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STABLE LIQUID SHAMPOOS

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The present invention relates to opaque liquid shampoos and, more particularly, to such liquid shampoo compositions of the type of the anionic synthetic sulfated and sulfonated detergent salts.

This application is a continuation-in-part of my co-pending application Serial No. 175,013, filed July 20, 1950, now Patent No. 2,674,580, issued April 6, 1954, which discloses compositions consisting essentially of such a detergent salt, an aqueous medium, and a minor amount of behenic acid or a water soluble soap thereof or a mixture of the same which serves as an opacifying and stabilizing agent.

Further experience with such compositions has shown that the stability against phase separation may be remarkably improved under adverse conditions, for example, summer heat and long shelf storage.

In accordance with the present invention, an opaque liquid shampoo of improved stability against separation at elevated temperatures consists essentially of a mixture of a deterative salt from the group consisting of the water-soluble anionic sulfated and sulfonated deterative salts, an aqueous medium, a minor proportion of behenic acid, and a minor proportion of a highly hydrogenated castor oil. Preferably the liquid shampoo also contains sufficient amounts of a lower amine to impart pourability at temperatures as low as about 50° F. and of an acid

The novel compositions of the present invention contain as the active ingredient a water-soluble anionic sulfated or sulfonated detergent, or suitable mixtures thereof. Included therein are the aliphatic sulfated or sulfonated agents, such as the aliphatic acyl-containing compounds wherein the acyl radical has about 8 to about 22 carbon atoms, and more particularly, the aliphatic carboxylic ester type, containing at least about 10 and preferably about 12 to about 26 carbon atoms to the molecule. As suitable examples of aliphatic detergents may be found the sulfuric acid esters of polyhydric alcohols incompletely esterified with higher fatty acids, e. g. higher fatty acid monoglyceride sulfate detergent salts such as coconut oil monoglyceride monosulfate and tallow diglyceride monosulfate; the long chain pure or mixed higher alkyl sulfates, e. g. lauryl sulfate, cetyl sulfate, higher fatty alcohol sulfates derived from reduced coconut oil fatty acids; the hydroxy sulfonated higher fatty acid esters, e. g. higher fatty acid esters of 2,3 di-hydroxy propane sulfonic acid; the higher fatty acid esters of low molecular weight alkylol sulfonic acids; higher fatty acid amides of amino alkyl sulfonic acids, e. g. lauric amide of taurine, and the like.

Within the ambit of the invention are the alkyl aryl sulfonate detergents also though these are not preferred generally because of their great drying power. These aromatic sulfonate detergents are also known in the art. They may be mononuclear or polynuclear in structure. More particularly the aromatic nucleus may be derived from benzene, toluene, xylene, phenol, cresols, naphthalene, etc. The alkyl substituent on the aromatic nu-

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cleus may vary widely, as long as the desired detergent power of the active ingredient is preserved. While the number of sulfonic acid groups present on the nucleus may vary it is usual to have one such group present in order to preserve as much as possible a balance between the hydrophilic and hydrophobic portions of the molecule.

More specific examples of suitable alkyl aromatic sulfonate detergents are the higher alkyl aromatic sulfonates. The higher alkyl substituent on the aromatic nucleus may be branched or straight-chain in structure; it comprises moreover such groups as decyl, dodecyl, keryl, pentadecyl, hexadecyl, mixed long-chain alkyls derived from long-chain fatty materials, cracked paraffin wax olefins, polymers of lower mono-olefins, etc. Preferred examples of this class are the higher alkyl mononuclear aryl sulfonates wherein the alkyl group is about 8 to about 22, and preferably about 12 to 18, carbon atoms.

These various anionic detergents are to be used in the form of their water soluble salts such as the alkali metal and alkaline earth metal salts. Their concentration in the liquid compositions of the present invention is generally at least about 5% and usually between about 10% to 35% though it is preferred to use from 15% to 30% by weight of the composition.

In the compositions of the present invention it has not been determined whether the behenic acid is present as soap, free acid or a mixture of both, since it may be partially or totally neutralized by the lower amine. The behenic acid constituent, whether present in the form of soap, free acid or a mixture of both, acts to opacify the liquid shampoo and helps to maintain its creaminess at somewhat elevated temperatures with maintenance of proper fluidity. Is also acts as a hair conditioner to leave the hair lustrous and manageable. The amount of behenic acid to be used in formulation is variable and should be integrated with the concentration of the detergent in the liquid mixture in order to maintain the proper consistency. The amount of behenic acid will ordinarily be from about 0.5% to 10% by weight of the final composition, the ingredients being so proportioned to form an opaque liquid emulsion. Generally highly satisfactory results may be obtained in amounts of behenic acid of about 1% to about 5%. Where excessive amounts of behenic acid are employed, the liquid shampoo becomes too thick to pour, in addition to other disadvantages thus destroying the characteristic features of the present invention.

It is important in the present invention to use a hydrogenated castor oil having a melting point of at least about 180° F., and preferably about 185° to 189° F. Such hydrogenated castor oil in the liquid mixtures of the present invention performs the function of stabilizing the liquid emulsions against separation at temperatures of the order of 110° F. The amount of such hydrogenated castor oil will ordinarily be from about 0.25% to 3% by weight of the final composition. Generally highly satisfactory results may be obtained with amounts of such hydrogenated castor oil of about 0.5% to 1.5%. Where excessive amounts of hydrogenated castor oil are employed, the liquid shampoo becomes too thick to pour. Hydrogenated castor oil having a melting point lower than about 180° F. does not impart satisfactory stability to the shampoo.

These ingredients are proportioned and mixed with an aqueous base to form an opaque emulsion, generally of the oil-in-water type, wherein the detergent is partially dissolved in the aqueous phase and partially dispersed in fine particles throughout said solution to yield a milky or creamy liquid. The amount of aqueous base is variable but must be sufficient to yield proper fluidity or pourability to the composition, using controlled

amounts of solid ingredients. The amount of water will usually be above about 50% by weight and preferably above about 60% for optimum results.

Where a lower amine is used in accordance with the invention it may be a primary, secondary or tertiary aliphatic amine and may have up to four carbon atoms in each radical. Preferred are the alkylolamines such as mono-, di-, and triethanolamine and isopropanolamine. The lower aliphatic amine is beneficial to lower the pour point of the shampoo and it generally will be present in an amount from about 1% to 5% by weight of the composition in excess of the stoichiometric equivalent of the behenic acid present in the composition, although its effect is evident when lower amounts of the order of about 0.5% by weight of the entire composition are employed. It is preferred to utilize sufficient amine to obtain a product which pours well at 50° F.

For optimum results, the pH of the liquid shampoo should be within the range of about 5 to about 7.5 and preferably 7 or less, e. g. 5.8 to 7. Such a shampoo composition in use would tend to neutralize alkaline residues on the hair and scalp and serve to tone up the stratum by restoring to it a beneficial mild acidity. Moreover, the formation of the insoluble types of soap produced in hard water is inhibited by the maintenance of pH values generally unsuitable for their production. Such pH ranges appear to be eminently suitable for the stabilization of the active ingredients per se, particularly for the aliphatic carboxylic ester type of detergent salts such as the higher fatty acid monoglyceride monosulfates which are more liable to decomposition on the alkaline side.

The employment of a quantity of a lower amine which is 1% to 5% by weight of the composition in excess of the stoichiometric equivalent of the behenic acid present raises the pH of the mixture above 7.5. Therefore sufficient acid, preferably a weakly ionizing acid such as citric acid, is added to the mixture to adjust the pH to within the desired range of 5 to 7.5. The use of citric acid has the additional beneficial effect of providing a buffer to help maintain the pH within the desired range. Other acids which may be used in place of part or all of the citric acid include tartaric acid, succinic acid, benzoic acid, phosphoric acid and the like.

It is common to add various adjuvant materials to shampoo compositions. Thus, the shampoo ordinarily will contain a perfume which should be selected so as to be compatible with the character of the shampoo. Other ingredients which may be used in shampoos for imparting desired qualities to the hair after washing may be incorporated in the present compositions. Thus, hair conditioners or superfatting materials such as lanolin, fatty alcohols, fatty amides and fatty acids, may generally be used in minor proportions, e. g. up to about 5%. The higher fatty alcohols such as myristyl, cetyl and stearyl alcohols have the advantage of maintaining the foaming properties of the composition at a desirable high level usually. Among suitable amides are the higher fatty acid amides such as myristamide, palmitylamide, stearyl amide, palmitylethanolamide and myristylpropanolamide. Glycerine may be added up to about 10% generally. Coloring materials or dyes may be added to tint the liquid if desired. Similarly, whitening 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, tragacanth and the like may similarly be used as desired.

The following specific examples are further illustrative of the nature of the present invention, but it is to be understood that the invention is not limited thereto.

Example I

The following composition is a white opaque liquid cream shampoo particularly intended for use by persons with oily hair and scalp.

Part 1:	Percent
Detergent salt ¹ -----	25.00
Methyl p-hydroxy benzoate -----	0.15
Sodium benzoate -----	0.50
Water -----	61.25
Part 2:	
Lanolin -----	0.50
Behenic acid -----	3.00
Hydrogenated castor oil of melting point 185° F. -----	0.50
Part 3:	
Triethanolamine -----	3.00
Citric acid -----	0.70
Water -----	5.00
Part 4:	
Perfume oil -----	0.40

¹ Sodium salt of sulfated monoglyceride of hydrogenated coconut oil fatty acids. It may contain about 10% by weight of inorganic sulfate formed in its manufacture.

Part 1, the detergent salt in the form of dry chips, the preservatives and water, is heated to 185° F. and Part 2, which has been heated to about 205° F., is added thereto. The ingredients are mixed to form a homogeneous mixture and Part 3 is added. Part 4 is added when the mixture, which is continuously stirred, has cooled to 120° F. Stirring is continued until the mixture has been cooled to 80–90° F.

This formulation having a pH of about 6.7 is subjected to oven storage at 110° F. Under such conditions, the composition maintains its creaminess with no separation for over two months.

A similar formulation lacking the hydrogenated castor oil separates within one week during oven storage at 110° F.

Example II

The following is a satisfactory opaque liquid shampoo for use by persons with normal hair and scalp.

Part 1:	Percent
Detergent salt (same as Example I) -----	21.00
Methyl p-hydroxy benzoate -----	0.15
Sodium benzoate -----	0.50
Water -----	64.92
Part 2:	
Lanolin -----	0.50
Behenic acid -----	3.00
Hydrogenated castor oil of melting point 187° F. -----	0.75
Part 3:	
Triethanolamine -----	3.00
Citric acid -----	0.78
Water -----	5.00
Part 4:	
Perfume -----	0.40

The parts are mixed as described in Example I. The pH of the product is about 6.6.

Example III

The composition of a satisfactory opaque liquid shampoo for use by persons with dry hair is as follows:

Part 1:	Percent
Detergent salt (same as Example I) -----	18.00
Methyl p-hydroxy benzoate -----	0.15
Sodium benzoate -----	0.50
Water -----	67.84
Part 2:	
Lanolin -----	0.50
Behenic acid -----	3.00
Hydrogenated castor oil of melting point 182° F. -----	0.75
Part 3:	
Triethanolamine -----	3.00
Citric acid -----	0.86
Water -----	5.00

	Percent
Part 4:	
Perfume oil	0.40

The parts are mixed according to the procedure outlined in Example I. The pH of the product is about 6.7

Example IV

A further satisfactory liquid cream shampoo may be prepared from the following formulation:

	Percent
Part 1:	
Detergent salt ¹	20.0
Water	63.65

Part 2:	
Behenic acid	3.5
Hydrogenated castor oil of melting point 183° F.	0.75

Part 3:	
Triisopropanolamine	3.0
Citric acid	0.8
Water	8.0

Part 4:	
Perfume oil	0.3

¹ Sodium lauryl sulfate.

The parts are mixed according to the procedure of Example I. The product has a pH of about 7.0

Example V

A further satisfactory liquid cream shampoo may be prepared from the following formulation:

	Percent
Detergent salt (sodium lauryl sulfate)	15.0
Behenic acid	3.5
Hydrogenated castor oil (M. P. about 187° F.)	0.5
Water	Balance

The pH is adjusted to about 7.0 by sodium hydroxide. Any other suitable alkaline material may also be used, as set forth in my said copending application.

As indicated above in Example I, the method of manufacture is relatively simple. In general, the solid ingredients are to be melted and stirred into the aqueous medium at elevated temperatures to form a homogeneous mixture, the mixture is partially cooled and perfume added, whereupon the opaque liquid shampoo may be further cooled and bottled or otherwise prepared for use. Other methods of manufacture may be employed if desired including continuous proportioning of the ingredients into a mixing apparatus where the ingredients are thoroughly blended at elevated temperatures and thereafter cooled to the desired temperature.

The term "consisting essentially of" as used in the definition of the ingredients present in the composition claimed is intended to exclude the presence of other materials in such amounts as to interfere substantially with the properties and characteristics possessed by the composition set forth but to permit the presence of other materials in such amounts as not substantially to affect said properties and characteristics adversely.

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 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. An opaque liquid shampoo consisting essentially of about 5 to 35% by weight of a detergent salt from the group consisting of water-soluble anionic sulfated and sulfonated detergent salts, about 0.5 to 10% by weight of behenic acid present therein as an opacifying and stabilizing agent, about 0.25 to 3% by weight of a highly hydrogenated castor oil having a melting point of at least about 180° F., and water in an amount sufficient to prepare a fluid composition, said shampoo having a pH of from 5 to 7.5.

2. An opaque liquid shampoo as set forth in claim 1 in which the behenic acid is present at least in part as a soap.

3. An opaque liquid shampoo as set forth in claim 1 in which a lower aliphatic amine is present in an amount sufficient to lower the pour point.

4. An opaque liquid shampoo as set forth in claim 3 which contains sufficient weakly ionizing acid to impart thereto said pH of about 5 to 7.5.

5. An opaque liquid shampoo consisting essentially of a mixture of about 5% to 35% by weight of an organic non-soap detergent selected from the group consisting of water-soluble anionic sulfated and sulfonated detergent salts, about 0.5% to 10% by weight of behenic acid, an amount of a lower aliphatic amine selected from the group consisting of primary, secondary, and tertiary alkyl or alkylolamines having up to 4 carbon atoms in each alkyl or alkylol radical which is 1% to 5% by weight of said liquid shampoo in excess of the stoichiometric equivalent of said behenic acid, sufficient citric acid to impart a pH of between 5 and 7.5 to said liquid, about 0.25% to 3% by weight of hydrogenated castor oil having a melting point of at least about 180° F., and at least about 50% by weight of water.

6. An opaque liquid shampoo as set forth in claim 5 wherein the detergent is a salt of a sulfated higher fatty alcohol.

7. An opaque liquid shampoo as set forth in claim 5 wherein the detergent is a salt of a sulfated higher fatty acid monoglyceride.

8. An opaque liquid shampoo as set forth in claim 5 wherein the lower aliphatic amine is triethanolamine.

9. An opaque liquid shampoo consisting essentially of a mixture of about 25% by weight of a water-soluble higher fatty acid monoglyceride sulfate detergent salt, about 3% by weight of behenic acid, about 3% by weight of triethanolamine, about 0.5% by weight of hydrogenated castor oil having a melting point not lower than about 180° F., about 0.7% by weight of citric acid, said mixture having a pH from 5 to 7.5, and at least about 50% by weight of water.

10. An opaque liquid shampoo consisting essentially of a mixture of about 21% by weight of a water soluble higher fatty acid monoglyceride sulfate detergent salt, about 3% by weight of behenic acid, about 3% by weight of triethanolamine, about 0.75% by weight of hydrogenated castor oil having a melting point not lower than about 180° F., about 0.78% by weight of citric acid, said mixture having a pH of from 5 to 7.5, and at least about 50% by weight of water.

11. An opaque liquid shampoo consisting essentially of a mixture of 18% by weight of a water soluble higher fatty monoglyceride sulfate detergent salt, about 3% by weight of behenic acid, about 3% by weight of triethanolamine, about 0.75% by weight of hydrogenated castor oil having a melting point not lower than about 180° F., about 0.86% by weight of citric acid, said mixture having a pH of from 5 to 7.5, and at least about 50% by weight of water.

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