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ACRYLIC OR METHACRYLIC ACID COPOLYMER IN RESINOUS AEROSOL HAIR PREPARATIONS

Ikuo Kubot, Sakai-shi, and Masakatsu Mikami and Seikichi Kitamura, Kyoto, Japan, assignors to Mitsubishi Rayon Co., Ltd., Tokyo, and Goo Chemical Industry Co., Ltd., Kyoto, Japan

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ABSTRACT OF THE DISCLOSURE

A composition suitable for use as an aerosol hair lacquer comprises 30–70% of an organic solution containing 1–10 weight percent of a copolymer of (1) 5–40 weight percent of an ester of an aliphatic alcohol with acrylic or methacrylic acid; (2) 6–35 weight percent acrylic or methacrylic acid; and (3) 25–89 weight percent of some other vinyl monomer neutralized with a water soluble base and 70–30% of a spraying agent.

The present invention relates to a method for producing a resinous composition which adheres to hair, displaying an excellent effect of hair preparation.

As the conventional adherents for hair preparation, shellac, polyvinyl pyrrolidone and polyvinyl ether are used but film formed by those of the shellac family is brittle so that when one of them is sprayed and made to adhere to hair, its film is impaired by combing or brushing and peeled off hair and educe like dandruff on its surface, presenting the so-called flaking phenomenon. Shellac is also defective in being hardly soluble in water. As to an adherent belonging to the family of polyvinyl pyrrolidone, when it is aerosolized, its solution in a water-soluble alcohol shows a good mutual solubility with a halogenated hydrocarbon, gaseous at atmospheric pressure, a liquefied petroleum gas or the like as a spraying agent but film formed by it is hard before it is humidified and becomes soft rapidly when humidified, a large change between such states being defective. When it is used in an especially high concentration, it presents the flaking phenomenon when it is dry and becomes humidified and sticky when it is wet, as the result of which hair sticks together, making its combing or brushing impossible. As to polyvinyl ether, it is more adhesive, as it is only added to shellac or polyvinyl pyrrolidone for giving a plasticizing effect to it.

For correcting the above-mentioned defects of the conventional adherents, there are saponified shellac and a copolymer of vinyl pyrrolidone and vinyl acetate. However, they cannot be prevented from flaking or adhering at a high temperature and a high humidity.

Further alkali metal or amine compounds of the polymers or copolymers of the esters of an alcohol having 1–4 carbons and acrylic or methacrylic acid or the copolymers of those monomers and vinylic monomers, copolymerizable with them, are known as the adherents (U.S. Pat. 2,897,172) but on their aerosolizing, they are soluble in a halogenated hydrocarbon but not in liquefied petroleum gas. They are produced by saponifying the above-mentioned polymers or copolymers with an alkali metal hydroxide. This manufacturing method is defective in an uneven quality of product and the low efficiency of production. Further film formed by these adherents are hard and cannot solve the problem of preventing flaking from taking place (British Pat. 796,318 and British Pat. 796,319).

An object of the present invention is to provide a resinous composition for hair preparation which is free from the above-mentioned defects. Another object of the present invention is to provide a method for producing such a resinous composition for hair preparation. These objects and other advantages can be attained by the method of the present invention which comprises subjecting a mixture of monomeric compounds consisting of (1) 5–40 (wt.) percent of the ester of an aliphatic alcohol having 8–18 carbons and acrylic or methacrylic acid, (2) 6–35 (wt.) percent of acrylic or methacrylic acid, (3) 25–89 (wt.) percent of some other vinylic monomer to solution polymerization and adding a water-soluble basic substance, several of the compounds of the groups (1)–(3) being able to be used concurrently.

According to the present invention, a resinous composition having necessary properties for obtaiinng an aerosolized agent for hair preparation, that is, a resinous composition which is soluble in water or water-soluble organic solvents, its solutions in those solvents present excellent mutual solubility with a common spraying agent and further it can be washed off with warm water or an ordinary shampoo on washing of the hair. Further the resinous composition of the present invention has such softness and adhesion as the conventional adherents have not, therefore causing no flaking nor becoming sticky at high temperature and humidity but keeping the effect of hair dressing for a long time.

In the practice of the present invention, when the content of a monomer belonging to the group (1) is below 5 (wt.) percent, a resinous composition thus obtained, when it is aerosolized, has an insufficient mutual solubility with a mixture of a halogenated hydrocarbon and a liquefied petroleum gas as a spraying agent. Film formed by it has insufficient softness, causing flaking to occur. On the other hand, when a monomer of (1) is used by more than 40 (wt.) percent, a resinous composiiton thus obtained becomes hardly soluble in water or a water-soluble organic solvent, particularly ethyl alcohol and its film becomes sticky.

It would be better to change the mixing ratio of acrylic or methacrylic acid belonging to the group (2) in accordance with those of an acrylic acid ester and a methacrylic acid ester belonging to the groups (1) and (3). That is, when the raw material monomers contain an acrylic acid ester but not a methacrylic acid ester, a transparent solution of the copolymer can be obtained at a high ratio of polymerization without white turbidity, using

only acrylic acid, or when they contain a methacrylic acid ester but not an acrylic acid ester, the same is possible, using only methacrylic acid. When the monomers contain both of them, it is preferable to use acrylic acid and methacrylic acid at such a mixing ratio as is generally proportional to their mixing ratio. When the total of the contents of monomers belonging to the group (2) is belw 6 (wt.) percent, film formed by a resinous composition thus obtained is hardly soluble in water, making it difficult to be washed off on washing of the hair. On the other hand, when it is above 35 (wt.) percent, the resinous composition is soluble in water but has no mutual solubility with a liquefied gas as a spraying agent, its white film is very hygroscopic and therefore becomes very sticky.

As the monomers of the group (3), esters of an aliphatic alcohol having 1–4 carbons and acrylic or methacrylic acid, acrylonitrile, acrylamide, styrene, vinyl toluene and vinyl acetate are suitable. They give to the copolymer an excellent adhesion and film obtained thereby is adequately soft. Of the monomers of the group (3), acrylic acid esters of a C_{1-4} aliphatic alcohol, acrylonitrile and acrylamide give comparatively soft film, which methacrylic acid esters of a C_{1-4} aliphatic alcohol, styrene, vinyl toluene and vinyl acetate give harder and less sticky film.

As solvents used for solution polymerization in the present invention, C_{1-4} aliphatic alcohols are suitable and can be used as mixture or a hydrous alcohol, for example, 98% ethyl alcohol. The polymerization is carried out at the boiling point of the solution or at a temperature near it with stirring. According to this method, the temperature can be controlled easily and a homogeneous polymer can be obtained.

As the catalysts of the polymerization, such peroxides as benzoyl peroxide, acetyl peroxide and lauroyl peroxide, and azo-bis-isobutylonitrile, for example, are preferable. The polymerization can be carried out at a ratio of polymerization over 90%, using these peroxides.

The mixture after the polymerization is partially or fully neutralized by adding a water-soluble basic substance which amount is at least 60% by mole of the carboxyl radical contained in the copolymer. As such basic substances, for example, ammonia water, lithium hydroxide, potassium hydroxide, sodium hydroxide, mono-, di- or tri-ethanolamine, mono-, di- or tripropanolamine, morpholine, amino ethyl ethanol amine, amino methyl propanol, amino methyl propanediol, hydroxy ethyl morpholine, ammonium salts of lysine or glycine and their mixtures are illustrated.

When only amines are used as a neutralizer, the composition thus obtained is excellent in mutual solubility with a spraying agent, particularly a liquefied petroleum gas, so the aerosol product in a high concentration can be produced as desired according to the specific purposes. In this case there is the advantage that the composition, nearly neutral, can be produced, compared with the case where an alkali metal hydroxide is used.

Tables 1 and 2 show the effect of the kinds of the monomer compositions and neutralizing agents in the present invention on the mutual solubility of a liquefied gas and the resinous composition and the pH of the solution. Table 1 presents the combination of the monomers and neutralizing agents and Table 2 the result of measuring the mutual solubility and the pH of the resultant compositions at 20° C. The degree of mutual solubility is expressed in the amounts of Freon gas and a liquefied petroleum gas which are dissolved in 50 g. alcohol solutions in various concentrations shown in the table. Freon gas used therein is a mixture of 80 (wt.) percent or dichlorodifluoromethane and 20 (wt.) percent of trichloromonofluoromethane. The values of pH are those measured relative to the alcohol or aqueous solutions in respective concentrations. A glass electrode combined with a mercurous chloride electrode was used as an apparatus for the measurement.

TABLE 1.—MONOMER COMPOSITION OF THE RESINOUS COMPOSITIONS AND NEUTRALIZING AGENTS

Composition No.	Monomer and neutralizing agent	Composition (weight part)
1-1	Ethyl acrylate	85
	Acrylic acid	14
	Methacrylic acid	1
	Potassium hydroxide	11.7
1-2	Ethyl acrylate	85
	Acrylic acid	14
	Methacrylic acid	1
	Ethanolamine	12.8
2-1	Butyl acrylate	90
	2-ethylhexyl acrylate	3
	Acrylic acid	6
	Methacrylic acid	1
	Sodium hydroxide	6.0
2-2	Butyl acrylate	90
	2-ethylhexyl acrylate	3
	Acrylic acid	6
	Methacrylic acid	1
	Morpholine	9.4
3-1	Dodecyl acrylate	40
	Ethyl methacrylate	23
	Acrylic acid	20
	Methacrylic acid	17
	Potassium hydroxide	24.3
3-2	Dodecyl acrylate	40
	Ethyl methacrylate	23
	Acrylic acid	20
	Methacrylic acid	17
	Diethanolamine	45.5
4-1	Ethyl acrylate	70
	Dodecyl methacrylate	15
	Acrylic acid	12
	Methacrylic acid	3
	Potassium hydroxide	9.0
4-2	Ethyl acrylate	70
	Dodecyl methacrylate	15
	Acrylic acid	12
	Methacrylic acid	3
	Triethanolamine	23.8

TABLE 2.—MUTUAL SOLUBILITY AND pH OF THE COMPOSITIONS OF TABLE 1

	Description				
				pH of solution	
Composition No.	Concentration (solid portion), percent	Freon gas, g.	Liquefied petroleum gas, g.	Alcohol solution	Aqueous solution
1-1	1	>75	8	10.1	8.5
	3	>75		10.1	8.5
	5	>75		10.0	8.5
1-2	1	>75	15	8.1	8.3
	3	>75	7	8.0	8.2
	5	>75		8.0	8.2
2-1	1	>75	21	10.0	8.5
	3	>75	5	10.0	8.4
	5	>75		9.8	8.4
2-2	1	>75	30	8.0	8.0
	3	>75	17	7.9	8.0
	5	>75	6	7.9	7.9
3-1	1	>75	10	10.3	8.7
	3	>75		10.3	8.6
	5	>75		10.2	8.6
3-2	1	>75	27	7.7	7.9
	3	>75	10	7.6	7.8
	5	>75		7.6	7.8
4-5	1	>75	>75	10.2	8.6
	3	>75	>75	10.2	8.5
	5	>75	>75	10.1	8.5
4-2	1	>75	>75	7.4	7.7
	3	>75	>75	7.3	7.6
	5	>75	>75	7.3	7.6

The resinous composition for hair preparation obtained by the present invention dissolved in such a water-soluble organic solvent as an aliphatic alcohol having 1–4 carbons, dioxane, methyl ethyl ketone, acetone, methyl Cellosolve, 2-methoxyethanol or ethyl Cellosolve, 2-ethoxyethanol is sealed under a superatmospheric pressure in a vessel, together with a spraying agent for delivery as the product.

The spraying agents used in the present method include halogenated hydrocarbons mainly composed of trichloromonofluoromethane, dichlorodifluoromethane or dichlorotetrafluoroethane in general use, liquefied petroleum gases mainly composed of propane or butane or their mixtures. Various additive can also be used such as glycerine, ethylene glycol, sorbitol, sorbit, polyethylene glycol, lanolin or dimethyl phthalate for modifying the hardness of the film according to the respective purposes, perfume, glazing agent, coloring agent, hair tonic and others.

As a hair lacquer product, the resinous composition obtained by the present invention, even in a high concentration does not cause flaking.

The resinous composition is superior in adhesion to the conventional adherents for hair lacquer. It enables to attain the object even in a smaller amount. For example, this resinous composition is dissolved in water at a ratio of 1–10 (wt.) percent of its solid. By mixing 30–70 (vol.) percent of the resultant solution with 70–30 (vol.) percent of a liquefied gas as a spraying agent, an excellent aerosol product is obtained.

Further the resinous composition obtained by the present invention is not only dissolved in water and a water-soluble organic solvent but also has mutual solubility with raw materials for making hair dressing agents, for example, castor oil, its derivatives or aliphatic higher alcohols. Hence it can be mixed as one of the raw materials for making hair dressing agents. Hair dressing agents containing this resinous composition are product possessing increased adhering property and excellent hair dressing effect.

Further this resinous composition can be used as one of the ingredients of hair cream, hair lotion or shaving cream or as adhesive, binding agent or coating agent in general.

The present invention may be more fully understood from the following examples which are offered by way of illustration and not by way of limitation.

EXAMPLE 1

Into a four-necked flask equipped with a reflux condenser, a dropping funnel, a thermometer and an agitator, 350 g. of ethyl acrylate, 30 g. of styrene, 70 g. of 2-ethylhexyl acrylate, 45 g. of acrylic acid, 5 g. of methacrylic acid and 600 g. of ethyl alcohol were introduced and with 7.5 g. of benzoyl peroxide added to them, were refluxed on heating at 80°–81° C. and polymerized for 3.5 hours. Further, with a solution of 5 g. of benzoyl peroxide in 70 g. of ethyl alcohol added to it, the content was heated at a refluxing temperature of 79°–80° C. for 1.5 hours. As a result, a solution of the copolymer in ethyl alcohol was obtained at a polymerization ratio of 98%. Next, a solution of 38 g. of caustic potash in a small amount of water and 430 g. of ethanol was added to the solution of copolymer through the dropping funnel and the resultant mixture was agitated, whereby a resinous composition having about 32 (wt.) percent of the solid portion was obtained. The viscosity of this composition at 20° C. was about 900 centipoises. The polymerization ratio was calculated by measuring its volatile portion and the viscosity was measured with a viscometer of a Brookfield type. The values of polymerization ratios and viscosities hereinafter were measured by the same procedures.

9.4 g. (10 ml.) (about 3 g. in terms of the solid portion) of the composition was dissolved in 90 g. (112 ml.) of ethyl alcohol. Further 1 g. of lanolin and 0.1 g. of a perfume and 120 g. (86 ml.) a mixture of equal amounts of trichloromonofluoromethane and dichloromonofluoromethane were added to the resultant solution. The mixture was charged in a closed vessel to make a hair lacquer. When the hair lacquer was used in the spray form of hair dressing, it was scarcely sticky even on a rainy day and kept the effect of hair dressing for several days. Flaking did not occur by combining or brushing.

EXAMPLE 2

Into the same four-necked flask as in Example 1, 110 g, of n-butyl acrylate, 10 g. of ethyl methacrylate, 30 g. of dodecyl methacrylate, 10 g. of dodecyl acrylate, 32 g. of acrylic acid, 8 g. of methacrylic acid, 100 g. of ethyl alcohol and 100 g. of isopropyl alcohol were introduced and, with 4 g. of lauroyl peroxide added to it, were heated, and while being refluxed at 84°–85° C., polymerized for 4 hours. Further, with 2 g. of lauroyl peroxide dissolved in 50 g. of isopropyl alcohol being added to it, the content was heated and maintained at a refluxing temperature for 2 hours. As a result, the copolymer was obtained at a polymerization ratio of 99%. Next, 15 g. of caustic potash and 23 g. of morpholine dissolved in 110 g. of ethyl alcohol were added to the copolymer through the dropping funnel. The mixture was agitated. As a result, a resinous composition having about 40 (wt.) percent of its solid portion was obtained. Its viscosity at 20° C. was about 1200 centipoises.

5 g. (5.2 ml.) (about 2 g. of its solid solution) of the composition was dissolved in 45 g. (56 ml.) of ethyl alcohol. With 1 g. of polyethylene glycol and some amount of a perfume added to it, the resultant solution and 50 g. (88 ml.) of a liquefied petroleum gas were charged in a closed vessel to obtain an aerosol product. When the product was used for hair dressing, a hair-setting with a soft touch was attained. It was scarcely sticky at high temperature and humidity, not causing flaking.

EXAMPLE 3

Into the same four-necked and round-bottom flask as in Example 1, 135 g. of methyl acrylate, 20 g. of acrylonitrile, 115 g. of 2-ethylhexyl methacrylate, 15 g. of acrylic acid, 15 g. of methacrylic acid and 470 g. of ethyl alcohol were introduced and with 3.5 g. of acetyl peroxide added to them, were refluxed on heating at 81–82° C. and polymerized for 4 hours. With 3 g. of acetyl peroxide dissolved in 50 g. of ethyl alcohol being added to it, the content was heated and kept being refluxed for 2 hours. As a result, a solution of the copolymer in ethyl alcohol was obtained at a polymerization ratio of 98%. Next, with 19 g. of diethanolamine and 30 g. of triethanolamine added to it, it was agitated. As a result, a water-soluble resinous composition having about 40 (wt.) percent of its solid portion was obtained. Its viscosity at 20° C. was about 900 centipoises.

The pH of a solution of 17.5 g. (18.5 ml.) (about 7 g. of its solid portion) of the composition in 82.5 g. (103 ml.) of ethyl alcohol was 7.3. As it was nearly neutral, it did not affect various additives. With 0.2 g. of phenyl ethyl alcohol added to it, it and 120 g. (120 ml.) of a mixture of equal amount of Freon, an equal weight mixture of monofluorotrichloromethane and difluorodichloromethane, and a liquefied petroleum gas were charged into a closed vessel to obtain a hair lacquer. When the product was used for hair dressing, it was scarcely sticky even at high temperature and humidity, causing no flaking.

What is claimed is:

1. A pressurized hair lacquer composition consisting essentially of (A) a resinous composition composed of a film-forming copolymer of (1) 5 to 40% by weight of an ester of a saturated aliphatic monohydric alcohol having 8 to 18 carbon atoms and an acid selected from the group consisting of acrylic acid and methacrylic acid, (2) 6 to 35% by weight of an acid selected from the group consisting of acrylic acid and methacrylic acid, (3) 25 to 89% by weight of a monomeric compound selected from the group consisting of acrylonitrile, acrylamide, styrene, vinyltoluene, vinyl acetate and esters of an aliphatic alcohol having 1 to 4 carbon atoms with acrylic or methacrylic acid, said copolymer having been neutralized with a water-soluble base added to the copolymer in an amount of at least 60 mol percent of the carboxyl group content of the copolymer, (B) a water-soluble organic solvent selected from the group consisting of a saturated aliphatic

alcohol having 1 to 4 carbon atoms, dioxane, methyl ethyl ketone, acetone, 2-methoxyethanol and 2-ethoxyethanol and (C) a spraying agent selected from the group consisting of halogenated hydrocarbons, liquefied petroleum gas and mixtures thereof, wherein said (A) component is dissolved in said (B) component in an amount of 1 to 10 weight percent of the solution, the solution of (A) and (B) is 30 to 70 volume percent of the aerosol composition and (C) is 70 to 30 volume percent of the aerosol composition.

2. An aerosol composition according to claim 1, wherein the (1) component is an ester selected from the group consisting of 2-ethylhexyl acrylate, 2-ethylhexyl methacrylate, dodecyl acrylate and dodecyl methacrylate.

3. An aerosol composition according to claim 1, wherein the (3) component is a monomeric compound selected from the group consisting of styrene, n-butyl acrylate, ethyl methacrylate, ethyl acrylate and methyl acrylate.

4. An aerosol composition according to claim 1, wherein the water-soluble base is a member selected from the group consisting of ammonia water, lithium hydroxide, potassium hydroxide, sodium hydroxide, monoethanolamine, diethanolamine, triethanolamine, monopropanolamine, dipropanolamine, tripropanolamine, morpholine,

aminoethylethanolamine, aminomethylpropanol, aminomethylpropanediol, hydroxyethyl morpholine, ammonium salts of lysine, ammonium salts of glycine and mixtures thereof.

5. An aerosol composition according to claim 1, wherein the water-soluble organic solvent is an alcohol selected from the group consisting of ethanol and isopropanol.

6. An aerosol composition according to claim 1, wherein the spraying agent is a member selected from the group consisting of trichloromonofluoromethane, dichlorodifluoromethane and dichlorotetrafluoroethane.

References Cited

UNITED STATES PATENTS

2,892,788	6/1959	Stewart et al.	260—80.73X
3,203,935	8/1965	Mirands et al.	260—80.73X

ALBERT T. MEYERS, Primary Examiner

V. C. CLARKE, Assistant Examiner

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