

Patented July 18, 1939

2,166,127

UNITED STATES PATENT OFFICE

2,166,127

SHAMPOO COMPOSITION

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Chicago, Ill.No Drawing. Application January 8, 1938,
Serial No. 184,030

13 Claims. (Cl. 87-5)

Our invention relates to new and useful improvements in solutions, and particularly aqueous solutions, of certain sulpho-carboxylic acid esters.

5 Broadly speaking, sulpho-carboxylic acid esters of alcohols are known, having been disclosed in various publications and patents, among which may be cited United States Patents Nos. 1,917,250 and 1,917,255. These compounds are generally
10 prepared and employed in the form of their alkali metal or ammonium salts. We have discovered that organic nitrogenous base salts of the sulpho-carboxylic acid esters have markedly increased solubility in water or in aqueous media
15 over the corresponding sodium, potassium, or ammonium salts. In addition, we have made the surprising discovery that solutions, particularly aqueous solutions, containing at least several percent of such organic nitrogenous base salts of sulpho-carboxylic acid esters tolerate super-cooling to a considerable extent. In other words,
20 when such solutions are super-cooled, the esters dissolved therein do not crystallize out despite the fact that the limit of solubility thereof may be exceeded. Instead of crystallization taking place, the solutions merely become more viscous. Just why this unusual phenomenon takes place has not been fully ascertained. At any rate, it does occur and the practical importance thereof
25 is evident so far as the stability of the solutions is concerned under conditions of storage and shipment wherein extreme cold is likely to be met.

We have also found that such solutions may be thickened in a novel and highly satisfactory manner. While an increase in thickness may, in certain cases, be accomplished by increasing the concentration of the organic nitrogenous base salt of the sulpho-carboxylic acid ester in its solvent,
35 this becomes impracticable in most cases since the esters are frequently soluble to only a limited extent in the particular solvent preferred to be used. In addition, the increase in the concentration of the esters, aside from other disadvantages emanating from such practice, is usually uneconomic since the degree of enhancement of thickness, consistency or increase in viscosity attainable by such method is insufficient to warrant the substantially greater cost involved.

Solutions, for example, aqueous solutions, containing as high as 20% to 25% or more, by weight, of some of the organic nitrogenous base salts of sulpho-carboxylic acid esters are almost as limp as water. When poured from a bottle and handled, there is a marked tendency for loss of
55 solution by spilling. It becomes highly advantageous in many instances to increase the thickness, consistency or viscosity of such solutions to facilitate the handling thereof and minimize the loss during pouring and the like from bottles or similar containers or receptacles.

Again, the employment of the thickening agents, hereinafter described in detail, enhances the stability of the solutions of the organic nitrogenous base salts of the sulpho-carboxylic acid esters with respect to low temperatures and appears to aid in preventing crystallization when the solutions are super-cooled. Other advantages accrue from the use of thickening agents in accordance with the present invention into which it does not appear to be necessary to go
10 into detail.

The solutions of the organic nitrogenous base salts of the sulpho-carboxylic acid esters, with or without the thickening agents, may be employed for various purposes for which surface or interface modifying agents may be employed. They may, for example, be employed in textile treating and dyeing baths, in margarine as emulsifying and antispattering agents, in ore flotation and agglomeration methods, and the like. Since
15 many of the organic nitrogenous base salts possess detergent, lathering, sudsing, frothing, foaming, penetrating and wetting properties, their solutions may be employed in the various arts where such functions are sought. Thus, for example, the high lathering and detergent powers of many of said nitrogenous base salts of the sulpho-carboxylic acid esters enables their solutions to be employed for general detergent purposes including the cleansing and laundering of
20 textiles and the like, the cleansing of the skin and the scalp, the washing or shampooing of hair on the human head, the cleansing or the brushing of the teeth, and the like. In such and similar uses, they overcome many of the disadvantages which normally attend the use of soap, particularly under adverse conditions of water supply.

It is accordingly an object of our invention to produce novel and useful solutions, particularly aqueous solutions, of organic nitrogenous base salts of sulpho-carboxylic acid esters.

Another object of our invention is the provision of aqueous solutions containing at least several percent of organic nitrogenous base salts of sulpho-carboxylic acid esters and which have good lathering, sudsing and detergent properties.

Still another object of our invention is to thicken solutions of organic nitrogenous base salts of sulpho-carboxylic acid esters, particularly aqueous solutions which contain at least several percent of such esters and which possess good lathering, sudsing and detergent properties.

Other objects and advantages of our invention will become apparent as the detailed description thereof proceeds.

The compounds of the present invention, in general, contain a relatively high molecular weight lipophile group and a relatively low molec-

ular weight hydrophile group, which latter group comprises sulpho-carboxylic or sulpho-fatty acid radicals. A more complete understanding of what may comprise the lipophile group and the particular character of the sulpho-carboxylic or sulpho-fatty acid group will be had as the detailed description progresses.

The function of the sulphonic acid group is to impart hydrophilic, that is, water wetting or water attracting properties, to the molecule as a whole. The group which are esterified by the sulpho-carboxylic or sulpho-fatty acid are, as indicated, of a lipophile character, the lipophilic properties being at times relatively strong and at other times moderately strong. In other words, and as will be seen in greater detail in connection with the examples hereinafter set forth, the lipophile group or groups, may be of relatively low molecular weight or higher molecular weight.

The lithophile groups entering into the molecular structure of the substances which we employ herein may be of simple character as, for example, in sulpho-acetates of straight chain alcohols such as octyl alcohol, decyl alcohol, lauryl alcohol and the like, or of similar lower molecular weight sulpho-carboxylic acid esters of branched chain alcohols such as 2-ethyl hexanol-1, 2-butyl octanol-1, and the like.

Others of the substances which we employ herein are lower molecular weight sulpho-carboxylic acid esters of polyhydroxy substances, at least one hydroxy group of the polyhydroxy substance being esterified with a carboxylic acid containing at least four carbon atoms and preferably between eight and eighteen carbon atoms.

It will be understood that, in all cases, the compounds are employed in the form of their organic nitrogenous base salts.

The following are examples of compounds which we may employ in accordance with the teachings of our invention:

- (1) Mono-ethanolamine salt of lauryl sulpho-acetate;
- (2) Tri-ethanolamine salt of sulpho-acetic acid ester of coconut oil mixed with fatty alcohols;
- (3) Piperidine salt of myristyl sulpho-propionate;
- (4) Pyridine salt of monolaurin sulpho-acetate;
- (5) Mono-ethanolamine salt of monopalmitin sulpho-butyrate;
- (6) Mono-ethanolamine salt of monolauric acid ester of diethylene glycol sulpho-acetate;
- (7) Di-ethanolamine salt of monolauryl ether of glycerol sulpho-acetate;
- (8) Ethylene diamine salt of decyl sulpho-acetate;
- (9) Diethyl mono-ethanolamine salt of cetyl sulpho-acetate;
- (10) Propanolamine salt of citronellol sulpho-acetate;
- (11) Methyl pyridinium salt of lauryl sulpho-propionate;
- (12) Pyridine salt of lauryl sulpho-acetate;
- (13) Piperidine salt of sulpho-acetic acid ester of coconut oil mixed fatty alcohols containing about 60% of lauryl alcohol.

We may select many different types of compounds as lipophile groups, particularly those having at least eight and preferably at least twelve carbon atoms, although, in some cases, the lipophile group or groups may contain as low as four carbon atoms. For example, the following compounds may be utilized as sources of lipophile groups, and sulpho-carboxylic acid esters thereof, such as sulpho-acetates, may be pre-

pared therefrom: aliphatic straight chain and branched chain alcohols such as butyl alcohol, amyl alcohol, hexyl alcohol, heptyl alcohol, octyl alcohol, nonyl alcohol, decyl alcohol, undecyl alcohol, lauryl alcohol, myristyl alcohol, cetyl alcohol, oleyl alcohol, linoleyl alcohol, stearyl alcohol, ricinoleyl alcohol, palmitoleyl alcohol, melissyl alcohol, ceryl alcohol, carnaubyl alcohol, myricyl alcohol, branched chain octyl, decyl, dodecyl, tetradecyl, hexadecyl and octadecyl aliphatic alcohols as, for example, 2-ethyl hexanol-1, 2-n butyl octanol-1, 2-butyl tetradecanol-1, and, in general, the higher molecular weight saturated and unsaturated aliphatic straight chain and branched chain alcohols. Preferably, the alcohols which are utilized are those corresponding to the fatty acids occurring in triglyceride oils and fats of vegetable or animal origin, natural or hydrogenated, such as corn oil, cottonseed oil, sesame oil, coconut oil, palm kernel oil, sunflower seed oil, lard, tallow, soya bean oil and the like, those alcohols containing from 12 to 18 carbon atoms being preferred. Other alcohols which may be employed are the cyclo-aliphatic or alicyclic alcohols such as the sterols, as, for example, cholesterol, iso-cholesterol, phytosterol, sitosterol, hydro-aromatic alcohols such as abietol, and such unsaturated alcohols as linalool, citronellol, geraniol and the like. Also included within the class of alcohols which may be employed are such compounds as the hydroxy and alpha-hydroxy higher aliphatic and fatty acids as, for example, ricinoleic acid, alpha-hydroxy stearic acid, alpha-hydroxy lauric acid, di-hydroxy stearic acid, 1-hydroxy-stearic acid, alpha-hydroxy palmitic acid, and the like, as well as esters of hydroxy-fatty acids, such as ethyl ricinoleate, castor oil, butyl α -hydroxy-stearate, cetyl hydroxystearate, and the like.

The term "alcohols", as employed herein, is intended to include alcohols which may or may not contain other groups such as carboxylic, halogen, sulphonic, sulphate, or other radicals. The alcohols obtainable by substituting alkyl or acyl radicals, preferably of high molecular weight, in place of the hydrogen of one or more hydroxy groups of polyhydroxy substances or polyhydric alcohols, it being understood that at least one hydroxy group attached to the nucleus of the polyhydroxy substance or polyhydric alcohol remains, are also within the scope of the alcohols from which the sulpho-carboxylic esters may be produced. As examples of such alcohols may be mentioned, partially esterified or partially etherified sugars and sugar alcohols such as monolauric acid ester of sucrose, monostearic acid ester of dextrose, monopalmitic acid ester of mannitol, dicaproic acid ester of maltose, mono-octyl ether of sorbitol, monolauryl ether of pentaerythritol, monolauric acid ester of pentaerythritol, and the like; the monoglycerides and di-glycerides, preferably of the higher fatty acids, as, for example, monolaurin, monomyristin, monostearin, distearin, diolein, dicaproin, mono-lauryl ether of glycerol, di-cetyl ether of glycerol, monostearic acid ester of diethylene glycol, monolauric acid ester of ethylene glycol, and the like.

It is, of course, obvious that the alcohols from which the sulpho-carboxylic esters are produced may be prepared in accordance with any desired method. For example, many of these alcohols may be prepared by the so-called Bouveault and Blanc method or, alternatively, by the reduction or catalytic reduction with hydrogen of natural or hydrogenated animal or vegetable fats and oils in accordance with well known practices.

Again the alcohols may be derived from synthetic processes such as by the oxidation of hydrocarbons or may be prepared by saponification of waxes and the like. Alternatively, they may be prepared by reduction of aldehydes or by the Grignard reaction.

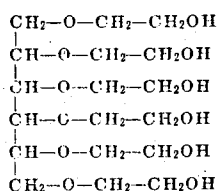
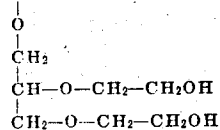
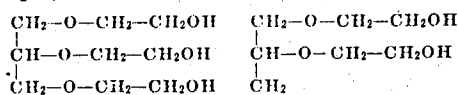
It is likewise apparent that mixtures of the foregoing or other alcohols may be utilized in the preparation of the sulpho-carboxylic acid esters as, for example, the mixture of alcohols resulting from the hydrogenation of coconut oil or the free fatty acids of coconut oil. Lauryl alcohol comprises about 45% of the total alcohol mixture, the remaining alcohols running from C₆ to C₁₈.

Again, mixtures of alcohols such as are present in the so-called sperm oil alcohols, as well as those present in wool-fat, may equally efficaciously be utilized. Indeed, these higher molecular weight alcohols are generally offered on the market in the form of mixtures of different alcohols. If desired for any specific purpose, special fractions which predominate in a certain particular higher molecular weight alcohol may be utilized or, if so desired, the products may be prepared from a single, substantially pure alcohol.

So far as the sulpho-carboxylic acid esters are concerned which are derivatives of polyhydroxy substances, we may select many different types of compounds as lipophile groups which are to be esterified or etherified with the polyhydroxy substances, principally compounds having lipophile radicals of relatively high molecular weight. For example, the following materials may be utilized as sources of lipophile groups: straight chain and branched chain carboxylic, aliphatic, and fatty acids such as butyric acid, caprylic acid, caproic acid, capric acid, saturated and unsaturated higher molecular weight aliphatic acids such as the higher fatty acids containing at least eight carbon atoms and including melissic acid, stearic acid, oleic acid, ricinoleic acid, linoleic acid, linolenic acid, lauric acid, myristic acid, palmitic acid, mixtures of any two or more of the above mentioned acids or other acids, mixed higher fatty acids derived from animal or vegetable sources, for example, lard, coconut oil, sesame oil, palm kernel oil, corn oil, cottonseed oil, sardine oil, tallow, partially or completely hydrogenated animal and vegetable oils such as those mentioned; hydroxy and alpha-hydroxy higher aliphatic and fatty acids such as i-hydroxy stearic acid, dihydroxystearic acid, alpha-hydroxy stearic acid, alpha-hydroxy palmitic acid, alpha-hydroxy lauric acid, alpha-hydroxy coconut oil mixed fatty acids, and the like; fatty acids derived from various waxes such as beeswax, spermaceti, montan wax, and carnauba wax and carboxylic acids derived, by oxidation and other methods, from petroleum; hydroaromatic acids such as naphthenic acid and abietic acid; aromatic acids such as benzoic acid and naphthoic acid, hydroxy aromatic acids such as hydroxy benzoic and naphthoic acid, and the like.

In those compounds which are derivatives of polyhydroxy substances and in which the polyhydroxy substance provides the linkage between the lipophile group and the sulpho-carboxylic acid radical, the polyhydroxy substances may be selected from a large class and include glycerol; glycols such as ethylene glycol, propylene glycol, trimethylene glycol; butylene glycol and the like; polyglycols such as diethylene glycol; pentaerythritol; polyglycerols such as diglycerol, triglycerol, tetraglycerol and the like including mixtures thereof; sugars such as dextrose, sucrose,

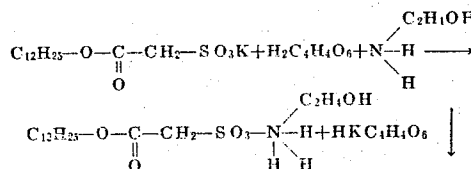
xylose, arabinose, galactose, fructose, maltose, mannose and the like; sugar alcohols such as arabitol, mannitol, sorbitol and dulcitol; and polyhydroxy-carboxylic acids such as tartaric acid, mucic acid, saccharic acid, gluconic acid, glucuronic acid, gulonic acid, mannonic acid, trihydroxyglutaric acid, glyceric acid, carboxylic oxidation products of polyglycerols, others of similar character, and hydroxyethyl and hydroxypropyl ether derivatives of the above, as, for example,



(For convenience, all hydroxyl groups are written facing one way.)

While the organic nitrogenous base derivatives of the sulpho-carboxylic acid esters may be prepared in various ways, we have found that a very satisfactory method comprises reacting an alkali metal or similar salt of a sulpho-carboxylic acid ester such as lauryl potassium sulphoacetate, with an organic nitrogenous base such as monoethanol amine, and with a compound which reacts with the cationic constituent of the sulphoacetate salt to produce a compound more insoluble than the sulphoacetate salt whereby the more insoluble compound precipitates out and may be removed by filtration or the like, leaving the monoethanolamine salt of the sulphoacetate in solution.

More specifically, unusually good results are obtained by reacting a sulpho-carboxylic ester such as lauryl potassium sulphoacetate, tartaric acid, and an organic nitrogenous base such as monoethanolamine. The reaction which takes place results in the formation of potassium acid tartrate which is quite insoluble in cold water and precipitates out, leaving the monoethanolamine salt of lauryl sulphoacetate. The reaction may be illustrated by the following equation:



The reaction takes place when the alkali metal or similar salt of the sulpho-carboxylic acid ester is more soluble or less insoluble than the salt or the like such as potassium acid tartrate which forms during the reaction. Thus, in the specific example referred to above, lauryl potassium sulphoacetate being more soluble or less insoluble than potassium acid tartrate, the reaction takes place. On the other hand, this particular reaction does not appear to take place when stearyl potassium sulphoacetate is substituted for lauryl

potassium sulphoacetate, presumably because stearyl potassium sulpho-acetate is less soluble than potassium acid tartrate. In such a case, other convenient methods may be employed, as, for example, by reacting sulpho-acetic acid with the desired alcohol to form the sulpho-acetic acid ester of the alcohol, and then neutralizing by means of the desired organic nitrogenous base. Other methods of making such compounds will readily suggest themselves to the skilled chemist in the light of our novel teachings herein.

In order to enable those skilled in the art to understand the nature of the invention even more fully, the following examples are given by way of illustration. It will be understood, however, that the specific reactants, the proportions thereof, and the times and temperatures may be varied within limits without departing from the spirit of the invention. The examples, therefore, are to be taken in an illustrative rather than in a limitative sense, the full scope of the invention being pointed out in the claims.

Example I

A. 200 grams of crystalline lauryl potassium sulpho-acetate, prepared from commercial lauryl alcohol, were dissolved in 400 cc. of water at 80 degrees C. to produce a relatively stiff paste.

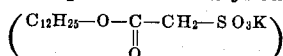
B. 150 grams of tartaric acid and 141 grams of triethanolamine were dissolved in 400 cc. of water.

C. Compositions A and B were then stirred together at a temperature of about 90 degrees C. A heavy precipitate came down and the previously viscous mixture became quite mobile. The precipitate, which comprises potassium acid tartrate, was filtered off and the filtrate was then neutralized with 50 grams of triethanolamine.

The final solution was quite viscous, containing in the neighborhood of 20% of lauryl triethanolamine sulpho-acetate. It possessed unusually good foaming, sudsing, lathering and detergent characteristics.

Example II

133.5 grams of potassium lauryl sulpho-acetate



were dissolved in 700 cc. of boiling water and were then mixed with a previously prepared solution containing 69.4 grams of tartaric acid and 28.7 grams of monoethanolamine in 200 cc. of water. These two solutions were mixed together at a temperature of about 90 degrees C. and the resulting mixture thereof was allowed to cool to room temperature. The liquid was then filtered from the precipitated potassium acid tartrate. The filtrate was a viscous, strongly foaming, substantially odorless and colorless liquid after having been neutralized with 6.7 grams of monoethanolamine to a litmus blue reaction. The solution contained 13.8% of the monoethanolamine salt of lauryl sulpho-acetate and 2.9% of the tartrate of monoethanolamine. The solution had excellent sudsing, foaming, lathering, and detergent properties.

Example III

133 grams of potassium lauryl sulpho-acetate were dissolved in 700 cc. of boiling water and the resulting solution was then mixed with a previously prepared solution containing 69 grams of tartaric acid, 36.6 grams of pyridine and 200 cc. of water. The two solutions were mixed at a temperature of about 90 degrees C. and were then allowed to cool to room temperature where-

upon the resulting solution was filtered from the potassium acid tartrate which had precipitated out.

Approximately 780 cc. of a yellow colored limpid solution were obtained which had excellent foaming, sudsing, lathering and detergent properties in hard water as well as in the presence of alkalies and acids. The solution contained a substantial proportion of the pyridine salt of the sulpho-acetate of lauryl alcohol.

Example IV

173 grams of lauryl potassium sulpho-acetate were dissolved in 1050 cc. of boiling water and mixed with a solution containing 93 grams of tartaric acid, 51 grams of piperidine and 300 cc. of water. After cooling to approximately room temperature, the solution was filtered off from the precipitated potassium acid tartrate and the solution was then neutralized to a methyl red yellow with 20 grams of piperidine. A water-white viscous liquid was obtained possessing strong foaming, sudsing, lathering and detergent properties in alkaline or acid aqueous media as well as in hard water.

Example V

453 grams of lauryl potassium sulpho-acetate, prepared from commercial lauryl alcohol containing about 75% lauryl alcohol, and containing about 40% water were dissolved in 1810 cc. of water previously heated to about 90 degrees C. To the above solution there was then added, at about 90 degrees C., a solution of monoethanolamine acid tartrate prepared by mixing together a solution of 60.9 grams of monoethanolamine (molecular weight 62.6) in 210 cc. of water with a solution of 146 grams of tartaric acid dissolved in 210 cc. of water.

The resulting solution was then allowed to cool for about a day at room temperature and was then decanted and filtered from the precipitate of potassium acid tartrate, the latter then being washed with 50 cc. of water and the wash water being added to the filtrate.

To the approximately 2660 grams of solution thus obtained, about 20 grams of monoethanolamine were added until methylred gave a yellow color. There was then added to said solution 110 cc. of a solution of monoethanolamine sulphate in order to thicken the solution.

The solution of monoethanolamine sulphate was prepared by adding a solution of 325 grams of monoethanolamine dissolved in 250 cc. of water to a solution of a stoichiometrically equivalent amount of 96% sulphuric acid dissolved in 580 cc. of water.

Example VI

An aqueous solution of 8.1 parts, by weight, of acid methylpyridinium tartrate in 17 parts, by weight, of water was prepared by mixing one mol of 0.166 normal methylpyridinium hydroxide solution with an aqueous solution of one mol of tartaric acid and evaporating down. This solution was then heated to a temperature of about 90 degrees C. and was then added to a previously heated solution, also at about 90 degrees C., containing 10.4 parts, by weight, of lauryl potassium sulpho-acetate and 50 parts, by weight, of water. The mass was permitted to cool to approximately 25 degrees C. and the acid potassium tartrate which had precipitated out was filtered off. The resulting clear filtrate was neutralized to yellow methylred with 20 volume parts of 0.167 normal methylpyridinium hydroxide solution.

The resulting solution, containing a substantial proportion of the methylpyridinium salt of lauryl sulpho-acetate, was water-white, relatively viscous, substantially odorless, and had excellent foaming, sudsing, lathering, and detergent properties in hard water as well as in aqueous acidulated media.

Those skilled in the art will readily be able to carry out the invention and make diverse variations all of which, however, are within the spirit of the invention in view of the detailed explanation and guiding principles set out hereinabove.

We have obtained unusually good results with organic nitrogenous base salts of sulpho-acetic acid esters of lauryl alcohol or higher molecular weight aliphatic alcohol mixtures containing at least 40% of lauryl alcohol and, preferably, from 60% to 80% or more of lauryl alcohol, the alkylamine salts such as monoethanolamine and triethanolamine being outstandingly satisfactory.

The preparation of the alkali metal sulphoacetates or the like, which are employed in the specific examples set forth hereinabove whereby the organic nitrogenous base derivatives are produced, may be effected, for example, as disclosed in said patents, by initially reacting a higher molecular weight alcohol, such as lauryl alcohol, with chloroacetic or bromoacetic acid or the like to produce the chloroacetic or bromoacetic ester of lauryl alcohol. The resulting product, preferably washed free of the formed hydrochloric acid and the unreacted chloroacetic acid or the like, is then treated with an aqueous solution of an alkali metal sulphite, such as K_2SO_3 , in accordance with the so-called Strecker reaction to produce the alkali metal sulpho-acetate which may, if desired, be purified in accordance with practices well known in the art.

It will be appreciated, for example, that other organic nitrogenous bases may be employed in place of those described hereinabove. Illustrative of bases of this type are, for example, alcohol amines and alkylolamines including mono-, di-, and tri-ethanolamine and mixtures thereof such as are, for example, present in so-called commercial triethanolamine, propanolamines, butanolamines, pentanolamines, hexanolamines, glycerolamines, dibutyl ethanolamine, diethanol ethyl amine, cyclohexyl ethanolamine, diethanol ethyl amine, cyclohexyl ethanolamine, alkylol polyamines such as alkylol derivatives of ethylene diamine, mono-methyl mono-ethanolamine, diethyl mono-ethanolamine, mono-, di-, and tri-ethyl triethanolamine, 1-amino-2, 3-propanediol, 1,2-diaminopropanol; alkylamines such as butylamine, dimethylamine, ethylene diamine, diethylene triamine, triethylene tetra-amine, mono-methyl ethylene diamine, mono-ethyl diethylene tetra-amine, aromatic and heterocyclic bases such as pyridine, quinaldine, methylpyridine, and homologues and derivatives thereof, quaternary ammonium bases or hydroxides such as tetra-methyl ammonium hydroxide, tetra-ethyl ammonium hydroxide, quaternary ammonium bases with dissimilar alkyl radicals such as methyl-triethyl ammonium hydroxide, propyl-trimethyl ammonium hydroxide, mixtures of any two or more thereof, and the like. It will be understood that these organic nitrogenous bases, as in the case of triethanolamine, for example, may be employed in pure, impure, or commercial form.

As previously pointed out, and as is evident, pure or single sulpho-carboxylic esters need not be employed. Mixtures are, in many cases, at least equally efficacious as, for example, the sul-

pho-carboxylic esters prepared from the product known as "Lorol Technical" which comprises a mixture of fatty alcohols derived from the hydrogenation of coconut oil or the free fatty acids of coconut oil. Lauryl alcohol comprises about 60% of the total alcohol mixture, the remaining alcohols running from C_8 to C_{18} . Similarly, it is apparent that mixtures of different organic nitrogenous bases, such as mixtures of those referred to hereinabove, may be employed with efficacious results. Indeed, in order to obtain varied solubility and other characteristics mixtures of different organic nitrogenous bases may be employed with mixtures of different sulpho-carboxylic acid esters.

As we have indicated above, it frequently becomes quite desirable to increase the thickness, consistency or viscosity of the aforementioned solutions. As a result of considerable research work, a large class of thickening agents has been discovered which are of marked utility for thickening solutions, particularly aqueous solutions, of sulpho-carboxylic acid esters, including those having good sudsing and detergent properties. These thickeners may be characterized as salts of organic nitrogenous bases, notably salts of such bases with water-soluble acids. Particularly useful are the salts of the alcohol amines, and of unusual utility are the salts of mono-ethanolamine, especially monoethanolamine sulphate.

In place of monoethanolamine, other organic nitrogenous bases may be employed, as, for example, alcohol amines and alkylolamines, including diethanolamine, triethanolamine, propanolamines, butanolamines, pentanolamines, hexanolamines, glycerolamines, dibutyl ethanolamine, diethanol ethyl amine, cyclohexyl ethanolamine, alkylol polyamines such as alkylol derivatives of ethylene diamine, mono-methyl mono-ethanolamine, diethyl monoethanolamine, mono-, di-, and triethyl triethanolamine, 1-amino-2, 3-propanediol, 1,2-diamine propanol; alkylamines such as butylamine, dimethylamine, ethylene diamine, diethylene triamine, triethylene tetra-amine, mono-methyl ethylene diamine, monoethyl diethylene tetra-amine, aromatic and heterocyclic bases such as pyridine, quinaldine, piperidine, methylpyridine, and homologues and derivatives thereof, quaternary ammonium bases or hydroxides such as tetra-methyl ammonium hydroxide, tetra-ethyl ammonium hydroxide, quaternary ammonium bases with dissimilar alkyl radicals such as methyl-triethyl ammonium hydroxide, propyl-trimethyl ammonium hydroxide, mixtures of any two or more thereof, and the like. It will be understood that these organic nitrogenous bases may be employed in pure, impure or commercial form such as, for example, commercial triethanolamine which contains minor proportions of mono- and di-ethanolamine.

As stated, these organic nitrogenous bases are employed in the form of their salts such as sulphates, phosphates, nitrate, acetates, chlorides, bromides, iodides, borates, lactates, citrates, tartrates, and the like or mixtures of any two or more thereof. The salts may be made in ways known in the art, for example, by neutralizing the base or mixtures of bases with the equivalent amount of acid or any desired mixture of two or more acids. For example, monoethanolamine acetate may be prepared by mixing equal molecular quantities of monoethanolamine and glacial acetic acid. The glacial acetic acid is added drop by drop to the monoethanolamine while constantly stirring the latter, the flask or the like

containing the monoethanolamine being surrounded by an ice bath to insure that the temperature does not rise too high and too rapidly. The monoethanolamine acetate is a brownish, viscous liquid. Triethanolamine acetate is made in the same manner and has the same general appearance as monoethanolamine acetate. Monoethanolamine sulphate may be prepared in solution, for example, by adding a solution of 325 grams of monoethanolamine dissolved in 250 cc. of water to a solution of a stoichiometrically equivalent amount of 96% sulphuric acid dissolved in 580 cc. of water.

As illustrative of thickeners falling within the scope of the invention may be mentioned, by way of example, monoethanolamine acetate, monoethanolamine sulphate, diethanolamine acetate, triethanolamine acetate, 1-amino-2, 3 propanediol acetate, 1,3-diaminopropanol acetate, monoethanolamine phosphate, triethanolamine phosphate, ethylenediamine sulphate, butylamine acetate, and the like.

It is convenient to prepare a solution of the thickener and add it in the desired amounts to the interface modifying agent solution although the manner of incorporation is optional and may be accomplished in various ways as, for example, in situ during the preparation of the solution of the sulpho-carboxylic acid ester. Since, in the main, aqueous solutions of sulpho-carboxylic acid esters are employed, the thickeners utilized in such solutions will be water-soluble. It will be understood that in all cases the thickener must be soluble in the solution of the interface modifier in which it is employed.

While, as stated and is obvious, the amount of thickener which may be employed is variable within relatively wide ranges of proportions, in order to indicate the remarkable and unusual aspects of this phase of the invention, the following facts should be understood. Aqueous solutions of many of the thickening agents which are disclosed herein, even in concentrations as high as 50%, are of a very limpid character with viscosity practically identical with or not much greater than that of ordinary water. Nevertheless, the addition of relatively small proportions of such limpid solutions to solutions of sulpho-carboxylic acid esters results in an entirely unexpected increase in thickness and viscosity of said latter solutions. That this happens in the face of and notwithstanding the mutual dilution which simultaneously occurs is all the more remarkable. The following table illustrates the nature of the results which have been obtained:

	Sulpho-Carboxylic Acid Ester Solution	Addition Agent	Results
1	10 cc. of a 10% aqueous solution of triethanolamine salt of lauryl sulphoacetate.	1 gram monoethanolamine acetate.....	Considerable increase in viscosity.
2	10 cc. of a 10% aqueous solution of triethanolamine salt of lauryl sulphoacetate.	2 grams monoethanolamine sulphate.....	Do.
3	10 cc. of an aqueous solution of rather low viscosity containing 2¼% of the triethanolamine salt of laurylsulphoacetate and 17¼% of triethanolamine phosphate.	Several drops of a 50% aqueous solution of monoethanolamine phosphate.	Considerable thickening.
4	5 cc. of a 15% aqueous solution of monoethanolamine salt of lauryl sulphoacetate.	¼ cc. of a 50% aqueous solution of butylamine acetate.	Do.
5	20 cc. of a 12% aqueous solution of	5 cc. of a 50% aqueous solution of monoethanolamine sulphate.	Considerable increase in viscosity.
70	$\text{C}_{11}\text{H}_{23}-\text{C}(=\text{O})-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-\text{C}(=\text{O})-\text{CH}_2-\text{S}(=\text{O})_2-\text{NH}_2$ $\text{CH}_2-\text{CH}_2\text{OH}$		

75 While it is preferred to carry out the inven-

tion with respect to the thickening of aqueous solutions of the sulpho-carboxylic acid esters, it must not be inferred that the invention is so limited. Alcoholic or other organic solvents may be employed, as well as aqueous-organic solvent mixtures, but for economic and other obvious reasons water is preferred.

Besides the salts of organic nitrogenous bases which are employed as thickeners, we have also found that various electrolytes such as ammonium sulphate, sodium sulphate, magnesium sulphate, disodium hydrogen phosphate treated with sufficient sulphuric acid to give a neutral reaction to litmus, and the like, may be utilized for a similar purpose although not nearly so satisfactorily as the salts of the organic nitrogenous bases.

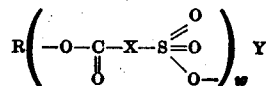
While the thickening effect increases with increasing concentrations of the sulpho-carboxylic acid esters and while it commences to become appreciable, in most cases, at concentrations of the order of magnitude of several percent or five to ten percent, nevertheless the invention is applicable, as well, at concentrations of said esters substantially below and beyond the above-mentioned range. Indeed the invention is applicable to the treatment of solutions of said esters of as low as about 0.5% strength and as high as 25% or 30% strength, or even higher.

Many of the sulpho-carboxylic acid esters employed herein may be represented by the general formula



wherein R denotes a lower molecular weight aliphatic radical containing at least one sulphonic acid radical the hydrogen of which is replaced by the radical of an organic nitrogenous base, and R₁ denotes a radical of a higher molecular weight mono- or polyhydric alcohol.

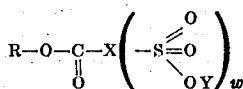
Many of the sulpho-carboxylic acid esters utilized herein may also be represented by the general formula



wherein R is a radical comprising or containing a lipophile group with at least four carbon atoms and preferably from twelve to eighteen carbon atoms, X is the carbon-hydrogen residue of the sulpho-carboxylic acid, Y is an organic nitrogenous base cation, and w is a small whole number, at least one.

Again, various of the sulpho-carboxylic acid 75

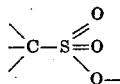
esters which may be employed herein may be represented by the general formula



wherein R is the residue of a polyhydroxy substance in which the hydrogen of at least one hydroxyl group is substituted by an alkyl or acyl group containing at least four carbon atoms and preferably between eight and eighteen carbon atoms, X is the carbon-hydrogen residue of the sulpho-carboxylic acid, Y is an organic nitrogenous base cation, and w is a small whole number, at least one.

So far as the sulpho-carboxylic or sulpho-fatty acid group of the compounds is concerned, it may be a sulpho-acetate, a sulpho-propionate, sulpho-butyrate, or other similar groups containing not more than seven carbon atoms and containing a sulphonic acid radical whose hydrogen is replaced by an organic nitrogenous base cation. In general, the sulpho-acetates are particularly useful and they possess the advantage of being relatively inexpensively produced from commercially available substances.

The term "sulpho-carboxylic acid" or "sulpho-fatty acid", as employed throughout the specification and claims is used in a strictly rigorous sense to cover an aliphatic linkage containing at least one



group, the various examples given being clear in this feature.

The term "residue", as used herein, is employed in its ordinarily understood chemical significance. For example, where one of the hydroxyl groups of glycerine is esterified with a higher fatty acid and another of the hydroxyl groups of the glycerine is esterified with a sulpho-carboxylic acid, that which remains of the glycerine molecule, for example



is the residue of the polyhydroxy substance, in this case, glycerine.

Similarly, the term "carbon-hydrogen residue" of a sulpho-carboxylic acid is employed as in conventional chemical nomenclature. Thus, for example, if sulpho-acetic acid ($\text{HOOC}-\text{CH}_2-\text{SO}_3\text{H}$) is esterified with glycerine, the group $-\text{CH}_2-$ is the "carbon hydrogen residue" of the sulpho-acetic acid.

The term "lipophile group", as employed herein, is intended to cover any radical having an affinity for oleaginous material such as oils, fats, hydrocarbons and the like and may comprise radicals such as hydrocarbon radicals, acyl or alkyl groups derived from aliphatic or fatty acids or their corresponding alcohols, and the like. The "hydrophile group" or groups, in other words, the groups having an affinity for aqueous materials are, as fully set forth hereinabove, sulpho-carboxylic or sulpho-fatty acid groups.

The term "solution" as employed herein and in the appended claims is employed in a broad sense to include not only true solutions but also colloidal dispersions.

Unless otherwise indicated, the term "higher",

wherever employed in the claims, will be understood to mean at least eight carbon atoms and, concomitantly, the term "lower" will mean less than eight carbon atoms.

The present application is a continuation-in-part of prior application, Serial No. 166,388, filed September 29, 1937.

What we claim as new and desire to protect by Letters Patent of the United States is:

1. A shampoo composition comprising an aqueous solution of at least 5% of a lower molecular weight sulpho-fatty acid ester of a higher molecular weight alcohol, the hydrogen of the sulphonic group of which is replaced by the radical of an organic nitrogenous base, the lower molecular weight sulpho-fatty acid radical containing less than eight carbon atoms and the higher molecular weight alcohol radical containing at least eight carbon atoms, said shampoo being stable against crystallization on being super-cooled.

2. A shampoo composition comprising an aqueous solution of at least 5% of a lower molecular weight sulpho-fatty acid ester of a higher molecular weight aliphatic alcohol corresponding to the higher fatty acids present in triglyceride oils and fats and waxes, the hydrogen of the sulphonic group of which is replaced by the radical of an organic nitrogenous base, the lower molecular weight sulpho-fatty acid radical containing less than eight carbon atoms and the higher molecular weight alcohol radical containing at least eight carbon atoms, said shampoo being stable against crystallization on being super-cooled.

3. A shampoo composition comprising an aqueous solution of at least 5% of a sulpho-acetic acid ester of a mixture of higher aliphatic alcohols containing a predominant amount of lauryl alcohol, the hydrogen of the sulphonic group of which is replaced by the radical of an organic nitrogenous base, said shampoo being stable against crystallization on being super-cooled.

4. A composition in accordance with claim 3, wherein the organic nitrogenous base comprises a member selected from the group consisting of monoethanolamine, diethanolamine, triethanolamine, and mixtures thereof.

5. A shampoo composition comprising an aqueous solution of at least 5% of lauryl monoethanolamine sulphoacetate, said shampoo being stable against crystallization on being super-cooled.

6. A viscous liquid shampoo in accordance with claim 1, and a salt of an alcohol amine as a thickening agent.

7. A viscous liquid shampoo in accordance with claim 3, and a salt of an alcohol amine as a thickening agent.

8. A viscous hair shampoo comprising an aqueous solution of at least 5% of lauryl monoethanolamine sulpho-acetate and monoethanolamine sulphate as a thickening agent, said shampoo being stable against crystallization on being super-cooled.

9. A viscous liquid shampoo comprising an aqueous solution of at least 5% of sulpho-acetic acid esters of a mixture of higher fatty alcohols containing at least 40% of lauryl alcohol, the hydrogen of the sulpho-acetic acid radical being replaced by the radical of an organic nitrogenous base, and a salt of an alcohol amine as a thickener, said shampoo being stable against crystallization on being super-cooled.

10. A composition in accordance with claim 9 wherein the organic nitrogenous base is a member selected from the group consisting of mono-

ethanolamine, diethanolamine, triethanolamine, and mixtures thereof, and the thickener is a salt of a strong inorganic acid with an organic nitrogenous base.

5 11. A shampoo composition comprising an aqueous solution of at least 5% of lauryl alkylol-
amine lower molecular weight sulpho-fatty acid
esters, the lower molecular weight sulpho-fatty
acid radical containing less than eight carbon
10 atoms, said shampoo being stable against crystallization on being super-cooled.

12. A shampoo composition comprising an aqueous solution of between about 5% and 20%.

by weight, of the monoethanolamine salt of the sulpho-acetic acid ester of a mixture of higher aliphatic alcohols containing in excess of 40% of lauryl alcohol, said shampoo being stable against crystallization on being super-cooled.

13. A viscous liquid shampoo comprising an aqueous solution of between 5% and 20% of lauryl monoethanolamine sulpho-acetate, and monoethanolamine sulphate as a thickener, said shampoo being stable against crystallization on
10 being super-cooled.

FRANK J. CAHN.
MORRIS B. KATZMAN.

CERTIFICATE OF CORRECTION.

Patent No. 2,166,127.

July 18, 1939.

FRANK J. CAHN, ET AL.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 2, first column, line 11, for the word "group" read groups; line 20, for "lithophile" read lipophile; line 45, strike out "with"; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 19th day of September, A. D. 1939.

(Seal)

Henry Van Arsdale,
Acting Commissioner of Patents.