

June 11, 1946.

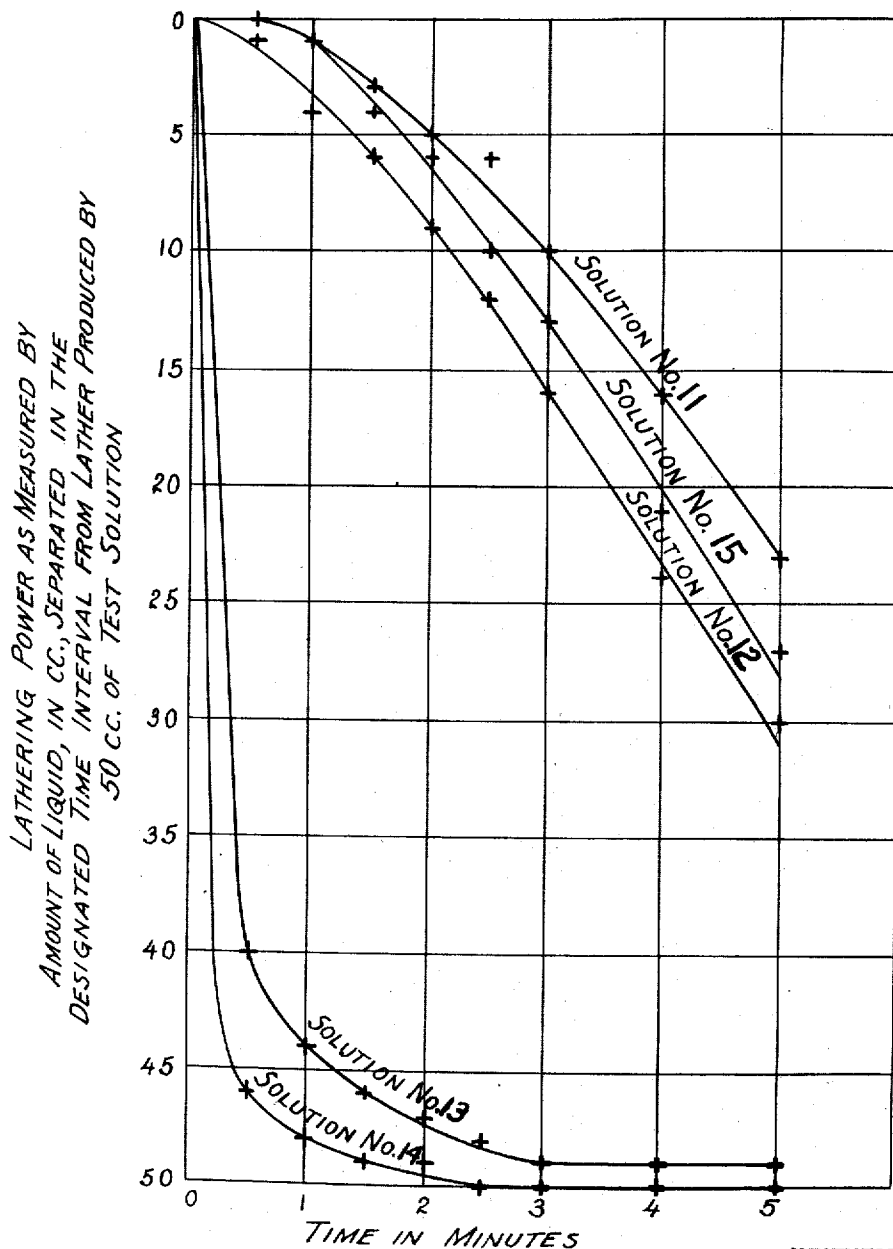
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2,401,726

DETERGENT COMPOSITION

Filed April 8, 1943

GRAPH OF TABLE 4, EXAMPLE 4,



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2,401,726

DETERGENT COMPOSITION

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Application April 8, 1943, Serial No. 482,286

15 Claims. (Cl. 252-161)

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The present invention relates to detergent compositions containing as an essential detergent ingredient one or more water-soluble salts of higher alkyl esters of sulfuric acid described more fully below, especially in the form of concentrated aqueous solutions.

The invention relates more particularly to detergent compositions comprising one or more of the said salts, which compositions in the dry form or in the form of solutions are especially adapted for use as shampoos.

The provision of a shampoo composition which will remove soil and body waste products from human hair without causing harmful or objectionable effects has occupied the attention of manufacturers of cosmetic products for a long time. Soaps of various kinds were tried, but even the best of them have the objection, being salts of fatty acids, that they hydrolyze in water, giving alkali which attacks the hair and makes it brittle. Further, soaps leave a scum on the surface of the hair, especially when used with hard water, necessitating the use of lemon, vinegar or other rinses to remove it.

The salts which constitute an essential detergent ingredient of the compositions of the present invention are the water-soluble detergent salts of long-chain monoalkyl esters of sulfuric acid containing at least 12 carbon atoms in the alkyl radicals thereof (herein termed "higher alkyl sulfates"). In their free acid form, they may be represented by the general formula



in which R stands for an alkyl radical of 12 or more carbon atoms, such as, lauryl, myristyl, cetyl, oleyl, etc. They are derivable from sulfuric acid and any of a wide variety of aliphatic alcohols (e. g., straight- and branched-chain aliphatic alcohols, including unsaturated alcohols) containing at least 12 carbon atoms, and especially 12 to 18 carbon atoms. Inasmuch as alcohols of this class derived from naturally-occurring fatty acids are frequently used in the preparation of the higher alkyl sulfates, when manufactured from said alcohols, the higher alkyl sulfates are ordinarily mixtures of compounds rather than single compounds. An outstanding example of this class of alkyl sulfates is the mixture of higher alkyl sulfates designated lauryl sulfate and prepared from commercial lauryl alcohol which is derived from the mixed fatty acid glycerides of coconut oil.

When the water-soluble detergent salts of long-chain monoalkyl esters of sulfuric acid were

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placed upon the market in the form of their sodium salts, a partial advance was made toward solution of the problem of providing satisfactory shampoo compositions, since the said detergent salts are not affected by hard water and their aqueous solutions are relatively neutral, with the result that the harmful effects of alkali and the scum resulting from the use of soap were absent. The problem was not fully solved, however, because certain of the properties of said detergent salts make them unsuitable for use in preparing shampoo compositions for use on the human scalp.

Thus, although the sodium salts of the compounds having the most desirable cleansing action (e. g., sodium lauryl sulfate), have good detergent power and are neutral in character, attempts to employ them alone or in an unmodified form for cleaning applications in which their lathering properties are especially desirable, and particularly for use in shampoos, have not been entirely successful. This is due to a number of factors related to the requirements of an acceptable shampoo, and the properties of the said higher alkyl sulfates. In order for a shampoo to be commercially acceptable, it should have good lathering power. Further, it should be an effective cleansing agent for the hair and scalp, but it should not possess the objectionable property of removing too much oil from the hair and scalp and leaving these in an excessively dry state. Further, the aqueous solutions of a shampoo preferably should be stable over a wide range of temperatures, and have a fair degree of viscosity.

The above higher alkyl sulfates in themselves do not have all these required properties. Thus for aqueous solutions of these salts alone to have strong lathering powers when the solutions are used in the usual small amounts, the salts must be present in substantial concentration. But when a concentrated aqueous solution of one of these salts is used in sufficient amounts to produce a satisfactory lather, its defatting power is, in general, too drastic; for, not only is it effective in cleansing the hair and scalp, but also it removes an excessive quantity of the natural oils from the hair and scalp. In the case of barbers and beauty parlor operators who, as a rule, manipulate shampoos with bare hands, this is especially objectionable because the removal of the natural oils from their hands by the continual use of the solutions leads to cracking of the skin. Solutions of this type obviously are objectionable if used as shampoos for dry hair and scalp. Attempts have been made to overcome such objec-

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tionable effects by emulsifying oils in the shampoo compositions or by adding rosin soap or other similar substances, but such a handling of the problem is obviously only a makeshift.

These concentrated solutions sometimes have a further disadvantage, resulting from the fact that the solubilities of the said salts in water vary greatly with changes in temperature. Thus, a concentrated aqueous solution of a higher alkyl sulfate in the form of a neutral alkali metal salt (e. g., a sodium salt) may be prepared so as to be perfectly clear at the temperature of preparation. However, on lowering the temperature of such a solution, it becomes supersaturated and for a time persists as a clear solution, but then it precipitates to yield a cloudy solution or unsightly mixture. This characteristic of the detergent salts is objectionable, particularly when they are to be used or marketed in the form of their concentrated solutions; accordingly, solutions containing the detergent salts, particularly when intended for small consumers or household users, frequently contain water-soluble solvents (as for example, monophenyl ether of ethylene glycol, cyclohexanol, carbitol, diethylene glycol, etc.) as aids to prevent precipitation and gelling. Additions of this kind are frequently of slight effect, and are objectionable because they are expensive and sometimes malodorous. Often their effect is only temporary, so that on prolonged standing the objectionable precipitates are formed. The tendency to form supersaturated solutions which on standing and/or cooling become unsightly, cloudy or gelatinous is common to all the higher alkyl sulfate detergents and is independent of the nature of the alkyl group, though it may vary in degree. Thus branching in the alkyl group or the presence of double bonds reduces the tendency somewhat.

In an attempt to produce solutions having the desired viscosity and solubility characteristics, the higher alkyl sulfates have been employed in the form of other detergent salts having greater solubility in water; such as their ammonium and ethanolamine salts, and particularly their triethanolamine salts. But the increased solubility only increases the difficulties arising in other respects; namely, the emulsifying and defatting action on the natural oils of the hair, scalp and skin.

It is an object of this invention to prepare detergent compositions which contain as the essential detergent ingredient one or more water-soluble detergent salts of long-chain monoalkyl esters of sulfuric acid containing at least 12 carbon atoms in the alkyl radical thereof, but which are particularly well adapted for use in shampoos and for related purposes, and are superior in their characteristics to compositions containing one or more of the said detergent salts only.

A further object of this invention is to provide compositions adapted for use as shampoos which contain as an essential detergent ingredient one or more of the above described detergent salts, which compositions do not have the objectionable properties of the known shampoos containing such detergent salts.

An additional object of the invention is to provide compositions comprising aqueous solutions containing one or more of the above described detergent salts, which compositions lather freely and may be produced economically.

Another object of the invention is to provide compositions comprising concentrated aqueous solutions containing one or more of the above

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described detergent salts, which solutions lather freely and have detergent power but limited defatting power, so that they may be used as shampoos without injury to the hair, scalp, or skin.

Other objects of the invention in part will be obvious and in part will appear hereinafter.

It has been discovered in accordance with the present invention that detergent compositions which contain as the essential detergent ingredient at least one water-soluble detergent salt of a long-chain monoalkyl ester of sulfuric acid containing at least 12 carbon atoms in the alkyl group thereof can be made substantially free from the above-discussed disadvantages of the said detergent salts when used alone, by associating, with one or a mixture of these detergent salts, one or a mixture of compounds of the class described more fully below, in certain proportions. (For simplicity in terminology, a compound of said class, whether used singly or in admixture with one or more other compounds of said class, is referred to herein as "a stabilizing agent.") The compositions may be in the form of dry mixtures which are readily soluble in water, and therefore can be applied directly to the hair and scalp. Because of their enhanced solubility and lower costs as compared with compositions which contain water-soluble solvents and the like, they are especially attractive as shampoos, washing agents for delicate fabrics, rugs, furniture, etc., and washing and cleaning generally in household arts and specialized washing processes of a similar nature. They may also be in the form of aqueous solutions, in which form they are particularly adapted for use as shampoos, especially for "dry" hair, and for the washing of fine fabrics, upholstery and rugs.

Thus, it has been found that by associating at least one-half part by weight of a stabilizing agent (such as sodium octyl sulfate) with about one part by weight of a higher alkyl sulfate of the above class (such as sodium lauryl sulfate), compositions are obtained which can be employed for the preparation of concentrated aqueous solutions that have lathering powers considerably in excess of the lathering powers of solutions containing the same amount of the higher alkyl sulfate, but omitting the stabilizing agent. In fact, aqueous solutions containing a mixture of a higher alkyl sulfate and a stabilizing agent in a certain total concentration of said components can be prepared which possess substantially the same lathering power as a solution having a concentration of the higher alkyl sulfate alone equal to this total concentration.

This result is surprising. Although it is known that aqueous solutions of the stabilizing agents have poor, if any, foaming properties, yet, according to the present invention, additions of the said stabilizing agents to aqueous solutions of the detergent salts have the unexpected effect of markedly increasing the foaming of the said solutions; as if the stabilizing agents functioned in place of an additive quantity of detergent salt.

The compositions of the present invention in the form of aqueous solutions have the important advantage over solutions of the detergent salts alone in that, while they have substantially equal lathering powers and satisfactory cleansing properties, they have weaker defatting properties and therefore, when used for shampooing the hair, do not remove an excessive amount of oil from the hair, scalp, or skin.

As before pointed out, it is important that commercial shampoos in the form of solutions should

remain clear at relatively low temperatures; that is, they should have relatively low turbidity points. The further surprising discovery has been made that, by adding the stabilizing agents to aqueous solutions of the above-described detergent salts of sufficient concentration to be turbid to solid at room temperature, solutions can be formed which not only do not have higher turbidity points than the aqueous solutions of the alkyl ester salts, but also in such cases the turbidity points are lower. Thus it has been found that the said detergent salts can be prevented from precipitating from their solutions and their solutions can be retained fluid and clear, even at temperatures of about 0° C., by associating a stabilizing agent with the detergent salt in aqueous solution. It has been found feasible to prepare from the compositions of the present invention highly concentrated aqueous solutions which remain clear even on long standing at average atmospheric temperatures (e. g., 20° to 30° C.) while aqueous solution of the same detergent salt at equal concentrations, but not containing a stabilizing agent, are very prone to precipitate and to gel when stored even for short periods of time at the said average temperatures. Because of this property of the stabilizing agents, it has been found that aqueous solutions can be prepared having sufficiently high total content of detergent salt and stabilizing agent to give the solutions excellent lathering properties, and yet, despite the highly concentrated nature of the solutions, their turbidity points are such that they may be handled and stored at ordinary household temperatures without developing turbidity. Even in the case of ammonium and ethanolamine salts of the higher alkyl sulfuric acids, which have improved solubility in water as compared with the sodium salts, the stability of their aqueous solutions is greatly improved by the addition of a stabilizing agent, such as, sodium 2-ethyl-hexyl sulfate) in accordance with the present invention.

The compositions of the present invention are distinctive in that they can be so compounded that desired viscosities and clarities of their aqueous solutions can be attained readily, and yet their content of detergent salt may be adjusted to their intended use on "oily" or "dry" hair and scalp. This advantage arises from the novel use, in these compositions, of the large proportions of stabilizing agents which have neither detergent nor degreasing qualities in themselves.

The stabilizing agents used in accordance with the present invention are composed of at least one organic compound which is an anion-active polar-nonpolar water-soluble salt having within its molecule a salt-forming group that induces solubility in water and at least one alkyl group containing 5 to 11 carbon atoms but not more than 9 carbon atoms in a straight carbon chain, and having no alkyl group containing more than 11 carbon atoms nor more than 9 carbon atoms in a straight carbon chain. Preferably the stabilizing agents are composed of at least one compound which is a water-soluble salt of a monoalkyl ester of an acid selected from the group consisting of sulfuric acid and sulfo-aliphatic mono-carboxylic acids containing 2 to 4 carbon atoms, said monoalkyl ester salt containing 5 to 11 carbon atoms but not more than 9 carbon atoms in a straight carbon chain in the alkyl radical thereof; that is, water-soluble salts of mono-alkyl esters of sulfuric acid containing 5 to 11 carbon atoms but not more than 9 carbon atoms in a straight carbon chain in the alkyl radicals thereof, and water-

soluble salts of monoalkyl esters of sulfo aliphatic mono-carboxylic acids containing 2 to 4 carbon atoms in the acyl radicals and containing 5 to 11 carbon atoms in the alkyl radicals but not more than 9 carbon atoms in a straight carbon chain. Thus, the preferred stabilizing agents are composed of one or more water-soluble monoalkyl esters of sulfuric acid, sulfoacetic acid, sulfopropionic acid, or sulfobutyric acid, wherein the alkyl groups contain 5 to 11 carbon atoms, but not more than 9 carbon atoms in a straight chain.

The stabilizing agents are preferably used in the form of their neutral salts, such as their alkali metal (including ammonium) salts and organic amine salts, particularly the sodium, potassium, ammonium, and ethanolamine salts. They include commercial forms of the salts which contain, in addition to water-soluble organic compounds of the type above defined, substantial amounts of inorganic salts, such as sodium chloride and sodium sulfate.

The stabilizing agents which contain 6 to 8 carbon atoms in the alkyl groups thereof are generally to be preferred for use in the compositions of the present invention; and those are especially preferred in which the alkyl groups are octyl groups, especially 2-ethyl-hexyl groups, particularly when in the form of monoalkyl esters of the above class.

Specific examples of compounds which may be used singly or in the form of mixtures as stabilizing agents in the compositions are the following: neutral sodium, potassium, ammonium, and ethanolamine salts of normal hexyl sulfoacetate, secondary hexyl sulfoacetate, mono-normal hexyl sulfate, mono-2-ethyl-butyl sulfate, heptyl sulfoacetates, normal octyl sulfate, normal octyl sulfoacetate, secondary octyl sulfoacetate, 2-ethyl-hexyl sulfoacetate, mono-2-ethyl-hexyl sulfate, 2'-ethyl-hexyl sulfobutyrate, mono-nonyl sulfate, and an undecyl sulfoacetate in which the alkyl group contains a branched carbon chain in which not more than 9 carbon atoms are in a straight chain.

The stabilizing agents alone are at best weak lathering agents and in some cases display no lathering properties at all. Nevertheless, these agents have surprisingly been found to possess the ability of increasing the lathering properties of the detergent salts described above. At the same time, since the stabilizing agents have substantially no defatting properties, the aqueous solutions of mixtures of the detergent salts and stabilizing agents in general are less drastic in their defatting action than aqueous solutions of the detergent salts alone having the same lathering properties. The reason why the stabilizing agents do not raise the turbidity points of aqueous solutions of the long-chain alkyl sulfates, but instead act to lower the turbidity points of such solutions, is not clearly understood. Whatever the theoretical explanation of the action of the stabilizing agents may be, the compositions of the present invention, containing the stabilizing agents in association with the long-chain alkyl sulfates, so combine the excellent cleansing and lathering powers of the latter compounds with the lather-inducing and stabilizing powers of the stabilizing agents that the concentrated aqueous solutions of the compositions are characterized by the controlled washing and high lathering qualities, the stability, and the clarity which are demanded of the highest quality shampoos; yet they do not have the excessive defatting powers that are an objectionable feature of the ordinary

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aqueous solutions of the long-chain alkyl sulfates.

As previously indicated, the long-chain alkyl sulfates used in the compositions of the present invention may be single compounds or mixtures of compounds. They may be in the form of pure compounds or in commercial forms, including mixtures of salts which contain, in addition to the long-chain alkyl sulfates, substantial amounts of inorganic salts, such as sodium chloride and sodium sulfate. They may be derived from any source, but preferably they are made from mixtures of alcohols prepared by hydrogenation of the lower alkyl esters of mixtures of higher fatty acids derived from fats and oils by saponification. Aqueous solutions of water soluble salts of monoalkyl sulfates in which the alkyl groups contain from 12 to 15 carbon atoms are far superior in foaming power to similar solutions of the monoalkyl sulfates with alkyl groups which contain more than 15 carbon atoms, and therefore the monoalkyl sulfates with 12 to 15 carbon atoms are preferred for use in shampoos. Aqueous solutions of monoalkyl sulfates in which the alkyl groups contain more than 18 carbon atoms foam even less than similar solutions of monoalkyl sulfates in which the alkyl groups contain from 12 to 18 carbon atoms, which have limited foaming power; but minor amounts of alkyl sulfates with more than 15 carbon atoms may be present along with the alkyl sulfates of 12 to 15 carbon atoms without seriously affecting the foaming power of the mixture. Hence, a valuable mixture of monoalkyl sulfates can be made from commercial lauryl alcohol which is obtained as a mixture of alcohols from coconut oil, for example, by hydrogenation of the lower alkyl esters of the mixture of higher fatty acids resulting from saponification of coconut oil. Such a commercial mixture of monoalkyl sulfates contains a preponderating amount of mono-lauryl and mono-myristyl sulfates with relatively small amounts of higher and lower alkyl sulfates. (In referring to a lauryl sulfate or other long-chain alkyl sulfate herein and in the claims, it will be understood that unless otherwise specified the commercial product as well as the substantially pure compound is intended.) Particularly valuable compositions are obtained with the use of such commercial lauryl sulfates, preferably in the form of the sodium, ammonium or alkylolamine salts. Compositions containing these compounds and a stabilizing agent, especially a stabilizing agent containing a compound having a 2-ethylhexyl group, are particularly valuable for use as shampoos.

The compositions of the present invention are conveniently prepared in a simple manner by dissolving suitable amounts of the long-chain alkyl sulfate and the stabilizing agent in water, or by mixing the long-chain alkyl sulfate and the stabilizing agent in the dry state in proportions such that the resulting mixture may be dissolved in water to produce an aqueous solution having the desired properties of detergency, lathering, and solubility; the components and proportions to be employed in any particular case being dependent upon the properties which it is desired to have the resulting composition possess. Because of the variable properties of the compounds composing the stabilizing agents, in some cases it may be advantageous to employ a stabilizing agent composed of two or more of such compounds rather than one consisting of a single compound.

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In connection with the proportioning of the components of the compositions, it should also be noted that while the above-described long-chain alkyl sulfates, as a class, possess the properties described herein, individual members of the class differ one from another in the degree in which they possess one or more of these properties. Hence, no general rule as to the optimum specific proportions is applicable to all mixtures. However, it can be stated that, to produce the beneficial results of the present invention, the amount of stabilizing agent should be not less than one-half part by weight for each part by weight of the long-chain alkyl sulfate or mixture of long-chain alkyl sulfates; and, as a general rule, the compositions preferably should not contain more than four parts by weight of stabilizing agent for each part by weight of the long-chain alkyl sulfate or mixture of long-chain alkyl sulfates. The preferred compositions of the invention contain from about one to about two and one-half parts by weight of the stabilizing agent for each part by weight of the long chain alkyl sulfate or mixture of long-chain alkyl sulfates. While, as already noted, the long-chain alkyl sulfate detergents and the stabilizers may be used in forms which include substantial amounts of inorganic salts in addition to the desired organic salts, the proportions referred to herein and in the claims are based on the organic salt contents of the long-chain alkyl sulfate detergents and the stabilizers.

It is known that commercial forms of the long-chain alkyl sulfates derived from alcohols produced from coconut oil by hydrogenation, such as those known in the trade as "Gardinols," "Orvus WA," "Dreft," etc., may contain lower alkyl sulfates, such as monohexyl-, monooctyl-, and monodecyl-sulfates, incidentally present in small amounts. These lower alkyl sulfates, if present, are in such small amounts, however, in comparison with the total amounts of long-chain alkyl sulfates which are present, that they fail to exert a material effect upon the lathering properties of the alkyl sulfate mixtures, or upon the solubility of the alkyl sulfate mixtures in water at ordinary atmospheric temperatures, or upon the emulsifying and defatting action of the alkyl sulfate mixtures on the natural oils of the hair, scalp and skin.

In preparing the compositions of the invention in the form of aqueous solutions, in order for the solutions to possess adequate cleansing and lathering powers, it is necessary that the combined content of long-chain alkyl sulfate and stabilizing agent should constitute at least three and one-half per cent, and preferably at least ten per cent by weight of the solutions. Further, to avoid high turbidity points, the solutions preferably should not have more than 50 per cent combined content of long-chain alkyl ester salt and stabilizing agent. In fact, for most purposes, solutions having a combined content of said components of not more than 35 per cent are preferable. The preferred solutions, therefore, are those which have a total content of long-chain alkyl sulfate and stabilizing agent of from 10 to 35 per cent.

When making up these solutions, it will be understood that the proportioning of the ingredients will be dependent upon the concentrations of the solutions as well as upon the specific long-chain alkyl sulfates and stabilizing agents used. The preferred solutions of the present invention are those which remain clear above 10° C.

and, after being precipitated, clear up below 20° C. By applying the above principles with respect to the proportioning and selection of ingredients, concentrated solutions can be prepared having turbidity points of this nature.

A property of aqueous solutions of the long-chain alkyl sulfates intended for use as shampoos and for related purposes which is of some importance is the viscosity of the solutions. While this property is not an indication of the basic functional worth of the solutions, it does have an effect on their merchantability. As noted above, the viscosity of aqueous solutions of the higher alkyl sulfates may be controlled by the amount and character of stabilizing agent incorporated therein. Thus it has been found that as the amount of stabilizing agent is increased in proportion to the amount of higher alkyl sulfates, the viscosity of the solution decreases to a minimum and then increases rapidly.

In order to obtain a solution having the detergent and lathering properties in the degree desired in a particular instance, which properties are dependent in some measure upon the specific properties of the long-chain alkyl sulfate and the stabilizing agent, it may not be feasible to employ an amount of stabilizing agent such as to impart optimum viscosity characteristics to the solution. The viscosity may be increased, however, without adversely affecting the action of the stabilizing agent and, in some cases, with increased efficacy, by including one or more of the following additional substances in the compositions: a highly soluble salt of the type represented by ammonium sulfate, sodium citrate, sodium tartrate, and sodium maleate (especially in connection with compositions containing highly soluble stabilizing agents and a total concentration of long-chain alkyl sulfate and stabilizing agent of about 15 to about 50 per cent); a gum of the type represented by gum karaya, locust bean gum, and gum tragacanth (especially in connection with compositions containing a total concentration of long-chain alkyl sulfate and stabilizing agent of about 5 to about 15 per cent); and a water-soluble alkyl ether of cellulose (for example, a commercial methyl cellulose sold under the name of "Methocel"). The inclusion of a gum or cellulose ether in the compositions not only increases the viscosity of their aqueous solutions, but also increases the stability of the foam or lather which they produce on use.

The compositions also may contain one or more other substances tending to improve their appearance and salability in other respects; for example, a coloring agent, a perfume, etc.

The following examples are given to illustrate the invention. The parts are by weight and temperatures are in degrees centigrade.

Example 1.—Aqueous solutions were made of commercial sodium lauryl sulfate ("Gardinol 200," comprising about 70 per cent sodium higher monoalkyl sulfates and about 30 per cent of inorganic salt, mainly anhydrous sodium sulfate), with and without the addition of sodium 2-ethyl-hexyl sulfoacetate (technical grade, containing about 70 per cent of the sulfoacetate and about 30 per cent of inorganic salt, mostly sodium chloride). In preparing the solutions, the ingredients were warmed to obtain homogeneous solutions, and then slowly cooled. The temperatures at which turbidity appeared in the resulting solutions on cooling, and the temperatures at which the turbidity disappeared on

warming the turbid liquids were noted. The results obtained are set out in the following table:

Table 1

Solution No.	Composition of 100 parts of solution by weight			Turbidity appeared on cooling to—	Turbidity disappeared on heating to—
	Commercial sodium lauryl sulfate	Technical sodium 2-ethyl-hexyl sulfoacetate	Water		
1	26 (18.2)	None	74	80	85
2	10 (7)	None	90	18	27
3	10 (7)	16 (11.2)	74	3	14

¹ Content of organic salt.

Solution No. 1 above, a 26 per cent solution of commercial sodium lauryl sulfate in water, on being cooled slowly, became slightly turbid at about 80°, milky at about 36°, pasty at about 20°, and solid at about 5°. When heated slowly, the mass became clear liquid at about 85°.

The results recorded in the foregoing table show the surprising effect which the addition of a stabilizing agent composed of sodium 2-ethyl-hexyl sulfoacetate has on the turbidity points of aqueous solutions of a representative higher alkyl sulfate, sodium lauryl sulfate. Because of this effect, aqueous solutions of sodium lauryl sulfate which remain clear at low temperatures can be prepared containing an amount of sodium lauryl sulfate such that, in the absence of the sodium 2-ethyl-hexyl sulfoacetate, the solutions would become turbid at a higher temperature.

Example 2.—Aqueous solutions of ammonium lauryl sulfate prepared from commercial lauryl alcohol, and substantially free from inorganic salt were prepared alone and with the addition of sodium 2-ethyl-hexyl sulfate substantially free from inorganic salt, in a manner similar to that above described in Example 1. The temperatures at which turbidity appeared in the resulting solutions on cooling and the temperatures at which turbidity disappeared on warming the turbid liquids were noted and are set out in the following table:

Table 2

Solution No.	Composition of 100 parts of solution (by weight)			Turbidity appeared on cooling to—	Turbidity disappeared on heating to—
	Ammonium lauryl sulfate	Sodium 2-ethyl-hexyl sulfate	Water		
4	9	None	91	0	23
5	9	9	82	-2	0
6	9	18	73	-5	0

Example 3.—Aqueous solutions of commercial sodium lauryl sulfate ("Gardinol 140" comprising about 73.8 per cent sodium lauryl sulfate and about 26.2 per cent of inorganic salt, mainly sodium sulfate) were made with and without the addition of sodium n-octyl sulfate (technical grade containing 90 per cent of the organic sulfate and 10 per cent of inorganic salt) in a manner similar to that described in Example 1. The temperatures at which turbidity appeared in the resulting solutions on cooling and the temperatures at which turbidity disappeared on warming the turbid liquids were noted. The viscosities of the solutions were also measured by warming each of the solutions to about 32°, transferring it to a 25 cc. pipette in which it was allowed to cool to 30°.

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and noting the time in seconds required to run the solution at 30° out of the pipette from the 25 cc. mark. The results are set out in the following table in which parts are by weight.

Table 3

Solution No.	Composition of 100 parts of solution			Turbidity appeared on cooling to—	Turbidity disappeared on heating to—	Time in seconds required to run 25 cc. of solution at 30° from pipette
	Commercial sodium lauryl sulfate	Technical sodium n-octyl sulfate	Water			
7.....	10	0	90	Degrees 6	Degrees 31	24
8.....	10	10	80	—2	21	26
9.....	10	20	70	—4	0	32
10.....	10	30	60	—7	0	60
Control.....			100			23

The following examples illustrate the property of the stabilizing agent of increasing the lathering properties (used herein to denote generically foaming, frothing and lathering properties) of aqueous solutions of the higher alkyl sulfates.

In determining the lathering properties of the aqueous solutions, an apparatus was used consisting of a 500 cc. cylindrical graduate and a plunger consisting of a No. 9 rubber stopper, having a top diameter of about an inch and three-quarters, a bottom diameter of about an inch and five-eighths, a height of about a half inch, and six holes of about one-eighth inch diameter running from top to bottom of the stopper, placed equidistant from each other and about midway between the center and outer edge of the stopper, the said stopper being mounted along its longitudinal axis at the end of a glass-rod extending well above the top of the graduate. The stopper was of such size that it slipped easily inside the cylinder. To measure the lathering power of a solution, 50 cc. of said solution were placed in the graduate and a lather was generated by plunging the stopper into and withdrawing it from the solution in uniform strokes between the bottom and 200 cc. mark of the graduate at the rate of about two strokes per second for 30 seconds. The solutions were tested at the same temperature, and time intervals were measured by a stop watch. After lather had been generated, the volume of liquid at the bottom of the graduate was measured at half minute intervals for three minutes and at one minute intervals for the next two minutes. The smaller the amount of liquid separated, the greater was the lathering power of the solution under test.

Example 4.—The following solutions were prepared and tested for lathering power as described above:

Solution No. 11.—3.0 grams of "Gardinol 140" (a commercial sodium lauryl sulfate containing 73.8 per cent by weight of organic detergent and 26.2 per cent by weight of inorganic salt) were dissolved in 1000 cc. of water. (Content of organic salt=0.00221 gm./cc.)

Solution No. 12.—40 cc. of the above solution were diluted to 100 cc. with water. (Content of organic salt=0.000884 gm./cc.)

Solution No. 13.—3.0 grams of commercial sodium n-octyl sulfate (containing 90 per cent by weight of sodium n-octyl sulfate and 10 per cent by weight of inorganic salt) were dissolved in 1000 cc. of water. (Content of organic salt=0.0027 gm./cc.)

Solution No. 14.—60 cc. of the n-octyl sulfate

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solution were diluted to 1000 cc. with water. Content of organic salt=0.00162 gm./cc.)

Solution No. 15.—40 cc. of solution No. 11 were mixed with 60 cc. of solution No. 13 (Content of organic detergent=0.000884 gm./cc. Content of stabilizing agent=0.00162 gm./cc. Proportions by weight of stabilizing agent to long-chain alkyl sulfate=16.2:8.84.)

The results of the lathering tests are recorded in the following table, in which the average experimental error is about 2 units at the five-minute interval.

Table 4

Solution No.	Amount of liquid, in cc., separated from lather in designated time intervals (in minutes)							
	½	1	1½	2	2½	3	4	5
11.....	0	1	3	5	6	10	16	23
12.....	1	4	6	9	12	16	24	30
13.....	40	44	46	47	48	49	49	49
14.....	46	48	49	49	50	50	50	50
15.....	0	1	4	6	10	13	21	27

In order to illustrate more clearly the effect of the addition of the stabilizing agent upon the lathering power of the higher alkyl sulfate, the data of this table are shown plotted as a graph in the drawing, which is self-explanatory.

From the results obtained with solutions Nos. 11 and 15, it appears that by replacing 60 per cent of the "Gardinol 140" in solution No. 11 with sodium n-octyl sulfate, solution No. 15 is obtained which has nearly the same lathering properties as solution No. 11; furthermore, solution No. 15 has lathering properties which are superior to those of solution No. 12, a solution containing as much sodium lauryl sulfate as solution No. 15 but no sodium n-octyl sulfate. This is surprising since the results obtained with solutions Nos. 13 and 14 indicate that sodium n-octyl sulfate has only very weak lathering properties. This example, therefore, illustrates an important advantage characterizing the compositions of the present invention; namely, that of two aqueous solutions, one containing a selected concentration of higher alkyl sulfate alone, and the other containing the same concentration of a composition of the invention, the solution which contains the composition of the invention has lathering properties which are superior to those of the solution which contains the higher alkyl sulfate alone.

Example 5.—The following solutions were prepared and tested for lathering properties in the manner described above:

Solution No. 16.—1.2 grams of "Drene" shampoo were diluted to 100 grams with water. ("Drene" shampoo is a commercially available shampoo composition, manufactured by Proctor and Gamble Company. According to Bulletin of the National Formulary Committee of the American Pharmaceutical Association, Vol. X (1942), page 191, "Drene" is the triethanolamine salt of lauryl sulfate.)

Solution No. 17.—40 cc. of solution No. 16 were diluted to 100 cc. with water.

Solution No. 18.—0.3 gram of commercial sodium n-octyl sulfate (containing about 90 per cent by weight of sodium n-octyl sulfate and 10 per cent by weight of inorganic salts) was made up to 100 grams with water.

Solution No. 19.—60 cc. of solution No. 18 were diluted to 100 cc. with water.

Solution No. 20.—40 cc. of solution No. 16 and 60 cc. of solution No. 18 were mixed together.

The results of the lathering tests were recorded in the following table, in which the average experimental error is about 2 units at the five-minute interval.

Table 5

Solution No.	Amount of liquid, in cc., separated from lather in designated time intervals (in minutes)							
	1/2	1	1 1/2	2	2 1/2	3	4	5
16	4	7	9	14	18	21	30	36
17	12	20	27	31	35	38	41	44
18	40	44	46	47	48	49	49	49
19	46	48	49	49	50	50	50	50
20	3	5	8	12	15	20	29	36

The results obtained in the above described tests demonstrate the characteristic action of the stabilizing agents of the invention of enhancing the lathering properties of commercial type shampoo compositions. Solution No. 20, which contains 40 per cent of the "Drene" detergent contained in solution No. 16, together with 60 per cent of the amount of sodium n-octyl sulfate contained in solution No. 18, has lathering properties substantially equal to those of solution No. 16, which contains no sodium n-octyl sulfate. The lathering properties of solution No. 20 are superior to those of solution No. 17, which contains the same amount of "Drene" as solution No. 20 but no sodium n-octyl sulfate. Yet, as shown by the tests of solutions Nos. 18 and 19, the sodium n-octyl sulfate has substantially no lathering power per se.

It will be realized by those skilled in the art that changes may be made in the compositions and methods of preparing them, hereinbefore described without departing from the scope of the invention. Thus, in place of the long-chain alkyl sulfate detergent salts employed in the foregoing examples, one or more of the other water-soluble long-chain alkyl sulfate detergent salts of the class hereinbefore disclosed may be employed; and in place of the stabilizing agents employed in the foregoing examples or in the modifications thereof just mentioned, one or more of the other stabilizing agents of the class hereinbefore disclosed may be employed. The proportions of said detergent and stabilizing agent are not limited to those set out in the examples but may be varied in the manner hereinbefore disclosed.

Further, the compositions may be prepared in other ways than those described in the foregoing examples. Thus, mixtures of the long-chain alkyl sulfate detergent salts with lower alkyl sulfates of the class of stabilizing agents, in the proportions hereinbefore disclosed, may be directly prepared by sulfating corresponding mixtures of alcohols or other suitable starting materials by the usual sulfating procedures. For example, a mixture of sodium alkyl sulfates containing, per part by weight of technical sodium lauryl sulfate, about two and one-half parts by weight of sodium normal-octyl sulfate may be prepared by mixing commercial lauryl alcohol with normal-octyl alcohol in the proportions by weight of 186 parts of the former to 390 parts of the latter; cooling the mixture to 10° C.; then gradually adding chloresulfonic acid (in the proportion of about 490 parts by weight) to the agitated mixture of alcohols while maintaining the temperature between 10° and 16° C.; then allow-

ing the mixture to warm up to 20° to 25° C.; pouring the resulting reaction mixture, together with a 50 per cent aqueous solution of sodium hydroxide (containing about 176 parts by weight of sodium hydroxide), into an ice and water mixture (3000 parts by weight) in such quantities that the pH of the resulting mixture at all times is between 7 and 8 and the pH of the final solution is 7.5; and evaporating the resulting solution (to dryness on a rotary drum drier, if desired).

From the foregoing description it will be apparent that the present invention provides compositions having good lathering properties and controlled detergent power. In the form of aqueous solutions, the compositions remain clear over a wide range of temperatures and have good viscosity characteristics.

Since certain changes may be made in the compositions disclosed without departing from the scope of the invention, all matter contained in the above description should be taken as illustrative and not in a limiting sense.

We claim:

1. A detergent composition useful as a shampoo comprising a water-soluble detergent salt of a long-chain monoalkyl ester of sulfuric acid containing at least 12 carbon atoms in the alkyl radical thereof, and for each part by weight of said salt, at least one-half part by weight of a stabilizing agent composed of at least one organic compound which is an anion-active polar-nonpolar water-soluble salt having within its molecule a salt-forming group that induces solubility in water and at least one alkyl group containing 5 to 11 carbon atoms but not more than 9 carbon atoms in a straight chain, and having no alkyl group containing more than 11 carbon atoms nor more than 9 carbon atoms in a straight chain.

2. A detergent composition useful as a shampoo comprising an aqueous solution of a water-soluble detergent salt of a long-chain monoalkyl ester of sulfuric acid containing at least 12 carbon atoms in the alkyl radical thereof, and for each part by weight of said salt, one-half to four parts by weight of a stabilizing agent composed of at least one organic compound which is an anion-active polar-nonpolar water-soluble salt having within its molecule a salt-forming group that induces solubility in water and at least one alkyl group containing 5 to 11 carbon atoms but not more than 9 carbon atoms in a straight chain, and having no alkyl group containing more than 11 carbon atoms nor more than 9 carbon atoms in a straight chain, said aqueous solution having a total concentration of said detergent salt and said stabilized agent of 3½ to 50 per cent by weight.

3. A detergent composition useful as a shampoo comprising a mixture of water-soluble detergent salts of long-chain monoalkyl esters of sulfuric acid containing 12 to 18 carbon atoms in the alkyl radicals thereof, and for each part by weight of said salt mixture, at least one-half part by weight of a stabilizing agent composed of at least one compound which is a water-soluble salt of a monoalkyl ester of an acid selected from the group consisting of sulfuric acid and sulfo-aliphatic mono-carboxylic acids containing 2 to 4 carbon atoms, said monoalkyl ester salt containing 5 to 11 carbon atoms but not more than 9 carbon atoms in a straight chain in the alkyl radical thereof.

4. A detergent composition useful as a sham-

poo comprising an alkali metal salt of a long-chain monoalkyl ester of sulfuric acid containing 12 to 18 carbon atoms in the alkyl radical thereof, and for each part by weight of said alkali metal salt, one-half to four parts by weight of a stabilizing agent composed of at least one compound which is a water-soluble salt of a monoalkyl ester of sulfuric acid containing 5 to 11 carbon atoms but not more than 9 carbon atoms in a straight chain in the alkyl radical thereof.

5. A detergent composition useful as a shampoo comprising an organic amine salt of a long-chain monoalkyl ester of sulfuric acid containing 12 to 18 carbon atoms in the alkyl radical thereof, and for each part by weight of said organic amine salt, one-half to four parts by weight of a stabilizing agent composed of at least one compound which is a water-soluble salt of a monoalkyl ester of sulfuric acid containing 5 to 11 carbon atoms but not more than 9 carbon atoms in a straight chain in the alkyl radical thereof.

6. A detergent composition useful as a shampoo comprising an alkali metal salt of a long-chain monoalkyl ester of sulfuric acid containing 12 to 18 carbon atoms in the alkyl radical thereof, and for each part by weight of said salt, one-half to four parts by weight of a stabilizing agent composed of at least one compound which is a water-soluble salt of a monoalkyl ester of sulfacetic acid containing 5 to 11 carbon atoms, but not more than 9 carbon atoms in a straight chain, in the alkyl radical thereof.

7. A detergent composition useful as a shampoo comprising sodium lauryl sulfate, and for each part by weight of said sulfate, one to two and one-half parts by weight of a stabilizing agent composed of at least one compound which is a water-soluble salt of a monoalkyl ester of an acid selected from the group consisting of sulfuric acid and sulfo aliphatic mono-carboxylic acids containing 2 to 4 carbon atoms, said monoalkyl ester salt containing 6 to 8 carbon atoms in the alkyl radical thereof.

8. A detergent composition useful as a shampoo comprising an organic amine lauryl sulfate, and for each part by weight of said sulfate, one to two and one-half parts by weight of a stabilizing agent composed of at least one compound which is a water-soluble salt of a monoalkyl ester of an acid selected from the group consisting of sulfuric acid and sulfo aliphatic mono-carboxylic acids containing 2 to 4 carbon atoms, said monoalkyl ester salt containing 6 to 8 carbon atoms in the alkyl radical thereof.

9. A detergent composition useful as a shampoo comprising an aqueous solution of a water-soluble detergent salt of a long-chain monoalkyl ester of sulfuric acid containing 12 to 18 carbon atoms in the alkyl radical thereof, and for each part by weight of said salt, one-half to four parts by weight of a stabilizing agent composed of at least one compound which is a water-soluble salt of a monoalkyl ester of an acid selected from the group consisting of sulfuric acid and sulfo aliphatic mono-carboxylic acids containing 2 to 4 carbon atoms, said monoalkyl ester salt containing 5 to 11 carbon atoms but not more than 9 carbon atoms in a straight chain in the alkyl radical thereof, said aqueous solution having a total concentration of said detergent salt and said stabilizing agent of $3\frac{1}{2}$ to 50 per cent by weight.

10. A detergent composition useful as a shampoo comprising an aqueous solution of an alkali metal lauryl sulfate, and for each part by weight of said lauryl sulfate, at least one-half part by weight of a stabilizing agent composed of at least

one compound which is an alkali metal salt of a monoalkyl ester of an acid selected from the group consisting of sulfuric acid and sulfo aliphatic mono-carboxylic acids containing 2 to 4 carbon atoms, said monoalkyl ester salt containing 6 to 8 carbon atoms in the alkyl radical thereof, said aqueous solution having a total concentration of said lauryl sulfate and said stabilizing agent of $3\frac{1}{2}$ to 50 per cent by weight.

11. A detergent composition useful as a shampoo comprising an aqueous solution of a mixture of water-soluble detergent salts of long-chain monoalkyl esters of sulfuric acid containing 12 to 18 carbon atoms in the alkyl radicals thereof composed predominantly of a lauryl sulfate, and for each part by weight of said salt mixture, at least one-half part by weight of a stabilizing agent composed of at least one organic compound which is an ionic-active polar-non-polar water-soluble salt having within its molecule a salt-forming group that induces solubility in water and at least one alkyl group containing 5 to 11 carbon atoms but not more than 9 carbon atoms in a straight chain, and having no alkyl group containing more than 11 carbon atoms nor more than 9 carbon atoms in a straight chain, said aqueous solution having a total concentration of said detergent salt and said stabilizing agent of $3\frac{1}{2}$ to 50 per cent by weight.

12. A detergent composition useful as a shampoo comprising an aqueous solution of a mixture of water-soluble detergent salts of long-chain monoalkyl esters of sulfuric acid containing 12 to 18 carbon atoms in the alkyl radicals thereof composed predominantly of a lauryl sulfate, and for each part by weight of said salt mixture, at least one-half part by weight of a stabilizing agent composed of at least one compound which is a water-soluble salt of a monoalkyl ester of sulfacetic acid containing 5 to 11 carbon atoms, but not more than 9 carbon atoms in a straight chain, in the alkyl radical thereof, said aqueous solution having a total concentration of said detergent salt and said stabilizing agent of $3\frac{1}{2}$ to 50 per cent by weight.

13. A detergent composition useful as a shampoo comprising an aqueous solution of an organic amine lauryl sulfate, and for each part by weight of said lauryl sulfate, at least one-half part by weight of a stabilizing agent composed of at least one compound which is an organic amine salt of a monoalkyl ester of an acid selected from the group consisting of sulfuric acid and sulfo aliphatic mono-carboxylic acids containing 2 to 4 carbon atoms, said monoalkyl ester salt containing 6 to 8 carbon atoms in the alkyl radical thereof, said aqueous solution having a total concentration of said lauryl sulfate and said stabilizing agent of $3\frac{1}{2}$ to 50 per cent by weight.

14. A detergent composition useful as a shampoo comprising an aqueous solution of sodium lauryl sulfate, and for each part by weight of said lauryl sulfate, one to two and one-half parts by weight of a stabilizing agent composed of at least one compound which is a sodium salt of a monoalkyl ester of an acid selected from the group consisting of sulfuric acid and sulfo aliphatic mono-carboxylic acids containing 2 to 4 carbon atoms, said monoalkyl ester salt containing 6 to 8 carbon atoms in the alkyl radical thereof, said aqueous solution having a total concentration of said lauryl sulfate and said stabilizing agent of 10 to 35 per cent by weight.

15. A detergent composition useful as a shampoo comprising an aqueous solution of an ethanolamine lauryl sulfate, and for each part by

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weight of said lauryl sulfate, one to two and one-half parts by weight of a stabilizing agent composed of at least one compound which is an ethanolamine salt of a monoalkyl ester of an acid selected from the group consisting of sulfuric acid and sulfo aliphatic mono-carboxylic acids containing 2 to 4 carbon atoms, said monoalkyl

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ester salt containing 6 to 8 carbon atoms in the alkyl radical thereof, said aqueous solution having a total concentration of said lauryl sulfate and said stabilizing agent of 10 to 35 per cent by weight.

LAWRENCE H. FLETT.
GILBERT C. TOONE.

Certificate of Correction

Patent No. 2,401,726.

June 11, 1946.

LAWRENCE H. FLETT ET AL.

It is hereby certified that errors appear in the printed specification of the above numbered patent requiring correction as follows: Column 5, line 22, for "solution" read *solutions*; column 12, line 61, for "Proctor" read *Procter*; column 14, line 9, for "7:5" read *7.5*; line 58, claim 2, for "stabilized" read *stabilizing*; column 16, line 19, claim 11, for "an ionic-active" read *an anion-active*; and that the said Letters Patent should be read with these corrections therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 17th day of September, A. D. 1946.

[SEAL]

LESLIE FRAZER,

First Assistant Commissioner of Patents.

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weight of said lauryl sulfate, one to two and one-half parts by weight of a stabilizing agent composed of at least one compound which is an ethanolamine salt of a monoalkyl ester of an acid selected from the group consisting of sulfuric acid and sulfo aliphatic mono-carboxylic acids containing 2 to 4 carbon atoms, said monoalkyl

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ester salt containing 6 to 8 carbon atoms in the alkyl radical thereof, said aqueous solution having a total concentration of said lauryl sulfate and said stabilizing agent of 10 to 35 per cent by weight.

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