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SHAMPOO COMPOSITION

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ABSTRACT OF THE DISCLOSURE

A shampoo composition suitable for simultaneously cleansing and conditioning human hair, comprising in combination a water-soluble non-soap organic synthetic detergent salt having a hydrophobic long chain substituent containing at least 8 carbon atoms in its molecular structure and a normally liquid saturated branched-chain higher fatty acid material containing about 12–24 carbon atoms. Preferred compositions contain about 10–40% by weight of the detergent and 0.5 to 5.0% by weight of the fatty acid material in an aqueous medium.

BACKGROUND OF INVENTION

The invention relates to a substantially stable liquid shampoo composition comprising in combination a major proportion of a synthetic organic non-soap detergent salt having a hydrophobic long chain substituent containing at least 8 carbon atoms in its molecular structure and a minor proportion of a normally liquid, saturated, branched-chain fatty acid material in an aqueous medium which simultaneously cleanses and conditions the hair.

Shampoo compositions may be described generally as preparations comprising a surfactant or surface active material which when used under the conditions specified will remove surface grease, dirt and skin debris from the hair and scalp without adversely affecting the hair, scalp or health of the user.

Originally, the shampoos were made of soap or mixtures of soaps, whereas today synthetic detergents are the primary surfactants used in the commercial products. Although soap shampoos comprising primarily either salts of C_{10} – C_{12} or salts of C_{16} – C_{18} fatty acids had the respective disadvantages of being irritating to the skin and of possessing inadequate solubility properties, shampoos, containing mixtures of salts of C_{10} – C_{20} fatty acids, e.g., olive oil soaps, were found to have outstanding cleansing and conditioning properties in soft water. However, these same shampoos proved ineffective in medium and hard water due to the formation of insoluble calcium and magnesium soaps which were deposited as sticky films on the hair.

To avoid the problem of insoluble soap precipitates associated with hard water, non-soap synthetic detergents were used in place of soap as the primary surfactant in shampoo compositions. While use of certain non-soap synthetic detergents resulted in enhanced foaming and cleansing action, the resultant shampoo compositions had little or no hair conditioning properties. Accordingly, it became necessary to add special expensive finishing agents such as unsaponified oils, fatty acid esters, lanolin, synthetic gums and quaternary ammonium compounds to non-soap synthetic detergent shampoos to provide the desired conditioning effects.

The addition of the foregoing expensive finishing agents created new problems in shampoo formulation due to the relative insolubility and/or chemical incompatibility of the finishing agents. For example, use of stearic acid as a hair conditioning acid in shampoos either tended to cause instability in liquid shampoos by separation from the liquid phase or tended to thicken the liquid shampoo

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to a non-pourable paste form. To overcome these new problems, additional expensive emulsifying agents and suspending agents were incorporated to minimize problems of physical separation of the finishing agents; or, alternatively, significant quantities of organic coupling agents were incorporated to solubilize the finishing agents.

Further, the addition of the emulsifying agents, coupling agents, etc. to the shampoo compositions restricted the physical characteristics of the final products. Thus, the physical form of the final product could not be readily varied from a clear liquid to an opaque lotion without creating a host of new problems.

As an alternative to the foregoing mixtures of synthetic detergents and special conditioning agents, blends of synthetic detergents and soaps were evaluated. However, satisfactory soap-detergent conditioning shampoos proved difficult to formulate and expensive because of the need to use blends of individual fatty acids in order to achieve the desired balance of solubility, cleansing, foaming, luster and other characteristics needed in the finished shampoo. In view of the foregoing formulation problems, the only shampoos containing a blend of synthetic detergent and soap which proved commercially successful were those in which a stearic or behenic acid salt was present as an opacifying agent.

SUMMARY OF THE INVENTION

It has now been discovered that compositions having particular utility in the simultaneous cleansing and conditioning of human hair as well as other desirable properties comprise essentially in combination a synthetic organic non-soap detergent salt having a long chain containing at least 8 carbons in its molecular structure and a minor proportion of a normally liquid saturated branched-chain higher fatty acid material containing 12–24 carbon atoms, the ratio of synthetic detergent salt to the fatty acid material being from about 80:1 to about 1:1 by weight and effective to yield the desired properties. A preferred embodiment relates to a pourable aqueous liquid shampoo consisting of about 10 to 40% by weight of said detergent and about 0.5 to 5% by weight of isostearic acid having a titer of 10° C. maximum dissolved or solubilized in the aqueous medium having a pH from about 5 to 8.5, preferably 7 to 8. The preferred shampoo composition has been found to possess exceptional stability, foaming properties and conditioning effects.

These compositions have the dual function of washing and conditioning the hair, leaving the hair soft and more manageable after shampooing. The need for frequent combing is minimized and the act of combing the hair is accomplished with greater facility due to the elimination of tangled hair. The hair is rendered significantly anti-static and exhibits good sheen or luster and curl retention. Other important advantages include a desirable modification of the foaming power so that there is achieved superior foam volume and stability in comparison to similar compositions wherein stearic acid is substituted for a portion of the branched-chain acids.

An important property of the liquid shampoos achieved by the combination of the detergent and the branched chain fatty acid material in the aqueous medium is their stability. The isostearic acid or the like is partially neutralized to a mixture of the soap and said acid at a pH of about 5 to 8.5 and the resulting shampoo has stability at 75° F. and at an elevated temperature of 110° F. without separation, and a capacity to retain opacifying agents in suspension so as to form a stable opaque liquid shampoo.

Thus, the shampoo compositions of the invention may be formulated in the popular forms of a clear liquid or a creme lotion without the need for significant amounts of additional, expensive ingredients, thereby eliminating the

problems common to the incorporation of such additional ingredients. For example, the need for additional finishing or conditioning agents, such as synthetic or natural gums and unsaponified oils and the instability problems associated with the incorporation of such materials is eliminated. Similarly, the need for the organic, non-aqueous solvent-type coupling agents which have the adverse property of causing the hair to become dry and brittle is also minimized. Therefore, the described shampoo compositions provide flexibility in the formulation of liquid products that cleanse the hair and scalp while simultaneously imparting luster, beauty and manageability to the hair.

DETAILED DESCRIPTION OF THE INVENTION

The suitable liquid branched-chain higher fatty acids containing about 12 to 24 carbon atoms are known in the art. In general, they should have a titer of up to about 15° C., usually 3 to 15° C., and preferably about 10° C. maximum. The preferred materials productive of optimum results are C₁₆ to C₁₈ branched-chain fatty acids, e.g., iso-stearic acid which is a liquid C₁₈ saturated branched-chain isomeric material of the formula C₁₇H₃₅COOH having primarily methyl branching. For present purposes, it has been found that a suitable commercial material is iso-stearic acid which is a liquid isomer of stearic acid having a titer of 10° C. maximum and comprising essentially the 9-methyl and 10-methyl stearic acids. Other characteristics of the commercial isostearic acid are a molecular weight of about 284, an iodine value of about 10 maximum and a saponification value of about 180 minimum. Other branched-chain saturated fatty acids may be employed including similarly branched-chain lauric, myristic and palmitic acids which should be prepared in isomeric form so as to have at titer of up to 15° C. with methyl or ethyl branching preferably at about the middle of the chain. Further examples of suitable branched-chain fatty acids include the 8-10 methyl branched isomers of stearic acid, palmitic acid and the like. Such isomeric branched-chain materials may be formed in any suitable manner; one method being polymerization of an unsaturated acid which is broken down to yield an unsaturated monocarboxylic acid having methyl chain isomers and which is thereafter hydrogenated to a saturated material.

In the manufacture of the shampoo in aqueous form, the branched-chain fatty acid is desirably neutralized at least in part by the addition of any suitable alkali such as alkali metal hydroxide, or a lower amine, particularly an ethanolamine such as mono-, di- or tri-ethanolamine. The resulting water-soluble soap is formed at a pH of 5 to 8.5, preferably 6.5 to 8. The salts of the branched-chain material may be dissolved or solubilized in the water to the extent that a transparent solution is obtained in the absence of opacifying materials.

The water-soluble organic non-soap detergent may be selected from the group consisting of the anionic, non-ionic and amphoteric organic non-soap detergents (including suitable mixtures thereof). Suitable detergents have a hydrophobic long chain substituent, containing at least 8 carbon atoms, generally 8 to 26 carbon atoms and preferably 12 to 18 carbons in their molecular structure, and at least one water-solubilizing group selected from the group consisting of sulfate, sulfonate and carboxylate so as to form a water-soluble detergent.

Among the anionic organic compounds that may be used are the long chain sulfated and sulfonated detergents. Suitable examples of these long chain aliphatic detergents are the sulfuric acid esters of polyhydric alcohols incompletely esterified with higher fatty acids, either saturated or unsaturated, particularly those whose acyl groups contain from 12 to 18 carbon atoms, e.g., coconut oil monoglyceride monosulfate, hydrogenated coconut oil monoglyceride monosulfate, tallow monoglyceride monosulfate; the long chain pure or mixed higher alkyl sulfates of 12-18 carbons, e.g., lauryl sulfate, cetyl sulfate, higher fatty alcohol sulfates derived from hydrogenated or non-hydro-

genated coconut oil or tallow fatty acids; the higher fatty acid esters of hydroxy alkyl sulfonic acids, e.g., higher fatty acid esters of 2,3 dihydroxy propane sulfonic acid; higher fatty acid amides of amino alkyl sulfonic acids, e.g., the oleic acid amide of amino methyl sulfonic acid, the lauric acid amide of taurine, and the like.

Other appropriate aliphatic long chain sulf(on)ates include fatty sulfoacetates, e.g., coconut fatty alcohol sulfoacetates; sulfated fatty acyl monoethanolamides, e.g., sulfated lauroyl monoethanolamide; fatty sulfoacetamides, e.g., lauryl sulfoacetamide; lower alkyl sulfosuccinates, e.g., dioctyl sulfo-succinate; sulf(on)ated fatty oils such as sulf(on)ated castor oil and sulf(on)ated red oil, and lower alkyl esters of alpha-sulfonated higher fatty acids, e.g., methyl ester of alpha-sulfo myristic acid, sodium salt.

Synthetic detergents having a carboxylate group, and particularly the higher fatty acid amides of aliphatic long chain amino acid compounds may also be included, such as the higher fatty acyl sarcosinates having about 10 to 18 carbons, usually 12-24 carbons, in the acyl radical, preferably the water-soluble salts of N-lauroyl or N-cocoyl sarcosine. Other materials are the higher fatty acid amides of polypeptide amino acids obtained by protein hydrolysis known as the Lamepons and Maypons. Other suitable detergents with carboxylate groups are various amphoteric detergents described hereinafter.

Suitable ether-containing sulfates may be used also such as the alkylphenol polyglycol ether sulfates, e.g., lauryl phenol polyethyleneoxy sulfates, and alkyl polyglycol ether sulfates, e.g., lauryl ethyleneoxy sulfates, each containing about 10 to 18 carbons in said alkyl groups and about 2 to 10 moles of ethylene oxide, usually 3-4 moles, per molecule.

The alkyl aryl sulfonates may also be used as the anionic detergent although they are not usually preferred in shampoos because of their excessive drying power. Typical of this class of compounds are the higher alkyl aromatic sulfonates where the nucleus may be derived from benzene, toluene, xylene, phenol, cresols, naphthalene, etc. The alkyl substituents may be branched or straight chain, such as decyl, dodecyl, keryl, hexadecyl, mixed long-chain alkyls derived from long-chain fatty materials, cracked paraffin wax olefins, polymers of lower monoolefins, etc. Examples of the classes are the higher alkyl benzene sulfonates wherein the alkyl group contains 8 to 18 carbon atoms, and preferably about 12 to 15.

These various anionic detergents are used in the form of their water soluble or water dispersible salts such as the amine, alkali metal and alkaline earth metal salts. Examples are the sodium, potassium, magnesium salts, ammonium, monoethanolamine, diethanolamine, triethanolamine, triethanolamine salts, and mixtures thereof.

Further suitable organic detergents include non-ionic detergents such as the lower alkylene oxide condensation products of hydrophobic compounds, e.g., ethylene oxide condensates with higher fatty acids, higher fatty acid amides, higher fatty alcohols or alkyl aryl hydrocarbons, having at least 5 and usually from about 5 to 30 ethyleneoxy groups per molecular. The corresponding higher alkyl mercaptans of thioalcohols, or polyoxypropylene glycols of at least 900 molecular weight condensed with a sufficient number of ethylene oxide groups as known in the art may be used also. Other non-ionics are the alkylolamine condensates of higher fatty acids such as lauric and myristic diethanolamide, coconut fatty acid diethanolamide, and the like.

Other suitable surface-active agents which may be used include the higher alkyl amine oxides such as lauryl dimethyl amine oxide. In place of the lauryl radical, other long chain alkyl radicals, preferably having 10 to 18 carbon atoms, may be used also. In place of either or both methyl radicals, there may be other lower alkyl or hydroxyalkyl radicals such as having two carbon atoms each. Suitable examples include a mixture of higher alkyl di-

methy lamine oxides having essentially about 12-14 carbons in the higher alkyl groups.

Any of the usual amphoteric (ampholytic) deterative materials may be employed in the compositions of the present invention. Among those are fatty or higher alkyl imidazolines, such as 2-coco-1-hydroxyethyl-1 carboxymethyl imidazoline known as Miranol CM; and the higher alkyl beta-alanines such as dodecyl beta-alanine known as Deriphats, said materials having usually an alkyl group of 10 to 18 carbons and the carboxylate group being in the form of the water-soluble salt. Further examples are the disodium salt of 2-lauryl-cycloimidium-1-ethoxyethionic acid-1-ethionic acid and its corresponding 1-lauryl sulfate derivative.

The mixture of detergent material and branched-chained acid material should be suitably proportioned to achieve the desired results such as hair conditioning in the use of the shampoo, improved foam consistency or solubilization, etc. In general, the ratio of detergent material to said fatty acid will be within the range of about 80:1 to about 1:1 by weight, usually 30:1 to 3:1, and sufficient to obtain the desired beneficial effect therefrom. It has been determined that optimum effects are obtained when the fatty acid material is present as a minor proportion of the order of 0.1 to 10%, usually at least about 0.5% and up to 5%, by weight of the final composition, which is dissolved or dispersed in water. In the final composition, the synthetic detergents desirably comprise at least about 10%-40%, by weight, preferably 15 to 30% by weight, with water as primarily the balance in the liquid shampoos.

It is preferred to use said isostearic acid or the like in combination with an alkylolamide of a higher fatty acid, such as the diethanolamides, monoethanolamides, and isopropanolamides of higher fatty acids having 8 to 18, preferably 10 to 14 carbons. The higher fatty acid alkylolamide is present in a minor amount, such as from about 1 to 10% by weight of the composition. Such combination is selected from the range of about 10:1 to 1:10 by weight of fatty acid material to fatty acid alkylolamide so as to produce improved overall lathering properties. The products containing the blend exhibit a quick, copious and yet stable foam.

The resulting liquid shampoo having the solubilized branched fatty acid material has a desirable capacity for retaining opacifying agents in suspension even when the shampoo is highly fluid. Any suitable opacifying agents may be used to produce an opaque lotion-like product including excess detergent, lanolin, and preferably higher fatty acid esters such as ethylene glycol distearate and monostearate in sufficient amount to opacify the product and be retained in a stable suspension upon aging. The opacifying agents such as the ester are generally employed in a suitable amount from about 0.5 to 10%, preferably 1 to 5% by weight of the shampoo.

In general, the products are manufactured in the usual manner with the detergent, fatty acid and alkali being mixed in water at an elevated temperature to form a stable, homogeneous mixture. It is prepared preferably in a readily pourable form such as having a viscosity of about 10 to 400 seconds, preferably about 40 to 110 seconds, as determined on a No. 5 Raymond flowmeter. The specific gravity of the liquid shampoos is desirably at least about 1.02 and preferably within the range of 1.025-1.03.

It is common to add various adjuvant materials to shampoo compositions and the like. Thus, the shampoo ordinarily will contain a compatible perfume and color. Other ingredients may include a small amount of a buffer material to aid in the adjustment and maintenance of the desired pH of the finished product. Suitable buffering materials include borax, the various inorganic water-soluble phosphates such as disodium phosphate, or sodium pyrophosphate, citric acid, etc. Sequestering agents such as the water-soluble salts of ethylene diamine tetra-acetic acid may be employed also. Other ingredients which may be used in shampoos for imparting desired qualities and

may be incorporated in the present compositions include superfatting materials such as lanolin, liquid lanolin or ethoxylated lanolin, fatty alcohols, fatty acids, fatty acid esters, etc., generally in minor proportions, e.g., up to about 5% by weight. The higher fatty alcohols include myristyl, cetyl and stearyl alcohols, etc. Glycerine, ethanol or propylene glycol may be added in small amounts generally. Similarly, antiseptics or other anti-bacterial agents may be used if desired. Preservatives such as sodium benzoate and the like may be added to prevent mold growth. Gum mucilages such as carboxymethylcellulose, and the like may be used if desired. Preservatives such as sodium benzoate and the like may be added to prevent mold growth. Gum mucilages such as carboxymethylcellulose, and the like may be used as desired similarly.

The following specific examples are further illustrative of the nature of the present invention, and it is to be understood that the invention is not limited thereto. All parts are by weight unless otherwise indicated.

EXAMPLE I

Ingredients:	Percent
Sodium lauryl sulfate -----	17.6
Triethanolammonium lauryl sulfate -----	1.9
Isostearic acid -----	2.0
Ethylene glycol distearate -----	2.0
Lanolin -----	0.5
Potassium hydroxide (34.2% solution) -----	1.0
Lauric-myristic (70:30) diethanolamide -----	1.5
Water -----	Balance

The above components except for the amide are combined with heat sufficient to maintain a fluid state at about 160° F. for about 10 minutes and to form a uniform mixture. The sodium lauryl sulfate is listed on an active ingredient basis and is added as a 28% aqueous paste containing in addition about 2% unsulfated fatty alcohol and 0.2% sodium chloride. The triethanolamine lauryl sulfate is added as a 41% aqueous solution with about 1.5% unsulfated alcohol and 1.5% triethanolamine chloride as impurities also. The isostearic acid is a liquid material and comprises essentially 9- and 10-methyl stearic acid having a titer of 10° C. maximum. The resulting mixture is cooled with the amide being added at 130° F., and a very small amount of color and preservatives at about 110° F. The pH is adjusted with the addition of citric acid to 7.5. The product is a stable, readily pourable opaque lotion shampoo having a specific gravity of 1.03 and a viscosity of about 50 seconds using the No. 5 Raymond flowmeter.

This lotion shampoo provides excellent foam quality and hair-conditioning effects superior to a similar product containing stearic acid in place of a portion of the isostearic acid.

EXAMPLE II

Ingredients:	Percent
Sodium lauryl sulfate -----	17.6
Triethanolammonium lauryl sulfate -----	1.9
Isostearic acid -----	3.3
Potassium hydroxide (34.2%) -----	1.1
Lauric-myristic diethanolamide -----	1.5
Water -----	Balance

The above shampoo is prepared as in Example I and is a clear, stable, pourable liquid at room temperature having satisfactory foaming, cleansing and hair-conditioning properties.

EXAMPLES III-V

Ingredients:	Percent
Sodium lauryl sulfate -----	17.6
Triethanolammonium lauryl sulfate -----	1.9
Isostearic acid -----	1.5
Potassium hydroxide (34.2%) -----	1.1
Lauric-myristic diethanolamide -----	1.5
Ethylene glycol distearate -----	1.4
Water -----	Balance

The above shampoo formulations are prepared as in Example I with 1%, 2% and 4% distearate respectively. The 2% and 4% formulas were opaque and the 1% formula was slightly less opaque. All formulas had a satisfactory pH of about 8 and viscosities of about 30 seconds using the No. 5 Raymond flowmeter with desirable stability and effective cleansing and hair-conditioning properties.

EXAMPLE VI

A similar formulation is prepared as in Example III with a 1% content of isostearic acid, 0.5% double-pressed stearic acid and 3% ethylene glycol distearate. The resulting product is an effective, stable, pourable lotion shampoo whereas a similar product containing 1.5% stearic acid and free of isostearic acid is found to exhibit unsatisfactory stability.

EXAMPLE VII

Ingredients:	Percent
Sodium cocoyl N-methyl taurate -----	19
Isostearic acid -----	2
Ethylene glycol distearate -----	2
Potassium hydroxide (34.2%) -----	1
Lauric-myristic diethanolamide -----	1.5
Water -----	Balance

The above shampoo is prepared as in Example I and is a relatively thick, but pourable, effective foaming shampoo product also.

EXAMPLE VIII

Ingredients:	Percent
Disodium salt of 2-coco ¹ imidazolinium 1-lauryl sulfate 1-carboxymethoxyethyl 1-carboxymethyl -----	19
Isostearic acid -----	2
Ethylene glycol distearate -----	2
Potassium hydroxide (34.2%) -----	1
Lauric-myristic diethanolamide -----	1.5
Water -----	Balance

¹ Alkyl mixture derived from coconut oil comprising about 8% C₈, 7% C₁₀, 48% C₁₂, 18% C₁₄, 9% C₁₆ and 2% C₁₈.

The above formulation is prepared as in Example I and is an effective foaming shampoo product having a viscosity of 10 seconds using the No. 5 Raymond flowmeter.

EXAMPLE IX

Ingredients:	Percent
Triethanolammonium linear dodecyl benzene sulfonate -----	19
Isostearic acid -----	2
Ethylene glycol distearate -----	2
Potassium hydroxide (34.2%) -----	1
Lauric-myristic diethanolamide -----	1.5
Water -----	Balance

The above ingredients are prepared into a satisfactory lotion shampoo product having a 75 second viscosity using the Raymond flowmeter.

Although the present invention has been described with reference to particular embodiments and examples it will be apparent to those skilled in the art that variations and modifications of this invention can be made and that equivalents can be substituted therefor without departing from the principles and true spirit of the invention.

Having thus described the invention, what is claimed is:

1. A pourable, liquid shampoo consisting essentially of 15% to 30% by weight of an alkyl sulfate salt containing 12 to 18 carbon atoms in the alkyl group and selected from the group consisting of sodium and triethanolamine salts and mixtures thereof, 0.5% to 5% by weight of liquid isostearic acid having a titer of 10° C. maximum and containing a methyl group in the 8, 9 or 10 position, 1% to 5% by weight of ethylene glycol distearate, 1% to 10% by weight of a higher fatty acid alkylolamide selected from the group consisting of monoethanolamides, diethanolamides, and isopropanolamides of fatty acids containing 8 to 18 carbon atoms, and water, said shampoo being in the form of a stable, opaque lotion having a pH of 6.5 to 8.

References Cited

UNITED STATES PATENTS

2,812,342	11/1957	Peters -----	260—409
2,756,178	7/1956	Verblen -----	167—87
3,267,039	8/1966	Schneider -----	252—153

OTHER REFERENCES

Sagarin et al., *Cosmetics Science and Technology*, Sept. 16, 1957, pp. 387, 388, 390, 393, 398, 399, 403, 404.
Wells et al., *Cosmetics and the Skin*, 1954, pp. 397—413.
Rees, *American Perfumer and Cosmetic*, vol. 81, No. 4, pp. 37—42, April 1966.
Bennett, *The Chemical Formulary*, 1965, vol. XII, pp. 201—202.
The Condensed Chemical Dictionary, 7th edition, 1966, p. 527.

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