(54) Title: WATER-BASED HAIR SPRAY COMPOSITIONS CONTAINING MULTIPLE POLYMERS

(57) Abstract

A water-based hair spray composition is provided herein which is capable of delivering a fine finishing mist to provide a stiff resin film having excellent hair holding power, with superior shine, and feel, and within a relatively low drying time, approaching that of alcohol-based systems. The composition of the invention attains its unique attributes by including a predetermined blend of at least two hair spray resins, one being a water soluble resin, and the other resin being a water dispersible polyester or polyesteramide.
For the purposes of information only

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

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WATER-BASED HAIR SPRAY COMPOSITIONS CONTAINING MULTIPLE POLYMERS

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to hair spray resin compositions, and more particularly, to water-based compositions which contain a multiple polymer system.

2. Description of the Prior Art

Present hair spray compositions, both pump spray and aerosol spray formulations, are described in detail in U.S. Patents 3,145,147; 4,223,009; and 4,521,402. These compositions generally perform effectively in providing most of the properties considered desirable for hair preparation, including fine spray patterns, prolonged curl retention under humid conditions, good holding power, ease of removability, and resistance to build-up. However, these and other pump formulations available in the art contain a considerable amount of alcohol which is a volatile organic compound (VOC). Aerosol hair spray formulations also require hydrocarbons or other propellants which add to the VOC content of the composition. Recent state legislation, moreover, has required that hair spray compositions have a lower VOC level than is presently found in commercial hairspray compositions. More particularly, it is now necessary that such compositions contain VOC materials at a weight level of no more than 80% of the composition.
Accordingly, it is an object of the present invention to provide new water-based hair spray compositions which meet VOC standards while retaining the effective properties of presently available compositions for hair preparation and treatment.

Another object of the invention is to provide water-based hair spray compositions capable of providing a fine finishing mist at a high resin solids level and which is substantially moisture resistant, which also forms a stiff resin film on the hair of the user, and provides a good hold and curl retention, with superior shine, and feel, and low drying times, which approach the properties of alcohol-based systems.

These and other objects and features of the invention will be made apparent from the following more particular description thereof.

SUMMARY OF THE INVENTION

A water-based hair spray composition is provided herein which is capable of delivering a fine finishing mist at a high resin solids level. The composition provides a stiff resin film having excellent hair holding power, with superior shine, and feel, and low drying times, which properties approach those of alcohol-based systems. The composition of the invention attains its unique attributes by including a predetermined blend of at least two hair spray polymers, one being a water soluble polymer, and the other being a water dispersible polyester or polyesteramide.
DETAILED DESCRIPTION OF THE INVENTION

The composition of the invention comprises
(a) one or more water soluble polymers and
(b) a water dispersible polyester or polyesteramide derived from:
   (1) at least one dicarboxylic acid or ester,
   (2) at least one diol, and
   (3) a difunctional monomer containing an $SO_3M$
       group attached to an aromatic nucleus,
       wherein $M$ is hydrogen, or metal ion or
       ammonium ion or the cationic radical of an
       organic amine;

whereby the inclusion of the linear polyester or
polyesteramide improves the set time (tac-free time) and
shine of the water soluble polymers thereby expanding the
use of commercially available water soluble polymers into
an aqueous-based hair spray composition which has a drying
character, time and feel which approaches to an
alcohol-based system.

Polymer blends particularly useful herein for
incorporation into the hair grooming composition comprise:
(a) about 99 to about 1 wt. % of a water soluble
    polymer, and
(b) about 1 to about 99 wt. % of a
    water-dispersible sulfonate group-containing
    polyester or polyesteramide.

A method for using these hair grooming
compositions comprises:

(i) contacting the following:
   A. one or more water soluble polymers, and
   B. a water-dispersible sulfonate
      group-containing polyester or polyesteramide,
   C. water, and, optionally,
D. a neutralizing agent to obtain 65 to 100% neutralization based on the acid monomer in the water soluble polymer, including metal hydroxides and aliphatic, cyclic, or aromatic amines;

(ii) applying the composition to hair, and evaporating the solvent, thereby holding the hair in place.

The final hair grooming composition preferably comprises:

(I) about 2 to about 28 weight % of a polymer blend comprising:

(a) about 99 to about 1 weight % of a water soluble polymer, and
(b) about 1 to about 99 weight % of a water-dispersible sulfonate group-containing polyester or polyesteramide,

(II) about 98 to about 40 weight % of water,

(III) 0 to about 30 weight % of an alcohol, and

(IV) 0 to about 5 weight % of a neutralizing base sufficient to neutralize the acid groups of the polymer blend.
Water-dispersible polyesters and polyesteramides useful herein are described in detail in U.S. Patents 3,734,874; 3,546,008; 4,335,220; and 3,779,993; and are available from Eastman Chemicals as Polymers AQ 38 and 55.

Preferably, the polyester or polyesteramide has an inherent viscosity of from about 0.28 to about 0.38, an acid moiety of from about 75 to about 84 mole % isophthalic acid and conversely from about 25 to about 16 mole % 5-sodiosulfoisophthalic acid, and a glycol moiety of from about 45 to about 60 mole % diethylene glycol and conversely from about 55 to about 40 mole % 1,4-cyclohexanediethanol or ethylene glycol or mixtures thereof.

Most preferably, the polyester or polyesteramide comprises an acid moiety comprising from about 80 to about 83 mole % isophthalic acid and conversely from about 20 to about 17 mole % 5-sodiosulfoisophthalic acid, and said glycol moiety comprises from about 52 to about 56 mole % diethylene glycol and conversely from about 48 to about 44 mole % 1,4-cyclohexanediethanol.

The water soluble polymers useful herein are preferably prepared from monomers of one or more of the following structures:

\[
\begin{align*}
\text{HC} &= \text{O} \\
\text{N} &= \text{O} \\
\text{COOR'} &\quad \text{CH}_2 = \text{C} \\
\text{R}_1 &\quad \text{CH}_3 - \text{CH} = \text{CHCOOH}, \\
\text{CH}_2 = \text{C} - \text{N} - \text{R}_3 &\quad \text{or} \quad \text{R}_5 - \text{C} - \text{O} - \text{C} = \text{C}
\end{align*}
\]
wherein

R¹ is a C₁-C₅ aliphatic group, preferably a C₁-C₃ alkyl group, or is of the structure

\[ \text{H}_3\text{C-CH}_2\text{-N}^{\text{R}^6} \]

wherein R⁶ and R⁷ are, independently, a C₁-C₅ alkyl group,

R² is a C₁-C₁₀ aliphatic group, preferably a C₁-C₃ alkyl group,

R³ is a C₁-C₁₆ aliphatic group, preferably a C₈ alkyl group,

R⁴ is H or a C₁-C₈ aliphatic group, preferably H or a C₈ group,

R⁵ is a C₁-C₁₀ aliphatic group, preferably a C₉ alkyl group.

Accordingly, suitable water soluble polymers include polyvinyl pyrrolidone (PVP), polyvinyl caprolactam (PVC), polyvinyl acetate (VA), polyacrylates and methacrylates, and copolymers and terpolymers of such monomers, such as VP/VA, VA/crotonic acid/vinyl neodecanoate, VA/crotonic acid, or octylacrylamide/acrylates/butyl aminoethyl methacrylate, VA, mono-n-butyl maleate and isobornyl acrylate; and VP/VC/dimethylaminoethyl methacrylate.
1. **Gaffix® VC-713** (GAF Chemicals Corporation) which is a terpolymer derived from the polymerization of vinyl caprolactam, vinylpyrrolidone and an ammonium derivative monomer having from 6-12 carbon atoms selected from the group consisting of dialkyl dialkenyl ammonium halide and a dialkylamino alkyl acrylate or methacrylate (see U.S. Patent 4,521,404). The commercial product is available as a ethanolic solution having a 37% solids level.

2. **Gantrez® SP-215** (GAF Chemicals Corporation) is the ethyl half-ester of a linear copolymer of methyl vinyl ether and maleic anhydride.

3. **Gantrez® ES-225** (GAF Chemicals Corporation) is the ethyl half-ester of a linear copolymer of methyl vinyl ether and maleic anhydride having a molecular weight of 978,000.

4. **Gantrez® ES-425** (GAF Chemicals Corporation) is the butyl half-ester of a linear copolymer of methyl vinyl ether and maleic anhydride having a molecular weight of 1,000,000.

5. **Resin 1212** (GAF Chemicals Corporation) is a terpolymer derived from the polymerization of vinyl acetate, mono-n-butyl maleate and isobornyl acrylate (see U.S. Patent 4,689,373), having a molecular weight of about 250,000.
In a preferred embodiment, the polymer blend is prepared as follows: the sulfonate group-containing polymer is prepared, generally by melt polymerization, and an aqueous dispersion containing from about 10% to 30% total solids is prepared from the polyester or polyesteramide directly. Then the water soluble polymer or polymers are added to the aqueous dispersion of the polyester or polyesteramide to produce an aqueous dispersion. The aqueous dispersion so produced can be prepared with a total solids content of from about 1 to about 30. Preferably, the pH is, or is adjusted to be, within the range of about 4-8 in order to minimize hydrolysis of the polyester.

A preferred polymer blend system comprises:

(a) water soluble polymer;

GAFFIX® VC-713 (ISP) having the formula:

\[
\begin{align*}
\text{H} & \quad \text{H} \\
\text{C} & \quad \text{C} \\
\text{H} & \\
\text{H}_2\text{C} & \quad \text{N} \quad \text{C=O} \\
\text{H}_2\text{C} & \quad \text{CH}_2 \\
\text{H}_2\text{C} & \quad \text{CH}_2 \\
\text{H}_n & \\
\end{align*}
\]

and

\[
\begin{align*}
\text{H} & \quad \text{H} \\
\text{C} & \quad \text{C} \\
\text{H} & \\
\text{H}_2\text{C} & \quad \text{O} \\
\text{H}_2\text{C} & \quad \text{CH}_2 \\
\text{H}_2\text{C} & \quad \text{CH}_2 \\
\text{H}_n & \quad \text{CH}_n \\
\end{align*}
\]
(b) water dispersible polymer Eastman AQ Polymer having the formula:

\[
\text{HO} - \text{G} - \text{A} - \text{G} - \text{A} - \text{G} - \text{A} - \text{G} - \text{OH}
\]

\[
\text{SO}_3^-\text{Na}^+ \quad \text{SO}_3^-\text{Na}^+
\]

A = An aromatic dicarboxylic acid moiety

G = An aliphatic or cycloaliphatic glycol residue, and

-\text{OH} = hydroxy end groups

A typical formulation of the composition of the invention is the following:

**EXAMPLE**

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<td>Gaffix\textsuperscript{\textregistered} VC-713 (37% in ethanol)</td>
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The above formulation was a one-phase system. Upon testing as a pump hair spray, it was observed that the spray patterns developed were fine, broad and dry, with a soft hold, and excellent shine, and low drying times; the properties were comparable to those of commercial alcohol-based systems.

While the invention has been described with particular reference to certain embodiments thereof, it will be understood that changes and modifications may be made which are within the skill of the art. Accordingly, it is intended to be bound only by the following claims, in which:
WHAT IS CLAIMED IS:

1. A water-based hair spray composition comprising
   
   (a) a water soluble polymer,
   
   (b) a water dispersible polyester or polyesteramide derived from:

   (1) at least one dicarboxylic acid or ester,
   
   (2) at least one diol, and
   
   (3) a difunctional monomer containing an \( \text{SO}_3\text{M} \) group attached to an aromatic nucleus, wherein \( \text{M} \) is hydrogen, or metal ion or ammonium ion or the cationic radical of an organic amine; and

   (c) water, wherein the water soluble polymer is prepared from monomers having one or more of the following structures:

\[
\begin{align*}
\text{HC=O} & \quad \text{COOR'} \\
\text{CH}_2=\text{C} & \quad \text{CH}_3-\text{CH}=\text{CHCOOH}, \\
\text{H}_2\text{C=C} & \quad \text{or} \quad \text{R}^2-\text{C}=\text{O}=\text{C}=	ext{H} \\
\text{CH}_2-\text{C}=\text{N-OR}^3 & \\
\text{H} & \quad \text{or} \quad \text{R}^3-\text{C}=\text{O}=\text{C}=	ext{H}
\end{align*}
\]
wherein

\[ R^1 \text{ is a } C_1-C_5 \text{ aliphatic group, preferably a } C_1-C_3 \text{ alkyl group, or is of the structure} \]

\[
\begin{array}{c}
  \text{H}_3\text{C-CH}_2-\text{N} \\
  \text{R}^6 \quad \text{wherein } \text{R}^6 \text{ and } \text{R}^7 \text{ are,} \\
  \text{R}^7
\end{array}
\]

independently, a \( C_1-C_5 \) alkyl group,

\[ R^2 \text{ is a } C_1-C_{10} \text{ aliphatic group, preferably a } C_1-C_3 \text{ alkyl group,} \]

\[ R^3 \text{ is a } C_1-C_{16} \text{ aliphatic group, preferably a } C_8 \text{ alkyl group,} \]

\[ R^4 \text{ is H or a } C_1-C_8 \text{ aliphatic group, preferably H or a } C_8 \text{ group,} \]

\[ R^5 \text{ is a } C_1-C_{10} \text{ aliphatic group, preferably a } C_9 \text{ alkyl group, and wherein said water soluble polymers include one or more of polyvinyl pyrrolidone (PVP), polyvinyl caprolactam (PVC), polyvinyl acetate (VA), polyacrylates and methacrylates, and copolymers and terpolymers of such monomers, such as VP/VA, VA/crotonic acid/vinyl neodecanoate, VA/crotonic acid, or octylacrylamide/acrylates/butyl aminoethyl methacrylate, VA, mono-n-butyl maleate and isobornyl acrylate, such as a terpolymer derived from the polymerization of vinyl caprolactam, vinylpyrrolidone and an ammonium derivative monomer having from 6-12 carbon atoms selected from the group consisting of dialkyl dialkenyl ammonium halide and a dialkylamino alkyl acrylate or methacrylate, or the ethyl or butyl half-ester of a linear copolymer of methyl vinyl ether and maleic anhydride, or a terpolymer derived from the polymerization of vinyl acetate, mono-n-butyl maleate and isobornyl acrylate.} \]
2. A water-based hair spray composition according to claim 1 wherein the polyester or polyesteramide has an acid moiety of from about 75 to about 84 mole % isophthalic acid and conversely from about 25 to about 16 mole % 5-sodiosulfoisophthalic acid, and a glycol moiety of from about 45 to about 60 mole % diethylene glycol and conversely from about 55 to about 40 mole % 1,4-cyclohexanediethanol or ethylene glycol or mixtures thereof.

3. A water-based hair spray composition according to claim 1 wherein the polyester or polyesteramide comprises an acid moiety comprising from about 80 to about 83 mole % isophthalic acid and conversely from about 20 to about 17 mole % 5-sodiosulfoisophthalic acid, and said glycol moiety comprises from about 52 to about 56 mole % diethylene glycol and conversely from about 48 to about 44 mole % 1,4-cyclohexanediethanol.

4. A water-based hair spray composition according to claim 1 comprises about 2 to about 28 weight % of said polymer blend comprising
   (a) about 99 to about 1 weight % of said water soluble polymer, and
   (b) about 1 to about 99 weight % of said water-dispersible sulfonate group-containing polyester or polyesteramide;

about 98 to about 40 weight % of water;
  0 to about 30 weight % of an alcohol; and
  0 to about 5 weight % of a neutralizing base.
5. A water-based hair spray composition according to claim 4 wherein (b) the water dispersible polymer has the formula:

\[
\text{SO}_3^-\text{Na}^+ \quad \text{SO}_3^-\text{Na}^+
\]

where:
A = an aromatic dicarboxylic acid moiety
G = an aliphatic or cycloaliphatic glycol residue, and
\(-\text{OH}\) = hydroxy end groups.
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
IPC(5): A61K 7/11
US CL.: 424/47
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED
Minimum documentation searched (classification system followed by classification symbols)
U.S.: 424/47, 70, 71

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
APS - (PVP or VA or PVC) and (Gaffix VC 713 or Gantrez SP-215 or Gantrez ES-225 or Gantrez ES-425 or Resin 1212) and dicarboxylic acid or ester.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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<td>X</td>
<td>US, A, 4,223,009 (CHAKRABARTI) 16 SEPTEMBER 1980; See entire document.</td>
<td>1</td>
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<td>Y</td>
<td>US, A, 3,937,802 (FUJIMOTO) 10 FEBRUARY 1976; See entire document.</td>
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<td>Y</td>
<td>US, A, 5,068,099 (SRAMEK) 26 NOVEMBER 1991 See column 9.</td>
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<td>Y</td>
<td>US, A, 4,946,932 (JENKINS) 07 AUGUST 1990 See entire document.</td>
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☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
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  *L* Document which may throw doubt on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
  *O* Document referring to an oral disclosure, use, exhibition or other means
  *P* Document published prior to the international filing date but later than the priority date claimed
  *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
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  *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
  *A* Document member of the same patent family

Date of the actual completion of the international search
26 MARCH 1993

Date of mailing of the international search report
19 MAY 1993

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Telephone No. (703) 308-2351

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