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3,280,179

PROCESSES FOR PRODUCING ACYCLIC SURFACTANT SULFOBETAINES

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This invention relates to sulfobetaines of purity and constitution suitable for incorporation into soaps and other toilet articles, and which are substantially free of harsh and corrosive inorganic salts, and also to methods for preparation thereof, and to soaps and other toilet articles which contain such sulfobetaines.

Tertiary amines having hydrophobic groups have been employed in forming salts by neutralization with an acid or by conversion into quaternary salts which have surfactant activity and are cationic. Usually, unless so neutralized, either by salt formation or quaternization, such tertiary amines are not dispersible in water, being hydrophobic. Such quaternary salts react in stoichiometric proportions with anionic surface active agents to form poorly soluble or water insoluble, and therefore generally undesirable, electroneutral complexes. The presence of such amine salts or quaternary compounds is therefore detrimental where anionic surface active agents are component parts of preparations as in the manufacture of shampoos, toilet soaps, shaving cream and numerous other preparations of surfactants. Furthermore, the presence of halide salts will impart corrosive properties under most conditions.

I have now discovered that another class of compounds containing a quaternary nitrogen, which are "ionic neutral" and are thus stable and substantially non-reactive in acid, neutral and alkaline solutions, have a strong surfactant activity and are particularly useful for the above indicated and other purposes, when prepared in substantially salt-free form. These compounds are the so-called sulfobetaines. They are classed here as "ionic neutral," to distinguish them from the ionic surfactants, to wit, anionic, cationic and the ampholytes, which are reactive with acids or bases, and the non-ionic surfactants.

As a result of my investigations, I have found that sulfobetaines of a constitution hereinafter more specifically described have surprising surfactant properties which distinguish them, and for this reason I have described them as acyclic surfactant sulfobetaines, to distinguish them from the aromatic and other sulfobetaines which show substantially no surfactant activity.

A significant property of the "ionic neutral" acyclic sulfobetaine surfactants of my invention is their compatibility with all classes of surface active agents, i.e., cationic, anionic, non-ionic and ampholytic surface active agents. When incorporated in compositions containing such agents, these sulfobetaine compounds impart valuable properties and will not produce precipitates with or otherwise deactivate other surfactants present, whatever their ionic constitution may be.

The acyclic surfactant sulfobetaines of my invention have the property, when combined with anionic surfactants such as fatty acid soaps, of improving surfactant activity of the soap and inhibiting the formation of scum usually obtained with fatty acid soaps of the alkali metals, ammonium and amine soaps resulting usually from precipitation of lime and magnesium soaps, arising from the hardness of the water. The frothing action of the soap is also improved.

I have also found that an enhancement of the detergent action of the anionic surfactant is obtained. Thus, as I have found, the laundering activity of soaps may be substantially improved by adding the acyclic surfactant sulfo-

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betaines to soap. In fact, there appears to be a synergistic relationship between the soap and such sulfobetaines.

Thus, the sulfobetaines of my invention may be incorporated into soaps both of the laundering and cosmetic grade, to improve their functions. It is a particularly useful additive to bar soaps and shaving soap sticks and other soaps in a solid state, whether in tablet form or as soap chips or soap powder.

The properties of the acyclic surfactant sulfobetaines of my invention also make them particularly useful in shampoos and liquid soaps. When used in combination with anionic surfactants in such toilet preparations, they counteract the undesirable properties of the anionics. For example, when employed in toilet articles applied to the skin or the hair, as in shampoos, they counteract the property of the anionics to embrittle and mat the hair, a property which, in shampoos, is usually attempted to be overcome by use of conditioners or by use of subsequent cationic rinses.

Contrary to the property of the prior art conditioners, the acyclic surfactant sulfobetaines of my invention, while counteracting the harshness of the anionic surfactants and their matting property, to leave the hair soft and manageable, do not impair the foaming and lathering properties of the shampoo or liquid soap, but may actually enhance such lathering and foaming properties.

Because of these inherent frothing and cleaning properties of the sulfobetaines of my invention, I may exclude the anionics from formulations of soaps and toilet articles and employ the acyclic surfactant sulfobetaines to the exclusion of the anionic surfactants.

The sulfobetaines of my invention are excellent wetting agents and are good foam formers, to produce profuse and stable foams and lathers in water and also in alkaline, acid and salt solutions. They are also excellent detergents and are unreactive and stable in acid and alkali solutions and in solutions containing electrolytes.

They may thus be added to quaternary ammonium compounds used as sanitary chemicals to impart sudsing and detergency values to the bacteriostatic and bacteriacidal solutions of these quaternary ammonium compounds. Other well known cationic materials, such as for example those used in hair rinses to condition hair shampooed with anionic shampoos, may have their foaming properties and detergency improved by adding the sulfobetaines of my invention, employing, for example, like percentages as are hereinafter given for shampoos containing anionics and the sulfobetaines of my invention. Because of their stability in highly alkaline or acid solutions, they may be added to such solutions employed as washing compounds in bottle washing and in other industrial cleaners, both of the alkaline and acid types.

Their stability in acid solutions makes them suitable for use as wetting agents to be added to metal plating electrolytes in plating baths and in the electrolytes employed in acid anodizing of aluminum.

A useful property of the sulfobetaines of my invention is as scale preventive agents in boilers and other applications where scale is formed. The addition of from 1 to 100 parts per million of the sulfobetaine to the water usefully inhibits hard scale formation.

Another use to which the sulfobetaines may be placed is in the preparation of emulsion polymers of various kinds where the sulfobetaine will act as an excellent dispersing agent, but will also enhance the "freeze-thaw" stability of the emulsion polymer.

Sulfobetaines have, in the prior art, been reported to be prepared from a compound assumed to be a chloroalkane sulfonic acid, particularly the chloro-hydroxyalkane sulfonic acid, by reaction of such acids with a tertiary amine, to produce compounds which are said to be unstable in concentrated alkali solutions. The reaction

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involves two moles of amine and one mole of the sulfonic acid, producing equimolar quantities of sulfobetaine and the amine hydrochloride. The subsequent neutralization and extraction of the tertiary amine leaves equimolar quantities of a chloride and of sulfobetaine. Such a process will not produce a product useful as a surfactant for toilet articles or for incorporation in soaps or for other end uses wherein the presence of substantial quantities of inorganic salts, or of tertiary amine salt having cationic properties, is detrimental. The resultant sulfobetaine produced by the above process contains about 50 molar percent of the chloride salt. Such a product is corrosive, harsh and highly deliquescent. For such reasons, compounds which contain a large amount of salt are usually excluded from preparations which are to be incorporated as surfactants in toilet articles. As far as applicant knows, sulfobetaines have not been used in soaps or toilet articles; and the surprising properties of the sulfobetaines which are included in the class of the acyclic surfactant sulfobetaines which applicant has discovered make them highly useful in soaps, shampoos and other toilet articles, is a novel discovery of applicant.

Further, as I have found, when the sulfobetaine is formed from an aromatic tertiary amine, the sulfobetaine is crystalline and may be separated by fractional crystallization. But, as I have found, aromatic sulfobetaines, even when substantially free of salts, form solutions which show substantially no surfactant activity when tested by standards accepted in this art. In the type of sulfobetaines which I have found to be useful as surfactants, the acyclic surfactant sulfobetaine is non-crystalline, amorphous, waxy or liquid. Such compounds, when formed by reaction with a chloroalkane sulfonic acid, may not be separated from the amine hydrochloride formed in the above reaction, by any economically useful process known to the applicant.

I have now discovered a procedure whereby the sulfobetaine may be formed substantially free of inorganic salts and substantially free of other salts such as amine salts of inorganic acids and of other contaminants, such as amines, in amounts which deleteriously affect the utility of the sulfobetaines of my invention. Small amounts of sulfonic acid salts and trace amines which sometimes are contained do not deleteriously affect the utility of the sulfobetaine surfactants of my invention. In fact, hydroxy alkane sulfonic acid salts which may be present in small amounts may add valuable properties to the surfactant sulfobetaines of my invention. The process of my invention results in a sulfobetaine which is a highly useful additive to toilet preparations and other quality surfactant preparations.

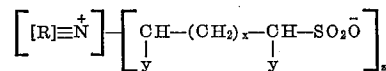
This procedure involves an adduct formation by reaction between an acyclic tertiary amine and an alkyl sultone, whereby the tertiary amine is alkylated to form a substituted ammonium alkyl sulfonic acid betaine, referred to herein as a sulfobetaine. Provided that the tertiary amine is of the proper chemical constitution, I can produce by such reaction sulfobetaines free of inorganic salts, having substantial and surprising surfactant activity.

Such products show a surprisingly broad usefulness as lathering agents, are water dispersible and produce stable foam, as detergents by themselves or in combination with soaps or other surfactants, as lime soap dispersing agents, as conditioning and softening agents, and as wetting agents. Several or all of these properties are exhibited by various of these sulfobetaines, not only in soft or tap water but also in sea water and in strong electrolyte solutions such as those of mineral acids, caustic alkalies and salts thereof. They are stable and will not be precipitated or decomposed or split up in acids or alkalis of even high concentration.

These surprisingly useful properties of the sulfobetaines make these materials unique among the surfactant materials.

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The class of sulfobetaines which I have found useful for the purposes of this invention, and which I designate as the acyclic surfactant sulfobetaines, are those which are characterized by the formula:



in which x is at least 1 and not more than 2, and y may be either a hydrogen or a methyl; and in which $[R] \equiv N$ is a quaternary radical chosen from the group as described below, and z is one or a number up to the number of tertiary amine nitrogens in the tertiary amine radical, if the tertiary amine contains more than one tertiary amine nitrogen.

In order to be of utility for the purposes of this invention for toilet preparations and surfactants of high quality, the compound should be substantially free of inorganic salts. Small amounts of such salts, as herein-after set forth, may be tolerated, but substantial quantities of corrosive or deliquescent salts, such as the metallic halides, such as the alkali metal or the alkali earth halides, and specifically the chlorides and bromides, as well as the cationic surfactant salts such as tertiary amine salts, should be excluded, as is more fully described below.

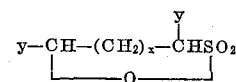
The products produced by employing the tertiary amines and sultones, according to my invention, and useful for incorporation in toilet articles and quality surfactants, are oily liquids or pasty semi-solids or waxy solids, and are not crystalline and may not be readily separated by crystallization for purposes of purification. In this way they are substantially distinguished from the aromatic sulfobetaines, in which an aromatic group is directly linked to or is heterocyclic with the quaternary nitrogen joined to the alkane group of the sulfonic acid radical. These types, while they may be produced by reaction of an aromatic tertiary amine with sultones in relatively pure form, do not show the surfactant activity of the sulfobetaines of my invention, and are therefore excluded from the groups of compounds which may thus be employed in soaps and other toilet articles for the purposes described above and hereinbelow.

By employing the adduct reaction described above, and as will be more fully described below, products may be directly produced in substantially pure forms so that they may be used directly without further purification as surfactants or additives as described above and described herein.

In forming the sulfobetaines of my invention, I employ the tertiary amines, $[R] \equiv N$, containing at least one higher acyclic radical as described below, which upon reaction with the alkanesultones will yield water soluble surface active quaternary ammonium alkane sulfonic acid betaines. The tertiary amines suitable in the preparation of these surface active, water soluble or dispersible, ammonium alkane sulfonic acid betaines through addition (alkylation) of alkanesultones upon such bases, may be acyclic, alicyclic or non-aromatic heterocyclic tertiary amines corresponding to the following general structure:

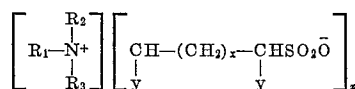


These tertiary amines are non-aromatic; that is to say, the tertiary amine nitrogen is not directly attached to a benzene ring, nor is a member of a heterocyclic aromatic ring such as in the pyridine or pyrazine or quinoline ring system or their homologs and analogs. Such non-aromatic tertiary amines, on reaction with the alkane sultones,



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form the substituted ammonium alkane sulfonic acid betaines (sulfobetaines):



When the



radical contains but one tertiary nitrogen, z is equal to one. When the radical contains more than one tertiary nitrogen, the value of z may be up to a number equal to the number of such tertiary nitrogens present in the above radical. Thus, one or all of the nitrogens may be in quaternary form, or some of the nitrogens may be unreacted and in tertiary nitrogen form. Thus, where the tertiary amine has only one tertiary amine nitrogen, $z=1$. Where the tertiary amine employed in the reaction is a polytertiary amine, all of the nitrogens may be quaternarized by the sultone, and are preferably so quaternarized where the sulfobetaine is the ionic neutral surfactant sulfobetaine of my invention. The value of z is therefore equal to the number of quaternary nitrogens in the sulfobetaine.

In the above tertiary amine and the corresponding sulfobetaine, x and y have the above significance; N is the quaternary nitrogen in the sulfobetaine. The radicals R_1 , R_2 and R_3 are chosen for purposes of forming the surfactant sulfobetaines of my invention, so as to produce water dispersible sulfobetaines having the surfactant activity described herein and to be ionic neutral. R_1 is a radical chosen from the group consisting of an acyclic radical having at least 8 and not more than 18 carbon atoms, chosen from the group consisting of the unbranched and uninterrupted straight carbon-carbon chain, and branched chain acyclic radicals having from 9 to 18 carbon atoms with at least one carbon-carbon chain of not less than 8 carbon atoms, herein referred to as higher acyclic, said higher acyclic group being joined to said quaternary nitrogen through a linking group, said linking group including an acyclic carbon joined directly to the nitrogen; that is, the carbon joined directly to the nitrogen is part of an acyclic group which may be the terminal carbon of the higher acyclic carbon-carbon chain or part of another acyclic radical containing one or more than one carbon atom in an uninterrupted straight carbon-carbon chain of not more than 6 carbon atoms, such acyclic radical herein referred to as lower acyclic, said other linking group being chosen from the group of radicals consisting of an amido group or other non-basic nitrogen group and an oxy group, each linked to the nitrogen through a lower acyclic group.

R_2 is a non-aromatic radical chosen from the group consisting of a lower acyclic radical, an alicyclic group and a non-aromatic heterocyclic group, each having not more than 6 carbon atoms in an uninterrupted carbon-carbon chain, a hydroxy acyclic group, an acyclic polyalkylene glycol, and an acyclic glycol ether group, the acyclic fraction thereof being an uninterrupted carbon-carbon chain of from 1 to 6 carbon atoms.

R_3 is chosen from the group consisting of R_1 and R_2 radicals; and R_1 , R_2 and R_3 are also chosen from the group of radicals consisting of the above radicals R_1 , R_2 and R_3 , in which at least two of said radicals are joined into a heterocyclic radical with said tertiary or quaternary nitrogen.

In the above compounds, the carbons of the groups may be substituted. For the purpose of forming ionic neutral higher acyclic surfactant sulfobetaines, these substituents should be groups incapable of forming salts in water solution with acids or bases. Naming such groups as non-ionic, the above substituents are definable as non-ionic and will be so named herein.

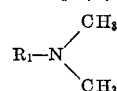
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Where the sulfobetaine contains more than one amino nitrogen, it is desired that they be all in quaternary ammonium form. Thus, for purposes of the ionic neutral surfactants of my invention, while non-basic amido or imido nitrogen may be included, primary, secondary or unquaternarized tertiary amines are preferably not included.

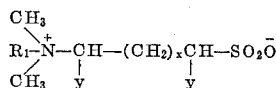
Such sulfobetaines, which conform to the description given above, are ionic neutral and have surfactant activity, which permits their identification as higher acyclic surfactant sulfobetaines which are ionic neutral and thus have utility described herein.

The following Groups (a) to (j) are specific examples, indicated for illustration only and not as a limitation of my invention:

Group (a)

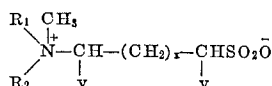


Higher acyclic dimethyl amine, on reaction with the alkane sultone, forms:



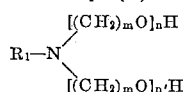
Higher acyclic dimethyl ammonium alkane sulfonic acid betaine, wherein the alkyl group R_1 is a higher acyclic radical chosen from a radical having at least 8 carbon atoms and not more than 18 in an uninterrupted carbon-carbon chain.

Such tertiary amines may be prepared by the Leuckart (Wallach) reaction or modification thereof (see also Kirby, U.S. Patent 2,366,534), as by reaction of formaldehyde and formic acid with higher primary or secondary amines. With secondary amines, tertiary amines may be formed having two higher acyclic groups such as indicated as R_1 . The methyl groups may, on the other hand, be replaced by other straight chain or branched acyclic hydrocarbons of 2 to 6 carbon atoms in an uninterrupted chain, or alicyclic or heterocyclic groups containing not over 6 carbon atoms, as described herein. Such compounds may be:

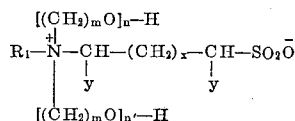


Where R_1 and R_2 are as stated above in this Group (a).

Group (b)



Higher acyclic di(hydroxyalkyl) amine, on reaction with alkane sultone, forms:

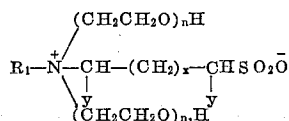


Higher acyclic di(hydroxy alkyl) ammonium propane-sulfonic acid betaine, wherein R_1 is chosen from a radical as in Group (a); when n and n' are each one and m may be from 1 to 6, and the hydroxyl may be on the terminal or other carbon of the alkyl group, for example, the hydroxy alkyl group may be hydroxy ethyl or hydroxy propyl. The amine is the corresponding alkanol amine. When n and n' are numbers greater than one, the compound is a polyglycol ether alkanol amine. The letter m may be a number from 2 to 6. The corresponding sulfobetaines result from these amines.

Such tertiary amines may be readily prepared by reacting primary or secondary higher acrylic amines with ethyl-

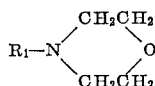
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ene oxide. Reacting each labile amino hydrogen with one mole ethylene oxide will result in the corresponding ethanamines, while further reaction with additional ethylene oxide will produce the di and polyglycol ether ethanol amines. In like manner, the reaction may be with propylene oxide or butylene oxide. The limit of the numerical value of n and n' may be one or a higher value, and m is selected to give uninterrupted carbon-carbon chains of from 1 to 6 carbon atoms. The chain lengths are chosen to result in alkane sulfonic acid betaines which have surfactant activity. Thus, for example, the polyglycol ether in which n and n_1 are 5 is given by the following general formula:

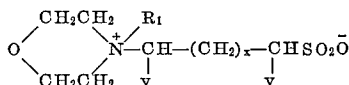


Propylene oxide or butylene oxide may be used instead of ethylene oxide to produce useful homologous products. Secondary amines may be used as starting materials, wherein there are two groups such as R_1 or R_1 and R_2 , to form the corresponding tertiary amine.

Group (c)



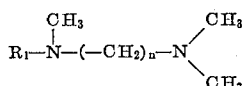
higher acyclic morpholine, on reaction with alkane sultone, forms:



Higher acyclic morpholinium alkane sulfonic acid betaine.

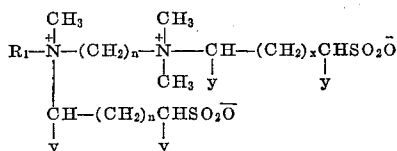
The radical R_1 is chosen from a group as outlined under Group (a).

Group (d)

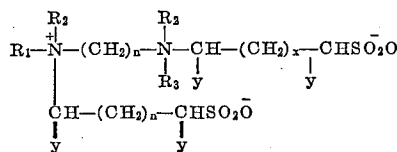


N-higher acyclic-N methyl N'N'dimethyl alkylene diamine.

On reaction with the alkane sultone, the sulfobetaine formed may be one in which the alkane sulfonic acid group may be attached to one or to both tertiary nitrogens, depending on the mol ratio of alkane sultone to tertiary amine; thus, where both nitrogens react:

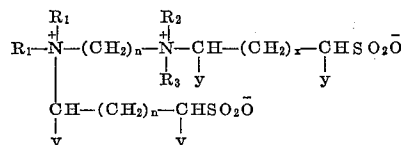


Wherein R_1 is chosen from a group such as outlined in Group (a), and n is a number from 1-6. One or more of the methyl groups may be replaced by a group such as is chosen from those included in R_2 or R_3 :



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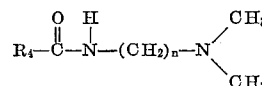
One only of the methyls joined to the tertiary N may be replaced by another radical like R_1 . Such compounds will have the formula, for example:



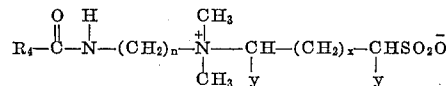
In the above, n is a number from 1-6.

The manufacture of the above amines may be accomplished by reaction of a higher primary or secondary alkylamine with acrylonitrile, followed by hydrogenation of the nitrile group into an amino group (while protected by the presence of ammonia) and subsequent alkylation of the primary and secondary amino groups with acyclic, alicyclic, heterocyclic, hydroxyalkyl or polyglycoether-alkanol groups as outlined in Groups (a) and (b). As in Group (c), the primary amino group can also be converted into a morpholine group by reacting the same with dichloroethyl ether, or to a pyrrolidine or other non-aromatic heterocyclic ring including the quaternary nitrogen.

Group (e)



Higher acyclic acyl amido alkyl dimethyl amine, on reaction with alkane sultone, forms:

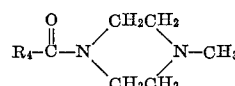


Higher acyclic amido alkyl dimethyl ammonium alkane sulfonic acid betaine.

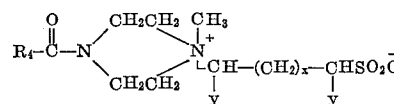
Wherein the acyl group R_4CO is a radical such as R_1 specified above, and is chosen as a radical having at least 8 and not more than 18 carbon atoms in an uninterrupted chain, including said carbonyl carbon, and n is a number from 1 to 6. One or more of the methyl groups may be replaced by any radical included in R_3 ; preferably one only of the methyl groups may be replaced by any radical included in R_1 . Thus, one methyl may be substituted by R_2 radical, and the other by an R_3 radical.

Such tertiary amines are readily produced by condensation of a fatty acid or other higher carboxylic acid or ester thereof with an aminoalkyl tertiary amine. Typical examples may be taken from Cook U.S. Patent 2,459,062.

Group (f)



1-(higher) acyclic acyl-4-methylpiperazine, when reacted with the alkane sultone, forms:

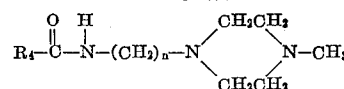


1-(higher) acyclic acyl-4-methylpiperazinium alkane sulfonic acid betaine.

Both the acyl group as well as the methyl group can be varied as in Group (e).

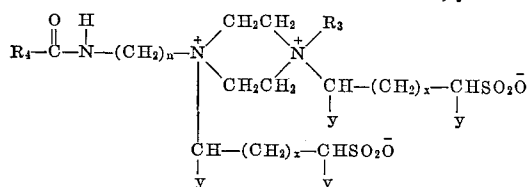
This compound is prepared by condensation of N-methylpiperazine or other N-substituted piperazine with a higher carboxylic acid or ester thereof.

Group (g)



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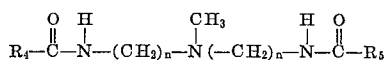
1-(higher) acyclic acyl alkylamido-4-alkyl piperazine, when reacted with two mols of alkane sultone, yields:



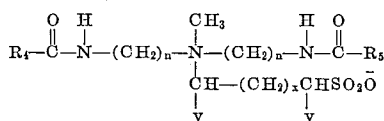
1-(higher) acyclic acyl alkylamido-4-R₃-piperazinium-1,4-bis-(alkane sulfonic acid betaine).

The acyl group R₄CO is the R₄CO specified in (e) above, and the R₃ may be a methyl group or any other group included in R₂. R₃ and the alkanesulfonic acid group together may be replaced, for example, by an acyl group, a urea group or a carbamate group. The integer *n* is one or a number up to 6. In like manner, the above sulfobetaine may be formed with one mole of sultone to give the mono sulfobetaine. This, however, leaves a tertiary nitrogen which is not desirable in the ionic neutral surfactants, as described herein.

Group (h)



Di(acyclic-acyl amidoalkyl) methyl amine, when reacted with alkane sultone, forms:

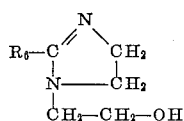


Di(acyclic-acyl amidoalkyl) methyl ammonium alkane sulfonic acid betaine. The R₄CO group is the R₄CO group referred to in (e) above.

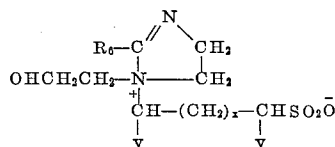
One or both of the acyl groups may be varied as in (g) above. The methyl group may be varied as under Group (g). *n* is one or a number not greater than 6.

These compounds may be prepared by reacting a lower primary amine such as methylamine with acrylonitrile, followed by hydrogenation into the corresponding triamine and condensing the same with higher carboxylic acids or esters, to mention a specific creation route as an illustration.

Group (i)



2 - (higher) acyclic - 1 - hydroxyethyl - 2 - imidazolium-1-alkane sulfonic acid betane:

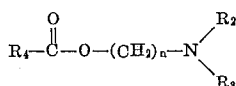


2 - (higher) acyclic - 11 - hydroxyethyl - 2 - imidazolium-1-alkane sulfonic acid betane.

R₆ is an acyclic radical forming with the ring C linked to quaternary nitrogen the acyclic carbon-carbon chain included in R₁ above. The hydroxyethyl group may also be replaced by R₂ above.

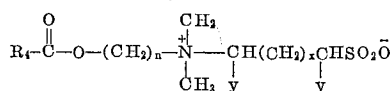
The amide linkages in Groups (e) through (h) may be replaced by ester linkages. For example, see below.

Group (j)



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(higher) acyclic acyloxy-alkyl dimethylamine, when reacted with alkane sultone, forms:

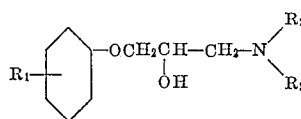


(higher) acyclic acyloxy-alkyl dimethylammonium alkane sulfonic acid betaine.

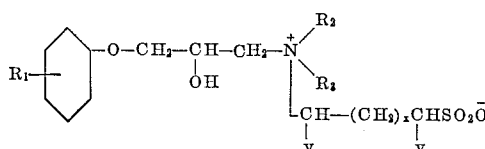
The acyl group R₄CO is an acyl group as described in Group (g). The methyl groups may be replaced as indicated in Group (g). *n* is one or a number no greater than 6.

The compounds are readily prepared by condensation of a lower hydroxyalkyl tertiary amine with a higher carboxylic acid or ester, such as for instance fatty acids or fatty methyl esters. Hydroxyalkyl dialkylamine, hydroxyalkyl morpholine, 1,4 di(hydroxyalkyl) piperazine, etc., may be considered useful starting materials in the preparation of such esters. The superior hydrolytic stability of the compounds (a) through (i) and (k) makes their selection in the preparation of the so-derived alkane sulfonic acid betaine preferable.

Group (k)



Higher acyclic phenoxy, hydroxy propyl tertiary amine, when reacted with alkane sultone, forms:



(higher) acyclic phenoxy, hydroxy propylammonium propanesulfonic acid betaine.

R₁ is higher acyclic radical and is usually para, but may be ortho or meta. The corresponding sulfobetaine is made by addition of the sultone to the tertiary nitrogen, as above.

The tertiary amines above indicated and similar compounds suitable for reaction with the sultone to produce sulfobetaines all contain at least one and not more than two higher acyclic or acyclic acyl groups having at least 8 uninterrupted carbon atoms and no more than 18 carbon atoms in the radical. These may be present as normal acyclic or normal acyclic acyl groups, such as are present in or may be derived from naturally occurring animal or vegetable oils or fatty acids derived therefrom, for example:

Acyclic radical (R₁):

- Caprylyl (n-octyl)
- Capryl (n-decyl)
- Lauryl (n-dodecyl)
- Myristyl (n-tetradecyl)
- Palmityl (n-hexadecyl)
- Stearyl (n-octadecyl)
- Palmitoleyl (9-hexadecenyl)
- Oleoyl (9-octadecenyl)
- Linoleyl (9,12-octadecadienyl)
- Linolenyl (9,12,15-octadecatrienyl)

Acyclic acyl radical (R₄CO=R₁):

- Capryloyl (n-octoyl)
- Caproyl (n-decanoyl)
- Lauroyl (n-dodecanoyl)
- Myristoyl (n-tetradecanoyl)
- Palmitoyl (n-hexadecanoyl)
- Stearoyl (n-octadecanoyl)
- Palmitoleoyl (9-hexadecenoyl)
- Oleoyl (9-octadecenoyl)
- Linoleoyl (9,12-octadecadienoyl)
- Linolenoyl (9,12,15-octadecatrienoyl)

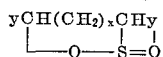
In addition to the above even numbered, unbranched higher acyclics, odd numbered unbranched acyclic or acyclic acyl groups may be used; for instance: nonyl or nonanoyl; undecyl or undecanoyl; tridecyl or tridecanoyl; etc. There may also be used the branched chain isomers of the above acyclic or acyclic acyl groups, for example, 1-heptyl undecyl, $C_7H_{15}CH(C_{10}H_{21})$ and 1-methyl heptadecyl, $C_{17}H_{35}(CH_3)$ and intermediate compounds, for example, trimethyl decyl, $(CH_3)_3C_{10}H_{19}$ and the acyl analogues thereof, wherein the terminal carbon is acyl.

Instead of using a single pure tertiary amine, in which all of the C_8 to C_{18} chains are the same, I may use mixtures of amines, where the nitrogen is substituted by different C_8 to C_{18} chains. Thus, for example, I may employ mixtures of tertiary amines containing different chain lengths of C_8 to C_{18} , or different chains of the same chain length, for example, any one of those specified above. Thus, I may use those tertiary amines derived from the acids or esters of natural oils and fats, for example, those derived from coconut oil, palm-kernal oil, babassu oil, cohune oil, murmur oil, all of which contain substantial percentages of the esters of lauric acid and myristic acid and will yield mixtures of lauryl and myristyl amines, or mixtures of lauroyl and myristoyl amido acyclic amines. Other natural oils and fats may also be used, such as soya bean oil, safflower oil, olive oil, corn oil, and tallow, all of which will yield mixtures of amines in which the tertiary amine or the amido acyclic tertiary amine are mixtures derived from the naturally-contained esters of the acids in the natural oil and fat.

For simplicity of naming, where the tertiary amine is a mixture derived from the natural oils, saturated or unsaturated, it will be named acyclic, with the natural oil or fat stated in parenthesis, as, for example, acyclic (coco-fatty), meaning that the amine group contains C_8 to C_{18} chain comprising mixtures of the kind present in the natural coconut oil; or acyl, with the natural fats in parenthesis, as, for example, acyl (coco-fatty), meaning that the C_8 to C_{18} chain is a mixture of compounds containing acyl groups comprising mixtures similar to the mixture of esters in the natural coconut oil. Similarly, the same significance will be attached to other similar notations in like parenthetical expressions for other natural oils. In each case the amine will be a mixture of tertiary amines in which the compounds contain C_8 to C_{18} chains or acyl groups which are in mixture similar to those in the corresponding natural oil. In each case the corresponding amine or the sulfobetaine derived from them is a mixture of amines or sulfobetaines in which the individual amines or sulfobetaine is substituted by different C_8 to C_{18} chains, all found in proportions similar to the proportions of the chains as found in the natural oil, for example, in the specific example given above, in the coconut oil. The proportions present may be different from those in the natural oil, because of the modifications by the reactions whereby such esters or the corresponding acids are used as starting reactants in process for conversion to the tertiary amines by procedures well known in the chemical arts.

The process for producing the sulfobetaines of my invention in a form to be substantially free of inorganic salts or amine salts, whether organic or inorganic, which, as I have found, are particularly useful as surfactants and surfactant additives to soaps, comprises reacting an alkane sultone with a tertiary amine such as is specified above for the formation of such sulfobetaines.

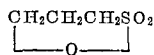
Such alkane sultones have the generic formula:



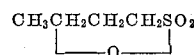
where y is either H or CH_3 , and x is 1 or 2.

For example:

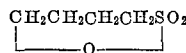
1,3-propane sultone:



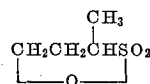
1,3-butane sultone:



5 1,4-butane sultone:



10 1,3-propane-1-methyl sultone:



15 Sultones of the higher molecular weight alkanes, such as pentane, isopentane and hexane and isohexane sultones, where the ring is closed on the 3 or 4 carbon (counting the carbon connecting the sulfo group as carbon 1), may also be used. Propane and butane sultone are preferred.

20 The reaction between the tertiary amine and the sultone is an alkylation, forming an adduct with substantially no side reaction. The reaction may be carried out, and I preferably do carry out the reaction, in an aqueous or alcoholic solution, or mixtures thereof, to control the reaction. The quantity of diluent employed is not critical. 25 A weight equal to the weight of reactants is a suitable ratio. More or less may be employed to moderate the reaction. The sultone ring opens up, and the methylene group to which the oxygen was originally joined forms a nitrogen-to-carbon bond through the unshared electron pair, thus giving a nitrogen compound of higher valence. 30 The sulfo acid group is ionically negative and neutralizes the residual positive charge on the quaternary nitrogen.

Applicant is of the opinion that the binding of the oxygen and nitrogen is ionic, but the compounds formed 35 are not ionogenic, as is the case of the ordinary quaternaries formed by reaction of a tertiary amine with a quaternarizing compound such as, for example, an aliphatic halide. The sulfobetaines of my invention are not ionogenic, since they form neutral solutions and may not be titrated by acid, for example, hydrochloric acid or 40 sulfuric acid, or by alkalis, such as sodium hydroxide or potassium hydroxide. They may, therefore, not be classed as cationics, as are the quaternaries, nor anionic, as are the sulfonate surfactants. They are not non-ionic, since they are an internal salt, but can also not be classed as amphoteric. They form, therefore, a separate class 45 of surfactants, and may be termed "ionic neutral" surfactants.

The alkane sulfonic acid betaines of this invention thus 50 formed from the tertiary amines specified above are, therefore, the alkane sulfonic acid betaines in which the alkane group is chosen from the group of the alkane radicals containing at least three and not more than six carbon atoms and in which the quaternary nitrogen is joined to 55 radicals R_1 , R_2 and R_3 in which the R_1 , R_2 and R_3 are chosen from the groups of radicals as stated above in connection with the tertiary amines stated as preferred for the formation of the sulfobetaines of this invention.

The above adduct reactions, however, are strongly affected by the structural character of the substituents on the tertiary nitrogen. When nitrogen is substituted by one or two substituents which contain the C_8 to C_{18} chain, as specified above, and the other remaining substituents are all methyl, the reaction is so rapid, even at low temperatures, that substantially all of the sultone is converted into the sulfobetaine. The reaction is so rapid that, even in the presence of large amounts of water or aqueous solutions of organic solvents, substantially no hydrolysis of the sultone occurs. Nor is there any substantial 70 reaction between the sultone and a reactive organic solvent. For example, where the organic solvent is an alcohol, there is substantially no alcoholysis.

When, however, one or both R_2 and R_3 of the remaining substituents other than R_1 is an oxygenated group such 75 as a hydroxy alkyl, polyglycoether, or morpholine group,

the reaction is more sluggish and requires elevated temperatures. If the reaction is carried out in an aqueous medium or in a medium containing compounds reactive with the sultones, such as alcohol, the higher temperature increases the rate of reaction between the sultone and the diluent or solvent, for example, increases the rate of hydrolysis or other side reactions, such as alcoholysis, to introduce undesirable impurities.

I have, however, found that I can catalyze the sultone tertiary amine adduct reaction in such cases to such a rate that the side reactions of the sultone are substantially suppressed, and the sulfobetaine is formed substantially free of product produced by such side reactions.

The catalysts which I have found useful are certain alkali metal halide salts, especially the alkali metal bromides and iodides, and particularly potassium iodide. The weight of the iodide required is about 3% or less, i.e., about 1% to about 3% based on the weight of the tertiary amine, and this amount of halide salt remains in the sulfobetaine but has been found not to interfere with the function or utility of the sulfobetaine for the purposes of my invention, and thus may be contained in a composition consisting essentially of the sulfobetaine within the meaning of this invention.

Usually the reaction proceeds substantially quantitatively, and an amount of sultone may be employed which is stoichiometrically equivalent to the amount of tertiary amine on the pure basis which is employed. Thus, where the tertiary amine has only one tertiary nitrogen, equal molar ratios may be employed; or, if the tertiary amine is a polytertiary amine, one mole of the sultone may be employed for each nitrogen to be reacted per mole of the polyamine.

Where, however, the tertiary amine contains impurities other than the tertiary amines or other compounds reactive with the sultone, the amount of sultone employed may need to be increased to compensate for the sultone consumed by such side reactions.

The mole ratio of sultone to the tertiary amine may be greater than one to one, based on the pure tertiary amine, where, when employing such one-to-one ratio, the residual tertiary amine left because of the incompleteness of the reaction to 100% conversion, is undesirable in the final product. In such case, I may use a molar excess of sultone in order to increase the percent conversion of the tertiary amine. Thus, for example, up to 5% to 10% molar excess, based on the tertiary amine, will usually be found to be sufficient to convert the tertiary amine, so as to reduce the tertiary amine to such low percentages as to make their presence not deleterious for the uses of the sulfobetaine as a surfactant, as described herein.

Some hydrolysis of the sultone occurs where the reaction is carried out in the presence of water to produce an hydroxyalkane sulfonic acid. This may be neutralized with sodium hydroxide to give the corresponding salt and any minor or even trace amounts of amines which result from the reaction. The resultant product thus contains the sulfobetaine, with substantially no salt, if no excess of sultone is employed or catalyst added. If an excess of sultone is used, an amount of the sodium salt of the corresponding hydroxyalkane sulfonic acid equivalent to the molar excess of the sultone employed, i.e., up to 5% to 10%, and residual unreacted tertiary amine may be present. If impurities are present in the reactants and side reactions occur, the resultant product may contain impurities so introduced. Since commercial grades of reactants are employed in commercial operations, the impurities should not be present in amounts such as would impair the surfactant properties of the resulting product, as will be well understood by those skilled in this art.

Products thus produced, containing the aforesaid impurities, which do not affect the useful properties of the sulfobetaine, may thus be classified as a product consisting essentially of the sulfobetaine.

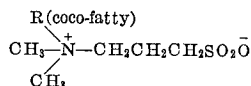
Where the tertiary amine contains an ester linkage, as

described above, I prefer to avoid the presence of water, to prevent the hydrolysis of the ester. In such cases, I may employ an entirely non-aqueous medium.

The following examples are given by way of illustration and not as a limitation of my invention.

Example 1

Preparation of acyclic (coco-fatty) dimethylammonium propanesulfonic acid betaine:



The tertiary amine employed was primarily a mixture of lauryl dimethylamine and myristyl dimethylamine, substantially in the ratios of the corresponding naturally-occurring glycerides in coconut oil. The fatty acids of the coconut oil are given for example, in Fieser & Fieser's Organic Chemistry, 1st edition, page 319. The relative percentages of the various acids depend upon the source of the coconut oil. Such mixed acids may also be stripped or topped, that is, have fractions removed, prior to or following conversion of the same into amines. Thus, for example, the acids derived from the coconut fatty oil may be converted to the nitrile by reaction with ammonia and reduced to the corresponding primary amines by hydrogenation. The corresponding dimethylamine may be obtained by alkylation with formaldehyde and formic acid, for example, by the process described in U.S. Patent 2,366,534.

The above chemistry is not given as a limitation on the methods of production of the tertiary amine, but to illustrate the characteristics of the mixed amines designated by the prefix acyclic (coco-fatty), or any other prefix employed in this specification, to indicate mixtures of the tertiary amines where the original source material from which the tertiary amines are formed is a natural oil, as identified in the parenthesis.

The reaction apparatus consisted of a 3-necked, 1000 ml. distilling flask, equipped with a stainless steel stirring assembly, a thermometer and inert gas inlet tube and an insulated dropping funnel. The flask was charged with one mole of acyclic (coco-fatty) dimethylamine, 234 g. (mol. weight). The insulated funnel was charged with 128.2 g. of propanesultone previously warmed to about 35° C. to melt the crystalline substance. The propanesultone was added drop by drop to the amine, with agitation, while mildly purging the amine with nitrogen (as the inert gas). The reaction was very exothermic, and the temperature rose quickly to 50° C. upon completion of addition over a 15-minute period. The reaction brought the temperature to 120° C. within an additional 10 minutes. The resulting compound solidified and prevented further agitation of the reaction mass or proper removal of the resulting sulfobetaine from the reaction vessel. The reaction mass proved insufficiently soluble in alcohol such as methanol or isopropanol, but readily dissolved in water. The reaction was therefore repeated with water present as a solvent.

An apparatus as described in the above example was charged with:

Acyclic (coco-fatty) dimethylamine, g. (0.7 mole) -----	163.8
Distilled water, g. -----	252.0

Agitation and nitrogen purging were started.

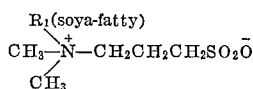
Propanesultone, 94.0 g. (0.77 mole), previously warmed to 35° C., was added over a period of 15 minutes. The agitation and purging with nitrogen were continued while the reaction temperature steadily rose to 64° C. in 12 minutes after completion of the propanesultone addition. During this period the emulsion gradually began to clear, and the viscosity of the resultant solution in-

15

creased. The reaction was continued for an additional 15 minutes. The resultant adduct, acyclic (coco-fatty) dimethylammonium propanesulfonic acid betaine, was soluble in water as well as in alkali solution, yielding a rich lather. The compound possessed a pleasant mild fatty odor. The solution was gradually cooled, and at room temperature it was a clear, amber colored fluid, having a slightly pinkish cast and a pH of 1.2, resulting from the excess propanesultone. 400 g. of the 501 g. yield obtained was neutralized with 11 g. of a 10% sodium hydroxide solution to a pH of 6.8. The color now turned pale amber (a color of one on the Gardner Hellige Varnish scale). The final composition contained 49.6% solids. This solution is now ready for use without further processing. Where desired, the water may be evaporated to obtain the anhydrous product. For analytical purposes only, a sample of the compound was dissolved in a small quantity of ethanol:water mixture and extracted 5 times with normal hexane, following neutralization with sodium hydroxide to phenolphthalein end point. Only 1.16% unconverted tertiary amine was found in this hexane soluble residue, indicating a yield of 98.84% based on the tertiary amine employed. The conversion was therefore nearly quantitative. The resultant sulfobetaine had the surfactant properties given in the tables below.

Example 2

Preparation of acyclic (soya-fatty) dimethylammonium propanesulfonic acid betaine:



In this case the tertiary amine is a mixture of dimethyl higher acyclic amines $(R(\text{CH}_2)_n(\text{CH}_3)_2\text{N})$, in which R is a higher acyclic radical, derived from the acids of soya bean oil. This soya bean oil is the glyceride composed primarily of linoleic and oleic acid and palmitic acid (and also contains a minor percentage of stearic acid glycerides), for example, having the composition given on page 398 of the above work by Fieser & Fieser, supra. The corresponding tertiary amine is a mixture of linoleyl dimethylamine, oleyl dimethylamine and palmityl dimethylamine, and a minor quantity of stearyl dimethylamine.

A reaction flask equipped as described under Example 1 is charged with:

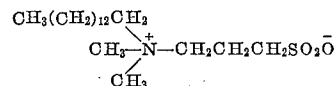
Acyclic (soya-fatty) dimethylamine, g. (0.6 mole) -- 195
Water, g. ----- 272

While the resulting creamy emulsion was agitated at room temperature, 76.9 g. of propanesultone (0.63 mole), warmed to about 40° C., was added from the dropping funnel over a period of about 15 minutes. The temperature at this point rose to 35° C., and within an additional 25 minutes the temperature reached 57° C. resulting from the exothermic reaction. The pH at this point was 4.5. By use of an electrically heated mantle, the temperature was gradually brought to 85° C. and held there for one hour. The pH thus dropped to 1.8, and the solution was cooled, resulting in a white paste. Addition of 10% ethanol based on total solution gave a clear solution. The resulting aqueous-alcoholic solution was then neutralized with 1 g. of 10% sodium hydroxide solution per 40 grams of sulfobetaine solution, to give a straw colored, low viscosity solution, Hellige VCS of below one, pH of 7.2, with a mild, pleasant odor and giving profuse and stable foam in hard and soft water. The water and alcohol may be removed by evaporation. The resultant sulfobetaine had the surfactant properties given in the tables below.

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Example 3

Preparation of myristyl dimethylammonium propanesulfonic acid betaine:



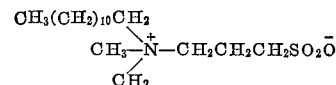
Using the apparatus of Example 1, the reaction flask was charged with:

Dimethylmyristylamine, g. (0.6 mole) ----- 151.8
Water, g. ----- 151.2

While the dispersion was agitated at room temperature and purged with nitrogen, 77 g. (0.63 mole) of propanesultone was added over a 10-minute period. Within 10 minutes after complete addition of the sultone, the temperature had risen to 75° C., and the mass began to solidify. 77 grams of ethanol (SDA3A) was now added, and the liquid resulting, which had now cooled to 56° C., was gently heated to 80° C. After one hour at about 80° C., the solution turned pale pinkish, showed a pH of 1.1 and was clearly soluble in distilled water, tap water and alkali solution and showed considerable foaminess. Upon cooling, the liquid was quite viscous, and 100 g. of ethyl alcohol was added to reduce viscosity. 3 g. of 50% sodium hydroxide was added, to bring the pH to 7.5. The pale straw-colored clear solution showed a Hellige VCS color of below one and had 42% solids. The sulfobetaine had the surfactant properties given in the tables below.

Example 4

Preparation of lauryl dimethylammonium propanesulfonic acid betaine:



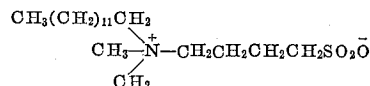
Following the procedure of Example 3, the following were reacted:

Dimethylaurylamine, g. (1.5 mole) ----- 322.5
Water, g. ----- 379.0
Ethanol, g. ----- 126.0
Propanesultone, g. (1.58 mole) ----- 192.15

The amine, alcohol and water were charged at once, and the sultone added over 15 minutes. The exothermic reaction brought the temperature to 70° C., where the reaction was held until the compound gave a clear, foaming solution in aqueous alkali. The product after neutralization had a pH of 7.3, a color Hellige VCS below one, and contained 50.8% solids. Unreacted amine was found to be less than one percent.

Example 5

Preparation of tridecyl dimethylammonium butanesulfonic acid betaine:



A 500 ml. three-neck reaction flask, equipped as in Example 1 and fitted with a "Glascol" heating mantle, was charged with the following:

N,N-dimethyl-N-tridecylamine¹ (M.W. 227), g. (0.4 mole) ----- 90.9
Water, g. ----- 157.0

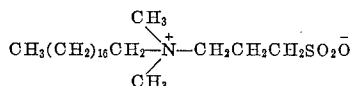
¹A reaction product of tridecyl chloride and dimethylamine (activity of 94%). The product being a derivative of the oxo reaction, therefore a mixture of isomers. (See I. Wender, Petroleum Refiner, 35 (12) 197 (1956).)

There was added in one increment butanesultone 66 g. (0.44 mole). The emulsion was agitated while purging with nitrogen. Within 40 minutes after addition of butanesultone, the internal temperature had risen to 45° C. as a result of the exothermic reaction which ensued.

The emulsion cleared up at this point, and the reaction mass was now gently heated to 70° C. and held at this temperature for one hour. At this point the clear solution had taken on a pinkish cast. The pH measured 0.8. The compound was soluble to a clear solution in distilled water and was equally soluble in alkali solution. The product was now neutralized with 10.5 g. of a 10% sodium hydroxide solution for each 100 g. yield of sulfobetaine solution to bring the pH to 6.9. The previously pinkish colored solution turned to a very light, straw colored liquid (Gardner Hellige VCS=2). The resulting solution contained 49.9% solids. Total yield was 308 g. A petroleum ether extraction of the solids showed the presence of 4.15% unconverted dimethyltridecylamine, indicating a 95.85% yield. It appears that the presence of the small residue of unconverted amine acts as a defoaming agent of the above sulfobetaine, since the foam of dilute aqueous solutions breaks quickly on standing. However, the compound is an excellent wetting agent. The free amine could be reduced by carrying the reaction out with greater excess of sultone. A 0.1% solution of this compound gave a 25 second sinking time in distilled as well as in hard water (200 p.p.m.) when measured at 25° C. by the Draves Wetting Test (Synthron tape method).

Example 6

Preparation of stearyl dimethylammonium propanesulfonic acid betaines:



The following materials were charged into a flask fitted as in Example 1:

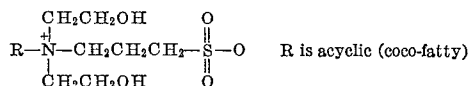
Dimethylstearylamine, g. (0.5 mole)	160.5
Water, g.	227.5
and to the resulting emulsion,	
Propanesultone, g. (0.55 mole)	67.0

was added over a 10-minute period.

The reaction was moderately exothermic, and the temperature rose to 48° C. in 30 minutes. Heat was then applied externally, and the temperature was raised to 70° C. for one hour. The resulting sulfobetaine was soluble in water and alkali solution. Upon cooling, the compound formed an ivory-colored paste, and the product was an essentially colorless paste upon bringing the pH to a neutral value. Total solids were found to be 54%, and the yield was approximately theoretical (445 g.). This agent was found to be particularly useful as a softening agent for hair and textile fibers. The surfactant properties of this compound are given in the tables below.

Example 7

Preparation of acyclic (coco-fatty) di(hydroxyethyl)ammonium propanesulfonic acid betaine:



This reaction, carried out in an apparatus as previously described, was promoted through a catalyst, potassium iodide, as a like run indicated a sluggishness of the reaction when conducted in the absence of a suitable catalyst.

Acyclic (coco-fatty) di(hydroxyethyl)amine, g. (M.W. 295)	443.4
Ethanol (SDA3A), g.	156.5
Water, g.	469.5
Potassium iodide, g. (2% on weight of amine)	8.86

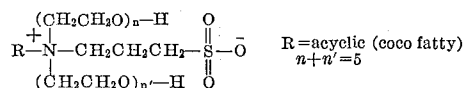
were charged into a 2000 ml. 4-neck round-bottom flask, equipped with heating mantle, condenser, stirrer, thermometer, insulated dropping funnel and inert gas inlet tube, and

Propanesultone, g. (10% molar excess) ----- 201.46
was charged into the agitated mixture over a 30-minute period.

The temperature rose from 22° to 36° C. without external heating, and then heat was gradually applied to bring the temperature to 86° C., to cause mild reflux. After one hour at top temperature, the foamy solution turned pinkish and was soluble in aqueous alkali, giving a clear solution. The pH was measured as 1.1. On cooling, 1 g. of 10% sodium hydroxide was added for each 100 g. of compound, to bring the pH to 7.3. A light amber solution resulted, having a color Hellige VCS of below 6. Total solids were found to be 48.6%. On standing, a thin film of insoluble matter developed on the surface and was decanted. The surfactant properties of the sulfobetaine are given in the tables below.

Example 8

Preparation of acyclic (coco-fatty) bis(polyethylene glycol) ammonium propanesulfonic acid betaine:



The reaction apparatus described under Example 7 was charged with:

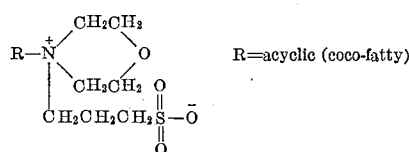
Ethomeen C 151, g. (0.9 mole)	369
Water, g.	544
Potassium iodide, as the catalyst, g.	7.4

¹A 5 mole adduct of ethylene oxide with cocofatty amine, sold by Armour & Co.

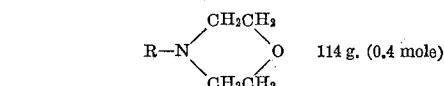
1 mole, 122.1 g., propanesultone (10% excess over stoichiometric amount) was added over a 10-minute period. The foamy solution was heated with mild purging with nitrogen to about 84° C. This temperature was held for 2 hours. The clear solution was an amber color. The compound was readily soluble in strong caustic soda solution. After cooling, the reaction product was neutralized with caustic soda to a pH of 6.8. This produced a clear amber-colored solution of very mild odor. The properties of this sulfobetaine are given in the tables below.

Example 9

Preparation of acyclic (coco-fatty) morpholinium propanesulfonic acid betaine:



An apparatus was used as in Example 1, but with the addition of an electrically heated "Glascot" mantle. Acyclic (coco-fatty) morpholine



was dispersed in

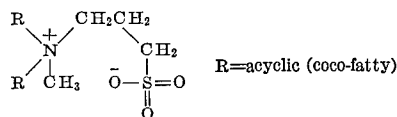
Water, g.	165.25
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51.25 g. (0.42 mole) of propanesultone, at 35° C., was added from a funnel over a 10-minute period. The exothermic temperature rise was very mild, too weak to complete the reaction. The reaction mass was heated to 85° C. for a period of two and a half hours. The liquid resulting had a pH of 1.1, contained 51.7% solids, was soluble in water, but gave cloudy solutions in alkali. A repeat run using 0.44 mole propanesultone and 2.28 g. potassium iodide gave clear solutions in alkali after 2 hours reaction time at 85° C. The surfactant properties of the sulfobetaine are as given in the tables below.

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Example 10

Preparation of di[acyclic (coco-fatty)] methyl ammonium propanesulfonic acid betaine:



The following were charged into the apparatus described in Example 1:

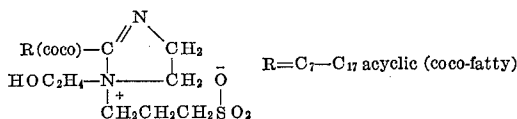
Di acyclic (coco-fatty) methylamine (M.W. 426 by titration), g. (0.4 mole)	170.4
Denatured alcohol (SDA3A), g.	112.0
Water, g.	112.0

Agitation and nitrogen purging were started, and Propanesultone, g. (0.44 mole) 53.75 was added.

Heat was applied by means of an electrically heated mantle. Upon reaching 80° C., the emulsion turned clear, and the temperature was held at reflux for a period of one hour. The clear fluid resulting dispersed in water to a clear foamy solution. The solution in alkali was slightly opalescent.

Example 11

Preparation of 2-acyclic (coco-fatty)-1-hydroxyethyl-2-imidazolinium-1-propanesulfonic acid betaine:



The imidazoline may be formed from the mixed fatty acids derived from coconut oil, as, for example, by the process disclosed in U.S. Patent 2,355,837.

A 1000 ml. reaction flask, equipped as in previous examples, was charged with:

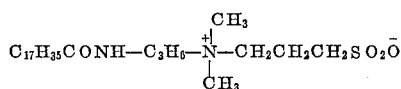
2-acyclic (coco-fatty)-1-hydroxy-ethyl-2-imidazoline (M.W. by titration 246)	246
Ethanol 190 proof	190
Water	190

4.92 g. potassium iodide (2% on the weight of the imidazoline) was then dissolved therein. While agitating the solution at room temperature and purging with nitrogen, 134.3 g. of propanesultone was run into the solution. Inside one hour the temperature rose from 24° C. to 55° C., as a result of the liberation of heat from the ensuing reaction. A sample then taken dissolved to a clear foaming solution in tap water, as well as in a 1% sodium hydroxide solution. To assure completion, the reaction was warmed for an additional hour through application of external heat to reflux temperature, which was found to be 82° C. Upon cooling, the product was found to have a pH of 1.4.

2.6 g. of a 50% sodium hydroxide solution was added to each 100 g. of finished product to bring the pH to 7.1. The resulting product showed 52% solids and was a pale amber colored, clear solution having relatively low viscosity and a pleasant fruit-like odor. The sulfobetaine had surfactant properties as given in the tables below.

Example 12

Preparation of stearylamidopropyl dimethylammonium propanesulfonic acid betaine:



Dimethylaminopropylstearamide (produced as indicated), g. (0.4 mole)	144.8
Isopropanol-water solution of 1:1 weight ratio, g.	144.8

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were charged into a 1000 ml. reaction apparatus, as in Example 1. This was warmed to 130° F. until dispersed.

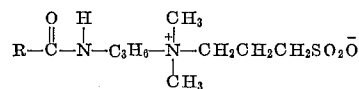
53.75 g. propanesultone was now charged from the funnel over a period of 10 minutes, with stirring and nitrogen purging. A vigorous exothermic reaction ensued, and the reaction mass quickly reached the reflux temperature of 184° F. The previously cloudy solution turned instantly clear. Within an additional 10 minutes, the temperature began to fall again, and the solution was heated externally to 182° F. (reflux) for 1 hour. A small sample was taken and dissolved in tap water. A soapy, very strongly foaming solution resulted, and the compound proved soluble to a clear, wetting and foaming solution in 1% aqueous sodium hydroxide. The cooled solution turned opaque and viscous, and 140 g. additional isopropanol:water solution was added to bring the compound to a clear solution of low viscosity. The pH was brought from 1.2 to 8 by addition of 6 g. sodium hydroxide (50% strength).

Total yield was 480 g. Color: Hellige VCS 4. Total solids: 40%.

As can be seen from the tables below, the compound has significant properties as a foaming, wetting and scouring agent. It is also an outstanding softening agent for cellulosic and protein fibres as well as hair. Terry cloth towels treated with as low a concentration as will cause 0.1% dry weight increase showed a very soft velvet-like "hand" and showed freedom from yellowing.

Example 13

Preparation of acyclic acyl (coco-fatty) amidopropyl dimethylammonium propanesulfonic acid betaine:



Proceeding as in Example 12, 440 g. of hydrogenated coconut fatty acid (2 moles) was reacted with 224.4 g. dimethylaminopropylamine (2.2 moles) in the presence of 400 g. benzene.

The resulting product was a low melting, soft, pasty solid having an acid number of 2.4 and an amine equivalent weight of 295 (as compared to theory of about 300), indicating the presence of about 1% free dimethylaminopropyl amine. The color measured 5 on the Gardner Hellige varnish color scale (VCS).

295 g. of the above acyclic amido tertiary amine was dispersed in:

Ethanol (190 proof)	173
Water	284

This emulsion-like dispersion was then charged into a 2000 ml. 4-neck flask equipped as outlined in previous examples.

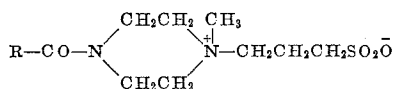
140.4 g. (1.15 moles) of propanesultone was then dropped in over a 5-minute period. The pronounced exothermic reaction resulting forced the internal temperature to 62° C. (144° F.) within 20 minutes after addition. The dispersion had now turned clear. After additional 15 minutes, the temperature began to drop, and the reactants were gently heated through the electrically heated mantle to bring the temperature to 77° C. (171° F.) or mild reflux, which temperature was maintained for one hour.

The acyl (coco-fatty) amidopropyl dimethylammonium propanesulfonic acid betaine so prepared dissolved readily in water as well as in a 1% solution of caustic soda, to give clear, foaming solutions. The pH of the reacted product was 1.2 and the compound was finally neutralized with 6.5 g. sodium hydroxide (added as a 10% aqueous solution). The finished product, having a yield of 910 g., had a pH of 7.1, total solids of 47%, and a color value on the Hellige Varnish scale of 3. As per

the tables below, the compound proved to have excellent foaming, wetting and detergent properties.

Example 14

Preparation of 4-(methyl)-1-(myristoyl) piperazinium propanesulfonic acid betaine:



4-(methyl)-1-(myristoyl) piperazine was prepared as a starting material (complex tertiary amine) in the preparation of the related alkane sulfobetaine. A 3-neck flask equipped with heating mantle, vacuum tight stirring assembly, nitrogen inlet tube, thermometer, Dry Ice condensate trap and connected to a vacuum pump was charged with:

726 g. (3 moles) of dry methyl myristate and 331 g. N-methylpiperazine M.W. 100.17; B.P. 138° C.

While agitating, 21 g. of a 25% solution of sodium methoxide in methanol was added as a catalyst. The reaction mixture was warmed to 140° F. and the heating mantle shut off, as an exothermic reaction ensued, bringing the reaction mass to 182° F. (84° C). Under mild purging with nitrogen, methanol steadily distilled and was collected in the ice trap. The exothermic reaction subsided after about 50 minutes, and the temperature of the distilling vapors reached a maximum of 59° C. during this time. Heat was then applied for 5 hours, during which time 110 g. of methanol was collected. Infrared analysis at this point proved substantially complete conversion of the methyl ester to the amide, with the ester carbonyl peak in the region of 5.74 microns having disappeared. A vacuum of 27" was applied for 30 minutes to remove the residual methanol and N-methylpiperazine. An amine equivalent weight of 266 showed that most of the excess amine originally charged still remained in the product. One-half of the batch was drained off, and the remaining portion was stripped at 250° F. and 2-3 mm. of Hg to an amine equivalent weight of 304 (theory about 309).

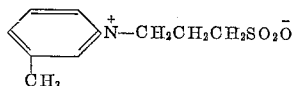
The finished product was an ivory colored, low melting, waxy solid, having a soap content expressed as sodium soap of 3.7% and an ash content of 0.37% expressed as Na₂O.

266 g. of the not fully stripped material, prepared as above, was dissolved in 130 g. of ethanol (SDA3A, 190 proof) and 260 g. of water.

This was charged into the reaction flask described in previous examples of this type. 134.3 g. (1.1 mole) of propanesultone was added at once while stirring. Reaction proved moderately exothermic and temperature rose to 36° C. from a starting point of 17° C. While purging with nitrogen, the substance was heated externally to 77° C. (mild reflux). The foam forming, settled when reaching reflux temperature. After one hour at reflux a sample gave still a hazy solution in water, and an additional 12.2 g. propanesultone was gradually added to overcome consumption of the propanesultone by the unreacted N-methylpiperazine still present. After an additional 3 hours at reflux temperature, the compound formed clear viscous solutions in water. A 1% solution had a viscosity of 60 cps. when measured on a Brookfield Synchroelectric viscosimeter, at 25° C. A clear solution also resulted in 1% aqueous sodium hydroxide. The product was further diluted with 100 g. ethanol (190 proof) and neutralized with 18 g. of a 10% sodium hydroxide solution to bring the pH to neutral. The final product showed 41% solids and had a color corresponding to a Gardner Hellige VCS of 3. As can be seen from the tables below, this compound shows outstanding detergent properties, coupled with good foaming and wetting properties. The foam proved exceptionally stable in the presence of oily soil.

Example 15

Preparation of beta-picolinium propanesulfonic acid betaine:



Beta-picoline (1 mole), 93 g. was dissolved in ethanol (190 proof), 113 g., and water 113 g.

This was charged to a reaction flask as described in Example 1, and 134.3 g. of propanesultone was added over an eight-minute period. The exothermic reaction brought the temperature to 182° F. within 5 minutes after completion of addition. After 5 minutes of strong reflux, the temperature began to fall again, and external heat was applied for 2 hours, keeping the temperature at reflux. The clear solution resulting had a pH of 1.2, and crystals developed on standing overnight. The compound was dried at 180° F. in an oven and then recrystallized from a solution of ethanol:isopropanol 1:1. The beta-picolinium propanesulfonic acid betaine was collected on the suction filter in the form of a white crystalline solid. These crystals instantly dissolved in water and alkali solution to a clear liquid. Such solutions, however, showed no properties of a surface active agent. Even relatively concentrated solutions, such as a 5% solution, failed to produce foam; and when tested for wetting power using the Draves Test, synthron tape method, the tape continued to float and did not wet even after one hour submersion in a 0.1% solution of the aromatic alkane sulfonic acid betaine described above.

Example 16

In this example, the tertiary amine was triauryllamine. 260 g. of this amine was dissolved in a mixture composed of 163.6 g. of ethanol and 163.6 g. of water, and the amount of propane sultone was 67.2 g. In other words, 0.5 mole of the amine was reacted with 0.55 mole of propane-sultone. The amine was dissolved in alcohol and water, and propanesultone at 40° C. was dropped into the amine, maintained at an internal temperature of 27° C., the addition of the sultone taking place over a period of 10 minutes. The mixture, which had an emulsion-like appearance, was stirred, but no reaction was noted, and the temperature did not increase at all after one hour of stirring. No temperature rise was noted, and the mixture was then heated in an effort to promote the reaction. The solution failed to clear up and remained an emulsion-like mixture during agitation, but separated into two layers when agitation was stopped. A composite sample of this reaction mass was tested after one hour of heating at 84° C., and showed a hydrolysis of the propane-sultone of above 60%, with hydrolysis proceeding when further heated under reflux.

The experiment was repeated, using 2% of potassium iodide as a catalyst, based on the weight of the tertiary amine. The result was similar to that given above, and no reaction occurred at room temperature, and hydrolysis resulted on heating for 4 hours.

Example 17

The above experiments were repeated with tris-octyl amine, following the procedure, with and without catalyst, and no noticeable reaction occurred.

Example 18

The above experiments, following the procedures of Example 1, were repeated with 2-ethyl hexyl dimethylamine and propanesultone, to form the 2-ethyl hexyl dimethylammonium propanesulfonic acid betaine. No catalyst was required. This product had substantially no wetting properties, as is shown further below.

In all of the above Examples 1-18, the solvent may be evaporated to obtain materials which are substantially free of solvent, such as water and alcohol, used in the examples.

To illustrate the highly useful properties of the surface active sulfobetaines obtained from examples given above, the sudsing action and wetting action of these agents are given in the tables below. Tests were conducted in distilled water, hard water, synthetic sea water, sulfuric acid and caustic soda solutions. The foaming properties and foam stability were determined using the well-established Ross-Miles foam test, as described in "Oil and Soap," 18, 99-102 (1941). In this procedure a sample of the surfactant solution is discharged from a container through an

betaines of my invention. The aromatic sulfobetaines and the lower acyclic sulfobetaines shown practically no foam forming properties. Thus, for example, see beta-picolinium propanesulfonic acid betaine and 2-ethyl hexyl dimethyl ammonium propane sulfonic acid betaine, Examples 15 and 18, as compared in the table with the higher acyclic surfactant sulfobetaines, Examples 1, 2, 3, 4, 7, 8, 11, 12 and 14.

In the following table, the concentration of sulfobetaine in each solution is 0.1% by weight.

TABLE I.—ROSS-MILES FOAM NUMBERS

Substituted (ammonium) propanesulfonic acid betaine	Distilled Water			Hard Water (200 p.p.m.)		
	Instantaneous	1 min.	5 min.	Instantaneous	1 min.	5 min.
Acyclic (coco-fatty) dimethyl (Example 1).....	150	140	135	150	145	140
Myristyl dimethyl (Ex. 3).....	165	150	145	165	155	147
Lauryl dimethyl (Ex. 4).....	150	140	130	150	140	130
Acyclic (soya) dimethyl (Ex. 2).....	105	95	90	125	115	110
Acyclic (coco-fatty) dihydroxy ethyl (Ex. 7).....	80	70	65	80	70	65
2-ethyl hexyl dimethyl (Ex. 18).....	Trace	0	0	-----	-----	-----
Acyclic (coco-fatty) bis(polyethylene glycol) (Ex. 8) ¹	125	115	110	135	125	120
Stearylamidopropyl dimethyl (Ex. 12).....	95	80	75	-----	-----	-----
4-(methyl)-1-(myristoyl) piperazinium (Ex. 14).....	140	120	115	-----	-----	-----
2-acyclic (coco-fatty)-1-hydroxyethyl-2-imidazolium (Ex. 11).....	145	135	130	-----	-----	-----

Betaine	10% solution H ₂ SO ₄			10% solution NaOH			Synthetic sea water		
	Instantaneous	1 min.	5 min.	Instantaneous	1 min.	5 min.	Instantaneous	1 min.	5 min.
Ex. 1.....	165	155	140	125	110	100	170	155	150
Ex. 3.....	180	165	160	Not compl. soluble			175	160	155
Ex. 4.....	180	160	145	130	115	105	190	170	160
Ex. 2.....	160	145	140	Not compl. soluble			190	170	160
Ex. 7.....	150	130	115	90	75	70	140	120	105
Ex. 18.....	-----	-----	-----	-----	-----	-----	-----	-----	-----
Ex. 8.....	145	135	125	110	100	70	140	135	125

¹ 5 mole ethylene oxide adduct of acyclic (coco-fatty) amine beta-picolinium ammonium propane sulfonic acid betaine (Example 15) showed no foam in distilled water either at 0.1% or 0.5% by weight solution.

orifice, to fall through a prescribed height into a pool of like solution. The concentration of the surfactant under test was 0.1% solids basis, and the temperature was controlled at 25° C. The foam height was indicated as measured immediately after discharge of the sample from the container (instantaneous), after 60 seconds, and after 300 seconds.

According to this test, a good foam producing surfactant is one showing an initial (instant.) foam height of 50 mm. or more, when dispersed in distilled water to a concentration of 0.1% by weight. The higher the foam height and the greater its persistence, the better the foam forming action of the surfactant. A like test using water containing electrolytes shows good foam forming properties in such solutions.

A reference to this table shows the excellent foam forming properties of the higher acyclic surfactant sulfo-

The wetting efficiency was evaluated by the "Draves Test," syntron tape method, as adopted from the tentative procedure presented to the Auxiliaries and Testing Group Meeting of the American Association of Textile Chemists and Colorists, Atlantic City Convention, October 14, 1949. Natural binding tape, 9 inches by 1.25 inches, weighing 1.85±0.1 g., was used along with a stainless steel hook weighing 1.25 g. The tape was obtained from the U.S. Testing Company, Hoboken, New Jersey.

According to this test, a material is not a good wetting agent, and therefore does not have sufficient wetting properties, unless it has a sinking time of less than 25 seconds at at least a 1% concentration and preferably at lower concentrations. A comparison of the times of sinking gives an indication of the relative wetting properties of the surfactants compared with the one having the lower value of time being the better wetting agent, according to this test.

TABLE II.—DRAVES TEST—SYNTHRON TAPE METHOD

[Sinking time in seconds measured at 25° C±0.5° C; 0.1% by weight solution of surfactant]

Substituted (ammonium) propane-sulfonic acid betaine	Distilled water	Hard water (200 p.p.m.)	10% soln. H ₂ SO ₄	10% soln. NaOH	Synthetic sea water
Acyclic (coco-fatty) dimethyl (Ex. 1).....	6	7	6	15	9
Myristyl dimethyl (Ex. 3).....	11	11	14	-----	14
Lauryl dimethyl (Ex. 4).....	6	7	4	13	12
Acyclic (soya-fatty) dimethyl (Ex. 2).....	19	18	24	-----	18
Acyclic (coco-fatty) dihydroxy ethyl (Ex. 7).....	9	10	6	21	12
Acyclic (coco-fatty) morpholinium (Ex. 9).....	22	23	18	-----	18
2-ethyl hexyl dimethyl (Ex. 18).....	250	115	-----	-----	-----
Acyclic (coco-fatty) bis(polyethylene glycol) (Ex. 8).....	24	23	32	30	28
Beta-picolinium (Ex. 15).....	(2)	-----	-----	-----	-----
Tridecyl dimethyl (Ex. 5).....	25	25	-----	-----	-----
Stearylamidopropyl dimethyl (Ex. 12).....	60	-----	-----	-----	-----
4-(methyl)-1-(myristoyl) piperazinium (Ex. 14).....	27	-----	-----	-----	-----
2-acyclic (coco-fatty)-1-hydroxyethyl-2-imidazolium (Ex. 11).....	80	-----	-----	-----	-----

¹ Using 1% solution. ² Did not wet in one hour.

It will be observed from Table II that neither the aromatic sulfobetaine (beta-picolinium propanesulfonic acid betaine) nor the lower acyclic sulfobetaine (2-ethyl hexyl dimethyl ammonium propanesulfonic acid betaine), which has only 6 carbons in an uninterrupted straight chain, show wetting properties according to this test, especially when compared with the higher acyclic surfactant sulfobetaines of my invention.

In order to be classed as a suitable surfactant, the product should be accepted under one or the other of such tests, or show activity as a detergent. Its utility will be wider to act as both a foam former and wetting agent when it satisfies both of these tests. Its utility as a detergent may be tested by produces described below, and this is also an aspect of surfactant activity.

As shown in Table I, the acyclic surfactant sulfobetaines, wherein the acyclic group is C₈ to C₁₈ in an uninterrupted, unbranched chain, as described above, are all excellent foam formers, with good foam stability; while the acyclic forms, when the acyclic group is less than C₈ (Example 18) or is an aromatic group (Example 15) do not show sufficient foaming properties to be classed as usable surfactants in the same class as the acrylic surfactant sulfobetaines of my invention.

Table II illustrates the wetting properties of the surfactants of my invention are much better wetting agents than the acyclic forms in which the acyclic is less than C₈, and are greatly superior to the aromatic type. However, they differ as between themselves in their activity as wetting agents more than they do as foam formers.

Since surfactant activity has various aspects, one of which is foam formation, another wetting power, and a third detergency, the various members of the class of the acyclic surfactant sulfobetaines of my invention, while all good foam formers and detergents, differ among themselves in the degree of their wetting power.

To illustrate the detergency values of the sulfobetaines of my invention and also their utility as soap additives, the following tests and tables are given below.

A series of wash tests was conducted using a Terg-O-Tometer, model No. BD-101, supplied by the United States Testing Company, Incorporated, as a laundering device. This device consists of washing vessels containing oscillating agitators positioned in a thermostatically controlled bath. The speed of agitation is controlled. The machine duplicates the action of agitator type home washers. One liter solutions using water of 300 p.p.m. hardness, calculated as CaCO₃, containing 0.25 "Ivory Flakes" soap (sold by Proctor & Gamble Co.), as well

as solutions of detergents wherein a portion of the soap was replaced with acyclic (coco-fatty) dimethyl ammonium propane sulfobetaine were investigated. Test runs were also made with various of the sulfobetaines in the absence of soap. No builders were used in these test runs. The temperature of the suds cycle was held at 140° F. for a duration of 30 minutes, followed by two rinse cycles at 100° F. for 5 minutes each. The agitation was set at 150 r.p.m. A swatch of artificially soiled cotton fabric supplied by Testfabrics, Incorporated, measuring 9" x 14" and weighing 14 g., was laundered with each run. A swatch is printed over one-half of its surface with a standard soil, the other half being white. The unsoiled portion, as well as the soiled portion of the fabric, was checked for reflectance by means of a Photovolt Photoelectric Reflection Meter, Model 610, using a 610-Y search unit and a green tristimulus filter.

This instrument measures the diffuse reflection intensity. By employing the green tristimulus filter, the luminous apparent reflectance or the degree of "whiteness" may be determined. The search unit comprises a light source and measuring photocell and galvanometer. On an arbitrary scale, the reflectance of two surfaces may be compared by comparing the relative value of the photocell reading when the reflectance of the two surfaces is compared.

The fabric before washing was tested by measuring the reflectance value of the white portion and of the soiled portion. The meter is adjusted so that the reflectance value of the white portion indicates a reflectance value of 95. The soiled portion then has a reflectance value of 25.

After washing according to the procedure described above, and air drying, the washed sample was measured to determine the reflectance of the soiled portion. The detergency value of the detergent employed is determined as follows:

E = Efficiency as a percent

W = Reflectance value of white portion before laundering (95)

G_1 = Reflectance value of soiled portion before laundering (25)

G_2 = Reflectance value of soiled portion after laundering.

$$E = \frac{G_2 - G_1}{W - G_1} \times 100; \text{ i.e., } E = \frac{G_2 - 25}{70} \times 100$$

On the following table is given the G_2 and E values of the various detergents listed in the table, when tested as above, employing in the wash water the samples of detergents in the concentrations given in the table.

TABLE III.—DETERGENCY EFFICIENCY

Sample	Percent by weight soln. conc.	Detergent used	G_2	E
				Percent
1	0.25	(Unwashed fabric, $W=95$, $G_1=25$)		
2	0.225	Ivory Soap Flakes	34	12.85
	0.025	Ivory Soap Flakes		
		Acyclic (coco-fatty) dimethyl ammonium propanesulfonic acid betaine (Example 1).	49	34.285
3	0.20	Ivory Soap Flakes		
	0.05	Acyclic (coco-fatty) dimethyl ammonium propanesulfonic acid betaine (Example 1).	55	42.85
4	0.175	Ivory Flakes		
	0.075	Acyclic (coco-fatty) (Example 1)	59	48.57
5	0.25	Acyclic (coco-fatty) (Example 1)	34	12.80
6	0.35	Lauryl dimethyl ammonium propanesulfonic acid betaine (Example 4).	33	11.42
7	0.25	Dimethyl myristyl ammonium propane sulfobetaine (Example 3).	33	11.42
8	0.25	Acyclic (soya) dimethyl ammonium propanesulfonic acid betaine (Example 2).	37	17.04
9	0.25	Stearoylamidopropyl dimethyl ammonium propanesulfonic acid betaine (Example 12).	40	21.4
10	0.25	4-(methyl)-1-(myristoyl) piperazinium propanesulfonic acid betaine (Example 14).	51	37.15
11	0.25	2-acyelic (coco-fatty)-1-hydroxyethyl-2-imidazolium-1-propanesulfonic acid betaine (Example 11).	30	7.15

Comparing the detergency efficiency of Ivory soap flakes, Sample 1, with the various sulfobetaines, it will be seen that they are all of about the same order of efficiency. When, however, mixtures of the soap and sulfobetaine are tested, they show a substantial increase in detergency efficiency, when compared with either the soap or the sulfobetaine used separately. Thus, the substitution of 10% of the soap flakes by the sulfobetaine, Sample 5, which had about the same detergency efficiency as the soap flakes, increased the detergency efficiency by a factor of 2.67 (see Sample 2). The substitution of 25% (Sample 3) increased the detergency efficiency by a factor of 3.3, and the substitution of 30% (Sample 4) increased the detergency efficiency by a factor of 3.86.

The remarkable enhancement of the detergency value of the soap and the sulfobetaines obtained by mixtures of these detergents indicates a strong synergistic action of the fatty acid soap and the acyclic surfactant sulfobetaines of my invention.

The outstanding lime soap dispersing power of the above-named sulfobetaines can further be demonstrated by the following lime soap dispersing test. The test procedure determines the minimum amount of lime soap dispersing agent required to prevent flocculation of a soap solution in hard water. The soap solution used was prepared by dissolving "Ivory" soap (sold by Proctor & Gamble Co.) in distilled water to a 0.15% solution based on solids. The solution was then aged for two weeks prior to use.

The hard water stock solution contained 0.1028 g. $MgCl_2 \cdot 6H_2O$ and 0.16667 g. $CaCl_2$ per liter of solution, and was therefore water of 200 p.p.m. hardness calculated as $CaCO_3$. 100 g. of the soap solution was now weighed out in an Ehrlenmeyer flask and combined with 100 g. of the hard water stock solution, so that the resulting solution had a hardness of 100 p.p.m. as $CaCO_3$ and contained 0.075% soap. Upon shaking, flocculation of the soap in the hard water environment set in. Small increments of acyclic (coco-fatty) dimethyl ammonium propanesulfonic acid betaine, based on the weight of soap present, was able to prevent precipitation of the lime soap, while 2% based on the soap content of such addition produced a small amount of stable froth with 5% producing ample stable foam.

TABLE IV.—LIME SOAP DISPERSION TEST IN WATER OF 100 P.P.M. HARDNESS

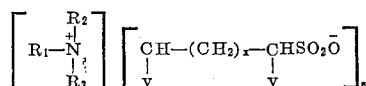
By weight, percent		Ratio	Results
Soap	Sulfobetaine		
0.075	0	-----	Precipitates; no foam.
0.075	0.00150	1:0.02	No precipitation; foams mildly.
0.075	0.00375	1:0.05	No precipitation; ample foam.
0.075	0.00750	1:0.1	Do.

Each of the above sulfobetaines produced comparable effects in the above test.

The above tables illustrate the surfactant activity of the sulfobetaines of my invention.

The lime dispersing, wetting, lathering and detergent properties, and particularly the detergency enhancing properties of the acyclic surfactant sulfobetaines of my invention make them particularly useful as additions to soap.

I may employ from about 2% to about 50% by weight of the higher acyclic surfactant sulfobetaines included within the general formula:



based on the total soap formula; and usually from about 10% to about 30% by weight, based on the soap in the soap formula, will be found to be preferable. The conventional soap may be an alkali metal (Na or K) salt of a soap-forming fatty acid, although ammonia or amine soap are also encountered.

Depending on its end use, soap may also contain perfumes, sequestering agents such as hydroxylaliphatic acids, bacteriostats and deodorizing materials, lubricants such as polyalcohols (for example, glycerine or polyalkylene-glycols) free soap-forming acids, fillers, dyes, pigments, opacifiers, stabilizers, and the like.

Sometimes additional anionic or non-ionic surfactants may be added, for example, fatty alcohol sulfates, fatty glyceride sulfates, fatty acyl amido alkane sulfonates, fatty acyl isethionates. Non-ionics such as higher alkyl phenol polyglycol ethers, such as nonyl or dodecyl phenol polyglycol ethers or fatty alcohols which have been reacted with ethylene oxide may be employed. Soaps may also contain super fattening agents such as the higher fatty acids, lanolin, stearin or glycerides. While conventional fillers are sometimes employed, deliquescent salts such as the halide salts, for example alkali metal chlorides, or sulfates, should be kept to a minimum, preferably below about 5% by weight based on the soap formula.

Such soap formulations are well known in the prior art and will be referred to herein as the soap formula, understanding this to be the entire composition, including soap and also including, if desired, the above and other additives which have been or may be incorporated into soap formulas to impart desirable properties to the soap.

Into such formulas, I may incorporate from 2%–50% by weight of the soap formula of an acyclic surfactant sulfobetaine of my invention. A practical range is from 5% to about 30% by weight for bar soaps and solid shaving sticks. The remaining portion of the soap formula may be composed of the fatty acid soap, to which may be added any of the additives usually added to soap, as described above. Since, however, the sulfobetaines will supply the surfactant properties of anionic and non-ionic surfactants, where these are added to soap, an amount of such surfactant equivalent to the weight of sulfobetaine may be omitted from the formula.

Thus, the soap formula of my invention comprises from about 2% to 50% by weight of an acyclic surfactant sulfobetaine and from 98% to 50% by weight of a soap formula, on an anhydrous basis. The cyclic surfactant sulfobetaines which may be employed are any of those stated above, but preferably I desire to employ the sulfobetaines having good lime soap dispersing properties and preferably good lathering properties; for example, and not as a limitation, those shown in Table I, above, to wit:

Parts by weight

Sulfobetaine ----- 2–50

Soap ----- 98–50

Such a formula thus consists essentially of from 2–50 parts by weight of the acyclic surfactant sulfobetaine and 98–50 parts by weight of soap, to which additives which do not impair the functioning of the mixture may be added.

In selecting the sulfobetaine and determining the percent composition, where it is desired to form a soap body with a hard surface, I prefer to employ the sulfobetaines which are waxy solids, as is obtained when using the C_8 to C_{18} acyclic substituent, which are predominantly saturated. The amount incorporated depends to some degree on the nature of the soap stock. Thus, where large percentages of fatty acid soaps made from the fatty acids of coconut oil, i.e., coconut fatty acid soaps, which are more readily dispersible in water than tallow acid soaps, are employed, I may incorporate the higher molecular weight saturated acyclic, i.e., C_{14} – C_{18} sulfobetaines. Where the soaps are tallow acid soaps or other soaps of equivalent hardness, the saturated or unsaturated C_8 – C_{18} sulfobetaines may be employed.

An example may be as follows:

Example 19

	Percent by weight
Sodium tallow soap (anhydrous) -----	30
Sodium palm-kernel soap (anhydrous) -----	30
Rosin -----	1.4
Sulfobetaine -----	39.6

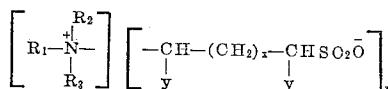
Example 20

	Percent by weight
Soap (anhydrous), such as tallow or mixed tallow and coconut fatty acid soaps -----	90-70
Acyclic (coco-fatty) dimethyl ammonium propanesulfonic acid betaine (anhydrous) (Example 1) -----	10-30

In both Examples 19 and 20, usual additives used in soap formulations may also be included.

The inert character of the sulfobetaines and their stability even in strong alkaline solutions permits the addition of these compounds directly to the saponification step of any conventional soap-making process, or by adding them to any of the saponification reactants prior to the saponification step. Thus, the sulfobetaine may be added to the fat or the alkali prior to saponification, where glycerine is left in the finished soap product and not removed by washing. It may be added to the soap stock prior to or during the crutching step after removal of the glycerine, if this is removed prior to crutching. The soap-sulfobetaine composition is then processed as is usual for soaps by drying and refining, depending upon the end product desired. Thus, the soap may be milled and passed through the plodder and then extruded into bar soap. It may be flaked after passing through the crutcher, and it may be spray dried.

The higher acyclic surfactant sulfobetaines of my invention having the composition:



are also particularly useful additives to shampoos.

Owing to the exceptional compatibility of the sulfobetaines of my invention with anionic and cationic surfactants, these sulfobetaines can be selected to be incorporated in the shampoo, to replace all or part of the anionic surfactant; or, when the shampoo is a rinse containing cationics, it may be added thereto to replace the cationic, to give equal or improved lathering properties and to impart to the hair softness and manageability. They counteract the harsh effects of the anionics without detracting from the detergent properties or the lathering properties of the anionic, but may improve the same. They may, therefore, be incorporated in one mixture with the anionic surfactant.

Since the sulfobetaines have the lathering and other surfactant properties of the anionics employed in shampoos and also provide the properties usually obtained from cationic rinses, as described below, I may replace some or all of the anionics in the shampoo formulations of the prior art which have been employed in shampoos such as in, for example, those stated herein, and thus obtain the desirable properties of the anionic shampoos and the cationic rinses in one formula.

Conventional anionic surfactants employed in such shampoos in the prior art comprise the sulfate salts of the higher acyclic alcohols such as lauryl sulfate salts, myristyl sulfate salts, coconut fatty alcohol sulfate salts, alkyl phenol polyglycol ether sulfates, for example, those described in U.S. Patent 2,758,977; isethionates, i.e., fatty esters of isethionic acid salts, fatty amides of sodium methyl taurine, or the higher alkyl benzene sulfonates, such as dodecyl and pentadecyl benzene sulfonate.

Non-ionic surfactants are sometimes added in addition to the anionic surfactants to modify viscosity and stabilize foam. Typical examples are the alkanolamides, such as

shown in Kritchevsky U.S. Patent No. 2,089,212, and in my copending application Serial No. 846,548, filed October 15, 1959, which is herewith incorporated by this reference, and fatty alcohols or other higher acyclic alcohols reacted with ethylene oxide, sorbitol esters and ethoxylated products thereof and other non-ionics such as have been employed in shampoos in the prior art, as stated herein.

A typical base for shampoos comprises sodium or triethanolamine salt of lauryl or myristyl sulfuric acid.

Such anionic surfactants have a drying effect on the skin and hair and tend to make the hair brittle. They also tend to tangle and clump the hair, and thus leave the hair unmanageable. This property is termed harshness. In order to attempt to overcome this difficulty, it is the practice in this art to add conditioning agents; for example, lanolin, lecithin, higher fatty amides, higher fatty acid esters of glycerol or polyethylene glycol and higher fatty alcohols have been added. However, these additives suppress foam formation and impair the lathering characteristics of the shampoo. In general, it is usually recommended that such materials may not be added in excess of 5%, and for some materials 1% or more suppresses lathering and foaming to an undesirable degree. The dilemma is that, if the addition is restricted to an amount which will not reduce the foaming and lathering characteristics to an undesirable degree, the conditioning action, i.e., the reduction in harshness, is insufficient, and is also insufficient to make the hair manageable, that is, soft and easy to comb and dress and maintain dressed.

Thus, the practice of providing a second cationic rinse has been proposed and used. The cationic rinses are used to neutralize the effect of the anionics and to leave the hair manageable. These cationics are employed as a separate rinse, since they may not be incorporated with the shampoo containing the anionic, due to their incompatibility.

As previously stated, the higher acyclic alkane sulfobetaines are exceptional softening agents for hair, and yet do not detract from and may enhance the froth-forming properties of anionic surfactants which may be used with the sulfobetaine.

Example 21

In this example, the sodium lauryl sulfate (sold as Sulfotex 4530 by Textilana Corporation) used was a composition containing 28% actives, conforming to the following specification:

	Percent
Methylene blue activity -----	28
Unsulfated alcohol -----	1.7
Chlorides as NaCl less than -----	0.1
pH -----	8.0
Color: Essentially colorless.	

This sulfate was prepared from a grade of commercial lauryl alcohol containing:

	Percent by weight
Decyl alcohol -----	2.0
Lauryl alcohol -----	65
Myristyl alcohol -----	26
Cetyl alcohol -----	7.0

A 20% by weight, active basis, solution in water of this lauryl sulfate was a cloudy, low viscosity dispersion at 24° C., and a clear solution at 40° C. The viscosity at 24° C. measured on the Brookfield Viscosimeter was 18 centipoises. Its Ross-Miles foam number is reported in the Table V below.

When 25% of the sodium lauryl sulfate actives was replaced with myristyl dimethyl ammonium propanesulfonic acid betaine of Example 3, the resulting mixture, containing 15% by weight sodium lauryl sulfate and 5% by weight of the sulfobetaine, was a viscous clear water white solution at 24° C. and had a viscosity of 1500 centipoises.

The Ross-Miles foam number of this mixture, when diluted to 0.1% by weight in water of 100 p.p.m. hardness

(calculated as CaCO_3), to simulate tap water, is reported in the table below. It will be observed that this mixture had a much greater viscosity and showed a large appreciation in foaming and lathering property. The addition of such a sulfobetaine to the lauryl sulfate base thus greatly improves the viscosity of the shampoo and eliminates or reduces the necessity of the addition of thickening agents. It improves its lathering properties and also overcomes the harshness effects of the anionic constituent and will leave the hair soft and manageable.

Example 22

A solution made of 15% by weight of the lauryl sulfate of Example 21 and 5% by weight of the acyclic (coco-fatty) pentaethylene glycol ammonium propanesulfonic acid betaine of Example 8 had a viscosity, when measured at 24° C. with the Brookfield Synchro-Lectric Viscosimeter, of 5200 centipoises.

The Ross-Miles foam numbers of this mixture, when diluted to 0.1% by weight in water as specified above, is given in Table V. The increase in viscosity and improvement in foaming properties is evident.

Example 23

Table V also gives like data for Ross-Miles foam numbers of other mixtures of 3 parts of the above lauryl sulfate and 1 part sulfobetaines, and the Ross-Miles foam numbers of the constituents. The increase in foaming properties of the blends over that of the individual components under comparable conditions is evident from the table. It will be observed from Table V that, as in the case of the detergency value of soap, the sulfobetaine, when used in combination with the anionic, has a synergistic action on the foaming properties of the anionics to raise them to a value greater than that of either the sulfobetaines or the anionics under comparable conditions. This, thus, illustrates another aspect of the enhancement of the surfactant activity of anionic surfactants described above in connection with Table III.

TABLE V

Compounds	Concentr. in water of 100 p.p.m. hardness as CaCO_3 , percent	Ross-Miles foam numbers		
		Foam height in mm.		
		Instantaneous	60 sec.	300 sec.
Sodium lauryl sulfate.....	¹ 0.1	150	130	125
Sodium lauryl sulfate.....	0.075	-----	-----	-----
Lauryl dimethylammonium propanesulfonic acid betaine.....	0.025	235	200	190
Sodium lauryl sulfate.....	0.075	-----	-----	-----
Myristyl dimethylammonium propanesulfonic acid betaine.....	0.025	205	180	175
Sodium lauryl sulfate.....	0.075	-----	-----	-----
Acyclic (coco-fatty) pentaethylene glycol ammonium propanesulfonic acid betaine.....	0.025	200	175	170
Sodium lauryl sulfate.....	0.075	-----	-----	-----
Stearoyl amidopropyl dimethyl ammonium propanesulfonic acid betaine.....	0.025	195	170	165
Lauryl dimethylammonium propanesulfonic acid betaine.....	² 0.1	150	140	135
Myristyl dimethylammonium propanesulfonic acid betaine.....	² 0.1	165	150	145
Acyclic (coco-fatty) pentaethylene glycol ammonium propanesulfonic acid betaine.....	² 0.1	125	115	110
Stearoyl amidopropyl dimethyl ammonium propanesulfonic acid betaine.....	² 0.1	95	80	75

¹ By weight. ² In distilled water. See Table I.

Practical shampooing tests proved the shampoos made of the composition given in the examples listed in Table V lather profusely, even in the presence of very oily hair and hair conditioned with various hair dressings, which generally have a great tendency to defoam shampoo preparations. The sulfobetaines serve as foam stabilizers (foam persistors) as well as conditioning agents and thickening agents.

The hair, after shampooing, was left soft, manageable and easy to comb and imparted a good luster.

It was found that greater softness was imparted with the use of the higher molecular weight sulfobetaines, such as those containing C_{14} to C_{18} chains. For example: stearyl amido dimethylammonium propanesulfonic acid betaine; palmityl dimethyl ammonium propanesulfonic acid betaine; 2-pentadecyl-1-hydroxyethyl-2-imidazolinium-1-propanesulfonic acid betaine.

In general, it can be stated that the sulfobetaines containing from C_{12} to C_{14} carbon atom chains produce the richest lather, while those containing from C_{16} to C_{18} carbon atoms produce the maximum softening action on the hair.

However, it was found that even the C_{18} -derived sulfobetaines gave profuse lather highly suitable for shampoos and other cosmetic purposes.

Thus, by employing the sulfobetaines to replace part or all of the anionic, an improved shampoo which will leave the hair soft and manageable may be formulated. Perfumes, dyes, thickening agents, opacifiers and other ingredients usually employed in shampoos may be added. Such acyclic surfactant sulfobetaines will have lathering and foaming properties which are comparable with and will be equal to and, by selecting the sulfobetaine, will actually improve the foaming and lathering property of the shampoo.

A useful shampoo can be formulated by mixing an anionic, such as is conventionally employed in shampoos, with a sulfobetaine and including therein, if desired, perfumes and thickening agents, opacifiers and other ingredients, such as used conventionally in shampoos. For formulations of shampoos, reference may be had to standard works describing shampoos: "Surface Active Agents and Detergents," vol. 2, Schwartz, Perry & Berch, published by Interscience Publishers, 1958, page 621 et seq; article by M. A. Lesser in "Soap & Sanitary Chemicals," 26, No. 12, 40-3, 143 (1950); 27, No. 1, 38-41,

115, 117, 119 (1951); and to "Cosmetics—Science and Technology," editor Edward Sagrin (1957), Chapter 17, published by Interscience Publishers, Inc., N.Y.

Specific formulations for liquid shampoos, liquid creme and creme lotion shampoos, and creme paste shampoos are given in detail in the above references. I may employ these formulations and replace all or some of the anionic materials there identified with the sulfobetaines

described herein. The trade names referred to in these references may be identified by reference to "Detergents & Emulsifiers," 1960, published by John W. McCutcheon, 475 5th Ave., New York, N.Y.

The sulfobetaines may be used in the formulations, as reported in the literature references given above, to replace all or part of the anionic surfactant employed in the above references. An effective and economical shampoo is obtained by replacing a part only of the anionic, because of the usually higher cost of the sulfobetaine. Thus, for example, from 5% by weight to 100% by weight of the total surfactant content of the shampoo may be sulfobetaine; the remaining 95% to 0% of the surfactant may be anionic, such as, for instance, those stated in the above references and elsewhere in this specification, as surfactants useful in shampoos.

For purposes of illustration, and not as a limitation of my invention, a shampoo base employing the sulfobetaines of my invention may have the following formulation. It is to be understood that to such base may be added the thickeners, opacifiers, dyes and perfumes and other additives, such as are employed in the prior art, but it will not be necessary to add conditioners, since such conditioning action is provided by the sulfobetaines.

Example 24

	Parts by weight
Anionics	98-25
Sulfobetaine	2-75

That is, the ratio of the anionic to the sulfobetaine is in the range of about 98/2 to about 25/75. The shampoo base is given on an anhydrous basis. To this base, water, opacifiers, perfumes, dyes and thickening agents may be added. Part of the anionic component may be replaced by non-ionic; thus, from 5% to 75% of the anionic may be replaced by non-ionic surfactant. Such anionics may be any of those referred to above useful in shampoos. Thus, for example, they may be the sulfates of the higher acyclic alcohols, such as lauryl sulfates and mixtures thereof with other sulfates of the higher acyclic alcohols.

Example 25

In Example 24, all of the anionic and non-ionic surfactant may be replaced by the sulfobetaine.

The compositions given in Examples 21-25 and those reported in Table V may form a suitable base for shampoos, to which may be added perfume, dyes and opacifiers, if desired. The water content, i.e., concentration, may be adjusted, or additional thickeners may be added to give the desired viscosity.

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

While I have described particular embodiments of my invention, it should be understood that various modifications and adaptations thereof may be made within the spirit of the invention, as set forth in the appended claims.

I claim:

1. A process for producing ionic neutral sulfobetaines which comprises mixing a tertiary amine with propane sultone

in a solvent chosen from the group consisting of water and mixtures of water and an alcohol chosen from the group consisting of ethanol and isopropanol,

said propane sultone being employed in a molar ratio of at least one mole of propane sultone per atom of tertiary nitrogen present in said tertiary amine, said tertiary amine containing substituents on the nitrogen which are all linked to the nitrogen through a nonaromatic carbon,

and at least one and not more than two of said substituents on the said tertiary nitrogen containing uninterrupted straight carbon-carbon chains linked to the tertiary nitrogen through a non-aromatic carbon, said chains being not less than C₈ and not more than C₁₈ and said substituents being substantially free of oxygenated groups selected from the group consisting of hydroxy alkyl and polyglycol ether groups, and maintaining said propane sultone and said tertiary amine at an elevated temperature to form the said sulfobetaine.

2. The process of claim 1, in which at least one and not more than two of the substituents on the tertiary nitrogen of said tertiary amine is methyl.

3. The process of claim 1, in which the tertiary amine is a higher acyclic dimethyl amine.

4. The process of claim 1, in which the tertiary amine is myristyl dimethyl amine.

5. A process for producing ionic neutral sulfobetaines which comprises mixing a tertiary amine with propane sultone

in a solvent chosen from the group consisting of water and mixtures thereof with an alcohol chosen from the group consisting of ethanol and isopropanol, containing about 1% to about 3% by weight of alkali metal halide salt, based on the weight of the tertiary amine, said propane sultone being employed in a molar ratio of at least one mole of propane sultone per atom of tertiary nitrogen present in said tertiary amine, said tertiary amine containing substituents on the nitrogen which are all linked to the nitrogen through a non-aromatic carbon,

and at least one and not more than two of said substituents on the said tertiary nitrogen containing uninterrupted straight carbon-carbon chains linked to the tertiary nitrogen through a non-aromatic carbon, said chains being not less than C₈ and not more than C₁₈, and at least one of said substituents containing an oxygenated group selected from the group consisting of hydroxy alkyl, polyglycol ether and morpholine groups,

and maintaining said propane sultone and said tertiary amine at an elevated temperature to form the said sulfobetaine.

6. The process of claim 5, in which the alkali metal halide salt is potassium iodide.

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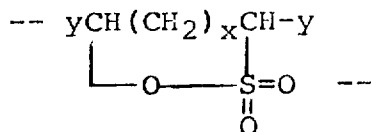
UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,280,179 Dated Oct. 18, 1966

Inventor(s) ROBERT ERNST

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

The formula at col. 11, lines 68 and 69, shall appear as shown below, instead of as in the patent:



SIGNED AND
SEALED
APR 21 1970

(SEAL)

Attest:

Edward M. Fletcher, Jr.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents