

[54] **HAIR SETTING COMPOSITION AND METHOD OF USE**

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[57] **ABSTRACT**

A hair setting composition comprising: (a) a film-forming carboxylic resin, (b) a polyvalent metal compound capable of forming metal salt linkages with the carboxylic moiety of the resin, and (c) a volatile alkaline compound which forms with the metal compound a complex which is initially soluble in the hair setting composition when the pH of the composition is 8.5–10.5. The compositions are formulated as lotions or aerosols and hair styling with the compositions is facilitated by application with hand-held, portable, hot air generating devices.

13 Claims, No Drawings

HAIR SETTING COMPOSITION AND METHOD OF USE

BACKGROUND OF THE INVENTION

The invention relates to hair setting compositions, and particularly to hair setting compositions which are applied in aqueous or aqueous alcoholic solutions.

While a great variety of hair setting compositions are known, based on a combination of numerous properties including substantivity to the hair without embrittlement, resistance to tack in a humid atmosphere, clarity of the compositions on storage and transparency when applied, good anti-static properties, and predictable removability depending on the type of shampoo, such compositions continue to suffer from several defects. For example, the hair holding properties of such compositions are substantially diminished when hair so treated is subjected to relatively high humidity at ambient temperatures. Additionally, the known hair setting compositions are too easily removed by conventional shampoos and must therefore be reapplied, thereby also subjecting the hair to undue resin buildup. Still further, the resin component of the hair setting compositions, after evaporation of the liquid vehicle, tends to be quite brittle and flakes badly from the hair, with the consequence that the hair is combed only with difficulty and frequent shampooing is required to keep the hair "clean" and comfortable.

While these tendencies are somewhat overcome by careful selection of the resin component, and by neutralization and/or plasticization of the resin, it is evident that such expedients add considerably to the complexity and expense of the composition.

OBJECTS AND SUMMARY

Accordingly, an object of the invention is to provide a new and improved hair setting composition which when applied to the hair will permit substantial retention of the initial shape imparted to the hair for a substantially longer duration than is presently possible at high humidities with known hair setting compositions, but without undue embrittlement of the resin or hair.

Another object is to provide a new and improved hair setting composition for which plasticizers are not required to provide flexibility of the hair after application of the composition and shaping of the hair.

Still another object is to provide a new and improved hair setting composition which is resistant to removal by conventional shampoos, especially acidic pH shampoos, such that when the treated hair is again shaped and dried, the hair will retain a substantial degree of its original shape for substantial periods at high humidities, thereby avoiding the undesirable resin buildup which normally results when a hair setting composition must be reapplied after shampooing.

These and other objects, features and advantages of the invention will in part be described below or will in part be obvious therefrom.

In summary, the hair setting compositions of the invention are based on the discovery that when a film-forming carboxylic hair setting resin, which is substantially completely soluble in the composition, is admixed with a polyvalent metal compound capable of forming metal salt linkages with the carboxylic moiety of the resin, and wherein the metal compound is initially maintained in the composition in a soluble state by

complexing with a volatile alkali, the resulting composition when applied to the hair, simultaneously with or followed by shaping and drying of the hair, provides a resin which is made more substantive or adherent to the hair, possibly by reason of cross-linking of the resin by reaction of the metal ions of the metal compound with the carboxyl groups of the resin after the alkali has volatilized.

Since the resulting modified resin sets harder than the same resin without the metal compound, the hair setting composition provides considerably improved resistance to loss of the set in high humidities, does not require plasticization, and has been found to be more resistant to removal by most shampoos, especially low pH (4.0 - 4.5) shampoos. The hair setting compositions of the invention therefore are retained in the hair for extended periods of time at high humidity without the need of reapplication of the hair setting composition, thereby avoiding resin "buildup" by reapplication of the resin, and also decreasing the need for frequent shampooing to keep the hair manageable and clean.

DETAILED DESCRIPTION

The resin component of the hair setting composition is any film-forming, carboxylic polymeric material useful in aqueous solution or alcoholic aqueous solution as a hair-holding or hair-fixing material. Therefore, while a wide variety of hair setting resins are known, including polyvinylpyrrolidone and various copolymers of vinylpyrrolidone and/or vinyl acetate with other ethylenically unsaturated monomers, only those of such resins which also include at least one monomer providing carboxylic moieties in the resin prepared therewith are suitable. The carboxylic moiety should be present in an amount of at least about 5% by weight of the resin. The preferred carboxylic content will vary according to the degree of hardness and adhesiveness desired in the resin, and in general, is at least about 10% by weight of the resin. The resin should be substantially soluble in the final composition (whether the composition be aqueous or hydroalcoholic), either by reason of the inherent character of the resin itself (that is due to the monomers and/or proportions thereof), or by reason of the presence of the volatile alkali in the composition.

Among the suitable resins may be mentioned four classes of materials: (1) copolymers of maleic acid and methyl vinyl ether; (2) copolymers of a monoalkyl ($C_1 - C_4$) ester of maleic acid and methyl vinyl ether; (3) copolymers of a vinyl ester of at least one alpha-branched saturated aliphatic carboxylic acid having at least five carbon atoms and an ethylenically unsaturated monocarboxylic acid; and (4) copolymers of acrylamide, *N-tert.* butylacrylamide, acrylic acid and *N*-vinyl pyrrolidone.

Resins of the first class, the maleic acid-methyl vinyl ether copolymers, are commercially available and are characterized by rapid solubility in water over the entire pH range, wide compatibility with other substances such as water-soluble gums, resins, plasticizers and most metal salts, and by low, medium and high molecular weight ranges. Preferred copolymers are those prepared from 1:1 weight ratios of the monomers.

Resins of the second variety, the copolymers of monoalkyl esters of maleic acid and methyl vinyl ether, on the other hand, have variable and selective solubility in various media depending upon the alkanol used for

esterification, the molecular weight of the copolymer, and the extent to which the copolymer is neutralized and the type of neutralizing agent employed. These resins are also commercially available and the relationship of solubility of the resin in various solvents to molecular weight, type of ester and neutralizing agent, and degree of neutralization is well known. For example, it is known that the higher alkyl monoesters (e.g., butyl) can produce softer and more water-resistant films, and that each of the monoalkyl esters, if neutralized to a high degree, becomes completely soluble in aqueous solution. Although films of certain of the copolymers, for example, the ethyl esters, become more water-sensitive by reason of increased neutralization, accompanied by an increase in the degree of tack, tack-free films may be obtained by employing the higher alkyl esters such as the butyl esters because, even with neutralization, such esters are inherently more resistant to water.

The third class of resins are characterized by the inclusion in the resin of a vinyl ester of at least one alpha-branched saturated aliphatic carboxylic acid having at least five carbon atoms, in addition to an ethylenically unsaturated monocarboxylic acid which provides the carboxylic moiety. One or more vinyl monomers different from the vinyl ester and unsaturated monocarboxylic acid monomers may also be included and preferably are included in the copolymer, such as vinyl acetate, methyl vinyl ether, or the like. The copolymers of this class are known, as described in British Patent No. 1,169,862, the complete specification of which was published Nov. 5, 1969.

Among the numerous copolymers disclosed in the British patent, which are useful in the hair setting compositions of the present invention, are the resinous reaction products of vinyl pivalate, crotonic acid and vinyl acetate; and of the vinyl esters of a mixture containing isomeric nine carbon atom acids (for example, 56% by weight of 2,2,4,4, -tetramethyl valeric acid and 27% by weight of 2-isopropyl-2,3-dimethyl butyric acid, the balance to make 100% being other isomers of the acids), with vinyl acetate and crotonic acid. In the latter product the proportions are 5-80% by weight of the vinyl ester mixture, 7-89% by weight of vinyl acetate and 6-13% by weight of crotonic acid. As another vinyl ester component of such copolymers may be mentioned the vinyl esters of a mixture of isomeric alpha-branched saturated aliphatic monocarboxylic acids containing ten carbon atoms.

As described in the foregoing British Patent, the water and alcohol solubility of the resins may be varied in known ways by the extent of neutralization as well as by control of the molecular weight and type of alkaline compound used for the neutralization. About 0.1-10% of stoichiometric neutralization will be sufficient, but neutralization may be complete, if desired.

The fourth class of representative resins useful in the invention are copolymers of acrylamide, *N-tert.* butylacrylamide, acrylic acid and *N*-vinylpyrrolidone. Resins of this class, modified and unmodified, are commercially available and may contain a wide range of monomer proportions. However, the acrylic acid content should be restricted to minor proportions, such as about 5-20% by weight of the copolymer. A preferred copolymer of this class contains about 9-10% by weight of acrylic acid and is sold by American Cyanamid Company as "Modified Quadramer Resin".

While the foregoing specific classes of resins are preferred for use in the compositions of the invention, it will be apparent that a wide variety of modifications of such resins may be made, provided the resins contain at least about 5% by weight of carboxylic moiety. For example, the copolymers may include other alpha-beta ethylenically unsaturated monocarboxylic acids, esters or amides, such as acrylic acid, alkyl acrylates, or acrylamides; other ethylenically unsaturated dicarboxylic acids, such as itaconic or citraconic acid, or anhydrides thereof; one or more other vinyl monomers copolymerizable therewith, such as *N*-vinyl pyrrolidone, or mixtures of any of the foregoing. However, the proportions of acrylic acid in the copolymers should be minimized since such monomers tend to provide films with reduced adhesion to hair. Molecular weights of the resins are not critical, and may range, for example, from about 30,000 to about 2,000,000, but preferably are from about 50,000 to about 750,000.

The amount of film-forming carboxylic resin component may vary widely depending upon the solubility of the particular resin in the vehicle employed, such as water or an alcohol-water system, and the degree of hair-holding properties desired. Generally, for a resin which is to be employed in a hair-setting lotion, from about 0.5% to about 6.0%, preferably 1.0% to 3.0%, by weight of resin based on the total composition will be useful.

The second significant component in the composition is a polyvalent metal compound which is capable of forming metal salt linkages with the carboxylic moiety of the resin. While many such polyvalent metal compounds will react with the carboxylic moieties in this manner, it is evident that not all will be suitable by virtue of the undue toxicity of certain polyvalent metals such as cadmium, mercury and copper, and because of color caused by formation of the metal salt linkages with certain metals. The preferred metals are divalent and are compounds of zinc or zirconium. The compounds may be oxides; hydroxides; acidic or neutral salts of such metals, or complexes of such compounds with other compounds such as ammonium carbonate. The metal compounds are employed in amounts sufficient to react substantially completely with the carboxylic moiety of the resin component. In the case of a divalent metal, the compound should provide at least about 1.5% of metal by weight of the resin, since such compounds provide two equivalents per molecule. However, if the resin contains a substantially higher proportion of carboxylic moiety, less than stoichiometric proportions of metal compound may be used. Consequently, the relative proportions of resin and metal compound may vary widely according to the degree of hair setting desired.

The volatile alkali of the composition is any alkaline compound sufficiently volatile to be substantially eliminated from the hair-setting composition after application to the hair, so that the metal salt compound will form metal salt linkages with the carboxylic moiety of the resin in a reasonably short period of time, and which will form with the metal of the polyvalent metal compound a complex which is soluble in the hair setting composition at the pH desired to maintain clarity in the composition, that is, a pH of at least 8.5, generally 8.5-10.5 but preferably 9.3-10.3. Although the preferred alkali from the standpoint of economy and ease of handling is ammonia, or an ammonium com-

pound such as ammonium carbonate, others are also suitable if they provide the desired degree of volatility and soluble complexing of the metal. Such compounds include the mono (lower alkyl) amines such as monomethylamine, monoethylamine, and monoisopropylamine, and heterocyclic compounds such as morpholine. They may be employed singly or in admixture.

In some cases it may be desirable to include compounds, alone or in admixture with the volatile alkali, which are known for their ability to increase the water solubility of the resin but which are less volatile than the aforementioned alkaline compounds. Among these may be mentioned alkali metal hydroxides, e.g., sodium and potassium hydroxide, primary, secondary and tertiary amines, alkanolamines, and hydroxy amines, e.g., triisopropanolamine, aminomethylpropanediol, and aminomethylpropanol.

The hair setting compositions of the invention may be formulated in a variety of ways. For example, when it is desired to apply the compositions in an aqueous medium in the form of a lotion, the resin is first dispersed in the water and the alkali is then added, followed by the metal compound. The concentrate is then agitated sufficiently to form a homogeneous solution, and then water or other medium may be added to bring the composition to the desired use concentration. Alternatively, the resin may be dispersed in the aqueous or alcoholic aqueous medium and a portion of the alkali added to bring the resin into solution. The metal compound then may be dissolved in the balance of the alkali in a separate vessel, the solution then being added to the resin solution while stirring. The composition is then diluted to the required strength, to provide concentrations of active ingredient of from about 1.0% to 10% by weight.

Formulation of the compositions as aerosols is also feasible, in accordance with known techniques such as set forth in "Aerosols: Science and Technology", ed. H. R. Shepherd, Interscience Publishers, New York, 1961. Although the compositions of the invention contain water even as concentrates, aerosol containers, valves and propellants are known which are compatible with aqueous or aqueous-alcoholic compositions. In fact, the presence of water has certain advantages for aerosol formulations since it facilitates the use of normally flammable propellants such as the hydrocarbon propellants (propane, butane, isobutane, and mixtures thereof). The hydrocarbon propellants, of course, may be admixed with non-flammable halocarbon propellants as a further precaution against flammability, e.g., a propellant containing 10% isobutane, the balance being a halocarbon. However, high proportions of halocarbon propellants are undesirable since they are not as soluble in the resin compositions of the invention as the other propellants, so as to cause retention of some product in the aerosol container after dissipation of the propellant.

Among the common liquified propellants which are preferred may be mentioned the chlorofluorocarbon Propellants 11, 12, 114, and 142-A; the fluorocarbon 152-B; and the chlorinated hydrocarbons such as methylene dichloride and 1,1,1-trichloroethane. The propellants may be employed singly or in admixture, as is known. The gaseous propellants may also be employed. Among these may be mentioned carbon dioxide, nitrous oxide, and nitrogen, and mixtures thereof. Generally, any propellant (liquified gas or gaseous) which is

sufficiently soluble in the compositions of the invention at the pressure for the form of emission desired (fine mist, droplets, fog, foam, liquid stream, and the like) so that substantially all of the hair setting composition in the container may be forced out, may be employed. If, as in the case of carbon dioxide, the alkalinity of the composition may be diminished by the propellant, suitable buffering agents may be added.

To minimize container and valve corrosion due to the alkalinity of the compositions, container materials such as plastics, glass, tin plate or other protected metal such as epoxy lined aluminum may be employed. One such material is acetal copolymer plastic, sold by Celanese Corporation as "Celcon". Other plastics include nylon, polyolefins such as high density polypropylene, and methacrylics.

The propellant may comprise from about 6% to 99% by volume of the container, the lower the volume of propellant the "wetter" the composition emitted. A typical aerosol composition comprises a hair composition of the invention containing about 90-97% by weight of water in a container with about 70% by volume of nitrous oxide under about 80 psig. pressure.

Other additives normally present in hair-setting compositions may be incorporated if desired. For example, the dispersion medium may comprise a major proportion of an organic solvent such as a lower alcohol, e.g., ethanol or isopropanol, to decrease drying time after application to the hair. Any tendency of the alcohol to cause precipitation or loss of the metal compound complex may be avoided by including effective amounts of coupling agents such as the glycols and alcohol ethers. Likewise, perfumes, plasticizers, emollients, lubricants and penetrants may be employed. Furthermore, buffering agents, surfactants, dyes and other colorants may be added, as well as preservatives, other polymeric binding agents to increase resistance of the composition to shampoos, and the like.

The compositions of the invention are applied to the hair in various ways, such as by pouring, dabbing, or spraying, to moisten the hair to the desired degree. The hair then may be combed to remove excess liquid and shaped as by curlers, followed by drying. Alternatively, the hair may be shaped first, as by hair curlers, followed by application of the composition, preferably as a spray (aerosol or non-aerosol). Substantially improved curl retention is evident by either mode of application, even when the hair is subjected to high humidity, for example, 90 - 95% at 70°- 74° F. Moreover, the hair when so treated exhibits improved resistance to loss of curl even after several shampoos with acidic shampoos.

While stationary, beauty parlor or home hair dryers afford a means of accelerating the drying of the thus-treated hair, electric hand hair curlers offer the additional advantage of permitting shaping or styling simultaneously with acceleration of drying. Recent improvements in lightweight, hand-held, portable devices offer still further advantages and constitute preferred methods of hair styling employing the compositions of the invention.

One form of such devices generates hot air in a directed stream, so as to confine the acceleration of drying to selected areas of the hair. This form of device has now been combined with either or both of a reservoir for a liquid and a comb, as permanent parts of the device or as removable attachments, and is commercially

available. The liquid reservoir is channeled to an outlet, usually a spray head, and a pump mechanism is provided for forceable emission of the liquid.

Greatly improved convenience, control and speed of hair styling is achieved by use of such combination devices. For example, the device having the liquid reservoir and spray head permits application of the composition followed by, or simultaneous with, drying of the composition. Thus, it is possible simply to hold a hair tress in a desired configuration while setting. This one-step process is then repeated for each of the hair tresses it is desired to stylize.

In another example, using the device which also incorporates a comb over which the liquid and hot air may be caused to flow (in separate or common streams), the hair may be combed and shaped while the hair setting composition is flowed therethrough, or shaping may follow distribution of the composition throughout the hair by the combing. The shaped hair then may be quickly dried by applying hot air from the device. In some cases, for example, where shaping and setting of individual tresses is important, as in male hair styling, the composition and hot air may be flowed over and through the comb onto the hair at the same time

water and about one-half the alkali, to form a first solution. The zinc oxide was dissolved in the remaining alkali and this second solution was added to the first solution with stirring. Sufficient water was then added to make 100 grams.

Test hair tresses were saturated with each of the solutions and the tresses combed to remove excess liquid, wound on $\frac{3}{4}$ inch diameter curlers, and dried. The curlers were then removed and the curled tresses placed in a constant temperature (70°-74° F) and humidity (90-95%) chamber, and observed for curl retention. All samples gave curl retention of better than 85% after 120 hours (5 days) storage.

EXAMPLES 4 AND 5

The following compositions were prepared by stirring the resin with 70 grams of water and then adding the alkali to form a solution. The metal salt was then stirred into the solution and sufficient water added to make 100 grams. The hexanediol and sulfonic acid are optional ingredients.

	Examples	
	4	5
Resin 28-2930	2.0g	2.0g
Ammonium hydroxide (28% NH_3)	1.5ml	1.5ml
Zinc Acetate $\cdot 2\text{H}_2\text{O}$ (5% w/w in distilled water)	3.5ml	3.5ml
2-ethyl-1, 3-hexanediol	0.2g	—
p-toluene sulfonic acid (0.01%)	—	1.0ml
Distilled water to make	100.0g	100.0g

that the comb is being used to distribute the composition and shape the tress.

The following examples are intended as further illustration of the invention but are not necessarily limitative except as set forth in the claims. All parts and percentages are by weight unless otherwise indicated.

The following table illustrates three compositions of the invention:

TABLE I

	Examples					
	1		2		3	
Resin 28-2930 ¹	2.0	g	2.0	g	2.0	g
Ammonium hydroxide (28% NH_3)	1.5	ml	—	—	—	—
Ammonium Carbonate (10% w/w in water)	—	—	15.0	ml	25.0	ml
Zinc Acetate $\cdot 2\text{H}_2\text{O}$ (5% w/w in water)	3.5	ml	—	—	—	—
Zinc Oxide	—	—	0.065	g	—	—
Zirconium sulfate $\cdot 4\text{H}_2\text{O}$ (5% w/w in water)	—	—	—	—	3.5	ml
Distilled water to make	100.0	g	100.0	g	100.0	g

¹Resin 28-2930 — A terpolymer sold by National Starch Company and disclosed in British Pat. No. 1,169,862.

In Examples 1 and 3, the composition was prepared by stirring the resin in 70 grams of water and then adding the alkali to form a solution. The metal salt was then stirred into the solution and sufficient water was added to make 100 grams. In Example 2, the composition was prepared by stirring the resin with 70 grams of

In separate experiments hair tresses were saturated with the solutions and combed to remove excess liquid. The hair tresses were placed on curlers and dried. The curlers were removed and the tresses shampooed with an acidic pH shampoo. Thereafter, the tresses were again wound on $\frac{3}{4}$ inch diameter curlers, dried, removed from the curlers, and placed in a constant temperature and humidity chamber as in Examples 1-3. It

was noted that the hair tresses retained more than 70% of their curl after 48 hours storage in the chamber.

EXAMPLES 6-11

Table II below illustrates other compositions of the invention.

TABLE II

	6	7	8	9	10	11
¹ Gantrez HY-L	2.0g	—	—	—	—	—
¹ Gantrez HY-M	—	2.0g	—	—	2.0g	2.0g
¹ Gantrez HY-H	—	—	2.0g	—	—	—
Ammonium Carbonate (10% w/w in distilled water)	50.0g	50.0g	65.0g	30.0g	70.0g	70.0g
Ammonium Carbonate	—	—	—	—	2.0g	5.0g
Zinc Oxide	0.47g	0.47g	0.47g	0.07g	0.47g	0.94g
Dodecyl benzene sulfonate	—	—	—	0.006g	0.006g	0.006g
² Modified Quadramer Resin	—	—	—	2.0g	—	—
Distilled water to make	100.0g	100.0g	100.0g	100.0g	100.0g	100.0g

¹Maleic acid - methyl vinyl ether copolymers of low (L), medium (M) and high (H) molecular weight, sold by GAF Corporation

²Available from American Cyanamid Company.

Each of the above compositions was prepared by dissolving the resin in 20 grams of water while stirring. The ammonium carbonate solution was then added where indicated. In Examples 10 and 11, the zinc oxide was dissolved in ammonium carbonate solution and then added to the batch, whereas in Examples 6-9 the zinc oxide was stirred directly into the resin solution. The dodecyl benzene sulfonate where indicated was then added. Sufficient water was added to the compositions to make 100 grams.

Hair tresses were saturated with the solutions, combed to remove excess liquid, wound on $\frac{3}{4}$ inch diameter curlers, and dried. The curlers were removed and the tresses placed in a constant temperature and humidity chamber as in Examples 1-3 and observed for curl retention. All samples gave curl retention of better than 70% after a minimum of 48 hours of storage.

EXAMPLE 12

An aerosol hair composition is prepared by pressurizing an acetal copolymer plastic pressure container at 82 psig. with sufficient nitrous oxide to provide about 30% by volume headspace over a hair setting composition of Example 1 above. The composition is emitted as a spray and provides excellent hair setting results.

EXAMPLE 13

A commercially available hand-held, portable electrically powered, hot-air generating device having a removable liquid reservoir, spray-head, and comb, is filled with a composition of the invention, such as a composition of Examples 1-11. The composition is sprayed on hair tresses which have been set in curlers, and the spray application is followed by directing a stream of hot air from the device onto the moistened tresses. The hair dries and sets quickly in the desired configuration, which is retained through several shampooings.

What is claimed is

1. A hair setting composition comprising an aqueous or alcoholic aqueous medium having dispersed therein:

- a. an effective amount of a film-forming carboxylic resin having a molecular weight of at least 30,000 wherein the carboxylic moiety comprises at least about 5% by weight of the resin, said resin being substantially completely soluble in said composition and selected from:

- i. a copolymer of maleic acid and methyl vinyl ether,
 - ii. a copolymer of a monoalkyl ester (C1-C4) of maleic acid and methyl vinyl ether,
 - iii. a copolymer of vinyl acetate, crotonic acid and at least one vinyl ester of an alpha-branched saturated aliphatic carboxylic acid having at least five carbon atoms, and
 - iv. a copolymer of acrylamide, N-tert. butylacrylamide, acrylic acid and N-vinylpyrrolidone,
- b. a non-toxic and non-color generating zinc or zirconium metal compound in an amount effective to form metal salt linkages with said carboxylic moiety, and
 - c. a volatile alkali in an amount effective to form with said metal compound a complex which is initially soluble in said hair setting composition when the pH of the composition is at least 8.5.

2. A hair setting composition as in claim 1 wherein said carboxylic resin (iii) contains 7-89% of vinyl acetate, 6-13% of crotonic acid and 5-80% of vinyl ester.

3. A hair setting composition as in claim 1 wherein the vinyl ester component of said carboxylic resin (iii) is a mixture of the vinyl esters of alpha-branched saturated aliphatic carboxylic acids containing 9 carbon atoms.

4. A hair setting composition as in claim 1 wherein said volatile alkali is ammonia.

5. A hair setting composition as in claim 1 wherein:

- a. is a copolymer of the vinyl ester of at least one alpha-branched saturated aliphatic carboxylic acid having 5-10 carbon atoms, crotonic acid and vinyl acetate,
- b. is zinc oxide or zinc acetate, and
- c. is ammonium hydroxide or ammonium carbonate.

6. A hair setting composition as in claim 1 wherein:

- a. is a copolymer of the vinyl ester of at least one alpha-branched saturated aliphatic carboxylic acid having 5-10 carbon atoms, crotonic acid and vinyl acetate.
- b. is zirconium sulfate, and
- c. is ammonium hydroxide or ammonium carbonate.

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7. A hair setting composition as in claim 1 wherein the amount of
- a. is about 0.5–6.0% of the total weight of the composition,
- the amount of
- b. as metal is at least about 1.5% based on the weight of (a), and
 - c. is present in an amount effective to provide a pH of 9.3–10.3.
8. A hair styling method which comprises applying to the hair a composition as in claim 1, shaping the hair while said composition is fluid, and drying the hair.
9. A method as in claim 8 wherein the hair is shaped before application of said composition to the hair.

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10. A method as in claim 8 wherein the hair is shaped simultaneously with application of said composition to the hair.
11. A hair styling method which comprises applying to the hair a composition as in claim 3, shaping the hair while said composition is fluid and drying the hair.
12. A method as in claim 11 wherein the hair is shaped before application of said composition to the hair.
13. A method as in claim 11 wherein the hair is shaped simultaneously with application of said composition to the hair.

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