

[54] **HAIR SPRAY CONTAINING VINYL
ESTER-ESTER OF α,β -UNSATURATED
MONO-OR DICARBOXYLIC ACID
COPOLYMER**

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doned.

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[51] **Int. Cl.****A61k 7/10**
[58] **Field of Search**.....424/DIG. 1, DIG. 2, 47, 71;
260/78.5 BB, 80.75

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[57] **ABSTRACT**

Hair sprays containing film forming copolymers of (a)
vinyl esters; (b) monoesters of aliphatic olefinically
unsaturated mono- or dicarboxylic acids with lower al-
kanediols, and where required; and (c) α,β -unsatu-
rated carboxylic acids are disclosed.

1 Claim, No Drawings

HAIR SPRAY CONTAINING VINYL ESTER-ESTER OF α,β -UNSATURATED MONO-OR DICARBOXYLIC ACID COPOLYMER

RELATED CASES

This case is a division of our U.S. Pat. application, Ser. No. 652,408, filed July 11, 1967, and now abandoned.

BACKGROUND OF THE INVENTION

Film forming substances used as hair fixatives or setting agents should be soluble both in water and in alcohols since preparations for hair setting are used as solutions in water-alcohol mixtures. Water solubility of the film former is desired even when a purely alcoholic preparation such as, for example, a sprayable preparation is used, in order that it can be readily removed from the hair, e.g., by shampooing.

Substances which are to be used as film formers for sprayable hair fixatives must fulfill a number of requirements, i.e., they must be good film formers and adhere well to the hair; they must have good solubility in the lower molecular weight solvents which are usually used in such preparations, e.g., ethanol and isopropanol; they must be miscible and compatible with the various propellants used in hair sprays, e.g., polyhalogenated lower hydrocarbons; they must give a glossy and clear film which is sufficiently flexible to hold the hair in place permanently despite the usual movements of the head or in wind, on the other hand, the film must be sufficiently brittle so the hair can be readily combed and brushed without collapsing and loss of the hair set through complete removal of the film coating; they must give a film which is soluble in cold water but which does not become sticky in moist atmospheres and, finally, they must be physiologically inoffensive. A polymer which is to be used as a hair fixative in the form of an aerosol preparation must thus, on the one hand, be water soluble or at least capable of swelling therein and therefore be removable by the usual shampoos, while, on the other hand, it must, at least in combination with organic solvents, be soluble in the liquid propellant medium. The solution of the polymer when sprayed on the hair should dry out to a glossy and clear film which is flexible and the film should adhere well to the hair in order to achieve a long-lasting action of the hair fixative.

The polymers hitherto used as film formers in hair dressing agents have numerous disadvantages. Many have the desired solubility properties but, as a consequence of high hygroscopicity, give the hair a sticky feel at high humidities. Other polymers have good hygroscopicity, but exhibit unsatisfactory solvent properties particularly being difficultly soluble in the alcohol-propellant mixtures generally used for hair sprays. Some polymers, however, have good hygroscopicity and are sufficiently soluble in the alcohol-propellant mixtures, but are not sufficiently water-soluble and therefore are difficult to wash out of the hair. Other polymers do not adhere to the hair well with the result that the hair to which it is applied sticks together and the individual hairs are not set so that when the hair is combed, it loses its set and collapses.

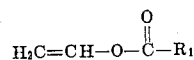
SUMMARY OF THE INVENTION

It has been discovered, according to this invention, that the properties required of film forming copolymers, particularly those intended for use in hair preparations, are fulfilled by film forming copolymers based on vinyl esters, hereinafter defined. This invention also comprehends hair fixatives containing the copolymers of this invention having carboxyl groups wholly or partially neutralized by salt-formation. In another aspect, this invention comprehends sprayable hair fixtures which contain the copolymers dissolved in a mixture of water-miscible solvents, advantageously lower alcohols and polyhalogenated lower hydrocarbons.

DETAILED DESCRIPTION OF THE INVENTION

The film forming copolymers of this invention are based on vinyl esters and contain essentially the following components:

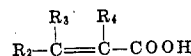
a. from about 90 to 40 percent by weight, preferably about 80 to 60 percent by weight of a vinyl ester or mixture of vinyl esters of the general formula



wherein R_1 signifies a hydrogen atom or a lower alkyl group containing up to four carbon atoms,

b. from about 10 to 60 percent by weight, preferably about 20 to 40 percent by weight of a monoester of substituted or unsubstituted lower aliphatic, olefinically unsaturated mono- or dicarboxylic acids containing up to seven carbon atoms with lower alkanediols containing up to four carbon atoms and

c. from about 0 to 10 percent by weight of an α,β -unsaturated carboxylic acid of the general formula



wherein R_2 signifies a hydrogen atom or a carboxyl group and R_3 and R_4 signify hydrogen or halogen atoms, e.g., fluorine, bromine, chlorine or iodine, or lower alkyl groups containing up to four carbon atoms.

Examples of suitable vinyl esters defined by component (a) are vinyl formate, vinyl propionate, vinyl butyrate, vinyl acetate and the like, or mixtures of such vinyl esters. Particularly advantageous is vinyl acetate or mixtures of vinyl esters containing vinyl acetate. Although it is indicated above that the copolymers of this invention contain as component (a) essentially vinyl esters with up to seven carbon atoms, it is to be understood that part of said component (a) can have a higher molecular structure. It has been found that said component (a) may contain up to 25 percent of vinyl esters derived from acids with up to 18 carbon atoms.

Examples of suitable esters defined by component (b) are those of α,β -unsaturated mono- and dicarboxylic acids, e.g., acrylic acid monoethyleneglycol ester, methacrylic acid monoethyleneglycol ester, crotonic acid monoethyleneglycol ester, crotonic acid monopropyleneglycol ester, maleic acid

monoethyleneglycol ester, α -chloroacrylic acid monoethyleneglycol ester and the like.

Examples of α,β -unsaturated carboxylic acids suitable for use as component (c) are acrylic acid, methacrylic acid, α -chloroacrylic acid, maleic acid, fumaric acid, crotonic acid and the like. Particularly suitable is crotonic acid (β -methacrylic acid).

When monohydroxyalkyl esters of dicarboxylic acids are used as component (b), it is not necessary to use component (c) unless specific properties are required since there are sufficient free carboxyl groups present.

Especially preferred are copolymers of vinyl acetate and/or vinyl propionate, β -methacrylic acid β -hydroxyethyl ester and β -methacrylic acid.

The amounts by weight of the components of the copolymerizates are governed by the desired properties of the end products.

Thus, component (a) affects the solubility of the end product so that the more of component (a) present the better the solubility in organic solvents and, the less the solubility in water and vice versa. The water solubility, however, is increased primarily by the content of component (c) and only secondarily by the content of component (b). The ethanol solubility depends for the most part on the content of component (b). The type of vinyl ester or esters used has particular influence on the consistency of the copolymerizates. Generally, the greater the carbon content of the carboxylic acids is the softer the products obtained will be. On the other hand, generally the more branched said acids are the harder the products obtained will be. In order to achieve the desired consistency, it is preferred to use mixtures of vinyl esters.

A convenient composition is the following:

About 90 to 40 parts by weight (preferably 80 to 60 parts by weight) of component (a), e.g., a vinyl ester or of a vinyl ester mixture whose composition is determined by the desired consistency of the end product, about 10 to 60 parts by weight (preferably 20 to 40 parts by weight) of component (b), e.g., a monoester of a substituted or unsubstituted aliphatic, olefinically unsaturated mono- or dicarboxylic acid and about 0 to 10 parts by weight of component (c), e.g., an α,β -unsaturated carboxylic acid, are used per 100 parts by weight of component mixture.

In the event it is desired to make the end products substantially water soluble, it is necessary to neutralize the carboxyl groups present in the copolymer. This can be accomplished with a base, e.g., diethanolamine, triethanolamine, 2-amino-2-methyl-1,3-propanediol and the like.

The production of the copolymers of this invention can be effected either by the block process, i.e., in an organic solvent, or in a mixture of such a solvent with water. However, it is preferred to effect the polymerization in suspension in water using free radical initiators.

Ethanol or methanol can, for example, serve as organic solvents, either alone or in admixture with water. Methyl ethyl ketone and/or acetone also can be used in admixture with water to serve as solvents in the process of this invention. Such solvents can also be used as regulators, since they limit, depending upon kind and amount, the molecular weight of the resulting copolymers, thus providing for a complete solubility of

said copolymers. Additional regulators, such as butyraldehyde or mercaptans, can be used to obtain copolymers with still lower molecular weight, which are of special value for certain purposes. One criterion generally used to characterize the molecular weight of polymers is the limiting viscosity number (or intrinsic viscosity), which is obtained by extrapolating to zero concentration the Huggins equation for the viscosity number (or specific viscosity). Organic and inorganic peroxides, alone or with accelerators, can be used as free radical initiators; typical suitable free radical initiators are, e.g., peroxides, such as, dibenzoyl peroxide, dilauroyl peroxide, potassium peroxydisulphate or thermolabile free radical forming compounds, e.g., azodiisobutyronitrile.

The copolymerization reaction is carried out in the absence of oxygen in stirring vessels fitted with reflux condensers. In this process all components of the monomer mixture can either be added to the oxygen-free solvent simultaneously with the initiators, or alternatively individual components of the monomer mixture, mixed with a portion of the initiators can be added during the reaction. The polymerization is generally initiated by heating the contents of the flask at reflux temperature, which is usually 60°–68°C. The completion of the reaction is indicated by a rise in temperature of the reaction mixture to 80°–90°C. The resulting copolymer product is separated from the reaction medium by methods known in the art, e.g., when water is the reaction medium, the polymeric end products can be coagulated in suitable vessels by briefly introducing steam or compressed air into the hot reaction medium and subsequently acidifying with a mineral acid.

The esters of aliphatic olefinically unsaturated carboxylic acids with lower alkanediols used in accordance with the invention as component (b) can be made by conventional means, e.g., by reaction of the appropriate carboxylic acids with ethylene oxide or simple alkyl derivatives thereof.

The copolymers produced by the process of this invention are suitable for use in hair sprays used to retain hair set without encountering the problems of solubility, consistency and elasticity mentioned previously. These copolymers can also be prepared for use in combination with water miscible solvents and can be made soluble in liquefied polyhalogenated hydrocarbons which are gaseous at normal temperature and pressure. It has been found that the hair fixative in accordance with the invention not only fulfills the conditions necessary for an aerosol preparation, especially, good adhesion to the hair, but also inhibits the formation of scale on the comb and hair.

The properties of the end products other than solubility which are controlled by suitable choice of the starting components (a), (b) and (c) are consistency and elasticity.

The composition of the vinyl ester component (a) determines the elasticity and consistency, i.e., "softness" or "hardness" of the end products. As stated above the copolymerizate becomes the softer the more the carbon content of the acid component in the vinyl ester is increased and the copolymerizate becomes the harder the more branched said acids are. It is convenient, instead of a single vinyl ester, to choose as the

copolymerization component a mixture of vinyl esters so that the desired consistency is obtained, e.g., vinyl acetate and vinyl propionate or mixtures of one of them with vinyl esters of higher aliphatic carboxylic acids with up to five carbon atoms. It has proved advantageous if about 5 to 25 percent of said vinyl ester was derived from higher molecular acids with up to 18 carbon atoms, such as acids with 9, 11 and 18 carbon atoms. The type of compound employed as components (b) and (c) in the reaction mixture likewise determines the consistency of the end product, depending on their proportion, and to a lesser extent, the chemical nature of the substances utilized determines the consistency. Thus, the pressure of structural elements derived from carboxylic acids which are alkylated at the unsaturated C-atom causes an increase in the hardness of the end product. The expert is thus enabled to adjust the consistency and elasticity of the end product by suitable composition of the amounts of the components (a) and (b).

The content of the components (a), (b) and (c) of the copolymers used can also be modified to achieve the desired water solubility of the film former. Thus, copolymers with increasing content of component (a) display increasing solubility in organic solvents and, decreasing solubility in water and vice versa. The water solubility, however, depends primarily on the content of component (c) and only secondarily on the content of the component (b). The ethanol solubility of the copolymers depend primarily on the content of component (b). Copolymers which contain 40 to 90 percent by weight of vinyl esters, and 60 to 10 percent by weight of monoesters of aliphatic, olefinically unsaturated mono- and dicarboxylic acids with lower alkanediols and 0 to 10 percent by weight of α,β -unsaturated carboxylic acids are generally used. Per 100 parts by weight of the monomer mixture, there are generally used as component (a) 90 to 40 parts by weight (preferably 80 to 60 parts by weight) of a vinyl ester or of a vinyl ester mixture whose composition is determined by the desired elasticity and consistency of the end product, and as component (b) 10 to 60 parts by weight (preferably 20 to 40 parts by weight) of an ester of an aliphatic α,β -unsaturated dicarboxylic acid with a lower alkanediol, or of a mixture of an ester of an aliphatic α,β -unsaturated monocarboxylic acid with a lower alkanediol and as component (c) 0 to 10 parts by weight of an α,β -unsaturated carboxylic acid whose proportion is governed by the amount of neutralizable carboxyl groups in the end product necessary for the achievement of the desired water solubility. This is determined by the acid number of the polymer, i.e., the amount of KOH in mg necessary to neutralize the free acids present in 1 g of the polymer. Generally polymers with an acid number of between 20 and 60 exhibit suitable water solubility upon complete neutralization. The neutralization of the carboxyl groups which is necessary for the achievement of the desired water solubility of the end products can be undertaken with a base, and effected either subsequent to the copolymerization, particularly if the copolymerization is carried out in a water soluble solvent such as, a lower-molecular aliphatic alcohol, acetone or methyl ethyl ketone, or the neutralization can be effected in a solution prepared from the unneutralized acidic resin

with a solvent preferably with a lower-molecular alcohol. The amount of the base to be used is governed by the desired degree of neutralization. In general, however, as complete as possible a neutralization of the carboxyl groups present in the copolymer is striven for.

Furthermore, the molecular weight influences the properties of the copolymers with a view to their technical usefulness. It has proved advantageous to use copolymers with low molecular weight, the limiting viscosity number of which ranges between about 0.08 and 0.30 dl/g copolymers of such kind can easily be prepared by using regulators such as buturaldehyde or mercaptans in the preparation of the copolymer.

For the manufacture of the sprayable hair fixative preparations, the copolymers generally in the form of powders, are conveniently dissolved in 5 to 15 parts by weight of a water-soluble solvent advantageously ethyl or isopropyl alcohol, with the addition of another organic solvent such as methylene chloride, if required. The resulting clear solution is neutralized by the addition of a base, preferably a higher-boiling alkanolamine. Additives which are usual in cosmetics, e.g., softeners, perfume essences, dyes, brightening agents and other hair dressing agents are then incorporated into the solution. The solutions conveniently contain not more than 9 to 12 percent of polymer, preferably about 10 percent. The polymer solution is filled into aerosol vessels and treated at room temperature under pressure with a suitable liquefied polyhalogenated hydrocarbon or mixtures thereof as a propellant. The solutions are used by spraying from these aerosol vessels by means of valves of known construction. The ratio between the polymer solution and the propellant can vary within moderately wide limits. It depends on the desired content of solids in the finished preparation and on the propellant power of the polyhalogenated hydrocarbons employed. Advantageously, the proportion by weight of polymer solution to propellant is between 1:1 and 1:4, preferably at 1:2:3.

The commercially available polyhalogenated hydrocarbon propellants, e.g., trichlorofluoromethane, dichlorodifluoromethane and sym. tetrafluoroethane are suitable. However, other suitable propellants, e.g., propane, butane, carbonic acid, vinyl chloride and the like can also be used. Mixtures of these propellants can be used to achieve desired propellant power.

In the following Examples, by "parts" are understood parts by weight and temperatures are in degrees C.

EXAMPLE 1

A mixture of 87 parts of vinyl acetate, 10 parts of crotonic acid β -hydroxyethyl ester, 3 parts of crotonic acid, 10 parts of butyraldehyde and 400 parts of water containing 1.4 parts of sodium bicarbonate is heated to 67° in a stirring flask under nitrogen. A mixture of 1.3 parts of dibenzoyl peroxide and 1.8 parts of potassium peroxydisulphate is then added and, during a time period of 4½ hours, the bath temperature is increased to 95°. After brief introduction of steam, the resin is precipitated by addition of 5 parts 2-N hydrochloric acid, isolated, and dried in vacuum. The product obtained is a yellowish brittle resin, whose limiting viscosity number in acetone, 25°, is 0.1 dl/g and its acid number is 21.5.

EXAMPLE 2

A mixture of 72 parts of vinyl acetate, 25 parts of crotonic acid β -hydroxyethyl ester, 5 parts of crotonic acid, 10 parts of butyraldehyde and 400 parts of water containing 1.4 parts of sodium bicarbonate is heated to 67° in a stirring flask under nitrogen. A mixture of 3.4 parts of potassium peroxydisulphate and 1.3 parts of dibenzoyl peroxide is then added and, during a time period of 7 hours, the bath temperature is increased to 95°. After brief introduction of steam, the resin is precipitated by addition of 15 parts of 2-N hydrochloric acid, isolated, and dried in vacuum. The end product is a yellowish, brittle resin whose limiting viscosity number in acetone, 25°, is 0.08 dl./g and its acid number is 32.6.

EXAMPLE 3

A mixture of 65.5 parts of vinyl acetate, 29.5 parts of crotonic acid β -hydroxyethyl ester, 5 parts of crotonic acid, 10 parts of butyraldehyde and 400 parts of water containing 2.4 parts of sodium bicarbonate is heated to 67° in a stirring flask under nitrogen. A mixture of 3.9 parts of potassium peroxydisulphate and 1.5 parts of dibenzoyl peroxide is then added and, within a time period of 7 hours, the bath temperature is increased to 95°. After brief introduction of compressed air, the resin is precipitated in a separate flask by addition of 15 parts of 2-N hydrochloric acid, isolated, and dried in vacuum. The end product is a yellowish, brittle resin whose limiting viscosity number in acetone, 25° is 0.08 dl./g and its acid number is 29.3.

EXAMPLE 4

A mixture of 72 parts of vinyl acetate, 5 parts of vinyl propionate, 20 parts of crotonic acid β -hydroxyethyl ester, 3 parts of crotonic acid, 10 parts of butyraldehyde and 400 parts of water containing 1.4 parts of sodium bicarbonate is heated to 67° in a stirring flask under nitrogen. A mixture of 2.9 parts of potassium peroxydisulphate and 1.3 parts of dibenzoyl peroxide is then added and, within a time period of 6 hours, the bath temperature is increased to 95°. After brief introduction of steam, the resin is precipitated by addition of 15 parts of 2-N hydrochloric acid, isolated, and dried in vacuum. The end product is a yellowish, brittle resin whose limiting viscosity number in acetone, 25° is 0.09 dl./g and its acid number is 37.8.

EXAMPLE 5

A mixture of 57 parts of vinyl acetate, 15 parts of vinyl propionate, 20 parts of crotonic acid β -hydroxyethyl ester, 8 parts of crotonic acid and 400 parts of water containing 3.9 parts of sodium bicarbonate is heated to 67° in a stirring flask under nitrogen. A mixture of 2.9 parts of potassium peroxydisulphate and 1.3 parts of dibenzoyl peroxide is then added and, within a time period of 10 hours, the bath temperature is increased to 95°. After brief introduction of steam, the resin is precipitated by addition of 15 parts of 2-N hydrochloric acid, isolated, and dried in vacuum; the product obtained is a colorless, viscous/hard resin whose limiting viscosity number in acetone, 25° is 0.28 dl./g and its acid number is 35.8.

EXAMPLE 6

A mixture of 57 parts of vinyl acetate, 20 parts of crotonic acid β -hydroxypropyl ester, 8 parts of crotonic acid, 15 parts of vinyl propionate, 10 parts of butyraldehyde and 400 parts of water containing 3.9 parts of sodium bicarbonate is heated to 68° in a stirring flask under nitrogen. A mixture of 3 parts of potassium peroxydisulphate and 1.2 parts of dibenzoylperoxide is then added and, within a time period of 4.6 hours, the bath temperature is increased to 95°. After brief introduction of steam, the resin is isolated by addition of 1.5 parts of 2-N hydrochloric acid and dried in vacuum. The product obtained is a yellowish, viscous/hard resin whose limiting viscosity number in acetone, 25° is 0.09 dl./g and its acid number is 52.8.

EXAMPLE 7

A mixture of 70 parts of vinyl acetate, 30 parts of acrylic acid β -hydroxyethyl ester, 670 parts of methyl ethyl ketone and 170 parts of water is heated at 80° in a stirring flask under nitrogen in a heating bath, then a mixture of 1.8 parts of potassium peroxydisulphate is added and the mixture is polymerized for 20 hours. The polymer is precipitated from the resulting clear solution by addition of acetone, isolated, and dried in vacuum. The end product is a colorless, soft resin whose limiting viscosity number in water, 25° is 0.1 dl./g.

EXAMPLE 8

A mixture of 87 parts of vinyl acetate, 13 parts of maleic acid mono- β -hydroxyethyl ester, 0.6 parts of dioctyl sodium sulphosuccinate and 200 parts of water containing 3.2 parts of sodium bicarbonate is heated to 68° in a stirring flask under nitrogen. A mixture of 1.3 parts of dibenzoyl peroxide and 1.4 parts of potassium peroxydisulphate is added and, within 1.3 hours, the temperature is raised to 95°. After brief introduction of steam, the resin is then precipitated by addition of 15 parts of 2-N hydrochloric acid, isolated and dried in vacuum. The product obtained is a colorless, viscous/hard, odorless resin whose limiting viscosity number in acetone, 25° is 0.5 dl./g.

EXAMPLE 9

One Part of the product of Example 1 is dissolved in 9 parts of absolute ethanol and neutralized by addition of 0.04 parts of diethanolamine. 0.01 parts of a silicone oil and 0.05 parts of perfume oil are thereupon added, and the mixture is filled into aerosol pressure vessels. 18 parts of fluorotrichloromethane and 12 parts of difluorodichloromethane are then added under pressure. The resulting hair spray gives the hair a high gloss and satisfactory fixation. The hair containing this spray can be combed without loss of its set. The hair lacquer may be removed from the hair by a normal shampoo, but is not hygroscopic and is completely resistant to moist atmospheres.

EXAMPLE 10

One part of the product of Example 2 is dissolved in 9 parts of absolute ethanol and neutralized by addition of 0.06 parts of diethanolamine. 0.01 parts of a silicone oil and 0.05 parts of perfume oil are then added, and

the mixture is filled into aerosol pressure vessels. 18 parts of fluorotrichloromethane and 12 parts of difluorodichloromethane are then added under pressure. Hair treated with the preparation obtained is fixed well and is capable of being combed without trouble, practically no formation of scale on the comb and hair occurring. The good adhesive power of the resin prevents the collapse of the hairdo. By simple rinsing of the hair with water, the resin is completely removable therefrom. The film is not hygroscopic and its properties are unaffected by atmospheric moisture.

EXAMPLE 11

One part of the product of example 3 is dissolved in 9 parts of absolute ethanol and neutralized by addition of 0.08 parts of triethanolamine. After the addition of 0.01 parts of a silicone oil and 0.05 parts of perfume, the mixture is filled into aerosol pressure vessels. 18 parts of fluoro-trichloromethane and 12 parts of dichloromethane are then added under pressure.

A sprayable hair dressing agent is thus obtained which binds the hair well and, because of its good adhesive power, permits no formation of scale on the comb and hair on combing. The resin can be completely removed from the hair by simple shampooing.

EXAMPLE 12

One part of the product of Example 4 is dissolved in 9 parts of absolute ethanol and neutralized by addition of 0.04 parts of diethanolamine. 0.01 parts of a silicone oil and 0.05 parts of perfume oil are thereupon added. The mixture is then filled into aerosol pressure vessels to which 18 parts of fluorotrichloromethane and 12 parts of difluorodichloromethane are then added under pressure. A sprayable hair fixative is thus obtained which binds the hair well and is capable of being combed without the formation of scale on comb and hair. The resin can be completely removed from the hair by simple shampooing, and is resistant to moist atmospheres.

EXAMPLE 13

0.8 parts of the product of Example 5 is dissolved in 9 parts of absolute ethanol and neutralized by addition of 0.11 parts of diethanolamine. 0.01 parts of a silicone oil and 0.05 parts of perfume oil are thereupon added. The mixture is then filled into aerosol pressure vessels to which 18 parts of fluorotrichloromethane and 12 parts of difluorodichloromethane are then added under pressure. Hair sprayed with the hair fixative obtained is solidly bound, exhibits a fine gloss and low susceptibility to electrostatic charge. It can be rapidly and completely removed from the hair by a simple shampoo, and is resistant to moist atmospheres.

EXAMPLE 14

One part of the product of Example 6 is dissolved in 9 parts of absolute ethanol and neutralized by addition of 0.1 parts of diethanolamine. After the addition of about 0.05 to 0.06 parts of cosmetic additives, the mixture is filled into aerosol pressure vessels. 18 parts of fluorotrichloromethane and 12 parts of difluorodichloromethane are then added under pressure.

Hair treated with this hair dressing agent is well bound, displays fine gloss and low susceptibility to electrostatic charge. The hair lacquer may be removed from the hair by normal shampooing and is resistant to moist atmospheres.

EXAMPLE 15

One part of the product of Example 8 in 9 parts of absolute ethanol is neutralized by addition of 0.06 parts of diethanolamine, treated with 0.05 parts of cosmetic additives and diluted by addition of 30 parts of water.

Hair, which can also be moist from preceding hair-cosmetic processes, which is treated with this aqueous-alcoholic solution is, after drying and combing, well and lastingly fixed and retains its natural appearance. The hair dressing agent can be removed from the hair by simple washing.

EXAMPLE 16

A mixture of 52 parts of vinyl acetate, 20 parts of vinyl propionate, 8 parts of crotonic acid, 20 parts of crotonic acid β -hydroxyethyl ester and 20 parts of methyl ethyl ketone is heated at 75° in a stirring flask under pure nitrogen, then a mixture of 1 part of dibenzoyl peroxide and 1.7 parts of dilauroyl peroxide is added and the mixture is polymerized for 16-20 hours at 80°-85°. The clear solution obtained is mixed with 95 parts of acetone and the polymer precipitated in 350-420 parts of a petroleum ether - diisopropyl ether mixture (1:3,3 volumes), isolated and dried in vacuo. The end product is a colorless and odorless brittle resin whose limiting viscosity number in acetone, 25° is 0.1 dl/g and its acid number is 58.6.

EXAMPLE 17

One part of the resin obtained in Example 16 is dissolved in 9 parts of absolute ethanol and neutralized by addition of 0.11 part of diethanolamine. 0.01 part of a silicone oil and 0.05 part of perfume oil are then added, and the mixture is filled into aerosol pressure vessels. 18 parts of fluorotrichloro-methane and 12 parts of difluorodichloro-methane are then added under pressure. Hair treated with the preparation obtained has a high gloss and is capable of being combed without trouble, practically no formation of scale on the comb and hair occurring. By simple rinsing of the hair with water, the resin is completely removable therefrom.

EXAMPLE 18

A mixture of 520 parts of vinyl acetate, 200 parts of crotonic acid β -hydroxyethyl ester, 80 parts of crotonic acid, 200 parts of a vinyl ester mixture of branched aliphatic carboxylic acids with nine to 11 carbon atoms and 200 parts of methyl ethyl ketone is placed in a flask fitted with a stirrer, a thermometer, a gas inlet tube and a reflux column, and heated to 75° under pure nitrogen. An initiator mixture of 9.2 parts of dibenzoyl peroxide and 15.8 parts of dilauroyl peroxide is then added, and the polymerization is carried out for 16 hours at 80°. The clear viscous solution thus obtained is dissolved in 630 parts of acetone, and the polymer is precipitated therefrom in a mixture of 1.45 parts diisopropyl ether and 2.6 parts of petroleum ether. After drying in vacuo, a colorless brittle resin is obtained, whose limiting

viscosity number in acetone, 25° is 0.1 dl/g and its acid number is 56.6.

EXAMPLE 19

A mixture of 57 parts of vinyl acetate, 15 parts of vinyl isostearate, 8 parts of crotonic acid, 20 parts of crotonic acid β -hydroxyethyl ester and 25 parts of methyl ethyl ketone is heated at 75° in a stirring flask under pure nitrogen, then a mixture of 1 part of dibenzoyl peroxide and 1.7 parts of dilauroyl peroxide is added and the mixture is polymerized for 17-20 hours at 80°-85°. The clear solution obtained is mixed with 95 parts of acetone and the polymer precipitated in 350 parts of a petroleum ether — diisopropyl ether mixture (1:3.3 volumes), isolated and dried in vacuo. The end product is a colorless and odorless brittle resin whose limiting viscosity number in acetone, 25° is 0.1 dl/g and its acid number is 61.9.

EXAMPLE 20

One part of the resin obtained in Example 19 is dissolved in 9 parts of absolute ethanol and neutralized by addition of 0.11 part of diethanolamine. 0.01 part of a silicone oil and 0.06 part of perfume oil are then added, and the mixture is filled into aerosol pressure vessels. 18 parts of fluorotrichloromethane and 12 parts of difluorodichloro-methane are then added under pressure. The hair dressing agent thus obtained binds the hair softly and imparts an agreeable grasping to it. The resin can be completely removed from the hair by simple washing.

I claim:

1. A pressurized aerosol hair spray composition containing for each part by weight of a 9 to 12 percent ethanolic or isopropanolic solution of a neutral film

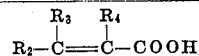
forming copolymer having an acid number of about 20 to about 60 prior to neutralization and having a limiting viscosity number of from about 0.08 to 0.30 dl./g. comprising essentially

- a. from about 90 to 40 percent by weight of a vinyl ester or mixtures thereof represented by the formula



wherein R_1 is selected from the group consisting of hydrogen and lower alkyl containing up to four carbon atoms,

- b. from about 10 to 60 percent by weight of a monoester selected from the group consisting of acrylic acid monoethyleneglycol ester, methacrylic acid monoethyleneglycol ester, crotonic acid monoethyleneglycol ester, crotonic acid monopropyleneglycol ester, maleic acid monoethyleneglycol ester and α -chloroacrylic acid monoethyleneglycol ester; and
- c. from 0 to about 10 percent by weight of an α,β -unsaturated carboxylic acid represented by the formula



wherein R_2 is selected from the group consisting of hydrogen and carboxyl; R_3 and R_4 each are selected from the group consisting of hydrogen, halogen and lower alkyl containing up to four carbon atoms; about 1 to about 4 parts by weight of a propellant.

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