

[54] HAIR CARE PREPARATIONS CONTAINING
N-VINYL PYRROLIDONE HOMO- AND
COPOLYMERS AND A QUATERNIZED
COPOLYMER OF VINYL PYRROLIDONE

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[58] Field of Search 260/80.3 R, 80.3 N, 80.72;
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[57] ABSTRACT

Hair care and hair cosmetic preparations, i. e., aerosol hair sprays, hair conditioners, and hair setting lotions, etc. containing as the film-forming resin homo- and copolymers of N-vinyl pyrrolidone admixed with a quaternized copolymer of vinyl pyrrolidone and a vinyl monomer copolymerizable therewith, i. e., a di-loweralkyl aminoalkyl acrylate or methacrylate. Such compositions containing N-vinyl pyrrolidone polymers and the quaternized copolymer exhibit excellent adhesion and holding power when employed for hair care preparations.

17 Claims, No Drawings

HAIR CARE PREPARATIONS CONTAINING N-VINYL PYRROLIDONE HOMO- AND COPOLYMERS AND A QUATERNIZED COPOLYMER OF VINYL PYRROLIDONE

BACKGROUND OF THE INVENTION

The present invention is directed to certain novel cosmetic compositions, i.e., aerosol hair sprays, hair conditioners, and hair setting lotions, creams, etc., containing polymeric N-vinyl pyrrolidone homo- and copolymers thereof, (i.e., with vinyl acetate), referred to as "PVP" and "VP/VA", respectively; and a minor amount of a quaternary copolymer of vinyl pyrrolidone; more particularly, the present invention is directed to such cosmetic compositions containing PVP or vinyl pyrrolidone/vinyl acetate copolymers (VP/VA) admixed with quaternary copolymer of vinyl pyrrolidone and a further copolymerizable vinyl monomer, such admixed copolymers providing greater adhesion, holding power, and less flaking than conventional synthetic polymers or the quaternized copolymer alone, when used in hair and similar cosmetic preparations.

A number of synthetic polymers are presently used in hair sprays, hair wave set lotions, hair conditioners, etc., the function of such synthetic polymers being generally to contribute "body" and holding power to the hair-do sets. The holding phenomena of hair sprays and setting lotions are, however, not very well defined. In this regard, in hair sprays a polymer globule holds several keratin fibers together so as to produce the necessary holding of the hair in place. In setting and conditioning lotions, however, polymers are deposited over the surface of the hair and again several hair strands are adhered together. In both cases it can be seen that polymer adhesion to the hair is a very important factor which influences the usefulness of a particular synthetic polymer or resin in a hair preparation. In this regard, many of the currently employed synthetic polymers or resins exhibit poor adhesion thereby causing poor holding of the hair and excessive flaking when the hair is combed or brushed.

At the present time, the principal synthetic polymers or resins employed in hair sprays, wave set lotions, and hair conditioners include polyvinyl pyrrolidone homopolymers and copolymers, half esters of polyvinyl ethers — maleic anhydride, polyvinyl acetate — crotonic acid co- and terpolymers, half esters of ethylene — maleic anhydride and various others.

In an attempt to improve the poor humidity stability of PVP-based hair care preparations, U.S. Pat. No. 3,145,147 teaches polymer compositions of PVP/VA which give improved humidity stability and decrease the tacky effect. However, it is taught therein that only polymers containing 50 percent or more vinyl acetate exhibit this improvement. Said copolymers (i.e., those with 50 percent or more vinyl acetate by weight) exhibited less substantivity on the hair, resulting in more residue on the hair and comb. With the exception of vinyl pyrrolidone homopolymers, all of the above conventionally employed synthetic polymers and resins used in hair sprays, wave set lotions, and hair conditioners give stiff hair-does, thereby causing an unnatural look. In addition, such synthetic polymers or resins sometimes result in excessive flaking or excessive fly-away, thereby making preparations containing same unsatisfactory from a commercial and cosmetic standpoint.

Although polyvinyl pyrrolidone homopolymers by themselves provide a more natural look in that the same are free from some of the disadvantages of other commercially available products, the use of such homopolymer alone does not provide satisfactory holding of the hair at high-humidity levels. Accordingly, this is one disadvantage of the use of only a polyvinyl pyrrolidone homopolymer in hair care compositions which has created the desire and necessity for the development of further synthetic polymers and resins free from all of the above recited disadvantages. This has now been accomplished in accordance with the present invention.

Thus, briefly stated, it has been discovered in accordance with the present invention that the above disadvantages and inherent deficiencies of previously employed compositions have been eliminated by the use of a new type of two component admixed polymer or resin composition useful in hair setting compositions including aerosol hair sprays, hair conditioners and hair setting lotions and creams. Thus, it has been discovered in accordance with the present invention that the combination of PVP or VP/VA copolymers with a minor amount of certain quaternary derivatives of N-vinyl pyrrolidone copolymers are particularly useful in cosmetic compositions in that such polymeric composition provides excellent holding power, improved moisture resistance and contributes to excellent body without possessing the disadvantages of flaking and stiffening associated with previously employed polymer materials.

It has also been found that humidity stability (moisture resistance) can be improved by adding some of the quaternized copolymer to the PVP-based formulations. An addition of the quaternized copolymer to PVP/VA based formulations will improve humidity stability and substantivity as well. Since resins of that quaternized copolymer are considerably more expensive than PVP or VP/VA, economically feasible, improved formulations can be prepared by varying the amount of said quaternized copolymer resin.

SUMMARY OF THE INVENTION

Accordingly, it is a principal object of the present invention to provide novel hair care compositions which are free from the inherent deficiencies and disadvantages of previously employed compositions, particularly hair care preparations.

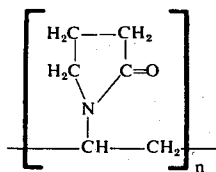
It is a further object of the present invention to provide such compositions, e.g., hair spray compositions, which contain PVP or VP/VA and a minor amount of a quaternary copolymer of vinyl pyrrolidone, which two component system contributes to the body and holding of the hair-do while eliminating the disadvantages of flaking and undue stiffness.

It is still a further object of the present invention to provide such novel compositions comprising PVP or VP/VA polymers and a quaternary copolymer of a) N-vinyl pyrrolidone and a b) di-loweralkylaminoalkyl acrylate or methacrylate and optionally a further monovinyl monomer different from a and b and copolymerizable therewith, in a suitable cosmetic vehicle, e.g., water, alcohol or water-alcohol mixtures.

Still further objects and advantages of the novel compositions of the present invention will become more apparent from the following more detailed description thereof.

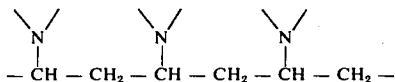
The above objects and advantages of the novel cosmetic compositions of the present invention are achieved by employing as the film-forming resin within such composition PVP or VP/VA polymers and a minor amount of quaternized derivative of a copolymer of N-vinyl pyrrolidone. In hair compositions, for example, such combined polymeric materials exhibit improved substantivity to the hair; by this it is meant that such materials are adsorbed onto the keratin surface thereby improving hair strength and increasing hair weight. Furthermore, such adsorption of the combined polymeric materials employed in the novel compositions of the present invention is more uniform and more continuous than the adsorption that can be obtained with currently available hair setting resins. Accordingly, this provides for a distinct advantage associated with the particular compositions of the present invention when compared, for example, with conventional prior art compositions.

Poly (N-vinyl pyrrolidone) utilized herein is represented by the following structural formula:



n represents a number indicative of the extent of polymerization, and is usually at least 3 or 4.

Depending upon the extent of polymerization, the poly (N-vinyl pyrrolidone) polymers will have molecular weights ranging from at least 400 up to 2,000,000 or more. Viscosity measurements are commonly used as an indication of the average molecular weight of polymeric compositions, the instant polymers being characterized by a chain of carbon atoms to which the lactam rings are attached through their nitrogen atoms:



The K value (Fikentscher) of any particular mixture of polymer is calculated from viscosity data and is useful as an indication of the average molecular weight of such mixture. Its determination is fully described in "Modern Plastics", 23, No. 3, 157-61, 212, 214, 216, 218 (1945), and is defined as 1,000 times k in the empirical relative viscosity equation:

$$\frac{\log_{10} n_{rel.}}{C} = \frac{75k^3}{1 + 1.5kC} + k$$

wherein C is the concentration in grams per hundred cc. of polymer solution and $n_{rel.}$ is the ratio of the viscosity of the solution to that of pure solvent. The K values are reported as 1000 times the calculated viscosity coefficient in order to avoid the use of decimals. For the purpose of the present invention, there may be employed those polymeric N-vinyl lactams having a K value of about 10 to 200, preferably of 30 to 100 because of their viscosity at lower concentrations.

K values and specific viscosities (n_{sp}) are interconvertible and are related through relative viscosity

($\pi_{rel.}$). Thus, when viscosity measurements are taken on solutions which have a concentration of 1.00 gram of polymer per deciliter of solution at 25°C. ($C=1$), the relationships are as follows: $\pi_{rel.} = n_{sp} + 1$ Relative viscosity = specific viscosity plus one. Relative viscosity = $10[0.001K + 0.000075K^2/(1 + 0.0015K)]$. Hence, $n_{sp} = -1 + 10[0.001K + 0.000075K^2/(1 + 0.0015K)]$.

Relative viscosity, specific viscosity and K are dimensionless, whereas inherent viscosity

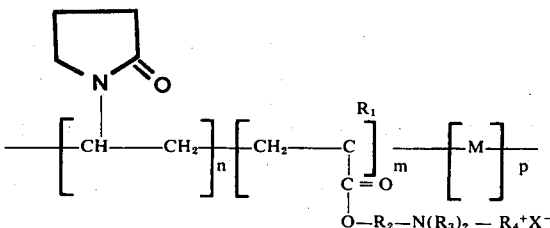
$$\frac{(\log_e n_{rel.})}{C}$$

and intrinsic viscosity (the limit of inherent viscosity as C approaches zero) have the dimensions of dilution, i.e., the reciprocal of concentration. Intrinsic viscosity and K are intended to be independent of concentration.

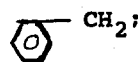
The number of recurring polymer units enclosed by brackets in the foregoing general structural formula, indicated by " n ," or the extent of degree of polymerization corresponds to a chain of roughly 4 to 20,000 monomer units or more. In actual practice, a mixture of polymeric molecules, each containing a different number (n) of monomer units, is always produced. The polymers are readily prepared by the procedural steps given in U.S. Pat. Nos. 2,265,450, 2,317,804 and 2,335,454 and in which working examples of all the species characterized by the above formula are given and all of which are incorporated herein by reference thereto.

Where the N-vinyl pyrrolidone is employed as a comonomer, to form vinyl pyrrolidone/vinyl acetate copolymers, operable ranges are 1:99 to 99:1, preferably 90:10 to 10:90, most preferably 20:70 vinyl pyrrolidone to 30:80 vinyl acetate. Also operative are 90:10 percent of a homopolymer of N-vinyl pyrrolidone admixed with said quaternized copolymer. These copolymers may be prepared in accordance with procedures known in the art.

The quaternary copolymers employed in the novel compositions of the present invention are those which have the following formula:



wherein n represents 40 - 90 percent, m is 5 - 40 mole percent, p is from 0 - 50 mole percent, and $n+m+p = 100$; R_1 is H or CH_3 ; R_2 is $CH_2CH_2CH_2$ or C_xH_2 where $x = 2-18$; R_3 is CH_3 or C_2H_5 ; R_4 is CH_3 , C_2H_5 ,



X is Cl, Br, I, SO_4 , HSO_4 , CH_3OSO_3 ; and M is a monomeric unit resulting from the heteropolymerization employing an optional mono vinyl new hydroxyl containing monomer different from and copolymerizable with the n and m units.

As indicated from the above formula, such quaternary copolymers are prepared by the copolymerization of N-vinyl pyrrolidone and di-loweralkylaminoalkyl acrylate or methacrylate, and optionally a further mono vinyl monomer different from and copolymerizable with n and m. The monomers are copolymerized in accordance with the present invention so that based upon 100 mole percent, the vinyl pyrrolidone units are present in an amount of 40 - 90 mole percent, the units derived from the diloweralkylaminoalkyl acrylate or methacrylate constitute from 5 to 40 mole percent, and the units derived from said further copolymerizable non-hydroxyl containing vinyl monomer constitute from 0 to 50 mole percent.

Exemplary di-loweralkylaminoalkyl acrylates or methacrylates suitably employed in the production of the quaternary copolymers of the present invention include such materials as:

dimethylaminomethyl acrylate
dimethylaminomethyl methacrylate
diethylaminomethyl acrylate
diethylaminomethyl methacrylate
diethylaminoethyl acrylate
dimethylaminoethyl methacrylate
dimethylaminobutyl acrylate
dimethylaminobutyl methacrylate
dimethylaminoamyl methacrylate
diethylaminoamyl methacrylate
dimethylaminoethyl acrylate
diethylaminoethyl methacrylate
dimethylaminoethyl acrylate
diethylaminoethyl methacrylate
dimethylaminodecyl methacrylate
dimethylaminodecyl methacrylate
diethylaminolauryl acrylate
diethylaminolauryl methacrylate
dimethylaminostearyl acrylate
dimethylaminostearyl methacrylate
diethylaminostearyl acrylate
diethylaminostearyl methacrylate, etc.

The optional monovinyl or vinylidene monomer represented by M in the above structural formula can comprise any conventional vinyl monomer copolymerizable with N-vinyl pyrrolidone. Thus, for example, suitable conventional vinyl monomers include the alkyl vinyl ethers, e.g. methyl vinyl ether, ethyl vinyl ether, octyl vinyl ethers, e.g. acrylic and methacrylic acid and esters thereof, e.g. methacrylate, methyl methacrylate, etc; vinyl aromatic monomers, e.g., styrene, α -methyl styrene, etc.; vinyl acetate; vinyl alcohol; vinylidene chloride; acrylonitrile and substituted derivatives thereof; methacrylonitrile and substituted derivatives thereof; acrylamide and methacrylamide and N-substituted derivatives thereof; vinyl chloride, crotonic acid and esters thereof; etc. Again, it is noted that such optional copolymerizable vinyl monomer can comprise any conventional vinyl monomer copolymerizable with N-vinyl pyrrolidone and said acrylate or methacrylate. Accordingly, the quaternized copolymers employed as a minor portion of the novel compositions of the present invention can be characterized as having a repeating structural unit derived from

A. 40 - 90 mole percent of vinyl pyrrolidone;

B. 5 - 40 mole percent of a di-loweralkylaminoalkyl acrylate or methacrylate

c. 0 - 50 mole percent of a vinyl monomer different from and copolymerizable with A and B.

Such copolymers are conveniently prepared by subjecting a solution of vinyl pyrrolidone and the amino acrylate or amino methacrylate monomer with or without an optional copolymerizable vinyl monomer to conditions conducive to vinyl polymerization through the double bond. Thus, for example, polymerization may suitably be initiated by the action of free radicals, the polymerization proceeding exothermically once initiated. Suitable free radical catalysts conveniently employed and suitably utilized in accordance with the production of the copolymers include organic and inorganic peroxides, e.g., hydrogen peroxide, t-butyl peroxide, etc. aliphatic azo compounds, e.g., azobisisobutyronitrile as well as other free radical forming catalysts well known in the polymerization art.

The polymerization is preferably carried out in solution at temperatures varying from about 50°C to 100°C or more; however, to avoid run away conditions and to obtain a copolymer of a desirable molecular weight it is sometimes preferred to carry out the copolymerization at a temperature of from about 75° to about 85°C. The copolymerization reaction is preferably carried out in the absence of free oxygen, conveniently under a blanket of an inert gas, such as, nitrogen, argon or the like, or at atmospheric pressure.

As indicated previously, the copolymers are in the form of their quaternary salts. Accordingly, after completion of the polymerization reaction the polymer is submitted to a treatment conducive to quaternization of the tertiary amino group, utilizing a conventional quaternizing agent. Thus, noting the above structural formula for the copolymers, suitable quaternizing agents include, such as, dialkyl sulfates, e.g., dimethyl sulfate, diethyl sulfate, etc.; alkyl sulfonic acid, e.g., methyl sulfonic acid, ethyl sulfonic acid, etc.; benzyl halides, e.g., benzyl chloride, benzyl bromide, benzyl iodide, etc.; alkyl halide, etc. Accordingly, any conventional quaternizing agent can be advantageously employed in the production of the quaternary N-vinyl pyrrolidone copolymers used in the cosmetic compositions of the present invention. The above quaternary copolymers employed in the compositions of the present invention can be prepared over a wide range of molecular weights. Generally, however, the molecular weight of the copolymer employed in the novel composition of the present invention is within the range of 10,000 to 1,000,000, the molecular weight being chosen somewhat with respect to the utility of the cosmetic composition. In this regard, the quaternary copolymers of the present invention are soluble in both water and alcohol as is the PVP and VP/VA polymers and, thus, the combination can be employed in hair spray and similar cosmetic compositions containing an alcoholic, aqueous, or mixed alcoholic-aqueous base. In addition, the high molecular weight quaternary polymers act as their own thickeners in aqueous or alcoholic solutions, such solutions displaying a slippery feel and an ease of application to the hair. Accordingly, the use thereof of such higher molecular weight quaternary copolymers, i.e., quaternary copolymers within the molecular weight range of 50,000 to 500,000 is particularly applicable to the preparation of hair setting lotions, creams, etc.

A further advantage of the use of pVP or VP/VA polymers and the quaternary copolymers in the hair setting and similar cosmetic preparations is that hair

sprayed or otherwise treated with a hair setting composition containing same is easy to comb and easy to roll on rollers. In addition, setting and conditioning lotions prepared utilizing same give a firm and stiff curl yet allow easy combing without comb drag. As indicated above, both polymeric materials employed in the novel compositions of the present invention are soluble in both alcohols and water, this makes them eminently suitable in hair spray and similar compositions which conventionally have an alcoholic, aqueous, or mixed aqueous-alcoholic base. Thus, they may be employed in the same manner as heretofore employed conventional film-forming resins, said mixture providing improvements as set forth above by their inclusion within the hair spray, setting lotion, or similar cosmetic preparation.

In the compositions of the present invention the film-forming polymers PVP or VP/VA with the quaternary copolymer of N-vinyl pyrrolidone is generally employed in an amount of from about 0.1 to 45.0 percent by weight, the precise amount depending somewhat on the end desired utility for the composition. The ratio of PVP or VP/VA to quaternary copolymer being in the range of 10 to 90 percent, preferably 50 to 50 percent. In addition, it is pointed out that for particular purposes it may be desirable to employ slightly less or greater amounts of the film-forming polymer, hereagain, the end use of the composition dictating the precise amount employed in in novel composition of the present invention.

As indicated above, for hair spray compositions, the base can either be aqueous, alcoholic, or a mixture of alcohols and water. The alcohol which is used as the alcoholic base or portion of the water-alcohol solvent system is generally a lower monohydric aliphatic alcohol, preferably, a monohydric aliphatic alcohol having from 2 to 3 carbon atoms, e.g., ethanol, isopropanol, or n-propanol, ethanol being preferred. Thus, for example, the alcoholic solvent can comprise the commercially and industrially available ethyl alcohols or any one of the denatured alcohol formulas which are permitted by law for use in hair care preparations, e. e. any one of those listed for this use in "Formulas for Denatured Alcohol," Part 212, Title 26 CFR, IRS publication 368. Representative formulas having current approval that can be used are, for example: SDA-40 which consists of 100 gallons of ethyl alcohol denatured with 1.5 oz. of brucine sulfate and one-eighth gallon of tertiary butyl alcohol; SDA-23 A which consists of ten gallons of acetone in each one hundred gallons of ethyl alcohol; and SDA-23 H which consists of 8 gallons of acetone and 1½ gallons of methyl isobutyl ketone in each 100 gallons of ethyl alcohol.

In addition to the two component film-forming polymeric composition and the solvent present in the system the hair spray or similar composition may contain minor amounts of other ingredients for their usual purposes. Thus for example, the compositions may include plasticizing agents i.e., ethoxylated and acetylated lanolin alcohols; polyoxyethylene sorbitan derivatives such as polyoxyethylene sorbitan monopalmitate, polyoxyethylene monostearate, polyoxyethylene sorbitan trioleate; glycol esters such as diethylene glycol, propylene glycol; dimethyl phthalates; isopropyl myristate and isopropyl palmitate; long chain fatty alcohols such as oleyl, isostearyl, cetyl alcohols, etc., conditioning agents such as water soluble and insoluble silicones;

hydralyzed polypeptide solutions and quaternary compounds such as stearyl dimethyl benzyl ammonium chloride, cetyl dimethyl benzyl ammonium chloride; preservative agents such as sorbic acid; 6-acetoxy - 2,4 diethyl m-dioxane; 2-bromo -2- nitropropane -1, 3-diol and others. All in amounts up to 5 percent by weight, preferably 0.1 to 2 percent.

in addition, when the aqueous, alcoholic, or mixed solvent system containing the two component polymer film-forming resins are utilized as a spray formulation, the usual aerosol type container and equipment and usual aerosol type propellant may be effectively utilized to propel the compositions to the hair, such propellants being liquified lower hydrocarbons such as propane, n-butane, and isobutane and the low boiling chlorofluoro hydrocarbons identified broadly as "Freons." Thus, for example, mention is made of "Freon 11"-trichlorofluoromethane, "Freon 12"-dichlorodifluoromethane and "Freon 114"-1,2-dichloro 1,1,2,2-tetrafluoroethane, and mixtures thereof. Preferred propellants may be F11 and F12 and F12 and F114. All propellants are used in a pressurizing amount.

In an aerosol type hair spray composition in accordance with the present invention, the propellant is generally employed in an amount of from about 25 percent to about 65 percent by weight based on the total composition. The film-forming two component polymer system constitutes from about 0.1 percent to about 5 percent by weight, preferably, between 0.1 and 2.5 percent with the remainder constituting the alcohol, water, or water-alcohol mixture. In addition, the hair spray composition can contain minor amounts, i.e., up to about 5 percent by weight of a surfactant or plasticizer and still lesser amounts of perfumes, i.e., up to about 0.5 percent by weight and similar agents.

In accordance with the preferred embodiment of the present invention, the sprayable hair composition is generally formed as an alcoholic or mixed aqueous-alcoholic solvent system. Accordingly, suitable amounts of the various components in such composition are as follows:

Component	Amount
two component polymeric system	0.1 - 5%
alcohol	30 - 70%
propellant	25 - 65%
water	0.25%

With respect to the above formulation, it is again pointed out that the use of the solvent system and propellant is conventional in the aerosol hair spray art, the improvement in accordance with the present invention residing in the use of the particular film-forming quaternary copolymer of N-vinyl pyrrolidone admixed with the PVP or VP/VA polymer.

Improved setting and conditioning lotions for the hair can also be provided by the employment of a minor amount, i.e., 0.1 - 5 percent by weight of the two component polymeric system in an aqueous or mixed aqueous and alcoholic system. Accordingly, in accordance with the present invention such a setting and conditioning lotion may comprise the following components:

Component	Amount
two component polymeric system	0.1 - 5%
Water	60 - 95%
Alcohol	0 - 35%

With respect to such setting and conditioning lotions, it is again pointed out that it is preferred in accordance with the present invention to employ the higher molecular weight quaternary copolymers of N-vinyl pyrrolidone as one of the two components. In this regard, when employing the higher molecular weight copolymers in the aqueous or mixed aqueousalcoholic solvent system such copolymers act as their own thickeners thereby providing more viscous lotion consistency to the composition. This is true even when employed in a minor amount of 0.1-5 percent by weight as set forth above.

As was the case with respect to the aerosol hair spray compositions, the setting and conditioning lotions may contain minor amounts of other conventional optional materials. These include such materials as perfumes, preservatives, additional organic solvents, lanolin and lanolin derivatives, silicone lubricity agents, etc. Here again, all of these optional components are conventional and employed in minor amounts, i.e., less than about 2 percent by weight. An optional surfactant or plasticizer for the film-forming copolymer can also be employed in an amount up to about 5 percent by weight.

In addition to the hair sprays and setting and conditioning lotions, it should be clear that the use of the film-forming quaternary copolymer of N-vinyl pyrrolidone in accordance with the present invention can provide for advantageous results in many similar cosmetic and related compositions wherein film-forming resins are utilized. Thus, for example, compositions can be prepared in the form of wig conditioners, hair coloring preparations, hand lotions, protective creams, moisturizing creams, anti-flash creams, deodorant sprays, cream rinses and shampoos as well as pet shampoos and industrial compositions such as sanitizer solutions, detergents, paper adhesive additives, carriers for pigments in printing inks, stencil inks, etc. Here again, it has been found that the use of the film-forming quaternized copolymer of N-vinyl pyrrolidone provides better results not heretofore obtainable with the use of conventional film-forming resins.

As indicated previously, the film-forming two component polymeric system is soluble in both the alcoholic and aqueous systems utilized in the preparation of the above and similar cosmetic and related preparations. Accordingly, in order to produce such formulations, it is merely necessary to dissolve the same in the suitable solvent with previous, simultaneous or subsequent addition of the other optional components. Solution of the same in the solvent system may be facilitated by mixing.

The novel compositions of the present invention will be illustrated by reference to the following specific examples.

EXAMPLE 1

Production of film-forming quaternary copolymer

A copolymer was produced utilizing polymerization apparatus comprising a 5 liter kettle equipped with me-

chanical stirrer, reflux condenser, thermometer, and gas inlet tube. Some 1,225 parts of ethanol as a solvent were charged into the kettle and 800 parts of vinyl pyrrolidone and 200 parts of dimethylaminoethyl methacrylate were added and agitation was started. To the system was added one part of azobisisobutyronitrile and the system was purged thoroughly with nitrogen. The temperature of the system was raised to gentle reflux at about 85° C.

The polymerization reaction was promoted with further additions of catalysts (one part each) until the amount of residual monomer was below 0.6 percent. The system was thereafter cooled to 25° C and the speed of the agitation was increased.

In order to provide the quaternary derivative of the copolymer 98.3 parts of diethyl sulfate were added from a dropping funnel over a period of thirty minutes. When the slightly exothermic reaction of quaternization was completed the mixture was agitated for an additional period of thirty minutes. An analysis of the product produced indicated that the same contained 49.19 percent solids with the residual monomer content being 0.57 percent.

EXAMPLE 2

An aerosol hair spray composition was produced by admixing the following components in the weight percent indicated:

	Weight %
VVP - K value - 30	1.5
Low molecular weight vinyl pyrrolidone/di methylaminoethyl methacrylate copolymer (80:20) quaternized with diethyl sulfate (50% solids in ethanol and produced in Ex. 1)	1.00
Dimethyl phthalate	0.1
Ethanol	37.40
Propellants: trichlorofluoromethane and dichlorodifluoromethane 50:50 ratio	60.00
	100.00

The aerosol hair spray formulation was prepared by dissolving the film-forming two component polymeric admixture in the ethanol solvent and thereafter adding the plasticizer with vigorous mixing. After such mixing, the perfume oil, lubricity agents and the like may be added and the composition filtered and transferred to an aerosol can where it is crimped and charged with the necessary propellants.

Such a hair spray composition was found to be easily applied to the hair, the same providing a natural look yet offering excellent holding power. The stiff look associated with the use of half esters of polyvinyl ethers, maleic anhydride or polyvinyl acetate, crotonic acid co-and terpolymer hair setting resins was not present and improved mixture resistance no flaking associated with the employment of the hair spray composition containing the film-forming two component polymeric admixture.

EXAMPLE 3

In a manner similar to Example 2, an aerosol hair spray particularly adapted for men was prepared in an alcohol-aqueous solvent system. Utilizing a mixing procedure as in Example 2.7 the following composition was prepared:

	Weight
VP/VA copolymer (90:10) (10-90) (50% sol in ETOH)	1.5
Low molecular weight vinyl pyrrolidone/di-methylaminoethyl methacrylate copolymer (80:20) quaternized with diethyl sulfate (50% solids in alcohol) and produced in Example 1	1.00
Isostearyl alcohol plus 3 E. O.	0.65
Perfume oil	0.10
Water deionized	16.50
Alcohol SD-40 anhydrous	50.25
Propellant - CCl ₂ F ₂ and CClF ₂ CClF ₂ 50:50 mixture	30.00
	100.00

As was the case with respect to Example 2, the hair spray composition was found to have improved moisture resistance and excellent holding properties providing a natural look to the hair. Here again, the use of the two component polymeric admixture was seen to be superior to PVP alone or VP/VA systems alone in that no flaking and no undue stiffness of the hair resulted.

EXAMPLE 4

A composition as in Example 3 was prepared except that the film-forming quaternized copolymer component of N-vinyl pyrrolidone and diethylaminoethyl methacrylate was replaced with a substantially equivalent amount of a quaternized copolymer of N-vinyl pyrrolidone and the following monomers:

- dimethylaminomethyl acrylate
- dimethylaminobutyl acrylate
- diethylaminooctyl acrylate
- diethylaminolauryl methacrylate
- diethylaminostearyl methacrylate

When the copolymers produced are admixed with PVP or VP/VA alone and are employed as the film-forming resin in a hair spray composition such as set forth in Example 3, substantially equivalent results are obtained.

EXAMPLE 5

A hair spray composition as set forth in Example 2 was produced except that the quaternized copolymer of N-vinyl pyrrolidone was prepared by employing the following comonomers in the following amounts:

- 800 parts of vinyl pyrrolidone — 100 parts dimethylaminoethyl methacrylate.
- 800 parts vinyl pyrrolidone — 300 parts dimethylaminoethyl acrylate.
- 800 parts vinyl pyrrolidone — 500 parts dimethylamino ethyl acrylate.
- 800 parts vinyl pyrrolidone — 600 parts dimethylaminoethyl acrylate.

Here again, such quaternized copolymers of N-vinyl pyrrolidone are found to be eminently suitable in hair spray compositions in that compositions having excellent characteristics are obtained.

EXAMPLE 6

A hair spray composition as set forth in Example 2 was again produced except that the quaternized copolymer component of N-vinyl pyrrolidone was one produced by the copolymerization system of Example 1 including the following further copolymerizable vinyl monomers:

- methylvinylether — 100 parts
- octylvinylether — 200 parts

- methacrylic acid — 150 parts
- methyl methacrylate — 300 parts
- styrene — 200 parts
- vinyl acetate 13 100 parts
- vinylidene chloride — 100 parts — vinyl chloride — 100 parts
- methacrylonitrile — 300 parts

When the above quaternized copolymers are admixed with PVP or VP/VA in the hair spray composition of Example 2 in substantially equivalent amounts, it is found that hair spray compositions of substantially equivalent properties are provided.

EXAMPLE 7

An anhydrous aerosol hair spray was produced through a procedure such as set forth in Example 2 by combining the following components:

	Weight %
PVP (K value 30)	1.5
Low molecular weight vinyl pyrrolidone/di-methylaminoethyl methacrylate copolymer (80:20) quaternized with diethyl sulfate and produced in Example 1	1.00
50% solution in ethanol	1.00
Isostearyl alcohol plus 3 E. O.	0.50
Perfume oil	0.10
Alcohol SD-40 anhydrous	51.90
Methylene chloride	15.00
Propellants trichlorofluoromethane and dichlorodifluoromethane 50:50 mixture	30.00
	100.00

The above composition containing no water was also found to be extremely suitable for hair spray purposes. In this regard, the composition exhibited excellent adhesion and holding power when employed as an aerosol hair spray, particularly adapted for men.

EXAMPLE 8

A concentrated setting and conditioning lotion for women's hair was produced as follows. A copolymer of vinyl pyrrolidone and dimethylaminoethyl methacrylate (80:20) quaternized with diethyl sulfate was thereafter dissolved in water and alcohol so as to provide a 2.0 percent solids content. After mixing the system well, a plasticizer, silicone lubricity agent, and perfume oil were added with additional mixing. Stirring was stopped and the system was allowed to rest for about 20 minutes so as to allow the escape of air bubbles. Such a formulation designed for use on damp or towel dried hair can then be packed in a plunger or tube type dispenser. The composition produced as above had the following formulation:

	Weight %
PVP (K value - 30)	20.00
High molecular weight vinyl pyrrolidone di-methylaminoethyl methacrylate copolymer (80:20) quaternized with diethyl sulfate	14.00
Isostearyl alcohol plus 10 E. O.	0.60
Propylene glycol	0.25
Ethanol	25.00
Water	39.90
	100.00

EXAMPLE 9

In a manner similar to Example 8, a setting and conditioning lotion was prepared from the following formulation:

	Weight %
VP/VA copolymer (90:10) (10:90)	20.00
High Molecular weight vinyl pyrrolidone dimethylaminoethyl methacrylate (90-10 copolymer) quaternized with diethyl sulfate (21.9% solids in H ₂ O)	14.00
Isostearyl alcohol plus 10 E. O.	

-Continued

	Weight %
Partially acetylated lanolin derived complex	
Perfume and preservative	q.s.
Water	100.00

Here again, the above components provide a setting and conditioning lotion having advantageous properties associated with the use of the copolymer of Example 8.

TABLE I

Comparative Humidity Stability Data Several Quaternized Copolymers Alone (QCP) vs. PVP or VP/VA Resins 2% Aqueous Solutions 90% RH. 80°F							
Time Interval/min. Polymer:	1 QCP ¹	2 QCP ²	3 QCP ³	4 QCP ⁴	PVP K-30	PVP K-90	VP/VA
5 min.	99	99.7	99	99	58	98	85
10	98	98	96	98	34	94	66
20	97	97	92	94	22	65	39
30	92	95	87	84	17	54	29
45	74	94	78	81	0	40	16
60	49	90	67	72	0	35	0
75	38	85	60	64	0	28	0
90	34	79	54	60	0	15	0

¹Low molecular weight in 50% in EtOH

²High molecular weight, 20% solution in H₂O

³Medium molecular weight, 20% solution in H₂O

⁴High molecular weight, ¼ quaternized as No. 2 above.

TABLE II

Comparative Humidity Stability Tests of 2% Aerosols (Anhydrous)					
(1) PVP K-30 vs.	(2) PVP K-30/QCP No. 1 blend vs. % Curl Retention		(3) QCP No. 1		
Time Intervals	PVP K-30	PVP-K-30	QCP No. 1		
5	69	99	99		
10	56	96	98		
20	34	88	94		
30	30	75	87		
45	27	57	77		
60	17	39	55		
(1) PVP K-30 100% Sol. Ethanol SDA-40	Wgt. % 2.0 48.0	(2) PVP K-30 100% Solids QCP No. 1 50% sol. in EtOH	Wgt. % 1.5 1.0	(3) QCP No. 1 50% sol. in EtOH Ethanol SDA-40	Wgt. % 4.0 46.0
Propellants F11/F12 & 50:50	50.0 100.0	Ethanol SDA-40 Propellants F11/F12 50:50	47.5 50.0 100.0	Propellants F11/F12 50:50	50.0 100.0

TABLE III

Comparative Humidity Test of 2% Aqueous Solutions 90% RH. 80°F			
(1) PVP K-30 vs.	(2) PVP K-30—QCP Blend vs. % Curl Retention		(3) QCP
Time Interval/min.	PVP K-30	PVP K-30—QCP Blend	QCP
5	64	92	99
10	41	88	98
20	33	31	94
30	21	74	89
45	12	62	84
60	0	50	78

TABLE III—Continued

Comparative Humidity Test of 2% Aqueous Solutions 90% RH. 80°F					
(1)	Wgt%	(2)	Wgt%	(3)	Wgt%
PVP K-30 100% sol. H ₂ O	2.0	PVP K-30 100% sol. QCP (20% sol. in H ₂ O) H ₂ O	1.0	QCP 20% sol in H ₂ O H ₂ O	10.0
	98		5.0		90.0
	100.0%				100.0
			94.0		
			100.0		

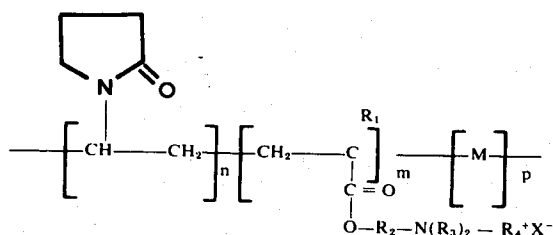
It can be clearly seen from the above that the objects and advantages of the novel compositions of the present invention are achieved through the employment of two component polymeric blend of a film-forming quaternized copolymer of N-vinyl pyrrolidone and PVP or VP/VA in lieu of conventional film-forming resins utilized in cosmetic compositions, principally compositions adapted for use on the hair.

Thus, the hair sprays of the present invention are seen to provide excellent adhesion and holding power without the disadvantages of previously employed compositions.

I claim:

1. A hair care composition comprising a solvent selected from the group consisting of water, a C₂₋₃ monohydric aliphatic alcohol and mixtures of each of these, said solvent containing a polymeric component approximately 0.1 to about 45 percent by weight of said composition, said polymeric component consisting essentially of.

1. 90 to 10 percent of a homopolymer of N-vinyl pyrrolidone or a copolymer thereof with up to about 90 percent vinyl acetate based on the weight of said copolymer; and
2. 10 to 90 percent of a quaternized copolymer having the following formula:



wherein n represents 40-90 percent, m is 5-40 mole percent, p is 0-50 mole percent, and $n+m+p=100$; R₁ is H or CH₃; R₂ is CH₂, CH₂CH₂, or C_xH_{2x} where x = 2-18; R₃ is CH₃ or C₂H₅; R₄ is CH₃, C₂H₅, or



X is Cl, Br, I, SO₄, or CH₃OSO₃; and M is a vinyl monomeric unit having no hydroxyl groups and different from and copolymerizable with the n and m units.

2. The composition of claim 1 wherein component 1 is poly (N-vinyl pyrrolidone).

3. The composition of claim 1 wherein component 1 is a copolymer of vinyl pyrrolidone and vinyl acetate.

4. The composition of claim 3 wherein said copolymer is composed of about (10:90) parts vinyl pyrrolidone and (90:10) parts vinyl/acetate.

5. The composition of claim 1 wherein unit m is dimethylaminoethyl methacrylate.

6. The composition of claim 5 wherein said quaternized copolymer is composed of vinyl pyrrolidone and dimethylaminoethyl methacrylate.

7. An aerosol hair spray containing a pressurizing amount of an aerosol propellant and the composition as defined in claim 1.

8. An aerosol hair spray composition comprising:

1. 30-70 percent by weight of a monohydric C₂₋₃ aliphatic alcohol solvent;
2. 0-25 percent by weight water;
3. 25-65 percent by weight of an aerosol propellant; and

4. 0.1-5 percent by weight of the polymeric component as defined in claim 1.

9. The composition of claim 8 wherein unit m is dimethylaminoethyl methacrylate.

10. A hair setting and conditioning lotion comprising:

- A. 60-95 percent by weight water;
- B. 0-35 percent by weight of a lower aliphatic alcohol; and
- C. 0.1-5 percent by weight of the polymeric component as defined in claim 1.

11. The hair setting and conditioning lotion of claim 10 wherein unit m is dimethylaminoethyl methacrylate.

12. The hair setting and conditioning lotion of claim 11 wherein component 2 is a quaternized copolymer of vinyl pyrrolidone and dimethylaminoethyl methacrylate.

13. The hair care composition of claim 1 wherein component 2 has a molecular weight within the range of 10,000 to 1,000,000 and component 1, when poly (N-vinyl pyrrolidone) has a molecular weight range of 20,000 to 1,000,000.

14. The composition of claim 8 wherein component 1 is poly (N-vinyl pyrrolidone).

15. The composition of claim 8 wherein component 1 is a copolymer of vinyl pyrrolidone and vinyl acetate.

16. The composition of claim 10 wherein component 1 is poly (N-vinyl pyrrolidone).

17. The composition of claim 10 wherein component 1 is a co-polymer of vinyl pyrrolidone and vinyl acetate.

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