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HAIR SPRAY

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No Drawing. Continuation-in-part of applications Ser. No. 567,856, July 26, 1966, now Patent No. 3,520,949, Ser. No. 650,259, June 30, 1967, and Ser. No. 654,044, July 5, 1967. This application is also a division of application Ser. No. 743,626, July 10, 1968. This application Sept. 9, 1970, Ser. No. 70,889

Int. Cl. A61k 7/10

U.S. Cl. 424—47 10 Claims

ABSTRACT OF THE DISCLOSURE

A hair straightening and/or hair setting formulation is prepared by adding a hydrophilic acrylate or methacrylate to an appropriate cosmetic formulation.

The present application relates to novel cosmetic preparations.

The present application is a continuation-in-part of application Ser. No. 567,856 filed July 26, 1966, now Pat. 3,520,949, July 21, 1970, application Ser. No. 650,259 filed June 30, 1967, now abandoned, application 654,044 filed July 5, 1967 and is a division of application 743,626 filed July 10, 1968.

Cosmetic manufacturers have sought in the past to produce compositions for use on human hair and skin which may be easily applied, exhibit no detrimental effect on the skin and retain their stability for a reasonable period of time. Some progress has been made in producing products of this type. However, there remains inherent defects in prior preparations such as creams, lotions, shampoos, dressings, sticks, and the like which impairs their cosmetic effectiveness. One example of this is the well-known tendency of conventional mascara to run when wet by tears or water.

As is well known, the various creams used on the body have a tendency to soil clothing, bedclothes and the like. Lipsticks and suntan creams have a tendency to be greasy and essences (e.g. perfume) and other volatile components present in lipstick, creams and lotions have a tendency to be lost on standing.

It has hitherto been proposed to employ lacquers for imparting a temporary set to the hair. However, since lacquers include a water-insoluble film-forming ingredient, it has been extremely difficult to remove them from the hair. When it is desired to change the hair style, it sometimes becomes necessary to employ a special solvent or a powerful detergent composition, neither of which is readily available in the home. Lacquers have generally been considered unsatisfactory for application to the hair for this reason. A number of water-soluble film-forming resinous materials have also been proposed for application to the hair in order to set it. However, such water-soluble materials have not been completely satisfactory because of the tendency for the resultant film to become tacky and for the hair to lose its set when exposed to conditions of high humidity.

Furthermore, at present there is no satisfactory method for straightening kinky hair.

A further object is to protect the body against the drying effects of cosmetics comprising alcohol solutions.

An important object of the invention is to straighten kinky or curly hair so that it can be manipulated as desired.

A related object is to set hair of any type.

A further object is to develop a hair setting composition and method which will provide a "permanent" set even under conditions of high humidity.

A related object is to give hair a "permanent" that does result in the treated hair developing static electrical charges under conditions of low humidity.

Another object is to apply a film having one or more of the above characteristics in relation to hair, but which can be readily removed.

A still further object is to develop novel aerosol compositions useful for application to the body.

Still further objects and the entire scope of applicability of the present invention will become apparent from the detailed description given hereinafter; it should be understood, however, that the detailed description and specific examples, while indicating preferred embodiment of the invention, are given by way of illustration only, since various changes and modifications within the spirit and scope of the invention will become apparent to those skilled in the art from this detailed description.

It has now been found that these objects can be attained by employing certain hydrophylic acrylate and methacrylate polymers in cosmetic compositions. For liquid cosmetics the hydrophylic polymer should not have substantial cross-linking (i.e. the cross-linking should not be sufficient to render the polymer insoluble in the solvent).

The hydrophylic monomer used to prepare the hydrophylic polymer is preferably a hydroxyalkyl monoacrylate or methacrylate such as 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, diethylene glycol monoacrylate, diethylene glycol monomethacrylate, hydroxypropyl acrylates and methacrylates, e.g. 2-hydroxypropyl acrylate, 2-hydroxypropyl methacrylate, 3-hydroxypropyl acrylate, 3-hydroxypropyl methacrylate, tetraethylene glycol monomethacrylate, pentaethylene glycol monomethacrylate, dipropylene glycol monomethacrylate. The most preferred monomer is 2-hydroxyethyl methacrylate and the next most preferred monomer is 2-hydroxyethyl acrylate.

In preparing hydroxyalkyl acrylates and methacrylates a small amount of the diacrylate or dimethacrylate is also formed. This need not be removed as it does not cause undue cross-linking.

When it is desired to shampoo out the hydrophylic polymer there are desirably included 0.1 to 15% of an ethylenically unsaturated acid to provide free acid groups. Typical examples of such acids include acrylic acid, methacrylic acid, itaconic acid, aconitic acid, cinamic acid, crotonic acid, citraconic acid, measaconic acid, maleic acid and fumaric acid. Less preferably there can also be used partial esters of poly-basic acids such as mono 2-hydroxypropyl itaconate, mono 2-hydroxyethyl itaconate, mono 2-hydroxyethyl citraconate, mono 2-hydroxypropyl aconitate, mono 2-hydroxyethyl maleate, mono 2-hydroxypropyl fumarate, monomethyl itaconate, monoethyl itaconate, mono methyl Cellosolve ester of itaconic acid (methyl Cellosolve is the monomethyl ether of diethylene glycol), mono methyl Cellosolve ester of maleic acid.

The use of such acid containing groups does not result in substantial cross-linking unless the polymer is heated for a substantial time above normal operating conditions for cosmetics or unless the polymerization time is prolonged using relatively high amounts of catalysts.

When cross-linked or cross-linkable hydrophylic polymers are prepared normally the cross-linking agent is preferably present in an amount of 0.1 to 2.5%, most preferably 0.1 to 1.0%, of the total monomers, although up to 15% of cross-linking agent can be used. Typical examples of cross-linking agents include ethylene glycol diacrylate, ethylene glycol dimethacrylate, 1,2-butylene dimethacrylate, 1,3-butylene dimethacrylate, 1,4-butylene dimethacrylate, propylene glycol diacrylate, propylene

glycol dimethacrylate, diethylene glycol dimethacrylate, dipropylene glycol diacrylate, divinyl benzene, divinyl toluene, diallyl tartrate, allyl pyruvate, allyl malate, divinyl tartrate, triallyl melamine, N,N'-methylene-bis-acrylamide, glycerine trimethacrylate, diallyl maleate, divinyl ether, diallyl mono ethylene glycol citrate, ethylene glycol vinyl allyl citrate, allyl vinyl maleate, diallyl itaconate, ethylene glycol diester of itaconic acid, divinyl sulfone, hexahydro-1,3,5-triacryltriazine, triallyl phosphite, diallyl ester of benzene phosphonic acid, polyester of maleic anhydride with triethylene glycol, polyallyl sucrose, polyallyl glucose, e.g. diallyl sucrose and triallyl glucose, sucrose diacrylate, glucose dimethacrylate, pentaerythritol diacrylate, sorbitol dimethacrylate.

Unless otherwise indicated all parts and percentages are by weight.

The hydrophylic polymers of this invention possess unique properties which are capable of improving a wide range of cosmetic products. In particular, they impart to such products a wide range of unusual and desirable properties and effects on the skin and hair, such as lubricity, emolliency, softening and smoothing, resistance to and protection against the drying effects of alcohol solutions, resistance to water and/or soap or detergents and water, freedom from tactile greasiness or oiliness due to mineral and/or vegetable oils, marked solvency and coupling effects for lanolin, lanolin isolates and derivatives either alone or in the presence of mineral and vegetable oils and freedom from tackiness or greasiness in preparations containing any of the above-mentioned materials.

The present invention overcomes the disadvantages pointed out supra of previous hair preparations. Even though the hydrophilic polymers of the invention are insoluble in water, they are easily removed, e.g. with conventional shampoo.

Hair sprays produced according to this invention comprise a soluble hydrophilic polymer such as previously described and a non-toxic organic solvent. When an aerosol is to be prepared thence propellant is also used. As the organic solvent there can be employed alcohols, particularly lower aliphatic saturated alcohols e.g. ethyl alcohol, isopropyl alcohol, propyl alcohol, glycols, e.g. ethylene glycol diethylene glycol, propylene glycol and dipropylene glycol, glycerine, ethylene glycol methyl ether, ethylene glycol ethyl ether, n-propylene glycol monomethyl ether, n-propylene glycol monoethyl ether, isopropylene glycol monomethyl ether, isopropylene glycol monoethyl ether, ethyl acetate. Mixtures of these solvents with minor amounts of water, e.g. up to 30% water, can be also employed. Glycols and glycerine and similar polyhydric alcohols act as plasticizers for the hydrophilic polymer.

Generally the amount of hydrophilic polymer will be about 0.5 to 10%, preferably 0.75 to 5%, by weight of the total hair spray composition.

Hair setting and hair straightening composiitons are also produced according to the invention using 0.5 to 10% of the hydrophylic polymer in the solvent.

Such compositions not only provide the desired temporary set-holding characteristic and maintains the hair in the desired configuration until removed, but do so even when the hair is exposed to conditions of high humidity without the development of any appreciable surface track. In addition, the hair thus treated, despite its resistance to moisture, is remarkably free from any tendency to develop static electrical changes when combed or brushed under conditions of low humidity. Furthermore, the treated hair is capable of being reset merely by use of water-dampened comb. Finally, the film on the hair may readily be removed, despite its resistance to moisture, by a mild shampoo.

The hydrophylic polymers can be used not only in solution, but also in compositions having the form of stable gels, creams and the like without requiring the presence of an emulsifying agent. They can have the

physical form of a jelly, paste, plastic mass, or the like and generally comprise the hydrophylic polymer in an amount of 2 to 15% by weight of the total composition. Advantageously there can be included 7 to 20% of a thixotropic agent such as Carbopol 961 (sucrose acrylate having free acid groups).

The amount of solvent is usually 10% or more of the total hair preparation. When a propellant is present the solvent is normally not over 60% and is preferably 25 to 40% of the total hair preparation by weight.

When the hydrophylic polymer is packaged in an aerosol container the propellant should be sufficient to force the composition out of the container as a spray. The propellant can vary considerably, but usually is about 25 to 85%, preferably 50 to 70%, of the total hair spray composition. As the aerosol propellants there can be used compressed gasses such as carbon dioxide, nitrous oxide and nitrogen, liquified volatile hydrocarbons such as propane, n-butane, isobutane, 2-methyl butane and fluorinated compounds including perhalogenated compounds and fluorinated hydrocarbons such as dichlorodifluoromethane, trichlorofluoromethane, 1,2-dichlorotetrafluoroethane, octofluorocyclobutane, chlorodifluoromethane, 1,1-difluoroethane, 1-chloro-1,1-difluoroethane. These fluorinated compounds are available under the names Freon and Genetron. The propellant should contain a substantial amount of volatile material boiling at not over 20° C., but there can also be present a significant amount of less volatile material boiling up to 50° C., e.g. methylene chloride can be present as a substantial part of the propellant. Of course perfumes or other essences can be included in the formulations.

As catalyst for carrying out the polymerization there is employed free radical catalyst in the range of 0.05 to 1% of the polymerizable hydroxyalkyl ester, for example, the preferred amount of catalyt is 0.1 to 0.2% of the monomer. Typical catalysts include t-butyl peroctoate, benzoyl peroxide, isopropyl percarbonate, methylethylketone peroxide, cumene hydroperoxide and dicumylperoxide. Irradiation, e.g., by ultra violet light or gamma rays, also can be employed to catalyze the polymerization. Polymerization can be done at 20 to 150° C., usually 40 to 90° C.

When cross-linked polymers are prepared the method of polymerization is not critical and the monomers can be polymerized in water, by suspension polymerization, in organic solvent or without any solvent. However, when hydrophylic soluble thermoplastic polymers are desired they are preferably prepared by suspension polymerization of the hydrophylic monomers in a non-polar medium such as silicone oil, mineral oil, xylene, toluene, benzene or the like. Alternatively they can be polymerized while in solution in ethyl alcohol, methyl alcohol, propyl alcohol, isopropyl alcohol, formamide, dimethyl sulfoxide or other appropriate solvent.

In the suspension polymerization procedure the catalyst containing monomer is dispersed in the non-polar medium in the form of small droplets which are polymerized to form finely divided spheres or beads. The beads are dissolved in the polar organic solvents, e.g., ethyl alcohol, isopropyl alcohol, ethyl alcohol-water (e.g. 95:5 or 70:30), glycols and glycol ethers for use as sprays, etc. or are mixed with other ingredients to make creams, powders or the like.

Suspension polymerization is preferably carried out at 50–105° C. until bead formation is completed. The ratio of suspension oil to monomer can be varied widely, but preferably is from 5:1 to 20:1. As stated the catalyst to monomer ratio is preferably from 0.05 to 1.0 part per 100 parts of monomer.

One method of incorporating the hydrophylic polymeric powders with cosmetic ingredients or essences dissolved in an appropriate solvent is to place the mixture on a mechanical roller so that the solution becomes intimately mixed with the powder. The mixture is dried by air

evaporation or forced heat. Upon evaporation of the solvent the cosmetic ingredients and/or essences are retained by the powder.

EXAMPLE 1

Into a flask equipped with an agitator and a heating mantle was charged 1000 grams of silicone oil; polydimethyl silicone, 100 grams of 2-hydroxyethyl methacrylate and 0.33 grams of isopropyl percarbonate. The flask was placed under a nitrogen atmosphere and the contents were rapidly agitated and heated to 100° C. After 15 minutes at 100° C., the polymer slurry obtained was filtered hot to isolate the polymer. The polymer powder was reslurried in 300 ml. of xylene, filtered and dried. A 98% yield of 2 to 5 micron particle size powder was obtained.

EXAMPLE 2

The thermoplastic, solvent soluble poly-(2-hydroxyethyl methacrylate)polymeric powder formed in Example 1 was mixed with an oil of orchids perfume essence and the resultant mixture placed on a mechanical roller for approximately 8 hours. The polymeric powder thus absorbed the essence. The mixture was filtered and the residue dried at room temperature.

EXAMPLE 3

Example 1 was repeated using xylene in place of the silicone oil. The amount of 2-hydroxyethyl methacrylate was increased from 100 grams to 300 grams and the quantity of isopropyl percarbonate was increased to 0.99 gram. An 85% yield of polymer beads was obtained.

EXAMPLE 4

Example 1 was repeated using mineral oil in place of the silicone oil, the amount of 2-hydroxyethyl methacrylate was increased from 100 grams to 200 grams and the quantity of isopropyl percarbonate was increased from 0.33 to 0.66 gram. A 98% yield of polymer beads ranging in diameter from 2 to 5 microns was obtained.

EXAMPLE 5

800 grams of ethylene glycol monomethyl ethers, 180 grams of 2-hydroxyethyl methacrylate, 20 grams of acrylic acid and 2 grams of t-butyl peroctoate were charged into a flask. The solution was heated and stirred under a carbon dioxide atmosphere at 85° C. for 6 hours. The thermoplastic hydrophylic polymer formed was precipitated by pouring the reaction solution into 10 liters of rapidly agitated water. The precipitated polymer was isolated by filtration and dried. The product of this example while thermoplastic and solvent soluble has the capability of curing to cross-linked solvent insoluble polymer by further heating, particularly if additional catalyst is added. In contrast, the polymers of Examples 1, 3, and 4 are permanently thermoplastic and solvent soluble.

EXAMPLE 6

The procedure of Example 1 was repeated replacing the 2-hydroxyethyl methacrylate by 100 grams of 2-hydroxypropyl methacrylate to produce a thermoplastic solvent soluble hydrophylic finely divided bead polymer.

EXAMPLE 7

A hair setting composition was prepared from 1.90 parts of the poly 2-hydroxyethyl methacrylate prepared in Example 1, 0.10 part of perfume (oil of orchids) and 28 parts of ethyl alcohol. This solution (50% of the total formulation) was packaged in a conventional aerosol pressure can container together with 45.5 parts (32% of the total formulation) of monofluorotrichloromethane and 24.5 parts (18% of the total) of methylene chloride.

The aerosol was sprayed on hair held in a desired configuration and allowed to dry, the formulation was found to provide satisfactory set-holding characteristics even under conditions of high humidity. The sprayed hair was natural looking, non-sticky, non-static and exhibited holding power for a relatively long period of time.

EXAMPLE 8

A 5% solution of the polymeric 2-hydroxyethyl methacrylate prepared in Example 1 in 95% ethyl alcohol (95% alcohol, 5% water) was applied to kinky hair. The hair was relaxed and then rolled on rollers and held in tension until dried. When dry, the hair was set and could be combed in conventional fashion. The permanent remained until the hair was wet.

Drying can be accomplished with or without a conventional hair dryer. In place of the rollers any other conventional means for holding the hair in tension can be employed.

EXAMPLE 9

A more flexible wave can be obtained by incorporating 5 to 100%, based on the polymer, of glycerol, sorbitol, diethylene glycol, dipropylene glycol, ethylene glycol, propylene glycol or other liquid polyhydric alcohol as a plasticizer.

Thus a more flexible wave than that of Example 8 was obtained by applying to the hair, a solution of 5 parts of the poly 2-hydroxyethyl methacrylate, 100 parts of 95% ethyl alcohol and 0.75 part of glycerol. After the hair was relaxed it was held in tension until dried using a hair dryer. The hair was then set and was combed in conventional manner. Not only was a more flexible wave obtained, but the use of glycerol prevented flaking of the polymer when the hair was combed.

EXAMPLE 10

To impart greater sheen to the hair a small amount, e.g. 2–3%, of silicone oil can be added to the formulation. Thus the formulation of Example 9 was modified by adding 3% of dimethyl polysiloxane oil based on the 2-hydroxy ethyl methacrylate polymer to give a flexible permanent wave having a high sheen.

The hair straightener compositions can be brushed on the hair, poured on the hair or combed on the hair. The preferred solvent is ethyl alcohol with or without minor amounts of water. There can also be employed other solvents such as isopropyl alcohol, monomethyl ether of ethylene glycol, monoethyl ether of ethylene glycol, normal or isopropylene glycol monomethyl ether, normal or isopropylene glycol monoethyl ether.

EXAMPLE 11

A hair setting gel was produced having the following formulation:

	Parts
Hydrophylic 2-hydroxyethyl methacrylate polymer of Example 1	10
95% ethyl alcohol	144
Water	36
Carbopol 940 (sucrose acrylate polymer having free acrylic acid groups)	1.2
Glycerine	1.4
Solulan 98 (acetylated polyoxyethylated lanolin)	1.0
Triton X–100 (polyoxyethylene (10)-nonylphenol condensate)	2.0
Essence (lavender oil)	0.6

The polymer was dissolved in the alcohol-water mixture to form a solution. The solution was then mixed with the remaining ingredients by rapid strring and the pH of the mixture adjusted to a pH of about 7.2 by adding a 10% solution of diisopropanolamine in 95% ethyl alcohol. This gel was suitable for setting hair. Thus a sample of curly hair was straightened by heat and pressure, coated with the above gel and soaked in water. A control sample of the curly hair was also straightened, but remained uncoated when soaked in water. The control sample returned to its original curly configuration after 30 seconds while

the coated sample remained straight for about 3 minutes.

In place of the dissopropanolamine there can also be used triethanolamine, diethanolamine or tripropanolamine as a gelling agent in this example.

What is claimed is:

1. In a process of improving the external appearance of hair on a human body by applying to the body a hair treating cosmetic comopsition the improvement comprising applying to the hair a cosmetic composition including a solvent soluble polymer of an acrylate or methacrylate seleceted from the group consisting of hydrophilic polymers of hydroxy lower alkyl acrylates, hydroxy lower alkyl methacrylates, hydroxy lower alkoxy lower alkyl acrylates and hydroxy lower alkoxy lower alkyl methacrylates.

2. A process according to calim 1 wherein said acrylate or methacrylate is a member of the group consisting of hydroxyethyl acrylate, hydroxyethyl methacrylate, hydroxypropyl acrylate and hydroxypropyl methacrylates.

3. A process according to claim 2 wherein the polmer is a polymer of 2-hydroxyethyl methacrylate.

4. A process according to claim 2 wherein the polymer is an organic solvent soluble polymer and is applied in a nontoxic organic solvent.

5. A process according to claim 4 wherein the solvent is a lower alkanol.

6. A process according to claim 5 wherein the polymer is essentially polymeric 2-hydroxyethyl methacrylate.

7. A process according to claim 2 where the hair is maintained under tension until it is dry enough to be in a new set condition.

8. A process according to claim 2 wherein the composition is applied to curly hair and the amount of curl is reduced by the application of the composition.

9. A process according to claim 8 wherein the polymer is a 2-hydroxyethyl methacrylate polymer.

10. A process according to claim 2 wherein the composition is applied in the form of an aerosol spray to the hair.

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Disclaimer

3,660,561.—*Thomas H. Shepherd*, Hopewell, and *Francis E. Gould*, Princeton, N.J. HAIR SPRAY. Patent dated May 2, 1972. Disclaimer filed Jan. 13, 1972, by the assignee, *National Patent Development Corporation.*

Hereby disclaims that portion of the term of the patent subsequent to May 4, 1988.

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