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2

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**RELATIVELY COLLAPSIBLE AEROSOL FOAM
 COMPOSITIONS**

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This invention relates to a composition capable of forming a relatively stable, shape-retaining mass of foam and more particularly to such a composition usable as a carrier substance for dyes, cosmetics, pharmaceuticals and other substances.

The present composition is particularly suited for use as a carrier for hair dyes, since it leaves little residue, can normally be used with no preconditioning of the hair and reduces the necessity for rinsing the hair following use. Hair coloring dyes are customarily supplied either in the form of dye solutions where deep coloring of the hair is desired or in the form of rinses or the like where only slight or moderate coloring or tinting of the hair is intended. Such solutions are generally applied in the form of liquids or sprays. In either case, contact with the skin or scalp of the user is inevitable with resultant staining and possible toxic effects on individuals who may be sensitive to the particular organic dye used. Furthermore, application in this manner is inconvenient and often requires careful preparation before application, careful attention during the application of the dye or rinse, and subsequent clean up to remove the results of spillage, etc.

In some instances compositions capable of forming a foam when being worked into the hair have been used to diffuse a dye or tinting material through the hair. These substances generally require a conditioning wash or rinse of the hair prior to the application of the dye in order that it will set and must contain rather substantial quantities of surface active agents, a soap or detergent base and additional thickening or foam stabilizing agents. Of course dispersion of the dye through the hair with foam generated by the fingers enables the dye to stain the fingers and may require substantial effort to remove it from the hands following treatment of the hair. Often, also, the hair must be rinsed following the dyeing operation, since the foam may deposit a relatively heavy residue on the hair which is not only unattractive but can also be potentially harmful to the hair.

The present foamable composition may not only be used as a carrier for applying hair coloring compositions, but may also find use as a carrier for cosmetic, pharmaceuticals, lubricants, shampoos and other related materials, since it can be readily applied to a particular area of the body with minimum difficulty. This method enables uniform application of material to the hair or body while reducing the difficulties encountered when other methods are used. For example, a pharmaceutical composition in a salve carrier such as petroleum jelly, may require special applicators or require the user to place the material on his hands or fingers to apply it to some other part of the body, whereas the foam carrier of the present invention can be directly applied and permitted to dry to deposit the pharmaceutical at the proper location.

It is therefore a principal object of this invention to provide a composition capable of forming a relatively dense, shape retaining mass of foam, to act as a carrier for various materials, which overcomes the risks and inconveniences of existing carrier compositions.

It is another object of this invention to provide a foamable carrier composition capable of forming a shape retaining mass of material having a relatively low content of nonvolatile or solid material.

Another object of this invention is to provide a foamable carrier composition using an amphoteric surface active agent which can be effectively used in combination with cationic, anionic, non-ionic, as well as other amphoteric substances.

It is an additional object of this invention to provide a carrier composition which can be formed into a shape retaining foam only with suitable liquid or gaseous propellants.

A further object of this invention is to provide a foamable carrier composition for pharmaceuticals, lubricants, shampoos, hair dyes and the like which includes a surface active agent which also acts as a stabilizer preventing the composition from being harmed by excessive heat or freezing.

Other objects and advantages of this invention will be apparent from the following description and the appended claims.

The present invention, as previously mentioned, makes possible the effective and simple application of various types of substances to the body, and is particularly adaptable for use in applying coloring materials to the hair. Therefore, the invention will be described principally with reference to the use of the material in conjunction with hair dyes and the like. Coloring materials may be applied to the hair by dissolving or dispersing the coloring dye in a foamable solution and then generating a dense, relatively stable and compact mass of foam which is substantially shape retaining. In other words, the dye solution is first formed into a mass or blob of an aqueous foam which is light in density and will remain stable without any substantial drainage of liquid therefrom. Thus, the foam in effect is in the form of a puff or similar mass which may be applied to the hair by means of a brush or similar applicator. In this way the dye solution is handled and applied not as a liquid but as a light, dispersed gas-liquid foam mass which is in effect semi-solid in nature, thus avoiding the disadvantages of liquid application even though the dye solution remains in liquid form within the foam mass.

This method of applying materials not only possesses the manipulative advantages referred to, but also has the advantage of avoiding contact of excessive liquid with the skin or scalp and is much cleaner and neater to use. Furthermore, the gas-liquid foam permits uniform dispersion of the coloring dye and thereby obtains non-streaking application of the dye to the hair. This is probably due to the fact that dispersion of the foam mass through the hair avoids concentration of the dye in localized areas, while the large surface area present permits thorough and uniform contact of the coloring matter present in the liquid film of the foam through the hair mass and around each individual hair. Additionally, it has been found that foam application of dye enables coloring of the hair to take place with smaller quantities of dye so that the possibility of incurring toxic effects is materially reduced.

A suitable foam structure having the desired stability, density and self-sustaining properties, permitting application in the manner desired, may be obtained by employing an aqueous solution of a foam forming composition containing surface active agents, coloring or dyeing materials, and a suitable propellant. These materials are combined in proper proportions in a container and released by means of a manually operable valve. Upon operation of the valve, the propellant is volatilized and carries with it a proportion of the water, dye and other ingredients to generate the desired foam mass. This same general type of arrangement is commonly used for dispersing insecticides, shaving creams, deodorants, lacquers and the like under the general designation of aerosol products.

The compositions of the invention should include water, a foaming agent such as a surface active material and other ingredients, when required, to modify the foam structure. Of course the surface active material, or surfactant, may serve the additional function of acting as a foam stabilizing agent or as an emulsifying agent, so that a separate stabilizer or emulsifier need not be added. In addition, where the aerosol foaming technique is used, the propellant must be incorporated with the foamable composition. When utilized for coloring hair in accordance with this invention, a suitable dye is incorporated either in solution or in suspension within the aqueous phase. Other ingredients, such as hair softening materials, perfumes, etc. may also be added as desired.

The present composition can be separated into two broad groups of substances, solids and non-solids, the non-solids referring to the volatile components and the solids referring to the non-volatile components. Since the purpose of the composition is to provide a means for carrying a particular material to some part of the body, it is desired that the solids part of the composition be kept as low as possible to eliminate deposition of excessive residue. The solids content in the invention falls within the range of from 1.5% to about 4.5% by weight of the total weight of the composition, these percentages being lower than those of existing foam compositions. Obviously after an application of the material the volatile components including water will evaporate and leave the solids or non-volatiles deposited on the hair or body. Thus, a composition which can operate with such low percentages of solids, without impairing the foaming characteristics, has advantages over compositions which must use relatively greater amounts of solids.

The preferred type of foamable carrier composition generates foam only when used in conjunction with an aerosol arrangement or its equivalent, so that the foam will tend to disappear after having performed its function of carrying an active agent to the desired location. Hereinafter, such a foam characteristic will be referred to as "relatively collapsible" to indicate that the foam will disappear once it has performed its function as a carrier. This property permits elimination of any rinsing operation following dyeing. The basic material, that is the material primarily responsible for the improved results, is an amphoteric quaternary surface active agent, which can be effectively used with other amphoteric, cationic, anionic or non-ionic substances such as the dyes, etc. The amphoteric nature of the quaternary surfactants reduces the necessity for rinsing or otherwise pre-treating the hair before using a dye carried in the composition.

The quaternary compound is the sodium alcoholate or the carboxylate and alcoholate of a cycloimido derivative such as might be obtained by reacting a fatty acid, as stearic or oleic or palmitic acid, with a diamine such as ethylene or propylene diamine, plus a poly-functional alcohol, such as ethylene glycol, or both a poly-functional alcohol and a hydroxy acid, such as lactic or glycollic acid.

The quaternary compounds are made by forming a condensation product of either sodium alcoholate or sodium carboxylate with one of the fatty acids mentioned and then further condensing this product with one of the hydrocarbon diamines. The bi- or poly-functional alcohol or the hydroxy acid is then added to complete formation of the amphoteric, quaternary surfactant.

Suitable surface active agents include, for example, ethylene cycloimido 1 alkyl bis (2 hydroxyethylene sodium alcoholate); alkyl dimethyl benzyl ammonium chloride; and ethylene cycloimido 1 alkyl 2 hydroxyethylene sodium alcoholate methylene sodium carboxylate. In certain situations it may be preferred to combine more than one of these quaternaries in a single car-

rier compound to regulate the amphoteric character of the material.

Generally, the carrier composition will consist of 1.5 to 4.5% by weight of surface active agents, as mentioned, minor additions of dye or other material to be carried, and water.

The dye stuffs selected will depend on the color desired and whether the foam is to be utilized on human hair or upon other materials such as fabrics or the like. For use on human hair the dye may be selected from those which have been certified by the Government as non-toxic, or those, which generally considered as non-toxic, will be essentially non-toxic when applied in accordance with the present invention. Such dyes should be water soluble or dispersible. These dyes include quinoline, monoazo, disazo, diphenolmethane, triphenolmethane, anthraquinone, xanthene, acridine and indigoid types. The concentration of the dye utilized will vary with the dye, the color desired, whether the product is to be used as a tint or for deep coloring etc. In general, a concentration of 0.001 to 0.5% by weight would be selected depending on color and intensity. Other organic dyes suitable for coloring hair include the aromatic amines such as paraphenylenediamine or the aminophenols and the like. Where water insoluble dyes are used, they may first be dissolved in water soluble solvents such as glycols or alcohols, or may be dispersed in the water with dispersant agents. Buffers may be added to insure maintenance of the pH range of the solution at the desired level for any particular dye.

The following examples are illustrative of acceptable compositions and are shown as including hair dye, the quaternaries being added as water diluted solutions, as indicated.

Example I

	Parts by weight
Ethylene cycloimido 1 alkyl bis (2 hydroxyethylene sodium alcoholate) — 35% solution	14.0
Alkyl dimethyl benzyl ammonium chloride — 28% solution	5.2
Water soluble color	0.5
Water	132.8

Example II

Alkyl aryl sulfonate — 60% solution	2.5
Ethylene cycloimido 1 alkyl bis(2 hydroxyethylene sodium alcoholate) — 35% solution	14.0
Alkyl dimethyl benzyl ammonium chloride — 28% solution	5.2
Water soluble color	0.5
Water	132.8

Example III

Ethylene cycloimido 1 alkyl 2 hydroxyethylene sodium alcoholate methylene sodium carboxylate — 35% solution	9.0
Ethylene cycloimido 1 alkyl bis(2 hydroxyethylene sodium alcoholate) — 35% solution	4.0
Polyglycol polyoxyethylene ether ester of stearic acid	1.5
Water soluble color	0.5
Water, bal. to 155 parts.	

Example IV

Amphoteric surface active material containing two hydrophilic sites one of which is anionic sulfate structure (Duponol XL)	8.0
Ethylene cycloimido 1 alkyl bis(2 hydroxyethylene sodium alcoholate) — 35% solution	4.0
Alkyl dimethyl benzyl ammonium chloride — 28% solution	1.5
Water soluble color	0.5
Water, bal. to 155 parts.	

The amphoteric surface active material cited in Ex-

ample IV is sold under the trade name of Duponol, by the E. I. du Pont de Nemours & Co. and represents a line of surface active agents of the alcohol sulfate type containing two hydrophilic sites, one of these sites being an anionic sulfate structure.

Additionally, if the compositions of the preceding examples are to be dispersed from aerosol pressure containers, about 18 parts of the propellant would be added to each of the compositions.

Propellant materials having little or no solubility in water and no destructive effects upon the foam are used, the "Freons" being a class of compounds which are highly suitable for this purpose. Examples of such propellants are the chlorine and fluorine substituted lower aliphatic hydrocarbons particularly the methane and ethane derivatives. Preferred propellants of this type are dichlorodifluoromethane, monochlorotrifluoromethane, monofluorotrifluoromethane, 1,2 dichlor, 1,1,2,2 tetrafluoroethane, trichlorotrifluoroethane, and mixtures of these. In general, organic materials which are gases at room temperature and liquid at elevated pressure may be utilized where the foamable composition and propellant are to be packaged under pressure. Other propellants which may be used include propane, butane, isobutane, methylchloride, nitrous oxide, and in general such other materials which will not adversely effect the foaming properties of the composition. The propellant is generally utilized in proportions of from 5 to about 25% of the weight by mixture.

The final composition is formed by preparing a mixture of the water with the appropriate surfactants and then applying heat until the water soluble portion of the molecules enters into a solution-like relation to the water. The resultant system tends to undergo a transition at temperatures from 110 to 130° F., when its viscosity sharply increases on cooling, and thixotropy appears.

In another form of the invention suitable surface active materials may be the fatty acid soaps, vegetable oil soaps, synthetic detergents, or wetting agents, including those of cationic, anionic or non-ionic character such as fatty alkyl sulfates, alkyl aromatic sulfonates, alkyl olamine soaps, sodium lauryl sulfate, triethanolamine lauryl sulfate, sulfated ethanolamine of coconut oil fatty acids, sodium dodecyl benzene sulfonate and others well known in the art. Mixtures of these may sometimes be advantageous, and in general, as mentioned, these agents are utilized in concentrations of from 0.5 to less than 5%.

When surface active materials such as those just described are used it is often desirable to add various foam stabilizing materials. For example such materials as glue, glycerin, albumin, thickening or viscosity increasing agents such as ethyl and methyl cellulose, hydroxyethylcellulose, carboxymethylcellulose, and so forth. These materials are also used in small proportions, generally less than 5%.

Foam structure modifying agents may be added to produce denser and smaller bubbled foams. These materials may also include small proportions of anti-foaming or modifying agents such as electrolytes or water soluble salts like sodium sulfate, silicon oil, hydrocarbon oils, ethyl or methyl alcohol, etc., which may be added in concentrations of 0.001% or the like.

Example V

	Parts by weight
Sulfated ethanolamide of coconut oil fatty acids	2.0
Sodium lauryl sulfate	1.0
Sodium stearate	1.0
Fast Black BB (D. & C. black #1, Color Index #307)	0.01
Water	95.0
Dichlorodifluoromethane (Freon 12)	6.0

Example VI

	Parts by weight
Triethanolamine stearate	3.0
Triethanolamine soap of coconut oil fatty acids	1.0
Hydroxyethylcellulose	1.0
Resorcin Brown (D. & C. brown #1, Color Index #234)	0.015
Water	95.0
Dichlorodifluoromethane	3.5
1,2 dichlor 1,1,2,2 tetrafluoroethane	4.5

Example VII

Dodecyltrimethylammoniumchloride	1.0
Sorbitan monostearate (Tween 60)	0.5
Animal glue	0.5
Naphthol blue black (Color Index #246)	0.02
Water	98.0
Dichlorodifluoromethane (Freon 12)	8.0

In utilizing the materials described in the preceding Examples V-VII to carry out the present invention, the foamable composition is first prepared by dissolving the ingredients thereof plus the dye in the water. Where an aerosol container is to be used, the solution is placed therein along with the propellant which is introduced under pressure in the liquid phase. The container is provided with a valve and a dispersing nozzle. Prior to use, the container is agitated and the contents mixed. On opening of the valve the propellant forces the foamable composition through the nozzle and simultaneously generates a thick creamy foam. The dispersion of the foamable material from the aerosol container is the same in each form of the invention.

In the coloring of hair the valve is opened for a long enough period to generate the desired mass or blob of foam. This mass is then applied to a brush or other applicator or directly to the hair, and the foam, while still in the foam state, is brushed or otherwise manipulated through the hair. By applying the foam in this manner progressively to selected areas of the hair, complete and uniform coverage can be obtained. The application of other materials to parts of the body other than the hair can be carried out in much the same manner so that upon evaporation or disintegration of the foam a uniform film or material is deposited at the proper location.

This application is a continuation-in-part of applicant's copending application Serial No. 553,188, filed December 15, 1955, now abandoned.

While the compositions herein described constitute preferred embodiments of the invention, it is to be understood that this invention is not limited to these precise compositions and that changes may be made therein without departing from the scope of the invention which is defined in the appended claims.

What is claimed is:

1. A composition for carrying a material, including hair dyes, pharmaceuticals, lubricants and shampoo, and for forming relatively collapsible foam bubbles carrying said material and which foam bubbles will collapse upon application and will form a non-foam drying film carrying said material, which composition comprises in liquid form for admixture with said material a foam-producing agent selected from the group consisting of ethylene cycloimido 1 alkyl bis (2 hydroxyethylene sodium alcoholate), alkyl dimethyl benzyl ammonium chloride, and ethylene cycloimido 1 alkyl 2 hydroxyethylene sodium alcoholate methylene sodium carboxylate, and mixtures thereof, a volatile aqueous solvent for said composition and a volatile foam-generating propellant, the non-volatile contents of said composition being between about 1.5% and 4.5% by weight.

2. A liquid hair dye composition adapted to form a mass of relatively collapsible foam bubbles carrying a hair dye, which bubbles collapse upon application to deposit a film of said dye on the hair, which comprises in combi-

7

nation a hair coloring dye, a volatile aqueous vehicle in which said dye is dissolved, a foam-producing amphoteric quaternary surface active agent, and a volatile compressed propellant for generating said foam, all said components being admixed and contained in a pressurized container in liquid form for generation of said collapsible foam bubbles by said propellant upon release of a portion of said composition from said container, and the non-volatile contents of said composition being between about 1.5% and 4.5% by weight.

3. A composition as set forth in claim 2 in which said hair dye is a basic hair dye.

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