethylsiloxane (PDMS) macromer-20,000 molecular weight
- (ii) dimethylaminoethyl methacrylate/isobutyl methacrylate/2-ethylhexyl-methacrylate/PDMS macromer-20,000 molecular weight
- (iii) t-butylacrylate/acrylic acid/PDMS macromer-10,000 25 molecular weight
- (iv) t-butylacrylate/acrylic acid/PDMS macromer-10,000 molecular weight

The ionic hair styling polymers, including both silicone-containing and non-silicone containing polymers, having carboxylate or other acidic functionalities will preferably be 30 utilized in at least partially neutralized form in the compositions hereof to promote solubility or dispersibility of the polymer in the vehicle. In addition, use of the neutralized form aids in shampoo removability of the hair spray compositions. In general, it is preferred that from about 10% to 100%, more 35 preferably from about 20% to about 90%, even more preferably from

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about 40% to about 85%, of the acidic monomers of the polymer be neutralized.

Any conventionally used base, organic or metallic, may be used for neutralization of acidic polymers. Hydroxides of alkali metal and alkaline earth metal are suitable neutralizers for use in the present hair spray compositions. It will be recognized by those skilled in the art that various of the cations supplied neutralizing the polymer will also contribute to the ionic strength modifier system, as described herein.

Preferred neutralizing agents for use in hair spray compositions of the present invention are potassium hydroxide and sodium hydroxide.

Examples of other suitable neutralizing agents which may be included in the hair spray compositions of the present invention include amines, especially amino alcohols such as 2-amino-2-methyl-1,3-propanediol (AMPD), 2-amine-2-ethyl-1,3-propanediol (AEPD), 2-amino-2-methyl-1-propanol (AMP), 2-amino-1-butanol (AB), monethanolamine (MEA), diethanolamine (DEA), triethanolamine (TEA), moniospropanolamine (MIPA), diisopropanol-amine (DIPA), triisopropanolamine (TIPA) and dimethyl steramine (DMS). Particularly useful for neutralization are mixtures of amines and metallic bases.

Polymers having basic functionalities, e.g., amino groups, are preferably at least partially neutralized with an acid, e.g., hydrogen chloride.

Liquid Vehicle

The hair spray compositions of the present invention also include a liquid vehicle. This can comprise any of those conventionally used in resin hair spray formulations. The liquid vehicle is present in the hair spray compositions at from about 80% to about 99%, preferably from about 85% to about 99%. More preferably, the liquid vehicle is present at from about 90% to about 98% of the total composition.

Organic solvents suitable for use in the liquid vehicle of the present compositions are C₁-C₆ alkanols, carbitol, acetone and mixtures thereof. C₁-C₆ alkanols preferred for use in the present

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compositions are C₂-C₄ monohydric alcohols such as ethanol, isopropanol and mixtures thereof. Water is also a preferred solvent for use in the liquid vehicle of the present hair spray compositions.

5 Preferably, the liquid vehicle for the present compositions is selected from the group consisting of C₁-C₆ alkanols, water, carbitol, acetone and mixtures thereof. More preferably, the liquid vehicle of the present composition is selected from the group consisting of water and C₂-C₄ monohydric alcohols such as
10 ethanol and isopropanol, and mixtures thereof.

In general, water may be absent from the liquid vehicle or may comprise all of the liquid vehicle. Most preferably, the liquid vehicle is a mixture of water and organic solvents.

Where water and organic solvent mixtures are used, for
15 instance, water-ethanol or water-isopropanol-ethanol, the water content of the compositions is generally in the range of from about 0.5% to about 99%, preferably from about 5% to about 50% by weight of the total composition. In such mixtures, the organic solvents are generally present in the range of from 0.5% to about
20 99%, preferably from about 50% to about 95%, by weight of the total composition.

In one aspect of the invention, the hair setting resin is of particularly high weight average molecular weight, i.e. weight average molecular weight above about 300,000, especially above
25 about 500,000. It has been found that surprisingly effective hair spray performance can be obtained using these high molecular weight resins in combination with ionic strength modifier system. This invention is especially effective at providing the resins with characteristics in hair spray compositions such that they can
30 be sprayed with good spray quality, especially with respect to silicone macromer-containing hair setting resins, which are preferably used at relatively high molecular weights.

In another aspect of the invention, what is provided is a low volatile organic solvent hairspray composition which comprises a
35 silicone macromer-containing ionic hair setting resin, an ionic strength modifier system as described herein, and a liquid

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vehicle. A reduced volatile organic solvent hair spray composition of the present invention comprises no more than 80% volatile organic solvents (which include, for purposes hereof, volatile silicone fluids and excludes water). In other embodiments hereof, the hair spray compositions can comprise no more than about 65%, 55%, 50%, or other levels of volatile organic solvents, as may be chosen by product formulators. In the reduced volatile organic solvent hair spray products hereof, the hair spray compositions comprise at least 10%, by weight, of water. It is also specifically contemplated that they may contain at least about 11%, 12%, 13%, 14%, 15%, or more water. The weight average molecular weight of the silicone macromer-containing hair setting resins can be of any level suitable for providing effective hair styling. Typically, it will be at least about 50,000, more typically at least about 70,000, preferably at least about 100,000. As used herein, volatile organic solvents means solvents which have at least one carbon atom and exhibit a vapor pressure of greater than 0.1 mm Hg at 20°C.

In the more preferred embodiments of this aspect of the invention, the weight average molecular weight of the resin is from about 70,000 to about 1,000,000, most preferably from about 100,000 to about 750,000.

In general, the reduced volatile organic solvent compositions hereof will comprise up to about 90%, preferably up to about 70%, more preferably up to about 60%, even more preferably up to about 50% water; and from about 10% to about 80%, preferably from about 20% to about 80%, more preferably from about 40% to about 80%, of volatile organic solvents. It is also specifically contemplated that the compositions can be limited to no more than other maximum limits on volatile organic solvents, eg., no more than about 75%, 65%, or 55%, etc..

In general, for the compositions hereof, the weight average molecular weight of the styling polymer is limited only by practical concerns. Generally, it will be below about 10,000,000, preferably below about 3,000,000, more preferably below about 1,000,000.

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Ionic Strength Modifier System

The compositions of the present invention include, as an essential element, an effective amount of an ionic strength modifier system for reducing the viscosity of the hair styling composition, relative to the same composition absent the ionic strength modifiers. In general, the present compositions will comprise at least about 0.01%, by weight, of the ionic strength modifier. As will be understood by those skilled in the art, as the ionic strength of the composition is increased, the hair styling polymer will eventually fall out of solution, or otherwise no longer remain solubilized or dispersed in the liquid carrier. The upper limit of the ionic strength modifier system level will vary depending upon the particular ionic strength modifiers, liquid vehicle, hair styling polymer, and other ingredients present in the composition. Thus, for example, the maximum amount of the ionic strength modifiers that can be used will tend to be lower for compositions with liquid vehicles containing less water, compared to compositions with more water. Generally, the compositions will comprise about 4%, by weight, or less of the ionic strength modifiers, more generally about 2% or less, and typically about 1% or less. Preferably, the compositions hereof will comprise from about 0.01% to about 0.5%, more preferably from about 0.01% to about 0.1%, of the ionic strength modifier system.

The ionic strength modifier system comprises a mixture of monomeric cations and anions. The ions of the ionic strength modifier system hereof are non-surface active, i.e. they do not significantly reduce surface tension. For purposes hereof, non-surface active shall mean the ions, which at a 0.5% aqueous solution concentration, reduce surface tension by no more than 5.0 dynes/cm². Generally, the ions of the ionic strength modifier system hereof will be characterized by having, at maximum, four or less carbon atoms per charge, preferably two or less carbon atoms, in any aliphatic chain or straight or branched organic hetero-chain.

The ionic strength modifier system comprises monomeric ions of the type which are products of acid-base reactions. Thus,

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basic and acidic ions OH^- and H^+ do not constitute part of the ionic strength modifier system hereof, although they may be present in the composition. The ions hereof are incorporated into the composition in a form such that they can exist in the composition as free ions, i.e., in dissociated form. It is not necessary that all of the ions added exist in the composition as free ions, but they must be at least partially soluble or dissociated in the composition. The ionic strength modifiers can be incorporated into the hair styling compositions, for example, by addition of soluble salts, or by addition of mixtures of acids and bases, or by a combination thereof. It is a necessary aspect of the invention that both anions and cations of the ionic strength modifier system be included in the composition.

Suitable cations for use include, for example, alkali metals, such as lithium, sodium, and potassium, and alkaline-earth metals, such as magnesium, calcium, and strontium. Preferred of the divalent cations is magnesium. Preferred monovalent metal ions are lithium, sodium, and potassium, particularly sodium and potassium. Suitable means of addition to the compositions hereof include, for example, addition as bases, eg., hydroxides, sodium hydroxide and potassium hydroxide, and such as salts that are soluble in the liquid carrier, eg. salts of monomeric anions such as those described below.

Other suitable cations include organic ions, such as quaternary ammonium ions and cationic amines, such as ammonium mono-, di-, and tri-ethanolamines, triethylamine, morpholine, aminomethylpropanol (AMP), aminoethylpropanediol, etc. Ammonium and the amines are preferably provided in the forms of salts, such as hydrochloride salts.

Monomeric anions that can be used include halogen ions, such as chloride, fluoride, bromide, and iodide, particularly chloride, sulfate, ethyl sulfate, methyl sulfate, cyclohexyl sulfamate, thiosulfate, toluene sulfonate, xylene sulfonate, citrate, nitrate, bicarbonate, adipate, succinate, saccharinate, benzoate, lactate, borate, isethionate, tartrate, and other monomeric anions

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that can exist in dissociated form in the hair styling composition. The anions can be added to the compositions hereof, for example, in the form of acids or salts which are at least partially soluble in the liquid vehicle, eg., sodium or potassium salts of acetate, citrate, nitrate, chloride, sulfate, etc. Preferably, such salts are entirely soluble in the vehicle.

The compositions hereof have a water-equivalent pH of about 10 or less, preferably from about 3 to about 10, more preferably from about 5 to about 10. For purposes hereof, water-equivalent pH shall correspond to the pH of a composition containing all of the components of the composition, except that any non-aqueous component of the carrier is replaced by an equal weight of double reverse osmosis (DRO) water.

A preferred reduced volatile organic solvent hairspray composition of the present invention contains from about .01% to about 2% of a fluorosurfactant; from about 0.1% to about 15% of an ionic resin, including those having a weight average molecular weight of 300,000 and above, as well as those below 300,000, and also including those having silicone macromer portions as well as those without; an ionic strength modifier system as described herein, and a liquid vehicle comprising about 10% to about 45%, by weight of the composition water and about 50% to about 80%, by weight of the composition, of an organic solvent, preferably selected from the group consisting of ethanol, isopropanol and mixtures thereof.

The level of ionic strength modifier system used, in general, is given above. It is to be recognized, however, that the particular level of ionic strength modifier system which must be used to achieve an improvement in hair spray performance, or to achieve optimum performance, for a particular hair spray composition can vary depending upon a variety of factors, including the particular type of resin chosen and its molecular weight, and level in the composition, the specific ionic strength modifier system, the level of water and the type and level of volatile organic solvent, and the presence of optional components in the system. In gene-

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ral, higher levels of ionic strength modifier system may be needed to achieve a performance benefit as resin molecular weight and/or water levels are reduced. In general, the compositions hereof should contain at least an effective amount of the ionic strength modifier system provide an improvement in hair feel for a given level of hair hold performance or for improved spray quality (?).

Optional Ingredients

In addition to the ionic strength modifier system described above, the compositions hereof can optionally contain other materials to improve sprayability of the compositions. In particular, it is contemplated to utilize ionic surfactants in combination with the non-surface active anions and cations of the ionic strength modifier system hereof.

A wide variety of surfactants may be advantageously incorporated into the compositions hereof. These include anionic, cationic, amphoteric, and zwitterionic surfactants, and further include both fluorinated surfactants, as described below, and nonfluorinated surfactants.

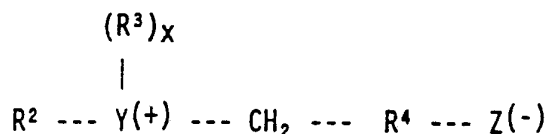
Anionic surfactants include, for example: alkyl and alkenyl sulfates; alkyl and alkenyl ethoxylated sulfates; (preferably having an average degree of ethoxylation of 1 to 10), succinamate surfactants, such as alkylsulfosuccinamates and dialkyl esters of sulfosuccinic acid; neutralized fatty acid esters of isethionic acid; and alkyl and alkenyl sulfonates, including, for example, olefin sulfonates and beta-alkoxy alkane sulfonates. Preferred are alkyl and alkenyl sulfates and alkyl and alkenyl ethoxylated sulfates such as the sodium and ammonium salts of C₁₂-C₁₈ sulfates and ethoxylated sulfates with a degree of ethoxylation of from 1 to about 6, preferably from 1 to about 4, e.g., lauryl sulfate and laureth (3.0) sulfate.

Amphoteric surfactants include those which can be broadly described as derivatives of aliphatic secondary and tertiary amines in which the aliphatic radical can be straight chain or branched and wherein one of the aliphatic substituents contains from about 8 to about 18 carbon atoms and one contains an anionic water solubilizing group, e.g., carboxy, sulfonate, sulfate,

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phosphate, or phosphonate. Examples of compounds falling within this definition are sodium 3-dodecylaminopropionate, N-alkyl-
 5 taurines such as the one prepared by reacting dodecylamine with sodium isethionate according to the teaching of U.S. Patent 2,658,072, N-higher alkyl aspartic acids such as those produced according to the teaching of U.S. Patent 2,438,091, and the products sold under the trade name "Miranol" and described in U.S. Patent 2,528,378. Others include alkyl, preferably C₆-C₂₂ and most preferably C₈-C₁₂, amphoglycinates; alkyl, preferably C₆-C₂₂
 10 and most preferably C₈-C₁₂, amphopropionates; and mixtures thereof.

Suitable zwitterionic surfactants for use in the present compositions can be exemplified by those which can be broadly described as derivatives of aliphatic quaternary ammonium, phosphonium, and sulfonium compounds, in which the aliphatic radicals
 15 can be straight chain or branched, and wherein one of the aliphatic substituents contains from about 8 to 18 carbon atoms and one contains an anionic water-solubilizing group, e.g., carboxy, sulfonate, sulfate, phosphate, or phosphonate. A general formula for these compounds is:
 20



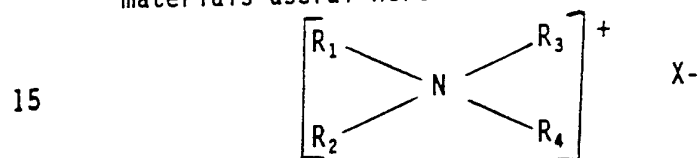
wherein R² contains an alkyl, alkenyl, or hydroxy alkyl radical of
 25 from about 8 to about 18 carbon atoms, from 0 to about 10 ethylene oxide moieties and from 0 to 1 glyceryl moiety; Y is selected from the group consisting of nitrogen, phosphorus, and sulfur atoms; R³ is an alkyl or monohydroxyalkyl group containing 1 to about 3 carbon atoms; x is 1 when Y is sulfur or phosphorus, 1 or 2 when Y is nitrogen; R⁴ is an alkylene or hydroxyalkylene of from 1 to
 30 about 4 carbon atoms and Z is a radical selected from the group consisting of carboxylate, sulfonate, sulfate, phosphonate, and phosphate groups. Classes of zwitterionics include alkyl amino sulfonates, alkyl betaines, and alkyl amido betaines.

35 Cationic surfactants useful in compositions of the present invention contain amino or quaternary ammonium hydrophilic moi-

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eties which are positively charged when dissolved in the aqueous composition of the present invention. Cationic surfactants among those useful herein are disclosed in the following documents, all incorporated by reference herein: M. C. Publishing Co., **McCutcheon's, Detergents & Emulsifiers**, (North American edition 1979); Schwartz, et al., **Surface Active Agents, Their Chemistry and Technology**, New York: Interscience Publishers, 1949; U.S. Pat. No. 3,155,591, Hilfer, issued Nov. 3, 1964; U.S. Pat. No. 3,929,678, Laughlin, et al., issued Dec. 30, 1975; U.S. Pat. No. 3,959,461, Bailey, et al., issued May 25, 1976; and U.S. Pat. No. 4,387,090, Bolich, Jr., issued June 7, 1983.

Among the quaternary ammonium-containing cationic surfactant materials useful herein are those of the general formula:



wherein R_1 is an aliphatic group of from 1 to 22 carbon atoms, or an aromatic, aryl or alkylaryl group having from 12 to 22 carbon atoms; R_2 is an aliphatic group having from 1 to 22 carbon atoms; R_3 and R_4 are each alkyl groups having from 1 to 3 carbon atoms, and X is an anion selected from halogen, acetate, phosphate, nitrate and alkylsulfate radicals. The aliphatic groups may contain, in addition to carbon and hydrogen atoms, ether linkages, and other groups such as amido groups. Other quaternary ammonium salts useful herein are diquaternary ammonium salts.

25 Preferred quaternary ammonium salts include dialkyldimethylammonium chlorides, wherein in the alkyl groups have from 12 to 22 carbon atoms and are derived from long-chain fatty acids, such as hydrogenated tallow fatty acid. (Tallow fatty acids give rise to quaternary compounds wherein R_1 and R_2 have predominately from 16 to 18 carbon atoms.)

35 Salts of primary, secondary and tertiary fatty amines are also suitable cationic surfactants for use herein. The alkyl groups of such amines preferably have from 12 to 22 carbon atoms, and may be substituted or unsubstituted. Secondary and tertiary amines are preferred, tertiary amines are particularly preferred. Such amines, useful herein, include stearamido propyl dimethyl

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amine, diethyl amino ethyl stearamide, dimethyl stearamine, dimethyl soyamine, soyamine, myristyl amine, tridecyl amine, ethyl stearylamine, N-tallowpropane diamine, ethoxylated (5 moles E.O.) stearylamine, dihydroxy ethyl stearylamine, and arachidyl-behenylamine. Cationic amine surfactants included among those useful in the present invention are disclosed in U.S. Pat. No. 4,275,055, Nachtigal, et al., issued June 23, 1981 (incorporated by reference herein).

Suitable cationic surfactant salts include the halogen, acetate, phosphate, nitrate, citrate, lactate and alkyl sulfate salts.

Nonionic surfactants can also be included in the compositions hereof. Preferably, the nonionic surfactants have an average HLB (Hydrophile-Lipophile Balance) of less than or equal to about 7.

Methods of determining HLB are well known in the art and any of such methods may be used for HLB determination. A description of the HLB System and methods for HLB determination are described in "The HLB System: a time saving guide to emulsifier selection," ICI Americas Inc.; Wilmington, Delaware; 1976.

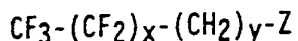
Nonionic surfactants include polyethylene oxide condensates of alkyl phenols (preferably C₆-C₁₂ alkyl, with a degree of ethoxylation of about 1 to about 6), condensation products of ethylene oxide with the reaction product of propylene oxide and ethylene diamine, condensation products of aliphatic alcohols with ethylene oxide, long chain (i.e., typically C₁₂-C₂₂) tertiary amine oxides, long chain tertiary phosphine oxides, dialkyl sulfoxides containing one long chain alkyl or hydroxy alkyl radical and one short chain (preferably C₁-C₃) radical, silicone copolyols, and C₁-C₄ alkanol amides of acids having a C₈-C₂₂ acyl moiety.

Fluorosurfactants (i.e., fluorinated surfactants) useful in the present compositions can be linear or branched alkyl, alkenyl or alkylaryl fluorohydrocarbons having a chain length of preferably 3 to 18 carbon atoms and being fully or partially fluorinated. The hydrophilic moiety can be, for example, sulfate,

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phosphate, phosphonate, sulfonate, amine, amine salts, quaternary ammonium, carboxylate, and any combination thereof. Also, there can be a bridging moiety between the hydrophilic and hydrophobic moieties, such as an amido alkalene group for example.

5 Ionic fluorosurfactants useful in the present compositions include perfluorinated compounds represented by the formula



where Z is a water solubilizing group of either organic or inorganic character, x is an integer which is generally from 2 to 10 17, particularly from 7 to 11, and y is an integer from 0 to 4, and said compounds may be cationic, anionic, amphoteric or zwitterionic, depending upon the nature of the grouping or groupings encompassed by Z. The Z groups may be or may comprise sulfate, sulfonate, carboxylate, amine salt, quaternary ammonium, phosphate, phosphonate, and combinations thereof. The perfluorinated 15 compounds are known in the art. These compounds are described in U.S. Patent 4,176,176, Cella et al., issued November 27, 1979; U.S. Patent 3,993,745, Cella et al., issued November 23, 1976, and U.S. Patent 3,993,744, Cella et al., issued November 23, 1976, 20 each being incorporated herein by reference.

Cationic fluorosurfactants preferred for use in the present compositions include fluorinated alkyl quaternary ammonium salts having a variety of anionic counter ions, including iodide, chloride, methosulfate, phosphate, and nitrate salts, preferably 25 an iodide; and those fluorosurfactants conforming to the formula $\text{R}_f\text{CH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{N}^+(\text{CH}_3)_3[\text{CH}_3\text{SO}_4]^-$ wherein $\text{R}_f=\text{F}(\text{CF}_2\text{CF}_2)_{3-8}$, such as ZONYL FSC supplied by E. I. DuPont deNemours and Company (Wilmington, Delaware, USA; DuPont). A preferred fluorinated alkyl quaternary ammonium iodide is FLUORAD FC-135 supplied by Minnesota 30 Mining & Manufacturing (St. Paul, Minnesota, USA; 3M).

Anionic fluorosurfactants preferred for use in the present compositions are mono-, and bis-perfluoroalkyl phosphates, such as ZONYL FSP supplied by DuPont and conforming to the general formulae 35 $(\text{R}_f\text{CH}_2\text{CH}_2\text{O})\text{P}(\text{O})(\text{ONH}_4)_2$ and $(\text{R}_f\text{CH}_2\text{CH}_2\text{O})_2\text{P}(\text{O})(\text{ONH}_4)$ wherein $\text{R}_f=\text{F}(\text{CF}_2\text{CF}_2)_{3-8}$; mono- and bis-fluoroalkyl phosphates, having a

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variety of cationic counterions such as ammonium, sodium, potassium, triethanolamine and diethanolamine salts, preferably ammonium salts, complexed with non-fluorinated quats, preferably aliphatic quaternary methosulfates, such as ZONYL FSJ supplied by DuPont; perfluoroalkyl sulfonic acid having a variety of cationic counterions such as ammonium, sodium, potassium, triethanolamine and diethanolamine salts, preferably ammonium salts, such as ZONYL TBS supplied by DuPont and conforming to the formula $R_fCH_2CH_2SO_3X$ wherein $R_f=F(CF_2CF_2)_{3-8}$ and $X=H$ or NH_4 ; telomer phosphates, having a variety of cationic counterions such as ammonium, sodium, potassium, triethanolamine and diethanolamine salts, preferably diethanolamine salts, such as ZONYL RP supplied by DuPont; amine perfluoroalkyl sulfonates, such as FLUORAD FC-99 supplied by 3M; ammonium perfluoroalkyl sulfonates, such as FLUORAD FC-93, FLUORAD FC-120 and L-12402, supplied by 3M; potassium perfluoroalkyl sulfonates, such as FLUORAD-95 and FLUORAD FC-98 supplied by 3M; potassium fluorinated alkyl carboxylates, such as FLUORAD FC-129 and FLUORAD FC-109 supplied by 3M; ammonium perfluoroalkyl carboxylates, such as Fluorad FC-143[®] supplied by 3M; and those fluorosurfactants conforming to the general formula $R_fCH_2CH_2SCH_2CH_2CO_2Li$ wherein $R_f=F(CF_2CF_2)_{3-8}$, such as ZONYL FSA supplied by DuPont.

Preferred anionic fluorosurfactants are mixed mono- and bis-perfluoroalkyl phosphates, ammonium salts; mixed mono- and bis-fluoroalkyl phosphate, ammonium salts, complexed with aliphatic quaternary methosulfates; perfluoroalkyl sulfonic acid, ammonium salts; mixed telomer phosphate diethanolamine salts; amine perfluoroalkyl sulfonates; ammonium perfluoroalkyl sulfonates; potassium perfluoroalkyl sulfonates; potassium fluorinated alkyl carboxylates; ammonium perfluoroalkyl sulfonates; and ammonium perfluoroalkyl carboxylates.

Amphoteric fluorosurfactants preferred for use in the present compositions are fluorinated alkyl amphoteric surfactants available commercially as FLUORAD FC-100 from 3M.

Zwitterionic fluorosurfactants preferred for use in the

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present compositions are those fluorosurfactants conforming to the formula $R_fCH_2CH(OCOCH_3)CH_2N^+(CH_3)_2CH_2CO_2^-$ wherein $R_f=F(CF_2CF_2)_{3-8}$ such as ZONYL FSK supplied by DuPont.

5 Preferably, mixtures of amphoteric or zwitterionic fluorosurfactants with anionic fluorosurfactants or mixtures of anionic and cationic fluorosurfactants are used.

The use of fluorosurfactants is especially desirable in reduced volatile organic solvent compositions, and most especially those with silicone macromer-containing polymers.

10 Surfactants are preferably included in the compositions at a level of from about 0.01% to about 2%, more preferably from about 0.01% to about 1.5%, most preferably from about 0.01% to about 1%.

Plasticizer

15 The performance of the hair styling polymers can be improved through the optional incorporation of a nonvolatile plasticizer into the composition. The plasticizer will generally be present in the compositions at a plasticizer: styling polymer weight ratio of about 1:20: to about 1:1, preferably from about 1:15 to about 20 1:2. As used herein, "nonvolatile" in regard to plasticizers means that the plasticizer exhibits essentially no vapor pressure at atmospheric pressure and 25°C. The polymer-liquid vehicle solution should not suffer from substantial plasticizer weight loss while the volatile carrier is evaporating, since this may 25 excessively reduce plasticization of the polymer during use. The plasticizers for use herein should generally have boiling points of about 250°C or higher.

Plasticizers are well known in the art and are generally described in Kirk-Othmer Encyclopedia of Chemical Technology, 30 second edition, Volume 15, pp. 720-789 (John Wiley & Sons, Inc. New York, 1968) under the topic heading "Plasticizers", and by J. Kern Sears and Joseph R. Darby in the text The Technology of Plasticizers (John Wiley & Sons, Inc., New York, 1982), both 35 incorporated herein by reference. See especially in the Appendix of Sears/Darby Table A.9 at pages 983-1063 where a wide variety of plasticizers are disclosed.

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Plasticizers include both cyclic and acyclic nonvolatile materials. Suitable categories of nonvolatile plasticizers include adipates, phthalates, isophthalates, azelates, stearates, citrates, trimellitates, silicone copolyols, iso C₁₄-C₂₂ alcohols, methyl alkyl silicones, carbonates, sebacates, isobutgrates, oleates, phosphates, myristates, ricinoleates, pelargonates, valerates, oleates, camphor, and castor oil, and silicone copolyols.

Examples of adipate plasticizers include adipic acid derivatives such as diisobutyl adipate, bis(2-ethylhexyl) adipate, diisodecyl adipate, bis(2-butoxyethyl) adipate, and di-n-hexyl adipate.

Examples of phthalate plasticizers include phthalic acid derivatives such as dibutyl phthalate, butyl octyl phthalate, di-n-octyl phthalate, diisooctyl phthalate, bis(2-ethylhexyl) phthalate, n-octyl n-decyl phthalate, di-n-hexyl phthalate, isooctyl isodecyl phthalate, diisodecyl phthalate, ditridecyl phthalate, butyl cyclohexyl phthalate, butyl benzyl phthalate, dicyclohexyl phthalate, diphenyl phthalate, isodecyl benzyl phthalate, and bis(2-butoxyethyl) phthalate.

Isophthalate plasticizers include bis(2-ethylhexyl) isophthalate.

Examples of azelate plasticizers include azelaic acid derivatives such as di(2-ethylhexyl) azelate, and bis(2-ethylhexyl) azelate.

Examples of stearate plasticizers include stearic acid derivatives such as n-butyl stearate, butyl acetoxystearate, and butoxyethyl stearate.

Examples of citrate plasticizers include citric acid derivatives such as acetyl tri-n-butyl citrate, tri-n-butyl citrate, and acetyl tri-2-ethylhexyl citrate.

Examples of trimellitate plasticizers include tri-(2-ethylhexyl) trimellitate, and triisooctyl trimellitate.

Other examples of plasticizers include dibutyl carbonate, butyl oleate, n-butyl, butyrate, isobutyl butyrate, isopropyl

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butyrate, dibutyl carbonate, ethyl palmitate, isooctyl palmitate, methyl ricinoleate, butyl ricinoleate, diisooctyl sebacate, triisobutyl phosphate, isodecyl pelargonate, ethyl valerate, isocetyl alcohol, octododecanol, isopropyl myristate, isostearyl alcohol and methyl alkyl silicones having C₂-C₂₀ alkyl and from 1 to about 500 siloxane monomer units, silicone copolyols, eg. dimethicone copolyol.

Hair Spray Compositions

Hair spray compositions of the present invention can be dispensed from containers which are aerosol dispensers or pump spray dispensers. Such dispensers, i.e., containers, are well known to those skilled in the art and are commercially available from a variety of manufacturers, including American National Can Corp. and Continental Can Corp.

When the hair spray compositions are to be dispensed from a pressurized aerosol container, a propellant which consists of one or more of the conventionally-known aerosol propellants may be used to propel the compositions. A suitable propellant for use can be generally any liquifiable gas conventionally used for aerosol containers.

Suitable propellants for use are volatile hydrocarbon propellants which can include liquified lower hydrocarbons of 3 to 4 carbon atoms such as propane, butane and isobutane. Other suitable propellants are hydrofluorocarbons such as 1,2-difluoroethane (Hydrofluorocarbon 152A) supplied as Dymel 152A by DuPont. Other examples of propellants are dimethylether, nitrogen, carbon dioxide, nitrous oxide and atmospheric gas.

The hydrocarbons, particularly isobutane, used singly or admixed with other hydrocarbons are preferred.

The aerosol propellant may be mixed with the present compositions and the amount of propellant to be mixed is governed by normal factors well known in the aerosol art. Generally, for liquifiable propellants, the level of propellant is from about 10% to about 60% by weight of the total composition, preferably from about 15% to about 50% by weight of the total composition.

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Alternatively, pressurized aerosol dispensers can be used where the propellant is separated from contact with the hair spray composition such as a two compartment can of the type sold under the tradename SEPRO from Americal National Can Corp.

5 Other suitable aerosol dispensers are those characterized by the propellant being compressed air which can be filled into the dispenser by means of a pump or equivalent device prior to use. Such dispensers are described in U.S. Patents 4,077,441, March 7, 1978, Olofsson and 4,850,577, July 25, 1989, TerStege, both
10 incorporated by reference herein, and in U.S. Serial No. 07/839,648, Gosselin et al., filed February 21, 1992, also incorporated by reference herein. Compressed air aerosol containers suitable for use are also currently marketed by The Procter & Gamble Company under their tradename VIDAL SASSOON
15 AIRSPRAY® hair sprays.

Conventional non-aerosol pump spray dispensers, i.e., atomizers, can also be used.

Other Ingredients

The hair spray formulations of the present invention can
20 optionally contain a variety of other hair spray adjuvants as are known in the art. Generally, the compositions will comprise from about 0.05% to 5%, by weight, preferably from about 0.1% to 3%, by weight, of adjuvants. Hair spray adjuvants include: silicones; emollients; lubricants and penetrants such as various lanolin
25 compounds; protein hydrolysates and other protein derivatives; ethylene adducts and polyoxyethylene cholesterol; dyes, tints and other colorants; sunscreens; and perfume.

METHOD OF USE

The hair spray compositions of the present invention are used
30 in conventional ways to provide the hair styling/holding benefits of the present invention. Such method generally involves spraying an effective amount of the product to dry or damp hair before or after the hair is styled, or both. By "effective amount" is meant an amount sufficient to provide the hair volume and style benefits
35 desired considering the length and texture of the hair.

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The following Examples illustrate the present invention. The Examples are given solely for the purposes of illustration and are not to be construed as limitations of the present invention as many variations of the invention are possible without departing from its spirit and scope.

EXAMPLES

Examples I-XVI

Hair spray compositions of the present invention are prepared according to the following formulations.

		Example # (Weight Percent)							
<u>Ingredient</u>		<u>I</u>	<u>II</u>	<u>III</u>	<u>IV</u>	<u>V</u>	<u>VI</u>	<u>VII</u>	<u>VIII</u>
10	Ethanol, 200 proof	79.3	79.3	79.2	79.2	79.1	79.1	79.2	79.2
	Isopropanol	--	10.4	10.4	10.4	10.4	10.4	10.4	10.4
	Hair Styling	4.0	2.6	2.6	2.6	2.6	2.6	2.6	2.6
15	Polymer ¹								
	KOH (45% aqueous solution) ²	0.82	0.7	0.8	0.8	0.8	0.8	0.8	0.8
	DRO Water ³	17.4	7.0	7.0	7.0	7.0	7.0	7.0	7.0
	Potassium Chloride	0.02	0.05	0.02	-	-	-	-	-
20	Potassium Acetate	-	-	-	-	0.09	-	-	-
	Magnesium Acetate	-	-	-	-	-	-	-	-
	Acetic Acid	-	-	-	0.06	-	-	-	0.06
	Fluorosurfactant ⁴	-	-	-	-	-	0.1	0.05	-
	AMP ⁵	-	-	-	-	-	-	-	-
25		Example # (Weight Percent)							
	<u>Ingredient</u>	<u>IX</u>	<u>X</u>	<u>XI</u>	<u>XII</u>	<u>XIII</u>	<u>XIV</u>	<u>XV</u>	<u>XVI</u>
	Ethanol, 200 proof	79.2	86.6	86.3	43.3	86.6	80.0	75.9	75.8
	Isopropanol	10.4	10.4	10.4	10.4	10.4	10.4	-	-
	Hair Styling	2.6	2.6	2.6	2.6	2.6	2.6	2.6	2.6
30	Polymer ¹								
	KOH ²	0.8	-	-	-	-	-	3.3	3.3
	DRO Water ³	7.0	0.1	0.3	42.9	-	7.0	15.0	15.0
	Potassium Chloride	-	0.03	-	-	-	0.03	-	-
	Potassium Acetate	0.09	-	0.1	-	-	-	-	0.2
35	Magnesium Acetate	-	-	-	-	-	-	0.1	-
	Acetic Acid	-	-	-	0.5	-	-	-	-

Fluorosurfactant ⁴	-	-	-	-	0.05	-	-	-
AMP ⁵	-	0.3	0.3	0.3	0.3	-	-	-

1 60% t-butyl acrylate/20% acrylic acid/20% silicone (PDMS) macromer - Example I, weight average molecular weight of about 150,000. Examples II-VI, weight average molecular weight of about 1.7 million; Examples VII-XIV, weight average molecular weight of about 800,000; Examples XV-XVI, weight average molecular weight of about 1.2 million.

2 Potassium hydroxide solution, containing 45% potassium hydroxide and 55% water and minors, except Examples XV and XVI, utilizing a 10% aqueous solution of potassium hydroxide.

3 Double reverse osmosis water.

4 ZONYL FSK containing 47% fluorosurfactant conforming to the formula $R_fCH_2CH(OCOCH_3)CH_2N^+(CH_3)_2(CH_2CO_2^-$ wherein $R_f=F(CF_2CF_2)_{3-8}$ and 53% Acetic Acid and minors, supplied by E.I. DuPont de Nemours & Co., Inc. (Wilmington, Delaware, USA).

5 2-Amino-2-methyl-1-propanol.

The hair spray formulations are prepared by forming a premix of the polymer in isopropanol, and then adding the ethanol. For Examples I, XV and XVI, the polymer is added directly to the ethanol. A magnetic or air driven stirrer is used to mix the ingredients until the polymer is dissolved, typically about 1 to 2 hours. If used, the neutralizing agent (KOH or AMP, or both) is then added and mixed into the premix. Then, fluorosurfactant, any of the salts, and water, as may be applicable, are mixed into the composition.

Adjuvants may also be added to the compositions, including, for example, perfume or fragrance. The hair spray compositions prepared are especially suitable for pump spray application. The compositions will be characterized by good sprayability characteristics and hair styling performance.

Example XVII

A hair spray composition, of the present invention, which is suitable for pump spray dispensers, is prepared as follows:

	<u>Ingredient</u>	<u>Weight %</u>
	Ethanol, 200 proof	78.5
	Isopropanol	10.4
	Hair Styling Polymer ¹	2.6
5	KOH (45%)	0.7
	DRO Water	7.0
	FLUORAD FC-120 ²	0.4
	ZONYL FSK	0.5

- 10 ¹ 60% t-butyl acrylate/20% acrylate acid/20% PDMS macromer, having a weight average molecular weight of about 1,700,000.
- ² FLUORAD FC-120 supplied by Minnesota Mining and Manufacturing Co. (3M), (St. Paul, Minnesota, USA) containing 25% ammonium perfluoroalkyl sulfonates, 37.5% ethanol and 37.5% water and minors.
- 15 Prepared as in Examples I-XVI.

Example XVIII

A hair spray composition, of the present invention, which is suitable for pump spray dispensers, is prepared as follows:

	<u>Ingredient</u>	<u>Weight %</u>
20	Ethanol, 200 proof	89.1
	Hair Styling Polymer ¹	2.6
	KOH (45%)	0.7
	DRO Water	7.0
25	FLUORAD FC-120 ²	0.1
	ZONYL FSK	0.5

- ¹ 60% t-butyl acrylate/20% acrylate acid/20% PDMS macromer, having a weight average molecular weight of about 1,700,000.
- 30 Prepared as in Examples I-XVI.

Example XIX

A hair spray composition of the present invention, which is suitable for pump spray dispensers, is prepared as follows:

	<u>Ingredient</u>	<u>Weight %</u>
35	Ethanol, 200 proof	78.8

	Isopropanol	10.4
	Hair Styling Polymer ¹	2.6
	KOH (45%)	0.8
	DRO Water	7.0
5	FLUORAD FC-120 ²	0.4
	ZONYL FSK	0.04

¹ 60% t-butyl acrylate/20% acrylate acid/20% PDMS macromer, having a weight average molecular weight of about 580,000. Prepared as in Examples I-XVI.

Examples XX-XXII

A hair spray composition, of the present invention, which is suitable for pump spray dispensers, is prepared as follows:

		Example	Example	Example
		<u>XX</u>	<u>XXI</u>	<u>XXII</u>
	<u>Ingredient</u>	(Wt %)	(Wt %)	(Wt %)
15	Ethanol, 200 proof	71.1	71.2	71.2
	Isopropanol	9.5	9.5	9.5
	Hair Styling Polymer ¹	2.4	2.4	2.4
20	KOH (45%)	0.6	0.6	0.6
	DRO Water	16.2	16.2	16.2
	ZONYL TBS ²	0.15	-	0.05
	ZONYL FSK	0.05	0.1	0.07

¹ 60% t-butyl acrylate/20% acrylic acid/20% PDMS macromer, having a weight average molecular weight of about 800,000.

² ZONYL TBS, an anionic surfactant supplied by DuPont, containing 30-35% perfluoralkyl sulfonic acid ammonium salt, 2.4% acetic acid and 65%-70% water.

Prepared as in Examples I-XVI.

Examples XXIII-XXV

		Example	Example	Example
		<u>XXIII</u>	<u>XXIV</u>	<u>XXV</u>
	<u>Ingredient</u>	(Wt %)	(Wt %)	(Wt %)
35	Ethanol, 200 proof	78.9	79.4	78.2
	Isopropanol	10.4	10.4	11.2

Examples XXVII-XXX

	<u>Ingredient (wt.%)</u>	<u>XXVII</u>	<u>XXVIII</u>	<u>XXIX</u>	<u>XXX</u>
	Ethanol, 200 proof	79.3	80.1	79.3	79.5
5	Isopropanol	10.4	10.4	10.4	10.4
	Hair Styling Polymer ¹	2.6	-	-	-
	Hair Styling Polymer ²	-	1.8	-	-
	Hair Styling Polymer ³	-	-	2.0	-
	Hair Styling Polymer ⁴	-	-	-	1.8
10	KOH (10% aqueous solution)	-	-	1.2	1.2
	HCl (10% aqueous solution)	0.6	0.6	-	-
	DRO Water	7.0	7.0	7.0	7.0
	Potassium Chloride	0.10	0.10	0.10	0.10

1 15% t-butylaminoethylmethacrylate/15% t-butylacrylamide/70% ethylmethacrylate, having a weight average molecular weight of about 1.2 million.

2 15% t-butylaminoethylmethacrylate/15% t-butylacrylamide/60% ethylmethacrylate/10% PDMS macromer (weight average molecular weight of about 10,000), having a weight average molecular weight of about 1.2 million.

3 15% N,N dimethylacrylamide/70% isobutylmethacrylate/15% acrylic acid, having a weight average molecular weight of about 1.2 million.

4 15% N,N dimethylacrylamide/60% isobutylmethacrylate/15% acrylic acid/10% PDMS macromer (weight average molecular weight of about 10,000), having a weight average molecular weight of about 1.2 million).

Prepared as in Examples I-XVI, except for Examples XXVII and XXVIII, the HCl is added as the neutralizer.

The above compositions will exhibit good sprayability and when applied to the hair, provide good hair styling benefits.

In the above examples and the compositions hereof utilizing silicone macromer-grafted styling resins, it can be desirable to purify the styling resin by removing unreacted silicone-containing monomer and silicone macromer-grafted polymer with viscosities at

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25°C of about 10,000,000 centistokes and less. This can be done, for the example, by hexane extraction. After drying the resin from its reaction solvent hexane extraction of the reaction product can be performed by adding an excess of hexane to the reaction product and heating to near the Tg of the non-silicone portion of the polymer. The mixture is held at this temperature with stirring for about 30 minutes and cooled to room temperature. The hexane is removed by vacuum suction. Two more hexane extraction cycles are preferably conducted in the same manner as above. After the third cycle, residual hexane remaining with the product is removed by distillation and vacuum drying.

Low molecular weight polysiloxane-containing monomer and polymer about 1 hour is solubilized by the supercritical carbon dioxide and transported away from the remaining polymer via a transfer line, which is maintained at identical temperature and pressure as the extraction vessel. The extracted materials are collected in an extraction vessel. Following extraction, the system is depressurized and dry, extracted polymer is recovered from the extraction vessel.

In the above examples and the compositions hereof utilizing silicone macromer-grafted styling resins, the resin can be purified by removing unreacted silicone-containing monomer and silicone macromer-grafted polymer with viscosities at 25°C of about 10,000,000 centistokes and less. This can be done, for the example, by hexane extraction. After drying the resin from its reaction solvent, hexane extraction of the reaction product can be performed by adding an excess of hexane to the reaction product and heating to near the Tg of the non-silicone portion of the polymer. The mixture is held at this temperature with stirring for about 30 minutes and cooled to room temperature. The hexane is removed by vacuum suction. Two more hexane extraction cycles are preferably conducted in the same manner as above. After the third cycle, residual hexane remaining with the product is removed by distillation and vacuum drying.

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CLAIMS:

1. A liquid hair styling composition useful for spray application to hair, said composition characterized in that it comprises:

- (a) an ionic hair styling polymer having a weight average molecular weight of at least 300,000;
 - (b) a liquid vehicle selected from the group consisting of water, C₁-C₆ monohydric alcohols, and mixtures thereof;
 - (c) an effective amount of an ionic strength modifier system for reducing viscosity of the composition, said system consisting essentially of a mixture of monomeric cations and monomeric anions, wherein said cations and anions are non-surface active and are at least partially soluble in said liquid vehicle;
- said composition having a pH of 10 or less.

2. A liquid hair styling composition as in Claim 1, comprising from 0.1% to 15%, by weight, of said ionic hair styling polymer, from 80% to 99.5%, by weight, of said liquid vehicle, and from 0.01% to 4%, by weight of said ionic strength modifier system.

3. A liquid hair styling composition as in Claim 1 or 2, wherein said ionic hair styling polymer comprises from 2% to 75% ionic monomers, and from 25% to 98% nonionic monomers.

4. A liquid hair styling composition useful for spray application to hair, said composition characterized in that it comprises:

- (a) an ionic hair styling polymer having a weight average molecular weight of at least 300,000; said ionic hair styling polymer comprising silicone-containing monomers, wherein when the composition is dried, the hair styling polymer separates into a discontinuous phase

which includes the silicone portion of said polymer and a continuous phase which includes the non-silicone portion;

- (b) a liquid vehicle selected from the group consisting of water, C₂-C₄ monohydric alcohols, and mixtures thereof;
- (c) an effective amount of an ionic strength modifier system for reducing viscosity of the composition, said system consisting essentially of a mixture of monomeric cations and monomeric anions, wherein said cations and anions are non-surface active and are at least partially soluble in said liquid vehicle; said composition having a pH of 10 or less.

5. A liquid hair styling composition as in Claim 4, wherein said polymer comprises at least 0.5% of silicone macromer-containing monomers.

6. A liquid hair styling composition as in Claim 4 or 5, comprising from 5% to 95% of ionic monomers and from 5% to 95% of nonionic monomers.

7. A liquid hair styling composition as in Claim 1, 2, 3, 4, 5, or 6, wherein said cations are sodium, potassium, magnesium, or a mixture thereof, and said anions are sulfate, acetate, chloride, or a mixture thereof.

8. A liquid hair styling composition as in Claim 1, 2, 3, 4, 5, 6, or 7, wherein said ionic hair styling polymer has a weight average molecular weight of at least 500,000.

9. A liquid hair spray composition as in Claim 3 or 6, wherein said ionic monomer is acrylic acid, methacrylic acid, dimethylaminoethyl methacrylate, quaternized dimethylaminoethyl

methacrylate, maleic acid, half esters of maleic anhydride, crotonic acid, itaconic acid, diallyldimethyl ammonium chloride, vinyl pyridine, vinyl imidazole, styrene sulfonate, or a mixture thereof, and said nonionic monomer is selected from the group consisting of acrylic acid esters of C₁-C₂₄ alcohols, methacrylic acid esters of C₁-C₂₄ alcohols, styrene, polystyrene macromer, vinyl acetate, vinyl chloride, vinyl propionate, vinylidene chloride, alphanethylstyrene, t-butylstyrene, butadiene, cyclohexadiene, ethylene, propylene, vinyl toluene, and mixtures thereof.

10. A liquid hairspray product comprising a hairspray composition and a spray dispenser means for containing and spraying said composition, said composition being contained in said spray dispenser means, said hairspray composition characterized in that it comprises:

- (a) an ionic, silicone macromer-containing hair styling polymer;
- (b) a liquid vehicle selected from the group consisting of water, C₁-C₆ monohydric alcohols, and mixtures thereof,
- (c) an effective amount of an ionic strength modifier system for reducing viscosity of the composition, said system consisting essentially of a mixture of monomeric cations and monomeric anions, wherein said cations and anions are non-surface active and are at least partially soluble in said liquid vehicle;

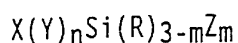
said composition having a pH of 10 or less and comprising from 10% to 90%, by weight, water, and from 10% to 80%, by weight, of said monohydric alcohols.

11. A liquid hairspray product as in Claim 10, comprising from 0.1% to 15%, by weight, of said hair styling polymer, from 80% to 99.5%, by weight, of said liquid vehicle selected from the group consisting of C₂-C₄ monohydric alcohols and water, and from 0.01% to 4%, by weight, of said ionic strength modifier system.

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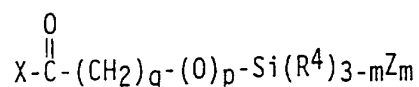
12. A liquid hairspray product as in Claim 10 or 11, wherein said cations are sodium, potassium, magnesium, or a mixture thereof, and said anions are sulfate, acetate, chloride, or a mixture thereof.

13. A liquid hair styling composition or product as in Claim 4, 5, 6, 10, 11, or 12, wherein said silicone macromer-containing monomers have the formula:



wherein X is a vinyl group; Y is a divalent linking group; R is a hydrogen, lower alkyl, aryl or alkoxy; Z is a monovalent siloxane polymeric moiety having a number average molecular weight of at least 500; n is 0 or 1; and m is an integer from 1 to 3.

14. A liquid hair spray composition or product as in Claim 13, wherein said silicone macromer-containing monomer is:

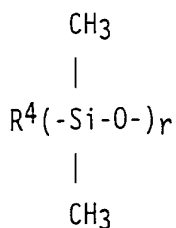


wherein m is 1, 2, or 3, p is 0 or 1, q is an integer from 2 to 6,

X is CH=C-



R¹ is -H or -COOH, R² is -H, -CH₃, or CH₂COOH, R⁴ is alkyl, alkoxy, alkylamino, aryl or hydroxyl, and Z is



wherein r is an integer from 5 to 700.

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15. A liquid hair spray product as in any of Claims 10-14, wherein said polymer comprises at least 0.5% of silicone macromer-containing monomers.

16. A liquid hair spray product as in any of Claims 10-15, comprising from 5% to 95% of ionic monomers and from 5% to 95% of nonionic monomers.

17. A liquid hair spray composition or product as in Claim 16, wherein said ionic monomer is acrylic acid, methacrylic acid, dimethylaminoethyl methacrylate, quaternized dimethylaminoethyl methacrylate, maleic acid, half esters of maleic anhydride, crotonic acid, itaconic acid, diallyldimethyl ammonium chloride, vinyl pyridine, vinyl imidazole, styrene sulfonate, or a mixture thereof.

18. A liquid hair spray composition or product as in Claim 17, wherein said polymer comprises 15% to 80% of said ionic monomer, 50% to 90% of nonionic monomer selected from the group consisting of acrylic acid esters of C₁-C₂₄ alcohols, methacrylic acid esters of C₁-C₂₄ alcohols, styrene, polystyrene macromer, vinyl acetate, vinyl chloride, vinyl propionate, vinylidene chloride, alphasubstituted styrene, t-butylstyrene, butadiene, cyclohexadiene, ethylene, propylene, vinyl toluene, and mixtures thereof and 2% to 25% of said silicone-containing monomer.

19. A method for providing hair setting benefits to the hair, comprising spraying an effective amount of any of the compositions of Claims 1-18 to hair.

INTERNATIONAL SEARCH REPORT

PCT/US 92/06975

International Application No

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int.Cl. 5 A61K7/06; A61K7/11		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
Int.Cl. 5	A61K	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹		
Category ^o	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
X	EP,A,0 412 704 (THE PROCTER & GAMBLE COMPANY) 13 February 1991 cited in the application see the whole document ---	1-19
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<p>^o Special categories of cited documents : ¹⁰</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search 18 DECEMBER 1992	Date of Mailing of this International Search Report 30.12.92	
International Searching Authority EUROPEAN PATENT OFFICE	Signature of Authorized Officer GAC G.	

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		Relevant to Claim No.
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SA 64051**

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SA 64051**

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