Patented Oct. 26, 1948 2,452,043

UNITED STATES PATENT OFFICE

2,452,043

DERIVATIVES OF SULFOSUCCINAMIC ACID

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No Drawing. Application December 11, 1945, Serial No. 634,398. In Canada May 11, 1943

5 Claims. (Cl. 260—501)

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This invention relates to new compounds which are wetting, washing, emulsifying, detergent, and surface-active agents and which are unusually effective as foaming or lathering agents. It relates more particularly to new derivatives of carboxylic mono-amides of sulfosuccinic acid, that is, to new derivatives of sulfosuccinamic acid, especially useful for the washing of human hair.

Shampoos for washing human hair present a number of problems to the cosmetic manufacturer. Soaps are objectionable in that they form alkaline solutions in water which are harmful to the hair and scalp. Soaps form precipitates with the calcium, magnesium and other salts present in hard waters, which not only interfere with the cleansing and rinsing of the hair washed with them, but tend to clog the pores of the scalp and to form precipitates on and within the hair, causing reduction in the luster of the hair and cracking of the hair itself.

Many soapless detergents which foam in aqueous solution are known, but they are generally characterized by a foam or froth this is light and that is formed of relatively large bubbles. They do not give thick lathers, such as are characteristic of soap when it is used in soft water.

An object of the present invention is to provide soapless detergents which dissolve in hard water as well as soft water, to give substantially neutral solutions which form thick lathers.

An additional object of this invention is to produce new and economical agents possessing lathering, wetting, washing, emulsifying, detergent and surface-active properties.

A further object of this invention is to provide derivatives of sulfosuccinamic acid which will give solutions in water that have a high foaming and lathering action and that retain their solubility at temperatures below normal room temperature, so that they can be used as components of shampoos.

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

The compounds of the present invention are N,N-di-substituted sulfosuccinamic acids, in the form of the di-monoethanolamine salts, in which one N-substituent (i. e., one of the substituents attached to the amidic nitrogen) is a methyl group and the other N-substituent is an open-chain hydrocarbon radical having 10 to 18 carbon atoms, more particularly an alkyl hydrocarbon radical of 12 to 16 carbon atoms, and especially 12 to 14 carbon atoms.

They include the di-monoethanolamine salts of the sulfosuccinamic acid derivatives of the following amines: N-methyl-decylamines, N-methyl-dodecylamines, N-methyl-tridecylamines, N-methyl-tetradecylamines, N-methyl-pentadecylamines, N-methyl-hexadecylamines, N-methyl-heptadecylamines, N-methyl-octadecylamines and corresponding N-methyl-unsaturated open-chain amines (for example, N-methyl-undecenylamines, N-methyl-dodecenylamines, and N-methyl-octadecenylamines).

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Specific instances of such compounds are the di-monoethanolamine salts of the following sulfosuccinamic acids:

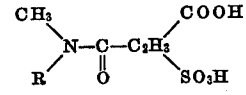
N-methyl, N-lauryl-sulfosuccinamic acid (i. e., N-methyl, N-normal-dodecyl-sulfosuccinamic acid)

N-methyl, N-cetyl-sulfosuccinamic acid (i. e., N-methyl, N-normal-hexadecyl-sulfosuccinamic acid)

N-methyl, N-normal-tetradecyl-sulfosuccinamic acid

N-methyl, N-oleyl-sulfosuccinamic acid (i. e., N-methyl, N-octadecenyl-sulfosuccinamic acid)

Thus the present invention comprehends the di-monoethanolamine salts of the N,N-dialkyl sulfosuccinamic acid compounds having, in the free acid form, the general formula:



wherein R represents an open-chain hydrocarbon radical which contains 10 to 18 carbon atoms, more particularly an alkyl hydrocarbon radical of 12 to 16 carbon atoms, and especially 12 to 14 carbon atoms.

The compounds of the invention are characterized by high water solubility and substantial neutrality of their aqueous solutions, which makes possible the preparation of stable solutions with high wetting, emulsifying, lathering and washing properties. Those of the compounds having, as N-substituents, carbon chains containing 12 to 16 carbon atoms are valuable detergents.

They are also generally soluble in organic solvents, such as benzene and toluene.

The compounds of the invention have the advantageous property of forming thick, creamy lathers in water solutions. In hard water, they do not form precipitates with the calcium and magnesium salts causing the hardness, and their foaming and lathering action is increased without impairment of their cleansing action.

They are unique in combining high solubility in water with exceptional foaming and lathering

power. This combination of properties makes the compounds particularly well suited for preparing concentrated liquid compositions for cleaning objects which cannot be cleaned by a usual laundering procedure. For example, the compounds of this invention are particularly useful for preparing shampoos, liquid dentifrices, rug cleaners and the like. Such cleaning compositions can be prepared in convenient concentrated liquid form without fear that the active detergent material will separate out in storage, even at temperatures which are considerably below average room temperature.

The compounds of the invention are very effective in aqueous solutions for wetting and detergent purposes even at low concentrations, being usually applied in concentrations which range from 0.1% to 2.0%. Thus, they can be used at such concentrations for laundry work; personal use; wetting and scouring raw cotton and wool; carbonizing wool; dispersing dyes in dyeing and printing preparations and applications; fire extinguishing mixtures; germicidal compositions; insecticidal sprays; dispersing materials in the manufacture of finely-divided pigments; dispersing active substances for impregnated textile materials, wood, leather, etc.; aiding in the dyeing or coloration of cellulose acetate and other cellulose esters or materials containing them. For any of these purposes for which soap or soap substitutes (such as alkyl aryl sulfonates or higher alkyl sulfates) are used, the compounds of this invention may be used with, or in place of, soap or the said soap substitutes.

They may be used as advantageous dispersing assistants in lubricants, treating and spinning oils, dust-laying sprays and compositions, and in suspension of pigments in lacquers.

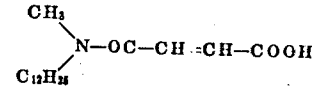
The compounds of this invention can be prepared in highly purified form; and because of the unusual cleansing properties of the compounds, their pure forms are especially suitable ingredients for cosmetic preparations. When applied to the skin, the pure compounds do not cause undesirable irritation which generally results from use of many soapless detergents and even of soap.

The compounds are particularly useful for processes of cleaning which are best effected with thick, creamy lathers; for example, the cleaning of rugs, upholstery, draperies, fur, and the like. They are especially effective in tonsorial shampoos for cleaning human hair.

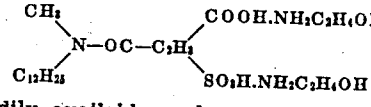
By virtue of their rapid wetting, emulsifying and dispersing properties, the compounds are very useful and valuable ingredients of dry preparations of dyestuffs and coloring matters which are applied as dispersions in water for dyeing or coloring natural silk or materials which are made of or contain cellulose esters and ethers, especially cellulose acetate. In such dye compositions the compounds of this invention play a two-fold part: they disrupt the dyestuff particles when the dry mixtures are added to water, and thereby prevent conglomeration of dye particles; and they wet and disperse thoroughly the dye particles throughout the dyebath liquid and thereby assure, without the aid of vigorous mechanical agitation, uniform distribution of dyestuff throughout the dyebath, and uniform dyeing of material dyed therein.

The compounds of the invention may be prepared in a number of ways. One method, which is readily carried out, involves converting the corresponding N,N-disubstituted mono-amide of an

ethylene dicarboxylic acid (for example, an N-methyl, higher N-alkyl mono-amide of maleic or fumaric acid) to the corresponding sulfosuccinamic acid and neutralizing with monoethanolamine. Thus, a particularly advantageous method for preparing the di-monoethanolamine salts in accordance with the present invention comprises forming an aqueous solution of a sulfite of monoethanolamine by passing sulfur dioxide into an aqueous solution of the amine, and reacting the resulting solution of monoethanolamine sulfite with an N-methyl, higher N-alkyl monoamide of an ethylene dicarboxylic acid. The di-monoethanolamine salt of the N,N-disubstituted sulfosuccinamic acid is thus directly obtained. For example, a mono-N-methyl, N-dodecylamide of maleic or fumaric acid:



can be reacted with monoethanolamine sulfite in aqueous solution to form directly the di-monoethanolamine salt of the corresponding mono-N-methyl,N-dodecylamide of sulfosuccinic acid:



Readily available and economically produced compositions of the present invention comprise mixtures of N-methyl, higher N-alkyl sulfosuccinamic acid derivatives of the above class in which the higher N-alkyl groups are derived from mixtures of amines which are obtainable from the fatty acids in coconut oil or from hydrocarbon mixtures, such as petroleum distillates, or the like.

For preparing such products according to one method of procedure in accordance with the invention, a mixture of N-methyl higher alkylamines containing 10 to 18 carbon atoms in the higher alkyl hydrocarbon radical (and derived from the mixture of acids obtainable by hydrolyzing coconut oil) is condensed with maleic anhydride or maleic acid or fumaric acid to form a mixture of mono-amides of maleic or fumaric acid, and the resulting mixture of mono-amides is converted to the corresponding mixture of N-methyl, higher N-alkyl sulfosuccinamic acid di-monoethanolamine salts; for example, by treatment with monoethanolamine sulfite. When using amines derived from higher fatty acids, it is preferred that the amines be substantially free of impurities (such as fatty acid amides, nitriles and substances which may form by decomposition when the amines are distilled without proper precautions). The quality of the N-methyl, higher N-alkyl sulfosuccinamates prepared from amines containing such impurities is impaired by the said impurities; they have a degrading effect upon such qualities as foaming power, color, taste, and odor of the said sulfosuccinamates and compositions prepared from them.

Instead of a mixture of N-methyl higher alkylamines derived from higher fatty acids, other mixtures of N-methyl higher alkylamines may be employed; for example, mixtures derived from mixtures of hydrocarbons (for example, a kerosene fraction of petroleum distillate having a boiling range that corresponds to a content of hydrocarbons which contain between 10 and 18 carbon atoms per molecule and an average carbon content of 14 to 16 carbon atoms) by chlorinating

the hydrocarbon mixture until the amount of organically combined chlorine contained in the chlorination product is equal to substantially that theoretically required for monochlorination of the hydrocarbon mixture, and converting the resulting mixture of chlorinated hydrocarbons to a mixture of N-methyl alkylamines by reaction with methylamine.

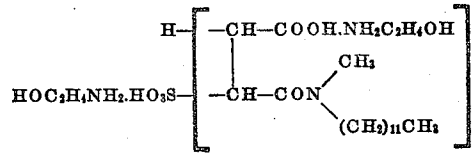
One of the preferred methods for making N-methyl, higher N-alkyl maleamic acids for use as intermediates in making the N,N-disubstituted sulfosuccinamic acids of this invention, is to add an N-methyl higher alkylamine to maleic anhydride at an elevated temperature in the absence of a solvent. When operating in this way, it is preferable to avoid the presence of substantial amounts of water in the amine. This preferred order of addition generally avoids undesirable side reactions which lead to the formation of impurities that contaminate the resulting maleamic acids, and subsequently degrade the quality of the N-methyl, higher N-alkyl sulfosuccinamates prepared from the maleamic acids. The impurities tend to degrade such qualities as foaming power, clarity and color of aqueous solutions of the sulfosuccinamates.

The invention will be illustrated by the following specific examples in which the parts are by weight. Since it is not definitely known to which of the two central carbon atoms of the succinic acid part of the molecule the sulfo group attaches itself, a bracket is used in the formulas as indicating that the sulfo group may be attached to one or the other of them.

Example 1

39.8 parts (1 mol) of N-methyl-laurylamine were mixed with 19.6 parts (1 mol) of maleic anhydride in granulated form. After the initial temperature rise was past, the reaction mixture was agitated and heated to 95° to 105° C. for 4 hours. Then a solution of di-monoethanolamine sulfite was made up by stirring 24.4 parts (2 mols) of monoethanolamine in 50 parts of water and passing in 12.8 parts of SO_2 gas (1 mol), maintaining the temperature at about 30° C. This solution, which had a faintly alkaline reaction to phenolphthalein, was added to the hot N-methyl-laurylamine-maleic anhydride reaction product. The resulting mixture was agitated and heated for 7 hours at 95° to 100° C. except for brief periods when the temperature had to be lowered slightly to counteract excessive foaming. The reaction mass was diluted with about an equal volume of water (about 135 parts) and, if necessary, the pH of the solution was adjusted to 7 to 7.5 or higher, depending on the use to which the product was to be put. The solution was subjected to a purification treatment with activated carbon "Darco," in the proportion of 10 parts for the total solution, at 55° to 60° C. for about one hour. It was then filtered, using "Super-Sel."

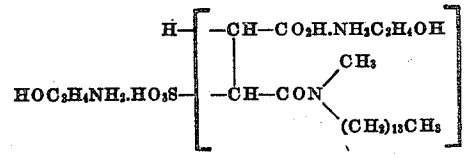
The product was a viscous solution having outstanding foaming and wetting power. It contained about 30% of active material, which was the di-monoethanolamine salt of N-methyl,N-lauryl-sulfosuccinamic acid, having the probable formula:



Example 2

22.7 parts (1 mol) of N-methyl-normal-tetradecylamine were added to 9.8 parts (1 mol) of maleic anhydride in granulated form. During the mixing of the reactants, cooling was used as required to prevent the temperature from rising above 105° C. The reaction mixture was agitated for four hours at a temperature of from about 95° to about 105° C. Thereafter, a solution of di-monoethanolamine sulfite which was made by stirring 12.2 parts (2 mols) of monoethanolamine in 30 parts of water and passing in 6.4 parts of SO_2 gas (1 mol) while maintaining the temperature at about 30° C., and which had a faintly alkaline reaction to phenolphthalein, was added to the hot N-methyl-normal-tetradecylamine-maleic anhydride reaction product. The resulting mixture was agitated and heated for 7 hours at 95° to 100° C., except when the temperature had to be lowered slightly to counteract excessive foaming. The reaction mass was diluted with about an equal volume of water (about 80 parts) and, if necessary, the pH of the solution was adjusted to 7 to 7.5 or higher. The solution was subjected to a purification treatment with activated carbon "Darco," in the proportion of 5.3 parts of the total solution, at 55° to 60° C. for about one hour. It was then filtered, using "Super-Cel."

The product so obtained was a viscous solution having outstanding foaming and wetting power. It contained about 30% of active material, which was the di-monoethanolamine salt of N-methyl,N-normal-tetradecyl-sulfosuccinamic acid, having the probable formula:



By evaporating the solutions obtained by the processes of the above examples under vacuum, the di-monoethanolamine N-methyl,higher N-alkyl sulfosuccinamates can be obtained in the form of viscous semi-solids.

In preparing shampoos for personal use, for which the compounds of the present invention are particularly valuable by reason of their high lathering power, there are mixed with the compounds a thickening agent (as, for example, sodium alignate or an alkyl ether of cellulose) and other customary ingredients (such as, a small amount of perfume, dye, etc.). An especially effective thickening agent for this purpose is a high viscosity cellulose ether such as a methyl cellulose which gives solutions of high viscosity.

It is possible further to improve the properties of shampoos made with the compounds of the present invention by admixing with them stabilizing agents which are anion-active, water-soluble organic salts having within their molecules, besides a salt-forming group that induces solubility in water, at least one alkyl group containing 5 to 11 carbon atoms but not more than 9 carbon atoms in a straight chain, and not having any alkyl group containing more than 11 carbon atoms nor more than 9 carbon atoms in a straight chain; such as the alkali metal, ammonium or alkylolamine salts of monoalkyl esters of sulfuric or sulfoacetic acids in which the alkyl groups are of said type (for example, the sodium, potassium, ammonium or ethanolamine salts of normal octyl sulfate or of 2-ethylhexyl sulfoacetate).

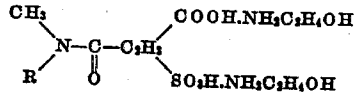
An important feature of such shampoos is their ability to form lathers which become thicker and creamier with increasing hardness of the water used. This increase in lather consistency is due to the fact that the percentage of shampoo solution retained in the foam increases with increasing hardness of the water, while the volume of foam simultaneously decreases or else remains substantially constant. The ability to give unusually thick, creamy lathers in hard water constitutes an important advantage of the products of this invention.

Since changes can be made in the products above described and the processes described for making them, without departing from the scope of the invention, it is intended that all matter contained in the above description shall be interpreted as illustrative and not in a limiting sense.

This application is a continuation-in-part of my application filed August 6, 1942, Serial No. 453,850, now abandoned.

I claim:

1. The di-monoethanolamine salts of N,N-disubstituted sulfosuccinamic acids having, as one N-substituent, an open-chain hydrocarbon radical of 10 to 18 carbon atoms, and, as the other N-substituent, the methyl radical, said salts corresponding with the formula



wherein R represents an open-chain hydrocarbon radical of 10 to 18 carbon atoms and being characterized by having high solubility in water and foaming and lathering power to a high degree.

2. The di-monoethanolamine salt of N-methyl, N-alkyl sulfosuccinamic acid having an alkyl hydrocarbon radical of 12 to 16 carbon atoms as the N-alkyl radical.

3. Di-monoethanolamine N-methyl,N-lauryl-sulfosuccinamate.

4. Di - monoethanolamine N - methyl,N - tetradecyl-sulfosuccinamate.

5. Di-monoethanolamine N-methyl,N-cetyl-sulfosuccinamate.

LAWRENCE H. FLETT.

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