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WATER RESISTANT HAIR GROOMING COMPOSITIONS

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ABSTRACT OF THE DISCLOSURE

This invention relates to novel hair grooming compositions capable of forming water resistant and alkali soluble films on hair comprising a proteinaceous substance and selective insolubilizing agent selected from the group consisting of formaldehyde and formaldehyde-evolving compounds, and heavy metal compounds and to a method of setting hair comprising applying said composition to hair and drying it on the hair to a water-resistant film, whereby the hair resists deformation on contact with rain or water but may be easily washed free of the applied film by simple shampooing with soaps and detergents.

BACKGROUND OF THE INVENTION

It is known that the shape of groomed hair may be changed by first treating with chemicals which break the disulfide cross-links native to the molecular structure of keratin, molding the hair to the shape desired, and administering a second chemical treatment to the molded hair which reintroduces cross-links to the keratin. The effect of repeating such "permanent" treatments of the hair with chemicals is damaging to the structure of the individual hair fibers. Damage may occur to a degree requiring conditioning treatments to restore the hair to its natural filamentary structure.

Supplementary to the permanent wave is the hair grooming practice of applying compositions in the form of lotions to permit temporary shaping of the hair. The mechanism by which this temporary hair setting is accomplished is primarily that of film deposition on the hair. The lotion comprises a polymer or colloid which dries to a film contributing its own property of continued stiffness or flexibility, dryness or tackiness and clarity or cloudiness to the hair mass. Film-forming colloids conventionally used in hair set lotions include gums, shellac, cellulose ethers, synthetic polymers, proteins and protein hydrolyzates singly or severally in solution in water, in alcohol or in combined solutions of water and alcohol. In addition, film-forming hair-grooming products are often formulated to permit their application as sprays.

Among the several types of film-formers above enumerated protein products are especially appropriate because of their similarity to the keratin protein of hair, giving rise to a high degree of affinity between film protein and hair protein and resulting in the physical effect of enveloping each hair with a substantive film. This unique property of protein film-formers explains their wide use in conditioning hair which has been damaged by repeated exposure to the chemicals of permanent hair setting.

While protein products have the above-mentioned advantages of substantivity of hair, they are deficient in the property of water-resistance, configuration of the protein-shaped hair being readily lost on chance contact with water as in a rain or on purposely contacting with water, as in bathing or swimming, or even on exposure to a damp atmosphere.

SUMMARY OF THE INVENTION

Proteinaceous hair-grooming compositions have now been found which can set hair into durable shapes and which resist deformation on contact with rain or water, while still maintaining removability from the hair by shampooing.

Briefly, our invention comprises a film-forming hair-grooming composition comprising a proteinaceous substance and a selective insolubilizing agent therefor selected from the group comprising formaldehyde, formaldehyde-evolving compounds, and protein-chelating compounds of heavy metals, said selective insolubilizing agent being present in an amount sufficient to cause the composition to form a water-insoluble, alkali-soluble film on keratinaceous substrates. The invention also comprises sprayable pre-mixed storage-stable compositions and the method of setting hair utilizing the novel compositions of the instant invention.

DETAILED DESCRIPTION

The proteinaceous substance that can be used in accordance with the present invention may be any one or a mixture of proteins and protein hydrolyzates including casein, collagen, gelatin, soy protein and their respective hydrolyzates. A necessary condition is that the protein be amenable to selective insolubilization by formaldehyde or heavy metal compounds. Of all the materials, casein is preferred because it has a chemical composition very similar to that of hair, extremely good adhesion to the keratin of hair, relatively low cost, a metabolizable nature, non-toxic properties and it provides a clear and colorless film as demanded by the beauty salon trade.

For optimum performance, casein hydrolyzate is preferred because the hydrolyzed material provides molecular fragments of sufficiently small size which fill the submicroscopic crevices characteristic of normal hair and thus protect the individual hair fibers along their entire length. Hydrolysis also reduces the viscosity of the casein in solution which permits use of higher concentrations in solution, thereby reducing the amount of solvent that must be evaporated per unit weight of applied film. Lastly, hydrolysis of casein also improves its tolerance to dilution by alcohol, thus insuring a solution that can be applied by pressure from an aerosol container. Our copending application, Ser. No. 326,378, filed Nov. 27, 1963 now Pat. No. 3,421,918, is descriptive of hydrolyzates suitable for this purpose.

As to insolubilizing agents, either formaldehyde, formaldehyde-evolving compounds, or certain heavy metal protein-chelating compounds can be used. Of these, the formaldehyde-evolving compound, methylol dimethyl hydantoin is preferred.

The heavy metal protein-chelating compounds utilizable are the salts of zinc, aluminum, titanium, zirconium, tin, magnesium, calcium, cadmium and mixtures thereof, as well as the oxides of these compounds that affect proteins to make them water-insoluble under the conditions prevailing in drying of hair. Moreover, the metal compounds may be water-soluble or water-insoluble. Specific examples are aluminum borate, formate, lactate, sulfate; zinc acetate, chloride, silicofluoride, sulfate, sulfide, oxide; ammonium sulfate; potassium sulfate; calcium acetate, chloride; and the like titanium, zirconium, tin and cadmium compounds. However, the zinc and aluminum compounds are preferred.

The formaldehyde used may be formalin, the 37% aqueous solution of formaldehyde or formaldehyde solutions of lower concentrations. Also suitable are paraformaldehyde and formaldehyde-evolving compounds such as glyoxal, hexamethylenetetramine, hydantoin compounds, and trimethylolnitromethane.

The use of solutions of formaldehyde is most suitable when the protein and selective insolubilizing agent are applied to the hair in successive rather than simultaneous steps, or when the mixture comprising the protein and agent components is made just prior to application to the hair. To avoid the high volatility of such solutions where formaldehyde solutions are added directly and also to produce solutions of acceptable viscosity we prefer that formaldehyde be provided from the formaldehyde-evolving compounds noted since the reaction rate is reasonably slow in the solution step and does not go to completion until the hair-drying step is reached.

Of the formaldehyde-evolving compounds it is preferred to use the hydantoin type of formaldehyde donor, as having an acceptable degree of reactivity and giving no by-products of reaction that might interfere with the purposes of this invention. Of these, preferred is monomethylol dimethyl hydantoin (MDMH), a soluble, odorless, white crystalline solid of 18.98% combined formaldehyde which is evolved on mild heating as at temperatures prevailing in the drying of the living hair.

The preservative value of formaldehyde in protecting protein solutions from microbiological decomposition supplements its selective insolubilizing effect and is an advantage over the use of the heavy metal compounds.

Also suitable substitutes for formaldehyde are acetaldehyde, propyl aldehyde, glutaraldehyde, and furfural.

As to proportions, the amount of protein substance used in the film-forming composition will vary dependent upon the level desired for different hair characteristics. For example, bleached hair and permanently waved hair vary significantly in their behavior in setting, as does the hair of people of varying races and nationalities. However, usual practice is to apply a water or alcohol solution of about 3% to about 5% protein content. Higher protein solids concentrations, as 20% to 30%, can be prepared, but these are diluted with water or alcohol to the lower concentrations for application.

As the selective insolubilizing agents, it is preferred to use, for each 100 parts by weight protein substance, from about 3 to about 7 parts by weight of formaldehyde calculated as molecular HCHO or from about 3 to about 9 parts, but preferably not more than 5 parts, by weight of heavy metal compound, calculated as zinc ion when casein is the protein.

The combining capacity of native casein for zinc and other metal ions cannot be stated in terms of precise equivalency because it varies with the freedom of the reactive groups as determined by the pH of the solution. However, an approximation of the combining capacity of native casein for the zinc ion has been well established as in the range equivalent to 7 to 9 weight percent or approximately 10.7 to 13.8 moles of Zn per mole of casein of average molecular weight 100,000. Since hydrolysis opens up the native molecule to additional metal-bonding groups the combining capacity is greater the higher the degree of hydrolysis. From the known combining capacity of zinc, equivalent values for the other metals can be readily determined for optimum performance for casein and the other protein substances; this being the standard procedure used by protein chemists.

When using formaldehyde-evolving compounds, such as the hydantoins, an amount is used which will supply between 3 and 7 parts by weight of molecular formaldehyde on a dry protein basis. With monomethylol dimethyl hydantoin, for example, between 15 and 35 parts by weight are required.

The foregoing proportions result in varying degrees of water-resistance of the dried film formed on the hair, but in all cases the films formed will be soluble in alkaline soaps and shampoos. Proportions of selective insolubilizing agents much above those set forth markedly increase the insolubility of the films, even in alkaline shampoos resulting in commercially unsuitable products.

Though not essential to the instant invention, various auxiliary components are included to complete a commercial product as applied to the hair and in their usual amounts. The protein concentrate, whether hydrolyzed or not, is preferably protected from attack by microorganisms by the addition of preservatives such as the esters of p-hydroxy benzoic acid, sodium o-phenylphenate, sodium ethyl mercuri thiosalicylate, and 1-hydroxypyridine-2-thione. Also, softeners may be added such as glycerin, sorbitol, the glycols, polyoxyethylene fatty derivatives, and the emollient ethoxylated lanolins. The formulation may also include supplementary film-formers such as polyvinyl-pyrrolidone and its copolymers, natural gums, cellulose ethers; the sterol emulsions; and foaming agents.

It is economical to market the protein with the selective insolubilizing agent as a relatively concentrated solution in water, at viscosity values which permit pouring, pumping and otherwise handling by the formulation of the complete wave set. Therefore, the concentrate may be formulated to permit dilution with water to whatever level is known from experience to be best for hair of differing characteristics.

As an alternative to marketing a concentrated solution of the combination of protein and agent, a dry mixture of the two essentials may be dissolved at some other intermediate point in progression of the product to its ultimate application to the hair. In the case of hydrolyzates these may be dried to a powder, then admixed dry with the agent.

In the special application technique of spraying the solution from a pressurized aerosol container, dilution of the aqueous concentrate with alcohol is practiced, thus obtaining an application of faster drying and setting properies than if water were the only vehicle. Water solutions of protein mixtures with the selective insolubilizing agent can be diluted with about an equal volume of alcohol of cosmetic-compounding grade. However, the use of hydrolyzed casein is particularly appropriate in that dilution with alcohol up to as much as four volumes of alcohol to one of water is possible.

In addition to applying the already combined solution of protein and selective insolubilizing agent, comparable results can be obtained by first applying a solution of the protein to the hair followed by application to the still wet hair of a solution or suspension of the selective insolubilizing agent. In this embodiment it is preferred to use the neutral, relatively inert agents to prevent irritation to the skin. Suitable agents are aluminum borate, aluminum lactate, zinc oxide, zinc carbonate, calcium acetate and the like.

The invention will be further described in connection with the following examples of the practice of it which are set forth for the purpose of illustration only and wherein proportions are in parts by weight unless specifically stated to the contrary.

Example 1

Four aqueous solutions of casein were prepared as follows:

(A) 20 grams of native casein were soaked in 80 mls. of water, 3 grams borax added, and heated at 180° F. with stirring. A film case at .02" thickness on glass was dried and immersed in water for one hour. The film, which is not an example of the instant invention, was completely soluble.

(B) An aqueous solution of native casein was prepared by the method of A above and 6 grams aluminum borate added. A film cast at .02" wet thickness and dried and immersed in water, as in Example A, was found to be only partially soluble after one hour's immersion.

(C) A solution of native casein prepared by the method of A above and treated respectively with 3 grams of zinc oxide and 2 grams of zinc oxide together with 2.5 grams ammonium chloride. A .02" wet film was dried and immersed in water for one hour. The film containing

zinc oxide was only partially soluble; the film containing also ammonium chloride had hardly dissolved at all.

(D) A native casein solution prepared as in A above was treated with 1 ml. of 10% formaldehyde solution. After 10 minutes of holding a film was cast at .02" wet thickness and dried. After 5 minutes immersion in water the film was only partially dissolved.

Example 2

Dolls' wigs composed of human hair were treated respectively with solutions A, B, C, and D described in Example 1. One hour after application the wigs were placed in a cabinet and subjected to a fine spray of moisture simulating rain for one-half hour. They were then allowed to dry in the air. The wig treated with the solution of A was completely dishevelled; the wigs treated with solutions of B, C, and D maintained a good portion of their initial crispness, and could be combed to look quite presentable.

Example 3

Casein was hydrolyzed by heating a mixture of 100 parts native casein, 430 parts water, 6 parts citric acid and 23 parts potassium hydroxide (pH 11.4) at 180° F. for one hour. Eleven parts 80% lactic acid were then added, reducing the pH to 8.9. Aliquots of this hydrolyzate were used for conversion to water-insoluble shampoo-soluble hair setting solutions and aerosol spray solutions as follows:

(A) To 100 ml. of the hydrolyzate there was added 1 gram of zinc potassium sulfate and a thin film was cast and dried at 120° F. for 45 minutes. Fragments of this film were found to be insoluble when immersed in water. On the other hand the film dissolved in a 1:1 mixture of hair shampoo and water. The time taken for solution was 40 seconds.

(B) The procedure of (A) above was followed excepting that zinc potassium sulfate was replaced by one gram of zinc ammonium sulfate. Again the film had not dissolved after exposure to water for 45 minutes. Solution was attained in the 1:1 aqueous dilution of hair shampoo in 1 minute and 15 seconds.

(C) The procedure of (A) above was followed excepting that zinc potassium sulfate was replaced by one gram of zinc sulfate. Again the film had not dissolved after exposure to water for 45 minutes. The solubility was attained in 1:1 aqueous dilution of hair shampoo in 1 minutes and 40 seconds.

(D) The procedure of (A) above was followed excepting that zinc potassium sulfate was replaced by one gram of zinc acetate. Again the film had not dissolved after exposure to water for 45 minutes. Solution was attained in the 1:1 aqueous dilution hair shampoo in 2 minutes.

The rate at which the hair-setting film could be washed out of the hair with shampoo was related to the solution times found in A, B, C, and D. These solution times are also related to the ratio of zinc to casein in the hair setting lotion, as shown by the following table:

Example	Zinc/casein, percent	Solution time, seconds
A	0.815	40
B	0.90	75
C	1.35	100
D	1.97	120

Example 4

(A) To 100 ml. of the hydrolyzate of Example 3 was added increasing amounts of aluminum sulfate

$(Al_2SO_4)_3/8H_2O$

as selective solubilizing agent. The conditions were adjusted to provide aluminum ion levels of 1, 2, and 3 parts respectively per 100 parts of hydrolyzed solids. The mixtures had pH values between 7.5 and 6.4. Films were prepared by casting at .02" wet thickness, dried at 140° F. for 15 minutes to .005" dry thickness. At all three levels of aluminum ion addition the films resisted solution in water but were completely soluble in solutions of shampoo in an equal volume of water.

(B) To 100 ml. of the casein hydrolyzate of Example 3 were added three grams of aluminum lactate. A film of 0.005 inch dry thickness was fragmented to simulate a broken film as it would exist on the hair. The fragments were insoluble in water but dissolved readily in shampoo solution.

Example 5

(A) A film of the casein hydrolyzate of Example 3 was cast and partially dried to a damp state. It was then sprayed with a solution of 1 gram aluminum lactate in 9 ml. water and dried thoroughly at 140° F. The film so treated resisted dissolution in water for at least 30 minutes but dissolved away in shampoo solution in a period of 5 minutes.

(B) A film of the casein hydrolyzate of Example 3 was cast, partially dried, and sprayed with a solution of 1 gram zinc acetate in 9 ml. water. After complete drying at 140° F. of the treated film, it was resistant to solution in water.

Example 6

(A) To 100 ml. of the hydrolyzate of Example 3 there was added 10 ml. of 10% formaldehyde solution, with no separation or gelling of the system occurring. A film was cast and dried to 0.005 inch thickness. The film was whole and could be torn into fragments for solubility tests in water and in shampoo solutions. The film dissolved in water in 30 minutes of immersion. When the proportion of formaldehyde solution to hydrolyzate was increased to 20 ml. of 10% formaldehyde solution, equivalent to about 8 percent molecular formaldehyde on casein hydrolyzate solids, the film was completely insoluble in water for at least 4 hours.

(B) To 100 ml. aliquots of the hydrolyzate solution of Example 3 there was added methylol dimethyl hydantoin (MDMH) in amounts of 13, 26, and 30 grams respectively. Films cast from these solutions were dried at 140° F. and found to be completely insoluble in water. The films were then immersed in a solution of shampoo and the times required for dissolution observed. The results given in the following table show that film insolubilization increases with increasing formaldehyde content:

MDMH, percent	Calculated formaldehyde released, percent	Solution time, minutes
0	0	40
13	2.5	45
26	4.9	48
39	7.4	60

(C) A film of the hydrolyzate of Example 3 was obtained by casting on release paper. When partially dry it was sprayed with a solution of 1 gram of MDMH in 10 ml. of water, then dried completely at 120° F. The hardened film was completely insoluble in water but dissolved completely in a solution of shampoo.

Example 7

(A) To 100 ml. of the hydrolyzate of Example 3 were added agents of both the metallic salt and the formaldehyde donor type. The proportions used provided 4 percent of zinc (from zinc acetate) and 2 percent of formaldehyde (from MDMH) to the casein hydrolyzate film. The film, dried on release paper, was whole, clear, and insoluble in water.

(B) To 100 ml. of the hydrolyzate of Example 3 were added increasing amounts of zinc acetate and decreasing amounts of the formaldehyde donor (methylol dimethyl

hydantoin). The dried films, as expected, showed varying degrees of solubility in shampoo solution, although all were completely insoluble in water. As shown below, the substitution of formaldehyde for zinc increased the solubility of the film in shampoo, thus indicating an improvement in washability of the wave set from the hair.

Zinc acetate, percent	Zinc in film, percent	MDMH, percent	Formaldehyde, percent	Solution time in shampoo, min.
1.53	0.54	33.3	6.33	60
2.30	0.82	33.3	6.33	100
0.77	0.27	50.0	9.50	60
0.77	0.27	66.7	12.67	35

Example 8

(A) To 100 ml. of the hydrolyzate of Example 3 was added zinc acetate in amounts to give 4.3 percent zinc to the dry film. The solution, of 16 percent solids in water was diluted with water to 4 percent solids, then applied as a lotion from a dispenser, actuated by finger pressure to swatches of human hair for observation as to drying rate, resistance of curl to exposure in damp atmosphere, and ease of washing out from the hair with shampoo. The results were observed and it was found that a zinc-reacted casein hydrolyzate film on hair permits exposure of the shaped hair to damp atmosphere without loss of contour and that said film is readily washed out with shampoo.

(B) To 100 ml. of the hydrolyzate of Example 3 were added 3 grams of methylol dimethyl hydantoin corresponding to 4 percent of formaldehyde on the dried film. The testing procedure of (A) gave results showing substantial resistance to curl to deformation on exposure to dampness and ready washability with shampoo.

Example 9

The hydrolyzate of Example 3, without any selective solubilizing agent, was diluted with alcohol of SD–40 formula to 6 percent solids, pressurized in an aerosol container with hair spray propellants Freon 11 and Freon 12 in 50:50 proportion. Freon 11 is made by Du Pont Inc. and chemically identified as trichloromonofluoromethane. Freon 12 is made by Du Pont Inc. and is chemically identified as dichlorodifluoromethane. The solution was applied as a spray to swatches of human hair. Curl retention was observed as the film dried on the hair exposed to ambient atmosphere. Curl retention was poor. When the same dilution was made of a solution of the hydrolyzate of Example 3 containing the formaldehyde donor, MDMH, curl was retained through at least one week of exposure to the atmosphere.

Example 10

The hydrolyzing process of Example 6 was applied to photographer's grade gelatin omitting the citric acid. The hydrolyzing alkali was adjusted upward to provide a pH of 11.4 for the hydrolyzing step, and sufficient lactic acid was then added to reduce the pH to 8.9. To 100 ml. of the clear, particle-free, solution was added 1 gram of zinc potassium sulfate. A film deposited from this solution and dried at 120° F. was found to be insoluble in water but soluble in a 1:1 aqueous dilution of hair shampoo. It was also found that the zinc salt was effective to insolubilize acid hydrolyzates of gelatin.

Example 11

To 100 ml. of the hydrolyzate of Example 10 were added 13 percent of methylol dimethyl hydantoin, dry basis. A film dried at 140° F., though insoluble in water, dissolved in shampoo in an immersion period of 20 minutes.

Example 12

50 grams of casein were dispersed in 450 ml. of water to which were then added 5 cc. of concentrated sulfuric acid. After a soak period of 10 minutes the system was heated at 180° F. for 30 minutes. As a measure of the degree of hydrolysis the viscosity of the hydrolyzate was only 24 cps. at 80° F. as compared to 40,000–50,000 cps. for a solution of unhydrolyzed casein at the same pH. After adjustment of the pH to 8.9, a film of this hydrolyzate was obtained by casting on release paper. When partially dry, it was sprayed with a solution of 1 gram methylol dimethyl hydantoin in 10 ml. of water, then dried completely at 120° F. The hardened film was completely insoluble in water but dissolved completely in a solution of shampoo.

Example 13

50 grams of casein were dispersed in 450 ml. of water and acidified to pH 3.7 with phosphoric acid. 0.2 gram of pepsin 1:3000 was added and the mixture held at 120° F. for 2 hours to permit peptic digestion of the casein. After destruction of the enzyme by heating to 180° F. the acidic solution had a viscosity of 480 cps. at 80° F. After adjustment of pH to 8.9, 100 ml. of this hydroylzate was treated with sufficient zinc acetate and methylol dimethyl hydantoin to deposit 4% zinc and 2% formaldehyde in a dried casein hydrolyzate film. The film, dried on release paper, was insoluble in water but dissolved in shampoo in 25 minutes.

Example 14

100 grams of casein were dispersed in 190 ml. of water and alkalized with 6 grams of potassium hydroxide. To this dispersion 0.3 gram of trypsin enzyme was added and the mixture held for 30 minutes at 120° F. Upon arresting the enzyme action by heating to 180° F. and dilution of the solution with 170 ml. of water, the viscosity was 390 cps. at 80° F., showing that a substantial cleavage of the casein molecule had occurred by the action of trypsin. After adjustment of pH to 8.9 this hydrolyzate was treated with 13% of methylol dimethyl hydantoin, dry basis. A film dried at 140° F. was insoluble in water and dissolved in shampoo in an immersion period of 20 minutes.

Example 15

The method and materials of Example 1B are used except that the casein there used is replaced separately and in turn by an equal amount of each of the other protein substances herein disclosed. In each case the dried film is water-insoluble and alkali-soluble.

Example 16

The method and materials of Example 1B are used except that the aluminum borate there used is replaced separately and in turn by an equivalent amount of each of the other metal salts and oxides herein disclosed. In each case the dried film is water-insoluble and alkali-soluble.

It will be understood that it is intended to cover all changes and modifications of the examples of the invention herein chosen for the purpose of illustration which do not constitute departures from the spirit and scope of the invention.

What is claimed is:

1. A method for setting hair comprising the steps of applying to the hair a composition comprising an aqueous based solution of a proteinaceous material selected from the group consisting of casein, collagen, gelatin, soy protein and the hydrolyzates thereof, and a selective insolubilizing agent therefor selected from the group consisting of (I) formaldehyde, acetaldehyde, propylaldehyde, glutaraldehyde, furfural; (II) formaldehyde-evolving compounds selected from the group consisting of glyoxal, hexamethylenetetramine, trimethylolnitromethane and methylol dimethyl hydantoin, and (III) protein-chelating compounds of metal compounds selected from the group consisting of salts and oxides of zinc, aluminum, titanium, zirconium, tin, magnesium, calcium, cadmium and mixtures thereof; said composition being water insoluble and

soap soluble, the proportion by weight being for each 100 parts by weight of proteinaceous substance, from about 3 to about 7 parts of (I) calculated as molecular HCHO, from about 3 to about 9 parts of (III), calculated as zinc ion when casein is the protein, and an amount of (II) sufficient to supply from about 3 to 7 parts of molecular formaldehyde on a dry basis; the concentration of proteinaceous material in the solution being from about 3% to about 30% and then drying the composition on the hair so as to form a water insoluble film thereon.

2. The method of claim **1** wherein the insolubilizing agent is methylol dimethyl hydantoin in a proportion from about 15 to about 35 parts by weight.

3. The method of claim **1** wherein the proteinaceous substance is casein-hydrolyzate and the insolubilizing agent is methylol dimethyl hydantoin, the proportions by weight of methylol dimethyl hydantoin being from about 15 to 35 parts by weight.

4. The method of claim **1** wherein the solution is a mixture of water and alcohol.

5. The method of setting hair which comprises applying to the hair an aqueous based solution comprising a proteinaceous substance selected from the group consisting of casein, collagen, gelatin, soy protein and the hydrolyzates thereof, allowing the resulting film to substantially dry, then applying a solution of an insolubilizing agent selected from the group consisting of (I) formaldehyde, acetaldehyde, propyl aldehyde, glutaraledhyde, furfural, (II) formaldehyde-evolving compounds selected from the group consisting of glyoxal, hexamethylenetetraamine, trimethylolnitromethane and methylol dimethyl hydantoin, and (III) protein chelating compounds of metal compounds selected from the group consisting of salts and oxides of zinc, aluminum, titanium, zirconium, tin, magnesium, calcium, cadmium and mixtures thereof; the proportion by weight being for each 100 parts by weight of proteinaceous substance, from about 3 to about 7 parts of (I) calculated as molecular HCHO, from about 3 to about 9 parts of (III), calculated as zinc ion when casein is the protein, and an amount of (II) sufficient to supply from about 3 to 7 parts of molecular formaldehyde on a dry basis, and the concentration of proteinaceous material in the solution being from about 3% to about 30% and then drying the composition on the hair to form a water-insoluble film thereon.

6. The method of claim **5** wherein the proteinaceous material is casein hydrolyzate and the insolubilizing agent is methylol dimethyl hydantoin.

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