United States Patent Office 3,026,250 Patented Mar. 20, 1962

3,026,250

AEROSOL HAIR-TREATING COMPOSITION

Eugene Casper Coyner, Wilmington, Del., assignor to E. I. du Pont de Nemours and Company, Wilmington, Del., a corporation of Delaware

No Drawing. Filed Sept. 10, 1957, Ser. No. 683,022
6 Claims. (Cl. 167—87.1)

This invention relates to a new composition of matter which is useful for treating hair. In particular, this invention relates to a novel volatile composition which may be expelled from a container as a spray. The composition comprises a solution of a copolymer which contains a number of amine salt groups, an alcohol and a fluorinated hydrocarbon. This novel composition is useful as a hair lacquer and has improved properties over hair lacquers known heretofore.

In the past many materials have been used as an aid to arranging and holding human hair in place for cosmetic purposes. For example, various natural synthetic oils, resins, and gums have been applied from solution for this purpose. A commonly used type of preparation at the present time is shellac and/or polyvinyl pyrrolidone. These are conveniently applied from self-propelled aerosol solutions which consist of a solution of shellac and/or polyvinyl pyrrolidone in an organic solvent (usually ethanol) and a halomethane and/or a haloethane as propellant. Such compositions are sprayed onto the hair from aerosol containers so that a fine mist penetrates the tresses and distributes the shellac or resin over the hair surfaces. The shellac or resin left after evaporation of the solvents tends to stiffen the individual hairs and causes them to adhere to one another at several points. This in turn tends to maintain the hair in its arrangement.

Although this treatment with shellac or synthetic resin is effective for the purpose of stabilizing the arrangement of the hair, these agents suffer from several disadvantages. Shellac is a natural product and produced under primitive conditions. It is therefore subject to variations in price, quality and availability. Solutions of shellac are corrosive to common metals such as tin-plated steel used in cans and cause trouble when incorporated in the aerosol container. Furthermore, shellac is relatively brittle when in the form of films on the hair. These films are often broken loose from the hair by combing and form objectionable dandruff-like scales. Thick deposits of shellac tend to cause trouble on aging in that difficulty often results in removing the shellac from the hair during the normal shampooing operation. Furthermore, build-up of shellac on the hair on repeated use of the lacquer is objectionable because of difficulty in removal.

Polyvinyl pyrrolidone is a synthetic resin which is potentially constant in quality. Its price, however, is higher than that of shellac. Films of polyvinyl pyrrolidone are relatively soft and weak and are both hygroscopic and readily soluble in water. These properties limit the utility of polyvinyl pyrrolidone as a hair treating agent because hair so treated tends to become more sticky in humid weather and as a result loses the desired arrangement. Also the polyvinyl pyrrolidone may be removed from the hair by wet combing and brushing or chance exposure to rain.

It is an object of this invention to provide a novel self-propelled composition which when sprayed onto hair leaves a film on the hair which holds the arrangement of the hair for several days.

It is an additional object to provide a hair-treating composition which leaves a film which is not hygroscopic and which will not absorb moisture in humid atmospheres.

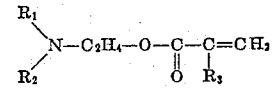
It is a further object to provide a hair-setting composition which gives a film that can readily be removed from the hair by ordinary shampooing methods.

A still further object is to provide a hair-treating composition giving films which do not scale and yield dandruff-like materials on repeated combing and brushing of the hair.

According to the present invention, copolymers similar to those disclosed in U.S. Patent No. 2,723,256 are the essential film-forming components which are to be deposited on the hair to hold the arrangement of the hair for an extended period of time, without being hygroscopic or subject to scaling and yet have the desirable characteristic of being easily removable by ordinary shampooing methods or by simply washing with soap and water.

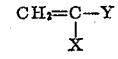
It has been found that when copolymers of the following type have a portion of the amino groups converted to salt groups, they are suitable for use in an aerosol composition and may be sprayed on the hair to form a film which is water sensitive and thus easily removed by ordinary soap and water.

These copolymers contain from 15–90% by weight of an amino group containing comonomer selected from the group represented by

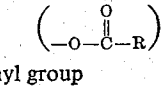


where R_1 and R_2 are lower alkyl groups and cycloalkyl groups which include R_1 and R_2, and R_3 is selected from the group consisting of H and CH_3.

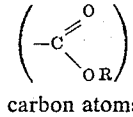
These amino group containing comonomers are polymerized with an ethylenic comonomer which will comprise from 10–85% by weight of the film-forming copolymer. These ethylenic compounds are selected from the group consisting of



where X is H or CH_3 and Y can be a polar group selected from either a nitrile group (—C≡N), an aliphatic acyloxy group containing from 1–18 carbon atoms



or an alkoxycarbonyl group



containing from 1–18 carbon atoms.

Polymerization is preferably carried out in an organic system until complete or substantially complete. This polymerization step may be carried out using as solvent lower monohydric aliphatic alcohols containing 1–4 carbon atoms as disclosed in Patent No. 2,723,256, although alcohols containing 2–4 carbon atoms are preferred. Preferably the organic system will include amounts of the alcohol solvent and comonomers that fall within the prescribed ratios of those components to be employed in the aerosol composition. By following this preferred procedure, it will be unnecessary to add additional alcohol, although the copolymer may be separated from the alcohol by any conventional method such as evaporating the solvent and redissolving in alcohol as indicated in the examples.

The degree to which polymerization proceeds is not critical when carried out in an organic system since it will not proceed to the point where it is insoluble in the organic system. One skilled in the art will readily appreciate that if the polymerization step is allowed to proceed to at least substantial completion, the copolymer will form

a film when applied to a surface by means of a solvent and propellant.

Polymerization is normally carried out in a lower monohydric aliphatic alcohol in the presence of a free radical generating catalyst such as a bis-azo nitrile as disclosed in the aforementioned U.S. patent. The copolymer so formed will be film forming when polymerization is substantially complete. A method of determining if the copolymer is film forming is to measure its intrinsic viscosity in benzene at 30° C., and copolymers of the type disclosed herein that have an intrinsic viscosity value within the range of from 0.04–0.5 will have film-forming characteristics. However, measurement of the intrinsic viscosity of the copolymer is not necessary when polymerization is carried out in an organic system as disclosed above since it will have suitable film-forming properties.

As examples of the amino group containing monomer, the following are representative of the compounds which may be used: dimethylaminoethyl acrylate, diethylaminoethyl acrylate, diethylaminoethyl methacrylate, dibutylaminoethyl methacrylate, 2-(N-piperidinoethyl)-methacrylate, etc.

Comonomers falling within the scope of

$$CH_2=\underset{\displaystyle X}{\overset{|}{C}}-Y$$

include methyl acrylate, ethyl acrylate, methyl methacrylate, butyl methacrylate, octyl methacrylate, isooctyl methacrylate, tridecyl methacrylate, octadecyl methacrylate, acrylonitrile, vinyl laurate, vinyl stearate, vinyl acetate, and the like. Mixtures of higher acrylate and methacrylate esters may be used in the polymerization process, as, for example, a mixture of isooctyl, hexadecyl, and octadecyl methacrylates.

In the patent to Hayek, No. 2,723,256, it is disclosed that the tertiary amine is preferably quaternized prior to polymerization since it is easier to obtain complete quaternization.

Unlike the copolymers disclosed in Patent No. 2,723,256, in which the nitrogen atoms of the amino groups are completely quaternized for use in aqueous solutions, copolymers useful in the present invention must have only a certain amount of salt groups present which enable the copolymer to be dissolved by the organic components in the spray composition and, at the same time, the copolymers must be sensitive to water, permitting easy removal from the hair when subjected to washing by ordinary soap and water.

According to the present invention, only a certain portion of the nitrogen atoms are converted to amine salts preferably after polymerization is carried out. The proper amount of salt agent to be added is added to the copolymer formed in the alcohol solvent. The amount of salt agent to be added is critical and must be within a certain range. Not only may quaternizing agents be added to render the copolymer water sensitive and at the same time suitable for use in an aerosol spray, but strong acids will also convert the nitrogen atoms in the amino group to amine salt groups.

These salts may be formed simply by the addition of strong acids such as hydrochloric acid, sulfuric acid, etc., or the nitrogen atoms may be quaternized with conventional quaternizing agents. Suitable quaternizing agents include alkyl halides such as methyl iodide, ethyl bromide, butyl chloride; alkyl sulfates such as dimethyl sulfate; alkyl sulfonates such as ethyl p'-toluene sulfonate; alkyl phosphates such as triethyl phosphate; and alkyl phosphites such as triethyl phosphite.

It has been found that if one equivalent of a salt group is present in from 500–1500 grams of salt group containing copolymer, the copolymer is made water sensitive and suitable for use in an aerosol composition. The above range is applicable when the amine salt group copolymer contains from 15–90% by weight of the amino group containing comonomer and is likewise applicable to all copolymers formed by copolymerizing any of the various comonomers falling within the scope of the above formulas.

The method of calculating the amount of salt groups needed to impart desirable characteristics to the copolymer is extremely simple and easily understood. It has the further advantage of enabling one skilled in the art to easily determine a range of amounts of any salt agent which may be added to convert the proper portion of nitrogen atoms to amine salt groups.

In order to practice the present invention, as stated before, it is essential that the proper portion of nitrogen atoms in the amino group containing comonomer be converted into salt groups. In order to prevent the copolymer from becoming too hydrophilic and insoluble in the propellant, it is necessary to predetermine the portion of nitrogen atoms which are to be converted to amine salt groups. Predetermination of the portion of nitrogen atoms which are to be converted may be readily calculated by employing the method disclosed herein.

To illustrate the simple mathematics involved, if one equivalent of a salt group, using dimethyl sulfate, for instance, is to be included in 500 grams of copolymer, it is only necessary to divide the atomic weight of sulfur, 32, by 500 and multiply the result by 100 to arrive at the percentage of sulfur required. Since one sulfur atom is required to convert one amino nitrogen to a salt group, this calculation will define a certain percentage of sulfur which may then be easily used to calculate the amount of a given salt-forming reagent to be added to the copolymer.

Percent S required

$$=\frac{32(\text{at. wt. of sulfur})\times 100}{500} \text{ or percent S}=6.4\%$$

The other limit may be calculated by substituting 1500 in place of 500 to arrive at 2.1%. Therefore, the amount of sulfur compound that may be added to quaternize the amino nitrogen will be an amount that will include between 2.1–6.4% by weight of sulfur in the salt group containing copolymer. Since the molecular weight of dimethyl sulfate is easily arrived at, one skilled in the art can readily determine the amount of dimethyl sulfate to add to a given amount of copolymer whereby water sensitivity is imparted to the film-forming copolymer. The copolymer still retains its solubility in organic solvents and may be used in an aerosol spray.

When salt reagents other than dimethyl sulfate are employed, the calculation will simply be based on the appropriate element which attaches itself to the amino nitrogen atom. In the instance of hydrochloric acid, the calculation will be based on the atomic weight of chlorine. Thus, one equivalent of a salt group should be included in every 500–1500 grams of salt group containing copolymer and it is a simple matter for one skilled in the art to determine the amount of any given salt-forming reagent which is to be added to the copolymer within this range.

From 0.5–5% of a salt group containing copolymer which includes comonomers in the proportions described above are suitable for use in an aerosol composition and are preferably included in a formulation which may be sprayed on the hair. The remainder of such a formulation will include a mixture of solvent and propellant and possibly small amounts of other ingredients, which mixture will have from about 10–50% by weight of a lower monohydric aliphatic alcohol having from 1–4 carbon atoms and a propellant. Alcohols that may be used include methanol, ethanol, propanol, tert.-butanol and others. The propellant used will usually comprise from about 50–90% by weight of the formulation. It is to be understood, however, that the essential part of the present invention is the composition of the film-forming copolymer.

A fluorinated propellant is preferably used in the aerosol

spray, which propellant comprises about 50–90% of the novel formulation. The propellant provides pressure which forces the solution through a valve of its container, and to do this the completed formulation should have a vapor pressure between about 10 and 75 p.s.i.g. at 25° C. The preferred propellant is a mixture of trichloromonofluoromethane and dichlorodifluoromethane, the mixture comprising about 20–50% by weight of dichlorodifluoromethane, the balance being trichloromonofluoromethane. Other operable propellants include a mixture of trichloromonofluoromethane (50–95% by weight) and chlorodifluoromethane (5–50% by weight), and also operable are dichlorotetrafluoroethane, 1-chloro-1,1-difluoroethane, 1,1-difluoroethane, and monobromomonochlorodifluoromethane. These may be used alone or in admixture with trichloromonofluoromethane or dichlorodifluoromethane so as to adjust the vapor pressure of the system to a preferred value. For example, 1,1-difluoroethane may be used alone as propellant in relatively high pressure systems. It may also be used in low pressure systems by mixing it with trichloromonofluoromethane to adjust the vapor pressure of the completed formulation to a lower value (see, for example, U.S. 2,742,321 and 2,529,092). In any event, the vapor pressure of the total formulation will be between about 10 and 75 p.s.i.g. at 25° C. The novel composition will contain about 50–90% by weight of propellant, although it is preferred for economic and practical purposes that the formulation contain about 70–80%. The formulations will be nonflammable because of the high percentages of the fluorinated propellants which are normally used. Other conventional propellants may be used, but fluorinated propellants are preferred because of the nonflammable characteristics.

Other ingredients may be compounded in the composition as, for example, perfume oils, lanolin, fatty oils, mineral oils, camphor and synthetic plasticizing oils, and these are normally added in small amounts.

In addition to its use as a hair lacquer, this composition is useful where films are desired which may be easily removed by washing. For example, the formulation may be used a spray for silverware to prevent tarnishing and it may be easily removed therefrom by a warm water wash with soap.

EXAMPLES

Example 1

A copolymer consisting of 54% by weight of lauryl methacrylate and 46% by weight of diethylaminoethyl methacrylate having an intrinsic viscosity of 0.30 in benzene at 30° C. is quaternized with dimethylsulfate so that 83% of the available tertiary nitrogen atoms are converted to salt groups. The quaternized copolymer contains 1 equivalent of quaternary ammonium groups for each 610 grams of copolymer.

The aerosol formulation is prepared by dissolving 2 parts of the above quaternized copolymer in 25 parts of ethyl alcohol containing 0.4 part of dibutyl phthalate plasticizer and 0.1 part of perfume. Then this solution is placed in a suitable aerosol dispenser and after chilling to −20° C., 72.6 parts of a mixture consisting of 35% by weight of dichlorodifluoromethane and 65% by weight of trichloromonofluoromethane is added. The dispenser is closed by inserting and fastening a valve assembly, and then the can is rolled while it is allowed to warm up to room temperature. The pressure within the aerosol container is 26 p.s.i.g. at room temperature.

When this composition is sprayed onto hair in repeated short bursts while holding the can 8 to 18 inches from the hair, it is observed that the hair is effectively held in its styled form for 2 to 3 days. Even after repeated stretching, the hair retains its set shape. The hair is soft and sweet smelling and no flaking occurs during combing or rubbing the hair. In humid atmospheres the hair remains dry to the touch.

When the treated hair is washed with a liquid coconut oil soap shampoo, the resin is completely removed.

Example 2

A copolymer consisting of 53% by weight of lauryl methacrylate and 47% by weight of diethylaminoethyl methacrylate having an intrinsic viscosity of 0.30 in benzene at 30° C. is quaternized with dimethylsulfate so that 37% of the available nitrogen atoms are converted to salt groups. The quaternized copolymer contains 2.7% sulfur which corresponds to 1 salt group for each 1190 grams of copolymer.

Two parts of the above quaternized copolymer is dissolved in 26.75 parts of ethyl alcohol containing 0.75 part of dimethylphthalate and 0.15 part of dibutylphthalate plasticizers and 0.35 part of perfume. Then this solution is placed in an aerosol container and is chilled to −20° C. and 70 parts of a mixture of 40% by weight of dichlorodifluoromethane and 60% trichloromonofluoromethane is added. The dispenser is fitted with a valve assembly and the can is rolled while allowed to warm to room temperature. Pressure within the aerosol container is 30 p.s.i.g. at room temperature.

When the above formulation is evaluated on hair as described in Example 1, essentially the same results are obtained.

Example 3

A copolymer consisting of 10% by weight of vinyl acetate and 90% by weight of 2-diethylaminoethyl methacrylate having an intrinsic viscosity of 0.17 in benzene at 30° C. is quaternized with dimethylsulfate so that 28% of the available tertiary nitrogen atoms are converted to salt groups. The quaternized copolymer contains one quaternary ammonium group for each 855 grams of copolymer.

The above copolymer in formulated in an aerosol composition comprising by weight

4.8% of the copolymer
30.0% of methyl alcohol
65.2% of propellant composed of 30% by weight of dichlorodifluoromethane and 70% by weight of 1,2-dichlorotetrafluoroethane

On evaluation as described in Example 1, the product is found to be equivalent.

Example 4

A copolymer consisting of 63% by weight of lauryl methacrylate and 37% by weight of diethylaminoethyl acrylate having an intrinsic viscosity of 0.28 in benzene at 30° C. is quaternized with dimethylsulfate so that 49% of the available tertiary nitrogen atoms are converted to salt groups. The quaternized copolymer contains one quaternary ammonium group for each 1070 grams of copolymer.

The above copolymer is formulated in an aerosol composition comprising by weight

1% of the copolymer
20% of ethanol
79% of propellant composed of a 1:1 weight ratio of trichloromonofluoromethane and dichlorodifluoromethane

Evaluation of the product as a hair lacquer showed it to be equivalent to that of Example 1.

Example 5

A copolymer consisting of 28% by weight of acrylonitrile and 72% by weight of diethylaminoethyl methacrylate having an intrinsic viscosity of 0.1 in benzene at 30° C. is quaternized with dimethylsulfate so that 29% of the available tertiary atoms are converted to salt groups. The quaternized copolymer contains one quaternary ammonium group for each 1020 grams of copolymer.

The above copolymer is formulated into an aerosol composition comprising by weight

1% of the copolymer
25% of ethanol
74% of the propellant mixture of Example 4

The product was quite satisfactory as a hair lacquer.

Example 6

A copolymer of 52% by weight of lauryl methacrylate and 48% by weight of 2-(N-piperidinoethyl) methacrylate having an intrinsic viscosity of 0.20 in benzene at 30° C. is treated in alcohol with dilute sulfuric acid to give one equivalent of salt groupings per 630 grams of copolymer.

This copolymer is formulated into an aerosol composition comprising by weight

0.5% copolymer
25.0% isopropyl alcohol
74.5% of the propellent of Example 1

Evaluation of the product as a hair lacquer showed it to have properties essentially the same as that described in Example 1.

Example 7

In accord with the procedures set out in Example 1, an aerosol composition was formulated from a copolymer containing 53% by weight of octadecyl methacrylate and 47% by weight of diethylaminoethyl methacrylate (intrinsic viscosity at 30° C. in benzene is 0.3) quaternized with dimethylsulfate so that 77% of the available nitrogen atoms were converted to salt groups. This corresponds to one salt group for every 635 grams of the quaternized copolymer.

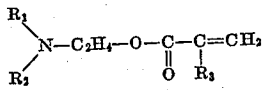
This copolymer was formulated into an aerosol composition comprising

2% by weight of copolymer
25% by weight of ethanol
73% by weight of the propellent of Example 1

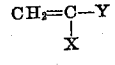
On evaluation, the product had properties essentially the same as that of Example 1.

I claim:

1. A hair-treating composition adapted for use as an aerosol spray, said composition comprising about 10–50% by weight of a lower monohydric aliphatic alcohol having 1–4 carbon atoms, about 50–90% by weight of a fluorinated propellant and 0.5–5% by weight of a film-forming copolymer, said copolymer consisting of 15–90% by weight of an amino group containing comonomer having the structure

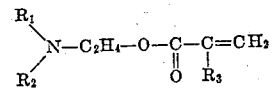


where R_1 and R_2 are selected from the group consisting of lower alkyl radicals and cycloalkyl radicals that include R_1 and R_2 and R_3 is selected from the group consisting of H and CH_3 and 10–85% by weight of a comonomer having the structure

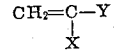


where X is a member selected from H and CH_3 and Y is a member selected from the polar group consisting of nitrile, acyloxy radicals having from 1–18 carbon atoms and alkoxycarbonyl radicals having from 1–18 carbon atoms, a portion of the nitrogen atoms of said copolymer being converted to amine salt groups by the addition of a salt agent in an amount to produce one equivalent salt group for every 500–1500 grams of the salt group containing copolymer, copolymer having an intrinsic viscosity value within the range of from 0.04 to 0.5 when measured in benzene at 30° C.

2. A hair-treating composition adapted for use as an aerosol spray, said composition comprising about 10–50% by weight of a lower monohydric aliphatic alcohol having 1–4 carbon atoms, about 50–90% by weight of a fluorinated propellant, said propellant consisting of 20–50% by weight of dichlorodifluoromethane and 50–80% by weight of trichloromonofluoromethane, and 0.5–5% by weight of a film-forming copolymer, said copolymer consisting of 15–90% by weight of an amino group containing comonomer having the structure

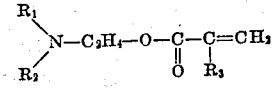


where R_1 and R_2 are selected from the group consisting of lower alkyl radicals and cycloalkyl radicals that include R_1 and R_2 and R_3 is selected from the group consisting of H and CH_3 and 10–85% by weight of a comonomer having the structure

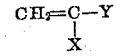


where X is a member selected from H and CH_3 and Y is a member selected from the polar group consisting of nitrile, acyloxy radicals having from 1–18 carbon atoms and alkoxycarbonyl radicals having from 1–18 carbon atoms, a portion of the nitrogen atoms of said copolymer being converted to amine salt groups by the addition of a salt agent in an amount to produce one equivalent salt group for every 500–1500 grams of the salt group containing copolymer, copolymer having an intrinsic viscosity value within the range of from 0.04 to 0.5 when measured in benzene at 30° C.

3. A hair-treating composition adapted for use as an aerosol spray, said composition comprising about 10–50% by weight of a lower monohydric aliphatic alcohol having 1–4 carbon atoms, about 50–90% by weight of a fluorinated propellant and 0.5–5% by weight of a film-forming copolymer, said copolymer consisting of 15–90% by weight of an amino group containing comonomer having the structure

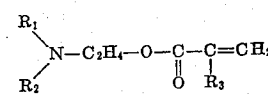


where R_1 and R_2 are selected from the group consisting of lower alkyl radicals and cycloalkyl radicals that include R_1 and R_2 and R_3 is selected from the group consisting of H and CH_3 and 10–85% by weight of a comonomer having the structure



where X is a member selected from H and CH_3 and Y is an alkoxycarbonyl radical having from 1–18 carbon atoms, a portion of the nitrogen atoms of said copolymer being converted to amine salt groups by the addition of a salt agent in an amount to produce one equivalent salt group for every 500–1500 grams of the salt group containing copolymer, copolymer having an intrinsic viscosity value within the range of from 0.04 to 0.5 when measured in benzene at 30° C.

4. A hair-treating composition adapted for use as an aerosol spray, said composition comprising about 10–50% by weight of a lower monohydric aliphatic alcohol having 1–4 carbon atoms, about 50–90% by weight of a fluorinated propellant and 0.5–5% by weight of a film-forming quaternizable copolymer, said copolymer consisting of 15–90% by weight of an amino group containing comonomer having the structure



where R_1 and R_2 are selected from the group consisting of lower alkyl radicals and cycloalkyl radicals that include R_1 and R_2 nd R_3 is selected from the group consisting of

H and CH_3 and 10–85% by weight of a comonomer having the structure

$$CH_2=\underset{\displaystyle X}{\overset{\displaystyle |}{C}}-Y$$

where X is a member selected from H and CH_3 and Y is a member selected from the polar group consisting of nitrile, acyloxy radicals having from 1–18 carbon atoms and alkoxycarbonyl radicals having from 1–18 carbon atoms, a portion of the nitrogen atoms of said copolymer being converted to quaternized amine salt groups by the addition of a salt agent in an amount to produce one equivalent salt group for every 500–1500 grams of the salt group containing copolymer, copolymer having an intrinsic viscosity value within the range of from 0.04 to 0.5 when measured in benzene at 30° C.

5. A hair-treating composition adapted for use as an aerosol spray, said composition comprising 25 parts of ethyl alcohol, 72.6 parts of a fluorinated propellant, said propellant consisting of 35% by weight of dichlorodifluoromethane and 65% by weight of trichloromonofluoromethane, and 2 parts of a film-forming copolymer, said copolymer consisting of 54% by weight of lauryl methacrylate and 46% by weight of diethylaminoethyl methacrylate, a portion of the nitrogen atoms of said copolymer being converted to quaternized amine salt groups by the addition of a salt agent in an amount to produce one equivalent salt group for every 610 grams of the salt group containing copolymer, copolymer having an intrinsic viscosity value within the range of from 0.04 to 0.5 when measured in benzene at 30° C.

6. A hair-treating composition adapted for use as an aerosol spray, said composition comprising 26.75 parts of ethyl alcohol, 70 parts of a fluorinated propellant, said propellant consisting of 40% by weight of dichlorodifluoromethane and 60% by weight of trichloromonofluoromethane, and 2 parts of a film-forming copolymer, said copolymer consisting of 53% by weight of lauryl methacrylate and 47% by weight of diethylaminoethyl methacrylate, a portion of the nitrogen atoms of said copolymer being converted to quaternized amine salt groups by the addition of a salt agent in an amount to produce one equivalent salt group for each 1190 grams of the salt group containing copolymer, copolymer having an intrinsic viscosity value within the range of from 0.04 to 0.5 when measured in benzene at 30° C.

References Cited in the file of this patent

UNITED STATES PATENTS

2,138,763	Graves	Nov. 29, 1938
2,305,356	Luckenbach	Dec. 15, 1942
2,677,679	Barney	May 4, 1954
2,677,699	Barney	May 4, 1954
2,723,256	Hayek	Nov. 8, 1955
2,766,157	Peterson	Oct 9, 1956
2,857,314	Phillips	Oct. 21, 1958
2,871,161	Spiegel	Jan. 27, 1959

FOREIGN PATENTS

747,806	Great Britain	April 11, 1956

OTHER REFERENCES

Reed; J. Society of Cosmetic Chemists, vol. 7, No. 2. March 1956, pp. 137–149.