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3,735,003

AEROSOL HAIR-SETTING COMPOSITION COMPRISING AN INTERPOLYMER OF AN N-3-OXOALKYLAMIDE AND α,β-UNSATURATED ALIPHATIC ACID

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U.S. Cl. 424—47 4 Claims

ABSTRACT OF THE DISCLOSURE

A hair-setting composition suitable for application to the hair preferably in the form of an aerosol spray is disclosed. The composition comprises a copolymer of an N-3-oxohydrocarbon-substituted amide of an α,β-unsaturated aliphatic carboxylic acid; α,β-unsaturated aliphatic mono-and/or dicarboxylic acids; and optionally a monoester of an α-unsaturated aliphatic mono-or dicarboxylic acid.

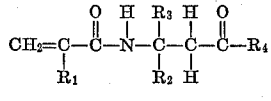
BACKGROUND OF THE INVENTION

The present invention is concerned with hair-fixative compositions especially suitable for application to the hair in the form of an aerosol spray preparation.

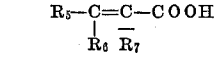
A hair-fixative composition must possess a specific set of properties in order to be effective. They must adhere well to the hair and hold the hair, yet, at the same time, allow the hair to be combed freely. In addition, the compositions should be capable of being easily, completely combed out of the hair without leaving residues and/or electrostatically charging the hair. Hair preparations such as the type contemplated herein must, in addition, maintain their holding properties without becoming tacky under humid atmospheric conditions. Such preparations should be easily removable from the hair by a single shampoo and, in addition, must be pleasant and easy to use by the consumer and impart a lustrious high gloss to the hair. Finally, such hair preparations must possess good water-solubility, low hygroscopicity, miscibility with the commonly utilized aerosol propellants and an inertness to perfumes and other ingredients normally incorporated into hair-fixative formulations. A spray formulation incorporating a hair-fixative should possess the above characteristics and, additionally, be easily manufacturable and have a cost factor which facilitates competition in the market place. It is the object of the present invention to provide an improved hair-fixative formulation which is clearly superior in reference to all of the above criteria in comparison to similar preparations now known in the art.

SUMMARY OF THE INVENTION

The hair-fixative composition, in accordance with the present invention, comprises as the essential ingredient an interpolymer of (A) an N-3-oxoalkyl amide of an α,β-unsaturated aliphatic carboxylic acid represented by the formula



wherein R_1 is hydrogen or lower alkyl of 1 to 3 carbons, and R_2, R_3 and R_4 are each lower alkyl of 1 to 3 carbons with (B) mono-unsaturated aliphatic mono-and/or dicarboxylic acids represented by the formula



wherein R_5 is hydrogen or a carboxyl group and R_6, and R_7 are hydrogen or a lower alkyl radical of 1 to 3 carbons and, as an optional third component (C), a monoester formed by the reaction of a monounsaturated aliphatic mono- or dicarboxylic acid with a member of the group consisting of alkanediols, alkanetriols and ethers of these alkanediols and alkanetriols. The composition is characterized by the presence of at least 60 percent and not more than 95 percent by weight of component (A). Also, the free carboxyl groups in the interpolymer are at least partially neutralized by salt formation.

DETAILED DESCRIPTION OF THE INVENTION

The following compounds are illustrative examples of the components of the interpolymer described above.

Specific examples of component (A) include: N-(1-propyl-1-methyl-3-oxohexyl-1)-acrylic acid amide, N-(1-ethyl-1-methyl-3-oxopentyl-1)-acrylic acid amide and, especially, N-(1,1-dimethyl-3-oxobutyl - 1) - acrylic acid amide.

Specific examples of component (B) include: methacrylic acid, crotonic acid, maleic acid and acrylic acid.

Specific examples of the optional monoester component designated as (C) above include: acrylic acid β-hydroxyethyl ester, methacrylic acid β-hydroxypropyl ester, maleic acid mono-β-hydroxyethyl ester, acrylic acid-2-hydroxy-3-butoxypropylester and crotonic acid β-hydroxyethyl ester. The latter is preferred.

Particularly preferred are copolymers of N-(1,1-dimethyl-3-oxobutyl-1)-acrylic acid amide, acrylic acid and crotonic acid-hydroxyethyl ester.

The interpolymers are prepared by methods well known in the art, such as the block process carried out in an organic solvent or a mixture of organic solvents. Preferably, a free radical initiator is utilized optionally with the addition of an accelerator as is well known in the art. Preferred among the free radical initiators well known in the art are the organic peroxides such as, for example, dibenzyl peroxide or dilauroyl peroxide. Thermolabile free radical-forming initiators, such as, for example, azodiisobutyronitrile, may also be employed in the copolymerization reaction.

As the organic solvent, it is preferred to utilize one or a mixture of such solvents as, for example, acetic acid ethyl ester, isopropanol, acetone and methyl ethyl ketone.

The copolymerizations can be carried out, with exclusion of oxygen, in any desired stirring vessel fitted with reflux condensers. In this case, either all the components of the monomer mixture can be added with the total initiators to the regulators or solvents provided, or individual components of the monomer mixture, mixed with a part of the initiators if desired, can be added separately during the reaction.

In order to regulate the molecular weight of the interpolymer, regulators well known in the art such as, for example, lower aliphatic aldehydes or alkylthiols may be added to the reaction mixture. These regulators are preferably utilized although the organic solvent utilized does act as a mild regulator. The polymerization reaction is generally initiated by mixing the monomers and other ingredients in a suitable reaction flask and heating to reflux temperature, which is generally about 60° to 70° C. The product may be purified by any expedient method recognized in the art. A preferred method of purification is carried out at a temperature of about 50° C. utilizing petroleum ether in a quantity at least double the weight of monomer mixture. Suitable high-boiling fluorinated hydrocarbons may be utlized in place of the petroleum ether.

The relative amounts by weight of the monomers utilized in forming the interpolymer of the present invention can be varied in relation to the desired properties of

the end-product. Thus, increasing the proportion of component (B) in the total monomer mixture results in an interpolymer of increased water-solubility, slightly decreased solubility in organic solvents and an unaltered brittleness. Replacing up to 30 percent by weight of component (A) and/or (B) with optional component (C) slightly increases water-solubility and produces a softer, more flexible interpolymer. An increase in the proportion by weight of component (A) results in a softer interpolymer with substantially unaltered solubility properties. Interpolymers with monoesters of monounsaturated mono or dicarboxylic acids with alkanetriols as component (C) show also an excellent cross linkage. Thus, it can be seen that by varying the relative amounts of the components of the interpolymer, the consistency, water-solubility and other properties thereof can be adjusted to a desired end.

Broadly stated, the interpolymer in accordance with the present invention contains in each 100 parts by weight, from about 60 to about 95 parts of component (A), from about 5 to about 15 parts by weight of component (B) and from 0 to about 30 parts by weight of component (C). Where only components (A) and (B) are utilized in forming the interpolymer, from about 85 to about 95 parts by weight of component (A) are utilized with the remainder being component (B). Especially preferred interpolymers are prepared from about 95 parts of component (A) and about 5 parts of component (B) by weight; and from about 75 parts of component (A), about 5 parts of component (B) and about 20 parts of component (C).

The interpolymers formed in accordance with the present invention may be applied to the hair by use of an atomizer or other suitable means. The preferred method of application is by means of spraying from an aerosol vessel such as is well known in the art. The interpolymers, according to the present invention, are incorporated into an aerosol preparation as a solution in a suitable water-miscible organic solvent system which may comprise a single solvent such as, for example, a lower aliphatic alcohol, such as ethanol or isopropanol. In addition, one or a mixture of poly-halogenated hydrocarbons which are gaseous at normal temperatures can be employed alone or in combination with said lower aliphatic alcohols as the solvent system for the interpolymers as described above. The interpolymer is dissolved in from about 5 to about 15 parts by weight of the solvent and the resulting clear solution is partially neutralized by the addition of any desired organic or inorganic base. Preferred bases include high boiling alkanolamines such as, for example, diethanolamine, triethanolamine and 2-amino-2-methyl-1,3-propanediol.

The partial neutralization process is for purposes of imparting water solubility to the interpolymer. The partial neutralization is carried out using an amount of base which is lower than that theoretically possible to neutralize all of the carboxyl groups in the interpolymer. The amount of base required for this operation can be readily established by prior experiment. The partial neutralization may be effected either subsequent to the completion of the polymerization reaction or by treating stock solutions of the unneutralized acidic interpolymer in the aforementioned organic solvent system just prior to filling into pressure vessels.

In addition to the above described interpolymers, the hair sprays prepared in accordance with the present invention can contain other optional additives commonly added to such preparations by those skilled in the art of cosmetic compounding. Exemplary of such additives are lubricants, emollients, plasticizers such as, for example, glycerine, silicones to impart water repellency to the hair, perfumes, gloss-agents and the like.

In preparing aerosol hair sprays in accordance with the invention, a solution of about 8 to 12 percent, preferably about 9 to 10 percent by weight of the interpolymer in the organic solvent system is filled into aerosol vessels along with optional ingredients such as described above. The vessels are then treated at room temperature under pressure with a liquified poly-halogenated hydrocarbon or a mixture of several such hydrocarbons suitable as a propellant. Commercially avilable polyhalogenated hydrocarbons such as, for example, trichlorofluoromethane, dichlorodifluoro-methane and symmetrical tetrafluoro-dichloroethane, are especially suitable as propellants. These may be utilized individually or in various combinations depending on the propellant force desired.

The ratio between the interpolymer solution and the propellant can vary within rather broad limits. The ratios utilized depend largely on the desired solids content of the finished product and on the propellant force of the poly-halogenated hydrocarbon system utilized. In the practice of the present invention, the weight-ratio of the resin solution to propellant is between 1:1 and 1:4, preferably about 1:2.6. The precent by weight of resin in the final aerosol prepartions is therefore between 1.6% by weight (an 8% by weight solution combined with propellant in a 1:4 weight ratio) and 6% (a 12% solution combined with propellant in a 1:1 weight ratio).

In the following examples which are illustrative of the invention, all parts are by weight and temperature in degrees centigrade.

EXAMPLE 1

A mixture of 95.0 parts of N-(1,1-dimethyl-3-oxo-butyl-1)-acrylic acid amide and 5.0 parts of crotonic acid were combined with 100 parts of methyl ethyl ketone and 0.8 part of dibenzoyl peroxide and the mixture was polymerized at 80° C. for about two hours, then cooled to 50° C. The interpolymer was extracted by stirring with 300.0 parts of petroleum ether (B.P. 50°–75° C.). The product was dried for 24 hours at a temperature of from 30°–40° C. The resultant interpolymer was very hard, brittle and odorless.

One part of the above interpolymer was dissolved in 13 parts absolute alcohol and partially neutralized by the addition of 0.06 part of 2-amino-2-methyl-1,3-propanediol. To the resulting mixture was added 0.015 of a silicone oil and 0.045 part of perfume oil. The solution was then filled into aerosol pressure vessels and 22.5 parts of fluorotrichloromethane and 15.0 parts of dichlorofluoromethane were added under pressure.

The fixative preparation formed above upon spraying on the hair quickly dried to a glossy lacquer film which imparted high gloss and good fixation to the air. The lacquer was readily combed out, did not statically charge the hair and proved to be insensitive to conditions of high atmospheric moisture.

EXAMPLE 2

A mixture of 95.0 parts of N-(1,1-dimethyl-3-oxo-butyl-1)acrylic acid amide and 5.0 parts of acrylic acid were combined with 150.0 parts of methyl ethyl ketone and 0.8 part of dibenzoyl peroxide and the mixture was polymerized at 80° C. in about 5 hours. The reaction mixture was cooled to 50° C. and was overlaid with 200.0 parts by weight of petroleum ether having a boiling point of from about 50° C. to about 75° C. and extracted by stirring for a short period of time. After ceasing the stirring, a petroleum ether phase separated and was decanted off. The residue was withdrawn from the reaction vessel and dried to a constant weight at 30°–40° C. under vacuum for 24 hours to yield a colorless, odorless brittle interpolymer.

One part of the interpolymer formed above was dissolved in 15.5 parts of absolute alcohol and partially neutralized by the addition of 0.06 part of 2-amino-2-methyl-1,3-propanediol. To the resulting mixture was added 0.015 of a silicone oil, 0.07 part of a softener and 0.05 part of perfume oil. The solution was then filled into an aerosol pressure vessel and 26.2 parts of fluoro-

trichloromethane and 17.5 parts of difluorodichloromethane were added under pressure.

The preparation obtained above produced a glossy, rapid-drying lacquer film when sprayed on the hair. The fixation could be completely combed out of the hair without electrostatically charging it or leaving undesirable residues. The hair lacquer was easily removed by a single shampoo. The lacquer was not affected by atmospheric moisture.

EXAMPLE 3

In an analogous manner, an interpolymer was formed from 95.0 parts by weight N-(1,1-dimethyl-3-oxobutyl-1)-acrylic acid amide and 5.0 parts of acrylic acid. The mixture was combined with 70.0 parts acetic acid ethyl ester and 80.0 parts methyl ethyl ketone and 0.8 part of dibenzoyl peroxide. The mixture was polymerized at 80° C. for 5 hours and the interpolymer was extracted with 200.0 parts of petroleum ether and dried. The resulting interpolymer was incorporated into an aerosol vessel in a manner analogous to that described in Examples 1 and 2. The resulting spray was found to be comparable in properties to the sprays prepared in Examples 1 and 2.

EXAMPLE 4

A mixture of 75.0 parts of N-(1,1-dimethyl-3-oxobutyl-1)-acrylic acid amide, 5.0 parts acrylic acid, 20.0 parts of the β-hydroxyethyl ester of crotonic acid and 0.8 part of dibenzoyl peroxide in 75.0 parts of methyl ethyl ketone was polymerized at 80° C. for about 7 hours. The interpolymer was extracted with 200.0 parts of petroleum ether and dried in vacuum to form a colorless, odorless brittle polymeric powder.

One part of the interpolymer formed above was dissolved in a mixture of 4.6 parts of ethyleneglycol monomethyl ether and 10.9 parts of methylene dichloride. The resulting solution was partially neutralized with 0.06 part of 2-amino-2-methyl-1,3-propanediol. The solution was then combined with 0.05 part of a perfume oil, 0.03 part of a softener and 0.015 part of a paraffin oil and filled into a suitable aerosol vessel. To this vessel was added, under pressure, 26.2 parts of monofluorotrichloromethane and 17.5 parts of difluorodichloromethane. The finished aerosol hair spray was entirely comparable in properties to those formed in Examples 1 through 3.

EXAMPLE 5

A mixture of 95.0 parts of N-(1,1-dimethyl-3-oxobutyl-1)-acrylic acid amide, 5.0 parts of maleic acid and 0.8 part of dibenzoyl peroxide were polymerized in a suitable vessel for about 2 hours at 80° C. The reaction mixture was then cooled to about 50° C. and the interpolymer extracted with 330.0 parts of petroleum ether. The resulting solution was dried under vacuum to produce a hard, brittle, odorless interpolymer.

One part of the interpolymer thus formed was dissolved in 13.0 parts of absolute alcohol and partially neutralized by the addition of 0.06 part of 2-amino-2-methyl-1,3-propanediol. To this mixture was added 0.04 part of a suitable perfume oil, 0.06 part of a softener, 0.015 part of a silicone oil and 0.0015 part of a non-ionic surface active agent. The resulting solution was filled into suitable aerosol containers which were then charged with a propellant mixture of 22.5 parts of monofluorotrichloromethane and 15.0 parts of difluorodichloromethane. The aerosol preparation thus formed exhibited the same excellent properties as those formed in the above examples.

EXAMPLE 6

Three parts of the interpolymer prepared in Example 2 were dissolved in 46.0 parts of absolute alcohol. The resulting solution was partially neutralized with 0.18 part of 2-amino-2-methyl-1,3-propanediol. To this solution was added 0.3 part of a perfume oil, 0.1 part of a water-soluble silicone oil, 0.2 part of a softener and 50.22 parts of demineralized water.

Eighteen parts of the above prepared aqueous-alcoholic solution were applied to hair which had been shampooed and towel-dried. The hair was thereafter set in curling papers and dried under a hood. The hair thus treated, when combed out, had a high gloss, was easily manageable and held the set very well. The hair thus treated, retained its set even under conditions of high atmospheric moisture.

EXAMPLE 7

2.5 parts of the interpolymer produced in Example 3 were dissolved in 46.0 parts absolute alcohol. The resulting solution was partially neutralized with 0.1 part potassium hydroxide. To the solution was added 0.3 part of a perfume oil, 0.1 part of water-soluble perfume oil, 0.2 part of a softener, 0.01 part of a wetting agent and 50.8 parts of demineralized water.

The above prepared aqueous-alcoholic solution was applied to shampooed, towel-dried hair which was then set in the manner described in Example 6. Appearance of the hair after being thus treated was entirely comparable to that described in Example 6.

EXAMPLE 8

One part of the interpolymer described below was dissolved in 13 parts of absolute alcohol and neutralized by the addition of 0.07 part of 2-amino-2-methyl-1,3-propanediol. To the resulting mixture was added 0.03 part of a silicone oil, 0.045 part of perfume oil and 0.03 part of a softener. The solution was then filled into aerosol pressure vessels and 22.5 parts of fluorotrichloromethane and 15.0 parts of dichlorofluoromethane were added under pressure. The fixative preparation formed above upon spraying on the hair produced a glossy, rapidly drying lacquer film when spraying on the hair. The fixation could be completely combed out of the hair without electrostatically charging it. The hair lacquer was easily removed by a single shampoo. The lacquer was not affected by atmospheric moisture.

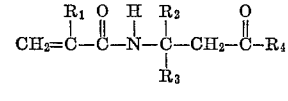
The resin can be prepared as follows:

A mixture of 79.0 parts of N-(1,1-dimethyl-3-oxobutyl-1)-acrylic acid amide, 6 parts of acrylic acid and 15.0 parts of acrylic acid-2-hydroxy-3-butoxy-propyl ester were combined with 110.0 parts of methyl ethyl ketone and 0.76 part of dibenzoyl peroxide and the mixture was polymerized at 80° in about 5 hours. The mixture was cooled to 50° and was extracted with 170.0 parts of petroleum ether having a boiling point from about 50–75° by stirring. The resin which contained some solvent was dried to a constant weight at 30–40° under vacuum for 24 hours to yield an odorless, brittle resin.

What is claimed is:

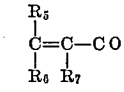
1. A hair-fixative aerosol composition comprising a lower alkanol, a polyhalogenated lower hydrocarbon propellant and between 1.6% and 6% by weight of a hair-fixative ingredient comprising an interpolymer of:

(A) from about 60 parts to about 95 parts by weight of a N-3-oxoalkylamide of an α,β-unsaturated aliphatic carboxylic acid represented by the formula



wherein R_1 is hydrogen or lower alkyl, and R_2, R_3 and R_4 are each lower alkyl;

(B) from about 5 parts to about 15 parts by weight of an α,β-unsaturated aliphatic acid represented by the formula



wherein R_5 is hydrogen or carboxyl and R_6 and R_7 are each hydrogen or lower alkyl; and

(C) from about 0 part to about 30 parts by weight of a compound selected from the group consisting of acrylic acid β-hydroxyethyl ester, methacrylic acid β-hydroxypropyl ester, maleic acid, mono-β-hydroxyethyl ester, acrylic acid-2-hydroxy-3-butoxypropyl ester and crotonic acid β-hydroxyethyl ester;

with the proviso that the free carboxyl groups in said interpolymer are at least partially neutralized by the formation of salts with a member selected from the group consisting of organic and inorganic bases.

2. The aerosol composition in accordance with claim 1 wherein said component (A) is N-(1,1-dimethyl-3-oxobutyl-1)-acrylamide, said component (B) is acrylic acid and said component (C) is acrylic acid-2-hydroxy-3-butoxypropyl ester.

3. A method of setting the hair, comprising the step of applying to said hair an effective amount of the hair-fixative composition of claim 1.

4. The method of setting the hair in accordance with

claim 3 wherein said component (A) is N-(1,1-dimethyl-3-oxobutyl-1)-acrylamide, said component (B) is acrylic acid and said component (C) is acrylic acid-2-hydroxy-3-butoxypropyl ester.

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U.S. Cl. X.R.

260—29.6 TA, 33.3 R, 33.8 UA, 63 N, 63 R, 18.5 BB, 80.3 N, 80.73; 424—Dig. 1 and 2, 11, 49.8

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,735,003 Dated May 22, 1973

Inventor(s) Gerhard Zimmer and Hermann Stein

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Cover page, Column 1, line following "Inventors:" insert

Assignee: Hoffmann-La Roche Inc., Nutley, N.J.

Signed and sealed this 1st day of January 1974.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

RENE D. TEGTMEYER
Acting Commissioner of Patents

FORM PO-1050 (10-69)

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