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[54] **PROTEIN CONDITIONER**

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[51] **Int. Cl.**[2] ... **A61K 7/04;** A61K 7/09; A61K 7/11

[58] **Field of Search** 260/112; 424/71, 61

[56] **References Cited**

UNITED STATES PATENTS

2,383,990	9/1945	Quisling	424/61
2,875,061	2/1959	Vogel et al.	260/112
2,960,442	11/1960	Schwarz	424/70

FOREIGN PATENTS OR APPLICATIONS

1,033,378	6/1966	United Kingdom	424/177
1,033,737	6/1966	United Kingdom	424/177
1,459,789	10/1966	France	424/359

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[57] **ABSTRACT**

A conditioner solution including alcohol and protein from fish milt is disclosed for use on human surface tissue such as skin, hair and fingernails. A method for preparing such protein solution is also disclosed.

7 Claims, No Drawings

PROTEIN CONDITIONER

The present invention relates to an alcoholic solution of protein such as may be used preferably as an aerosol hair spray. The alcohol solution may alternatively be used as a skin lotion or a fingernail polish.

Aerosol hair sprays are commonly used today. Such hair sprays typically include a film forming material, a plasticizer, a solvent and a propellant. The film forming material is usually a lacquer-like material such as ethyl cellulose, shellac or polyvinylpyrrolidene. The film forming material sets up or hardens when applied to the hair and serves to hold the hair in place. The plasticizer is typically diethylene glycol oleate. The plasticizer serves to control the film flexibility, modify setting properties and facilitate ultimate removal of the film from the hair by washing. The solvent serves as a carrier for the film forming material, the plasticizer and any other materials that may be present. The propellant is typically a freon. Such other materials typically include perfumes, anti-tack agents, silicones and lanolin.

The worth of a hair spray is judged on certain highly desirable characteristics. For example, hair sprays should have good hair fixing properties. In other words, the hair spray should hold the hair in the desired position over an extended period even under adverse conditions such as encountered during damp, humid weather. Certain hair sprays used in the past have provided excellent holding ability; however, they have resulted in a heavy, stiff film on the hair and have caused the hair to be stiff and somewhat brittle or straw like. Other hair sprays used in the past have provided a thin flexible film resulting in hair that is soft to the touch. These sprays, however, have had less desirable holding characteristics.

The present invention relates primarily to a hair setting agent and conditioner; however, in its broader aspects, the present invention also relates to a skin and fingernail conditioner. The present invention overcomes the disadvantages of the previously known hair sprays by including an alcohol soluble protein as a film forming material. The present hair spray provides excellent holding ability and yet results in hair that is soft to the touch. The present invention provides excellent conditioning of hair. Furthermore, the present hair spray adds body and sheen to the hair.

The present invention includes a protein prepared from fish milt, namely protamine, and an alcohol solvent. If desired, the present hair spray may include other materials conventionally used in hair sprays, typically perfumes and various hair conditioning materials. If desired, the present hair spray may contain additional film forming materials preferably of types and amounts which do not result in stiff hair.

Hair has been treated with protein in the past. For example, U.S. Pat. No. 3,483,008 shows a protein lotion for application to hair. The protein is egg white and the solvent is water. Although such a water based system is satisfactory in a lotion, it is not satisfactory in a hair spray. Hair spray containing water as the solvent is slow to vaporize when applied to the hair thus leaving the hair tacky and sticky. Water-based solutions tend to straighten the hair rather than hold the curl. Moreover, water tends to corrode the metal spray containers. Also, water soluble proteins do not function on the hair as well as the protein used in the present invention. Protein hydrolysates and their derivatives have been suggested for use in hair spray; however, they may be

required in an amount of 20 percent or more by weight based on the weight of the hair spray solution in order to obtain some functionality. They result in stickiness and poor holding. The protein used in the present invention provides excellent functionality even at only 1 percent by weight of the spray fluid.

The protein used in the present invention is obtained from fish milt. Fish milt is one of the waste products of the fish processing industry. It is made up primarily of the fish sperm surrounded by connective tissue. Analysis of the milt shows that it contains large amounts—i.e. 90 percent and more—of deoxyribonucleoprotein wherein the protein is protamine. Normally the milt is combined with other fish wastes and used to some extent as a hatchery feed. Some biochemical companies use the milt as raw material for the preparation of deoxyribonucleic acid. More often than not, the milt is simply disposed of with the rest of the fish waste products.

Protein obtained from fish milt is commercially available; however, such protein is unsatisfactory for the present hair spray since it is not soluble in nonaqueous alcohol solvent. The available fish milt protein is water soluble.

The protein or protamine used in the present invention may be obtained from any source of fish milt so long as the nucleoprotein content has not been degraded. For example, the fish milt may be fresh, frozen or dried. Also the fish milt may be treated in various ways to inhibit enzyme activity or deterioration. One excellent source of fish milt is from the Alaskan salmon canneries. The fish milt may be, and preferably is, removed from the connective tissue. To prevent autolysis or deterioration, the milt should be rapidly removed of its moisture or treated in such a way as to inactivate biological agents, such as microorganisms and enzymes. One way is to grind up the milt and then disperse the milt in a liquid or solvent which can extract the moisture but does not dissolve the nucleoprotein, such as acetone or the lower aliphatic alcohols using from 1 to about 30 volumes of the alcohol based on the volume of the milt. From an economic standpoint, the use of about 2 to about 10 volumes is especially preferred. The alcohol may be an alkanol having from 1 to 5 carbon atoms. The alcohol may be cold or heated to as high as its boiling point in the case of methanol, ethanol and isopropanol, or to about 90°C. in the case of the alcohols having boiling points above such temperature. The dispersion may be maintained for a period long enough to allow the alcohol to act upon the nucleoprotein, for example ½ to 1 hour. The residue including some connective tissue may then be removed, dried and ground to yield a creamy powdery product. The alcohol may be recovered by conventional techniques such as vacuum distillation. The moisture of fish milt may also be removed by such methods as vacuum drying, drum drying, freeze drying, etc.

In the present invention the fish milt or dry nucleoprotein material is dispersed in an aqueous medium, an organic and/or an inorganic salt is added thus forming a thick solution. The dispersion preferably contains between 0.01 to 1.0 percent by weight of the fish milt or nucleoprotein material based on the weight of the water present.

A wide variety of salts have been shown to bring about the formation of the thick solution. Representative of the inorganic salts are sodium chloride, sodium sulfate, sodium carbonate, sodium bicarbonate, sodium

bisulfate, calcium chloride, lithium chloride, ammonium sulfate, magnesium sulfate, ammonium nitrate and the like. The inorganic salts are preferably the alkali metal, alkaline earth metal or ammonium salts of the mineral acids and especially of sulfuric, sulfurous, hydrochloric and nitric acids. Representative of the organic salts are guanidine hydrochloride, hydroxylamine hydrochloride and the like. Salts of other amines and of other acids can also be used. A preferred group of organic salts are the soaps and detergents, especially synthetic anionic detergents—i.e. anionic surfactants. Representative soaps are sodium stearate, sodium palmitate and sodium oleate. Representative of the synthetic anionic detergents are sodium lauryl sulfate, alkylaryl sulfonate, dioctyl sodium sulfosuccinate and various other sulfates and sulfonates. If desired, mixtures of organic and inorganic salts may be used, for example a mixture of sodium chloride and sodium dodecyl sulfate. The preferred range of salt is between 0.04 to 25 percent by weight based on the weight of the water present.

The pH may be raised in order to precipitate the protamine from solution. The pH may be raised typically with sodium hydroxide, ammonium hydroxide or potassium hydroxide. The precipitated protein may be removed by filtration or centrifugation. The nucleic acid, salt and base remains in the supernatant liquid. It is desirable to wash the precipitated protein with water in order to remove salt, base and nucleic acid. The precipitated protein may be dried.

The precipitated protein is readily soluble in lower alcohols, such as methanol, ethanol and isopropanol, to give a clear solution. For example, it was found that a 20 percent solution (by weight based on the weight of the solution) could be prepared using ethanol as the sole solvent. The solution used in the present conditioning solution, however, may contain from 0.1 to 2 percent by weight, and will normally contain about 1 or 2 percent protein by weight. In fact, an excellent fingernail polish and conditioner, hair spray or skin conditioner can be prepared by using such a 1 or 2 percent solution. Such solution may be conveniently provided in a conventional aerosol applicator together with a conventional propellant such as freon. The following examples are illustrative of the preparation and use of the present invention.

EXAMPLE A

One hundred grams of frozen salmon milt were thawed and chopped into small pieces which were minced and dispersed in 300 milliliters of isopropanol. The dispersion was thoroughly stirred for 30 minutes. The dispersion was then filtered and the residue was washed with 300 milliliters of isopropanol. The alcoholic solution was dried in air at room temperature and the residue was finely ground by ball milling at 4°C. Most of the residue (i.e. about 90 percent) consisted of nucleoprotein. The residue weighed 21.0 grams. The residue was dispersed in 1360 milliliters of water using a Waring blender at low speed for about 2 minutes. About 140 milliliters of a 10 percent aqueous solution of sodium lauryl sulfate was added to the dispersion during continuous stirring and formed a thick viscoelastic solution. A solution containing 120 grams of sodium chloride dissolved in 500 milliliters of water was added to the viscoelastic solution during continued stirring. About 200 milliliters of one normal sodium hydroxide solution was added and thoroughly dispersed. Removal of the protein may be aided by applying a shearing action to the solution such as with a Waring blender either after addition of the sodium chloride or after addition of the sodium hydroxide. The resulting mixture was centrifuged at 2000 rpm for 20 minutes. The residue, which was protamine, was recovered and thoroughly washed with water. The residue was dried and ground into a fine white powder. The fine white powder weighed 8.5 grams. The powder was added to anhydrous ethanol to obtain a 1 percent solution.

EXAMPLE I

One hundred milliliters of the 1 percent protamine solution of Example A was placed in a conventional aerosol can. The propellant included 2.5 milliliters each of trichloromonofluoromethane and dichlorodifluoromethane. The pressure in the aerosol can was raised to 80 p.s.i.g. with nitrogen gas. A hair piece containing human hair was sprayed on one half with the present invention and on the other half with a leading commercial hair spray. The half sprayed with the present invention had a better body and appearance than the side sprayed with the leading commercial hair spray. The hair piece was placed for 24 hours in a room in which adverse weather was simulated. During the first 12 hours the temperature was 70°F. and the relative humidity was 65 percent. During the second 12 hours the temperature was 90°F. and the relative humidity was 65 percent. The side treated with the commercially available hair spray showed noticeably more drooping whereas the side sprayed with the present hair spray had more lustre and remained softer and better in body than the commercial hair spray.

EXAMPLE II

The solution of Example I, containing 1 percent protamine, was sprayed onto the hands and skin of a person and was found to act as a skin conditioner. In other words the ethanol solvent evaporated leaving the protamine on the hands and skin. The protamine made the hands and skin soft and smooth.

EXAMPLE III

The ethanol solution of Example A, containing 1 percent protamine, was brushed onto a woman's fingernails. The solution served as a fingernail polish. The ethanol evaporated and the protamine gave the fingernails a glossy appearance.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A conditioning solution for hair, skin and fingernails consisting essentially of an alcohol having from 1 to 3 carbon atoms and fish milt protamine, said protamine being present in an amount of from 0.1 to 20 percent by weight based on the total weight of the solution, said protamine being dissolved in said alcohol, said alcohol soluble protamine having been prepared by dispersing finely divided particles of fish milt material in water, adding an organic or an inorganic salt to said dispersion in an amount sufficient to produce a thickened solution, adding an alkaline material to raise the pH to a point at which the protamine precipitates from the solution, and removing the protamine from the water.

2. The solution of claim **1** wherein the alcohol is ethanol.

3. The solution of claim 2 wherein the protamine is present in an amount of between about 1 and 2 percent by weight.

4. A method of preparing a protein and alcohol conditioner solution comprising:

dispersing finely divided particles of fish milt material in water;

adding an organic or an inorganic salt to said dispersion in an amount sufficient to produce a thickened solution;

adding an alkaline material to raise the pH to a point at which the protein precipitates from the solution;

removing the protein from the water; and

dissolving the precipitate in an alcohol having from 1 to 3 carbon atoms.

5. The method of claim 4 wherein the finely divided fish milt material has been dispersed in an alcohol having from 1 to 5 carbon atoms and removed from said alcohol before dispersing in said water.

6. The method of claim 5 wherein the fish milt material is dried after being removed from said alcohol.

7. The method of claim 4 wherein the salt is a soap or synthetic anionic detergent.

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