The present invention relates to new surface active agents (surfactants) which are also lime soap dispersants, to soap and detergent compositions which contain these surfactants, to processes for the manufacture of these surfactants, and to processes for their use. The present invention is a continuation-in-part of presently co-pending United States patent application, Ser. No. 218,437, filed Aug. 21, 1962, now abandoned.

Soap has been and still is one of the most versatile and inexpensive surface active agents. General use of soap in the home, however, for example, for personal washing and bathing as well as for laundering, is often considered undesirable, because soap forms insoluble scum or curds in wash water that contains significant amounts of the so-called "hardness" ions such as calcium, magnesium and iron. The curds result from the reaction of the fatty acid anion to advantage with the hardness ions, thus yielding a greasy, water-insoluble film or curd which ordinarily floats on the surface of the water and sticks to the surfaces of sinks, tubs, clothes, etc., which it comes into contact and is removable therefrom only with difficulty.

The one method that has become most widely accepted for overcoming the most important of these difficulties which result from using soap in hard water (namely, the elimination or the substantial prevention of the formation of sticky scum [usually called "lime soap" in the trade] on the surface of the water, which scum often causes the so-called "bathtub ring" etc.) which is that which involves the use of a "lime soap dispersant." A lime soap dispersant is ordinarily a synthetic surface active agent which, when used in conjunction with the soap, lowers the "lime soap curds" to remain mostly dispersed through the water, and eliminates most of their stickiness so that the curds are formed to stick to the sinks, bathtubs, etc., in such an undesirable fashion as that described above.

Of the thousands of different synthetic organic surface active agents (often termed "surfactants") that have been made over the past thirty or more years, only a very few have the right physical and chemical properties, particularly of the hydrophilic portion, of known surfactants often have great, generally unpredictable effects on their over-all activity as lime soap dispersants. Because of the relative rarity of acceptable, efficient lime soap dispersants, manufacturers of soap products including bar soaps, soap chips and flakes, etc., have relatively few good lime soap dispersants from which to choose for use in their formulations. In addition, those lime soap dispersants that are presently known and utilized are generally fairly expensive. Thus, there is a strong need in the trade for surfactants that can be utilized to advantage as lime soap dispersants and that can also serve as excellent relatively inexpensive general purpose detergents.

It is an object of the present invention to provide novel vicinal acylamido- and N-substituted acylamido sulfonates and sulfonate surfactant compounds, which, in addition to being a valuable general purpose surfactant, are also excellent lime soap dispersants. It is another object of the present invention to provide valuable detergent compositions that contain the aforementioned surfactant compounds.

It is another object of this invention to provide valuable novel soap compositions that contain, in addition to soap, an effective lime soap dispersing amount of the aforementioned surfactant compounds, which compositions can be used in hard water without excessive formation of lime soap curd in a sticky, undesirable form.

It is still another object of the present invention to provide novel processes for the manufacture of the aforementioned surfactant compounds.

It is still another object of this invention to provide processes in which the aforesaid surfactant compounds can be used as lime soap dispersants.

Other objects of the present invention will become apparent from the following discussion of the compounds, compositions, and processes of this invention. The novel compounds of this invention include those vicinal acylamido-type sulfonates of the formula:

$$R_C^{-}O-C-R'$$

wherein $R$ and $R'$ contain a total of from 8 to 22 carbon atoms and are selected from a group consisting of hydrocarbon radicals, aliphatic hydrocarbon radicals, and aliphatic radicals containing at most about 8 carbon atoms, the combined total number of carbon atoms in $R$ plus $R'$ being at most about 10.

When $R$ or $R'$, or both $R$ and $R'$ in the formula above, are aromatic radicals, they can be branched or unbranched to practically any degree, although it is preferred that they be substantially unbranched (straight-chain). Still further preferred are those organic radicals in this class of compounds wherein the total number of carbon atoms in $R$ plus $R'$ is from about 10 to about 18. Also, compounds having structures as in the above formula wherein one of $R$ or $R'$ is hydrocarbon are particularly preferred embodiments of the present invention. $R$ and $R'$ can also contain substituents which do not render them substantially hydrophobic or water-soluble in nature, such as halide (including fluoride, chloride, bromide and iodide, for example), ester groups, ether groups, thioether groups, nitro groups, sulfone groups, sulfoxide groups, amide groups, carbonyl groups, nitroso groups, and the like, in their aliphatic or alicyclic radicals, without substantially eliminating the benefits that can result from the use of these compounds as detergent and/or lime soap dispersants. The test for hydrophobicity in this instance involves the mixing with an equal volume of water of compositions having the structure of the above formula wherein the acylamido-type group and the sulfone group are replaced with hydrogen. "Hydrophobic" compounds are those that do not dissolve significantly in the water. $R$ and $R'$ in the above formula can also contain heterocyclic, monocyclic, monocyclic hydrocarbyl and substituted cyclic hydrocarbyl radicals (whether the rings thereof are saturated or not) although it is preferred that they be al-
phatic or substituted phatic, rather than alicyclic or substituted alicyclic radicals. It is additionally preferred that R and R' be of the type that does not ordinarily react readily with sulfur trioxide (SO₃) at a temperature below about 35°C, such as, for example, saturated hydrocarbyl, and halide-, nitro-, sulfone-, ether-, thiocarbon-, amido-, and sulfone-substituted hydrocarbyl radicals and the like.

When R" is an aliphatic or an alicyclic group, it can contain practically any of the above-described substituent groups. It is preferred, however, that R" be either an ethenyl group, a lower alkyl group or a halogen-substituted lower alkyl group containing from 1 to 5 carbon atoms, and still more preferably that R" be either hydrogen, or a methyl group. M is usually a cation selected from the group consisting of alkali metal cation, ammonium cation, and alkaline earth metal cation (preferably alkali metal cation; and of these, preferably sodium or potassium).

For the sake of clarity herein, whenever the term "vicinal acylamido" sulfonate or sulfate (or their corresponding acids) is utilized in the present patent, the term is intended to encompass those materials having structures such as those shown in the above formula, wherein R₃ is hydrogen when the term "vicinal N-substituted acylamido" sulfonate or sulfate (or their corresponding acids) is utilized herein, it is intended to encompass those materials having structures as in the above formula, wherein R₃ is an organic group containing at least 1 carbon atom.

The term "vicinal acylamido-type" sulfonate (and their acids) as utilized herein, is intended to encompass both "acylamido" and N-substituted acylamido" sulfonate. Similarly, the term "sulfol compounds" is intended herein to include sulfonate, as well as their corresponding (sulfonic) acids.

The vicinal acylamido-type sulfonates of this invention can be utilized advantageously as general detergent active ingredients, either alone or in combination with practically any material with which they are compatible in aqueous systems and that can be conveniently employed in combination with known anionic surface active agents such as soap and the alkali metal alkylaryl sulfonates; for example, sodium dodecylbenzene sulfonate; alkyl sulfates, alkane sulfonates, as well as with other types of compatible surfactants. The types of materials that can be employed in the formulation of so-called polyphosphate "built" detergents, liquid "heavy-duty" detergents, flaked and powdered soap compositions (assuming the usual considerations of compatibility are applied), including such materials as other surface active materials, polyphosphate complexing agents and other surface active materials, polyphosphate complexing agents and other builders, antideposition agents, optical brighteners, bleaching agents and the like, are well known in the detergent art and need not be detailed here. It is interesting to note that the acylamido-type sulfo compounds of this invention can be utilized to advantage in practically any of the compositions in which the alkaryl sulfonates, for example, can be utilized. In order to utilize the compounds of this invention as general purpose surfactants, the compounds need merely be dissolved in effective amounts, generally at concentrations of at least about 0.005 weight percent or more in water. In order for optimum results to be obtained when they are used as lime soap dispersants, these vicinal acylamido-type sulfo compounds should be dissolved in the hard water either prior to the time, or at the same time, at which the soap is dissolved in the water.

The preferred acylamido-type sulfonates of the present invention have physical and chemical properties that make them particularly outstanding as lime soap dispersants. Therefore, their use as lime soap dispersants constitutes a particularly preferred embodiment of the present invention. Generally, for use as lime soap dispersants, the acylamido-type sulfonates (preferably the sodium salts, but other alkali metal salts such as potassium and lithium salts or even ammonium and alkaline earth metal salts can be used) can be blended with any conventional soap, (for example, one which is intended to be utilized as a personal or laundry bar soap, or ultimately in the form of soap "flakes" or "powder" for laundering purposes) prior to the time the soap is formed into the bar or before it is ground or flaked to yield the final soap composition. Any amount of the preferred acylamido-type sulfonate, and especially amounts above about 1 weight percent (based on the amount of soap in the soap composition into which the compounds of this invention are blended) has a beneficial effect on the lime soap curd that forms when the soap composition is dissolved in hard water. However, it is generally preferred that, in combination with a soap (i.e., the alkali metal salt of a fatty acid which usually contains from about 10 to about 22 carbon atoms), between about 5 and about 70 weight percent of one or more of the preferred vicinal acylamido-type sulfonates described above, be utilized. Actually, because they are generally solid at room temperature, and generally at temperatures through about 50°C. have a "soapy" feel, and dissolve relatively slowly (after they are initially compressed into a "bar" shape) when they are allowed to stand in water, these preferred compounds can even be utilized alone as detergents in the form of bars, flakes, chips, granules, etc., if desired.

The following Table 1 illustrates some of the benefits that can result from utilizing these preferred vicinal acylamido-type sulfonate compounds as lime soap dispersants. The lime soap dispersant test is one that involves the measurement of the relative stickiness of lime soap curd or curds. Lime soap curds are those that form at the surface of hard water after a soap has been dissolved therein. Effective lime soap dispersants decrease or minimize the stickiness of the lime soap curds. In the test, which is conducted at a temperature between 30 and 35°C., 250 parts per million hard water (calculated as CaCO₃) having a Ca:Mg ratio of 2:1 is utilized. Five ml's of a 1 weight percent soap solution (or soap-lime soap dispersant blend) are shaken vigorously in a 50 ml test tube. Then the resulting foam is immediately stirred slowly into 500 ml's of the hard water in a 600 ml beaker. After all of the foam is quenched and the solution has stood undisturbed for 2 hours, the amount and particle size of scum, or suspended lime soap curd, are observed, and are allowed in comparison with soap alone and a standard soap-lime soap dispersant composition. Soap gives a low rating of 10, while the standard lime soap dispersed composition is rated 3 in a test such as that just described.

<p>| TABLE 1—LIME SOAP DISPERSANCY TEST DATA |</p>
<table>
<thead>
<tr>
<th>Sample Tested</th>
<th>Rating</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. 100% soap control</td>
<td>10</td>
</tr>
<tr>
<td>2. n-C₆H₁₃-CH-CH₂SO₃Na</td>
<td>3</td>
</tr>
<tr>
<td>3. n-C₆H₁₃-CH₂SO₃Na</td>
<td>3</td>
</tr>
<tr>
<td>4. n-C₆H₁₃-CH₂NHC₆H₄SO₃</td>
<td>3</td>
</tr>
<tr>
<td>5. n-C₆H₁₃-CH₂NH₂SO₃</td>
<td>3</td>
</tr>
<tr>
<td>6. n-C₆H₁₃-CH₂NHC₆H₄</td>
<td>3</td>
</tr>
<tr>
<td>7. C₆H₄-CH₂-CH₂SO₃Na</td>
<td>1</td>
</tr>
<tr>
<td>8. C₆H₄-CH₂-CH₂SO₃Na</td>
<td>3</td>
</tr>
<tr>
<td>9. C₆H₄-CH₂-CH₂SO₃Na</td>
<td>3</td>
</tr>
</tbody>
</table>
3,344,174

TABLE I—Continued

<table>
<thead>
<tr>
<th>Sample Tested</th>
<th>Rating</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₆H₅—CH—CH₃</td>
<td>5 (i)</td>
</tr>
<tr>
<td>NH₂CO₂H</td>
<td>5</td>
</tr>
<tr>
<td>C₆H₅—CH—CH₃</td>
<td>2</td>
</tr>
<tr>
<td>NH₂CO₂H</td>
<td>10</td>
</tr>
<tr>
<td>C₆H₅—CH—CH₃</td>
<td>2</td>
</tr>
<tr>
<td>NH₂CO₂H</td>
<td>15</td>
</tr>
<tr>
<td>(C₆H₅—CH—CH₃)₂Mg</td>
<td>5</td>
</tr>
<tr>
<td>NH₂CO₂H</td>
<td>1</td>
</tr>
<tr>
<td>C₆H₅—CH—CH₃</td>
<td>2</td>
</tr>
<tr>
<td>NH₂CO₂H</td>
<td>15</td>
</tr>
<tr>
<td>C₆H₅—CH—CH₃</td>
<td>1</td>
</tr>
<tr>
<td>NH₂CO₂H</td>
<td>10</td>
</tr>
<tr>
<td>C₆H₅—CH—CH₃</td>
<td>2</td>
</tr>
<tr>
<td>NH₂CO₂H</td>
<td>3</td>
</tr>
<tr>
<td>C₆H₅—CH—CH₃</td>
<td>3</td>
</tr>
<tr>
<td>NH₂CO₂H</td>
<td>30</td>
</tr>
</tbody>
</table>

* Lime soap dispersants tested as a 15 weight percent blend of the dispersant with 85 weight percent of soap.

Other ways in which the valuable vicinal acylamido-type sulfonates (and their corresponding acids) can be utilized to advantage include such uses as oil additives, emulsifiers for biological toxicants, pharmaceuticals and cosmetics, as dry cleaning detergents, as active ingredients in high foaming shampoos, as well as many other uses. Although certain of the vicinal acylamido sulfonate compounds of the present invention; i.e., those having structures such as are shown in Formula 2:

\[(2) \quad \text{A} \quad \text{SO₃M} \]

\[\text{R}—\text{O}—\text{R'} \]

\[\text{H} \quad \text{N} \quad \text{B} \]

\[\text{O}—\text{O} \]

\[\text{R''} \]

wherein R, R', R'', Y, A and B have the same meaning as in Formula 1, above; can be manufactured via several different processes, it has been discovered that one of the most advantageous processes involves the hydrolysis and neutralization of a novel intermediate "inner anhydride" raw material; a 2-dioxo-1,2,5-oxathiazine compound which is believed to have a structure such as that shown in Formula 3 or Formula 4:

\[(3) \quad \text{R}—\text{C}—\text{O}—\text{R'} \]

\[\text{N} \quad \text{Y} \quad \text{O}_3 \]

\[\text{R''} \]

\[(4) \quad \text{A} \quad \text{B} \]

\[\text{N}—\text{Y}—\text{O}_3 \]

\[\text{C} 

\[\text{O} \]

\[\text{R''} \]

20 wherein R, R', R'', A and B have the same meaning in Formulas 3 and 4 as they do in Formula 1, above. Note that the 2-dioxo-1,2,5-oxathiazines that can be utilized to greatest advantage in the practice of the present invention are the 3- and/or 4- and/or 6-(aliphatic, allylic; preferably lower alkyl) substituted 2-dioxo-1,2,5-oxathiazines (and similarly substituted 2-dioxo-3,4-dihydro-1,2,5-oxathiazines, 2-dioxo-3,4-dihalo-1,2,5-oxathiazines, or 2-dioxo-3- and/or 4-mono or di lower alkyl-1,2,5-oxathiazines); wherein the total (combined) number of carbon atoms in the substituents at the 3- and 4-positions is from 8 to 22, and preferably from 12 to 18, and the preferred substituents at the 3- and 4-positions are saturated aliphatic in nature.

Still further preferred are those 2-dioxo-1,2,5-oxathiazines having this number of carbon atoms at the 3- or 4-position, but which are only mono-substituted in either the 3- or 4-position. In addition, for the desired lime soap dispersants that can be manufactured via these 2-dioxo-1,2,5-oxathiazine "intermediate" raw materials, the 6-position should contain either hydrogen or a saturated aliphatic hydrocarbyl or halogen-substituted saturated hydrocarbyl radical containing from 1 to 8, and preferably from 1 to 5 carbon atoms (i.e., preferably a lower alkyl radical). Thus, the 2-dioxo-1,2,5-oxathiazine intermediate compounds that can be used to greatest advantage in the processes of this invention are those 2-dioxo-3,4-dihydro-1,2,5-oxathiazine compounds that contain substituents in the 3- and 4-positions selected from the group consisting of hydrogen, aliphatic hydrocarbyl, and substituted aliphatic hydrocarbyl radicals containing a total of from about 8 to about 24 carbon atoms in said substituents in the 3- and 4-positions; said 2-dioxo-3,4-dihydro-1,2,5-oxathiazine compounds additionally containing in the 6-position a radical selected from the group consisting of hydrogen, aliphatic hydrocarbyl and substituted aliphatic hydrocarbyl radicals, containing at most about 8 carbon atoms. Still further preferred are those 2-dioxo-3,4-dihydro-1,2,5-oxathiazine compounds having substituents in the 3- and 4-positions that are selected from the group consisting of hydrogen, saturated aliphatic hydrocarbyl and saturated halogen-substituted aliphatic hydrocarbyl radicals containing a total of from 12 to 20 carbon atoms in the 3- and 4-positions; at most one of the 3- or 4-positions containing 2 hydrogens; said 2-dioxo-3,4-dihydro-1,2,5-oxathiazine compound additionally containing at the 6-position a radical selected from the group consisting of hydrogen, hydrocarbyl radicals and halogen-substituted hydrocarbyl radicals; said radical at the 6-position containing at most about 5 carbon atoms. Still further preferred are those 2-dioxo-1,2,5-oxathiazine compounds wherein any organic substituent at the 6-, 3- and/or 4-positions are straight-chain substituents and either the 3- or the 4-position contains 2 hydrogens. Typical, but non-limiting, examples of some of the 1,2,5-oxathiazine compounds from which the
desired vicinal acylamido sulfonates of this invention can be made are
2-dioxy-3,4-dihydro-4-tetradecyl-6-methyl-1,2,5-oxathiazine;
2-dioxy-3,4-dihydro-3-methyl-4-decyl-6-ethyl-1,2,5-
oxathiazine;
2-dioxy-3,4-dihydro-3-ethyl-4-nonyl-6-allyl-1,2,5-
oxathiazine;
2-dioxy-3-hexadecyl-6-phenyl-1,2,5-oxathiazine;
2-dioxy-3,4-dihydro-3,4-diisobutyl-6-phenyltetrahydro-1,2,
5-oxathiazine;
2-dioxy-3,4-dihydro-4-dodecyl-1,2,5-oxathiazine;
2-dioxy-3,4-difluoro-4-perfluoroethyl-6-trifluoromethyl-1,2,
5-oxathiazine;
2-dioxy-3,4-dihydro-3-(7,8-dichloroheptadecyl)-6-chloro-
methyl-1,2,5-oxathiazine;
2-dioxy-3,4-dihydro-4-(p-octyl phenyl)-6-methyl-1,2,5-
oxathiazine;
2-dioxy-3-carboxy-4-hexadecyl-6-phenyl-1,2,5-
oxathiazine;
2-dioxy-4-decy-4-propyl-1,2,5-oxathiazine;
2-dioxy-3,4-dihydro-3,4-cyclohexyl-6-hexyl-1,2,5-
oxathiazine and the like.
The 2-dioxy-1,2,5-oxathiazines described above can be
manufactured by reacting, usually in an appropriate sol-
vent and at a temperature between about 30° C. and
about 70° C., an organic nitrile containing from 2 to 9
atoms of carbon or hydrogen cyanide with either a β-sulfone or a
carbonyl sulfite type compound in accordance with one of the
following reactions:

\[ R - C = O + R'' + C\equiv N \rightarrow R - C = O - R'' \]

(sulfone nitrile)

\[ R - C = O + R'' + C\equiv N \rightarrow R - C = O - R'' \]

(urea sulfite nitrile)

wherein R, R', R'' and A and B have the same meanings as
those assigned for Formula 1 above. Additional details
relating to the manufacture of these 2-dioxy-1,2,5-
oxathiazines can be found in a co-pending patent applica-
No. 3,255,549.
In order to convert any of the above-described 2-dioxy-
1,2,5-oxathiazine compounds to the corresponding vicinal
acylamido sulfonic acid, one need merely intermix them
in any particularly desired or convenient manner with
at least about, but preferably considerably more than, one
mole of water per mole of inner anhydride compound and
warm the resulting mixture to a temperature above about
50° C., and preferably above about 75° C. If it is desired
to convert (hydrolyze) only a portion of the 2-dioxy-
1,2,5-oxathiazine material, less than this amount of water
can be used. Note that some 2-dioxy-1,2,5-oxathiazine
compounds can have more than one of the 2-dioxy-1,2,5-
oxathiazine rings (such as those shown in Formulas 3
and 4 above) per molecule. Thus, when more than one
2-dioxy-1,2,5-oxathiazine ring is present per molecule pro-
portionately more water than one mole per mole of the
oxathiazine compound must be utilized in order to hydro-
lyze all of the inner anhydride rings to the appropriate
vicinal acylamido sulfonic acid groups. In order to manu-
facture a vicinal acylamido sulfonate in accordance with
the processes outlined above, the vicinal acylamido sul-
fonic acids can be neutralized with any alkali metal,
alkaline earth metal or ammonium base in either water
or a non-aqueous solvent, depending upon the solubility
characteristics of the particular acid and base that are
utilized. Practically any alkali metal, alkaline earth metal
or ammonium base that is stable either per se or in aque-
ous solution within the range of from about room tem-
perature to about 105° C. and under about one atmos-
phere of pressure can ordinarily be utilized to convert
these sulfonic acids to the corresponding sulfonates. Par-
ticularly preferred are the alkali metal cation bases such as
alkali metal hydroxides, carbonates, silicates, bicar-
obonates and the like (and of these, sodium and potassium
bases are generally preferred because of economic as
well as other considerations) and alkaline earth metal
cation bases such as calcium carbonate, magnesium car-
bonate, magnesium hydroxide, magnesia carbonate and the
like. Ammonium hydroxide, as well as other alkaline am-
monium salts can also often be utilized to advantage in
the neutralization of these sulfonic acids. Water-soluble
and/or water-dispersible bases can conveniently be pre-
sent in the water that is utilized to hydrolyze the inner an-
hydrde compounds (described above) if desired, to
thereby effectively hydrolyze the 2-dioxy-1,2,5-oxathiazine
ring and neutralize the resulting acid at practically the
same time. Sometimes only a small amount of water (or
even none in some instances) is necessary when the
hydrolysis and neutralization steps are performed simul-
taneously. For example, when an alkali metal hydroxide
such as sodium, potassium or lithium hydroxide, is utilized
after it has been dissolved in an organic solvent such as
methanol or ethanol, essentially no additional water at all
is needed for the hydrolysis of the 2-dioxy-1,2,5-oxa-
thiazine compound and the formation of the correspond-
ing alkali metal vicinal acylamido sulfonate.
It is advantageous that the hydrolysis and neutraliza-
tion of the 2-dioxy-1,2,5-oxathiazine compounds can be
carried out while the oxathiazine is in physical contact
with soap. Thus, soap compositions that have excellent
over-all detergent properties, and that are additionally
valuable because they can form effectively dispersed limed
soap curds when they are dissolved in hard water, can be
manufactured directly, if desired, in conventional soap
equipment such as a crucher, or in practically any mix-
ing vessel that can be used to formulate soap (i.e., in
which molten soap can be handled), such as a conven-
tional amalgamator, a conventional "refiner," or even a
conventional soap mill. Since the temperature of the soap
when it is in a molten state is generally fairly high, essen-
tially all that is usually necessary is that the hydro-
lysis and neutralization of the 2-dioxy-1,2,5-oxa-
thiazine compound (admixed with the soap) is that both
an effective amount of the oxathiazine compound and a
sufficient quantity of the particular base that is to be em-
ployed for the neutralization step be well mixed through
the soap while the soap is in the molten state. Usually
the small amount of moisture that the molten soap con-
tains is enough for the hydrolysis and neutralization of
the oxathiazine to be performed without the necessity
of adding water to the molten soap-oxathiazine composi-
tion or blend, although some water can be added to
speed up the rate of hydrolysis and neutralization of the
oxathiazine compound if desired. For this particular neu-
tralization technique, the oxathiazine compound (and the
base) can be blended with the soap either before or after
the soap is made molten, depending upon the particular
manufacturing procedure desired. It is generally preferred,
however, that an alkali metal hydroxide such as potassium
or sodium hydroxide be used when the oxathiazine com-
pound is hydrolyzed and neutralized "in situ," i.e., in
physical contact with the soap.
After the conversion of the oxathiazine compound to
the corresponding vicinal acylamido sulfonate via this
 technique, the sulfonate compositions can generally be
handled via conventional techniques and equipment in
a manner similar to that in which plain or conventional
soap is handled; for example, through the usual pledging,
sizing, cooling, stamping and packaging operations.
Ordinarily materials that can be employed with soap (such as preservatives, pigments, dyes, perfumes, fillers, and chelating N-substituted vicinal acylamido sulfonates) can also be employed in soap compositions that additionally contain any one (or more) of the vicinal acylamido-type sulfo compounds of the present invention without detracting substantially from the advantages that can result from practicing the invention. In addition, any soap can be used advantageously in combination with one or more of the vicinal acylamido-type sulfo compounds of the present invention.

The 2 - dioxy - 1,2,5 - oxathiazine compounds that can be converted by hydrolysis and neutralization into the vicinal acylamido sulfonate compounds of this invention have the peculiar ability to apparently become converted to the corresponding vicinal acylamido sulfonic acids upon being heated in the presence of water (but in the absence of base) as described above, but to revert back to the original 2 - dioxy - 1,2,5 - oxathiazine compound when the temperatures of aquatic systems containing the sulfonic acids are lowered to about room temperature, for example, or sometimes to a degree or more above about 0° C. However, this reversion in neutral or acidic aqueous media does not ordinarily take place if the particular sulfonic acid utilized (hydrolyzed 2 - dioxy - 1,2,5 - oxathiazine has been reacted with one of the appropriate N-substituted vicinal acylamido sulfonic acids. The presence of one or more bases in the aqueous medium may, however, allow some of the above-described 2 - dioxy - 1,2,5 - oxathiazine intermediate compounds generally makes it possible to hydrolyze the "inner anhydride" (oxathiazine) ring at a lower temperature than would otherwise be expected (of the pure intermediate compounds in neutral or acidic aqueous media, for example).

The vicinal acylamido sulfates (and the corresponding acids) of the present invention can be manufactured by first sulfating an appropriate vicinal amino alcohol compound, which in turn can be prepared by reducing an appropriate vicinal amino carboxylic acid, such as, for example, an a-amino fatty acid containing from 10 to 24, and preferably from 14 to 20 carbon atoms. After sulfation, the resulting vicinal amino sulfuric acid ester can be reacted, for example, with a lower aliphatic carboxylic anhydride such as, for example, acetic, haloacetic or propionic anhydride, to yield the desired vicinal acylamido sulfate compound of the present invention. The vicinal N-substituted acylamido sulfates of this invention can be made via practically the same processes, except that instead of sulfating a vicinal amino alcohol, an appropriate vicinal amino alcohol is sulfated. To manufacture the corresponding thiono (or other chlalkogen) compounds of the present invention, one need merely substitute an appropriate thiono anhydride (for example, thionoacetic anhydride for acetic anhydride) in the foregoing discussion.

Another process wherein most of the vicinal acylamido sulfonates (and sulfonic acids) of the present invention can be manufactured is via the treatment (generally in a non-aqueous solvent such as carbon tetrachloride, ethyl ether, benzene and the like) of an appropriate vicinal amino sulfonate with an appropriate carboxylic acid-type anhydride, generally at temperatures above about 30° C., according to the reaction:

$$\text{R}^1-\text{C}_x-\text{C}_y=\text{H}^+\text{Y} + \text{B}^{-}\text{C}_x-\text{C}_y=\text{A} + \text{R}^2$$

wherein R', R", Y, A and B have the same meaning as in Formula 1, above. Instead of the carboxylic acid-type anhydride, the corresponding carboxylic acid-type halide, or even the carboxylic acid-type itself, can be used, when consideration is given to removal of by-product hydrohalic acid or water during the reaction. Addi-

tional details relating to the manufacture of these vicinal acylamido sulfonates (and sulfonic acids) from their corresponding vicinal amino sulfonates can be found in patent application, Ser. No. 321,696, filed concurrently herewith, and now abandoned.

The vicinal N-substituted acylamido sulfonates of the present invention can also be made by a reaction similar to that of Equation III, above (i.e., by acylating an appropriate vicinal N-substituted amino sulfonate). Details relating to the manufacture of these vicinal N-substituted acylamido sulfonates (and sulfonic acids) can also be found in the patent application, Ser. No. 321,696, filed concurrently herewith.

In the following examples, which are illustrative of some of the preferred embodiments of the present invention, all parts are by weight unless otherwise specified.

**Example I**

Into a conventional glass-lined reaction vessel fitted with a fairly efficient stirrer are dumped 1,000 parts of powdered 2 - dioxy - 3,4 - dihydro - 2 - methyl - 1,2,5 - oxathiazine and 10,000 parts of water. The resulting mixture is then warmed to and subsequently maintained at a temperature of about 90° C. for about 1 hour, during which time the carboxylic acid by-product is removed enough of a 50 weight percent solution of sodium hydroxide to bring the pH of the hot mixture to about 8. Upon subsequently being cooled to about 0° C., a white precipitate settles out of the aqueous mixture. The precipitate is removed by filtration and air-dried to yield a product which is an excellent general purpose detergent and lime soap dispersant. It is practically pure sodium 2 - acetamidoo - n-tetradecane - 1-sulfonate.

**Example II**

Two hundred parts of purified 2 - dioxy - 3,4 - dihydro - 3 - n - tetradecyl - 6 - ethyl - 1,2,5 - oxathiazine are dispersed in 4,000 parts of water in a conventional glass-lined mixing vessel fitted with a reasonably efficient stirrer and a water and/or steam jacket for heating and cooling the contents of the vessel. To the resulting slurry are added 50 parts of a 50 weight percent solution of sodium hydroxide. The resulting mixture is then warmed to a temperature of about 50° C. and held at about this temperature until the mixture becomes clear, at which point essentially all of the anhydride material is hydrolyzed and neutralized to the corresponding sodium sulfonate salt. The resulting compound, sodium 1 - propionamido - n - hexadecane - 2 - sulfonate, is then isolated from the water by drying the neutralized clear solution on a conventional stainless steel drum-drier.

**Example III**

In a mixing vessel such as that described in Example II, above, are blended 250 parts of 2-dioxy-3,4-dihydro-3-branched hexadecyl-6-benzyl-1,2,5-oxathiazine, 3,000 parts of water, and 150 parts of powdered magnesium carbonate. The resulting mixture is then heated to a temperature of 75° C., and maintained at about this temperature until the evolution of carbon dioxide from the mixture ceases. Then the mixture is filtered to remove excess magnesium carbonate. The resulting filtrate is then spray-dried in a conventional spray-drying tower from which the desired product, magnesium 2-phenylacetamidohexadecane-1-sulfonate, is recovered in a dry, powdered form.
Example IV

A detergent slurry containing the following ingredients is prepared by blending together in the following order:

**Ingredient:**

- Water: 4000 parts
- Sodium 2-acetamido-n-hexadecane-1-sulfonate: 1500
- Sodium tripolyphosphate hexahydrate (−20 mesh): 4000
- Sodium sulfate (−200 mesh): 300
- Sodium carboxymethyl cellulose: 100
- Optical brightener: 20

After being well blended, the slurry is then dried in a conventional spray tower via conventional techniques, yielding a product containing approximately 65% weight percent of sodium tripolyphosphate, 25% weight percent of surfactant, 5% weight percent of sodium sulfate, plus other minor ingredients. This product is an excellent laundry detergent.

Example V

A spray-dried detergent product is prepared as in Example IV, above, using sodium 2-N-propylacetamidom-n-hexadecane-1-sulfonate as the sole surfactant (in place of 2-acetamido-n-hexadecane-1-sulfonate) at the 25% weight percent level in the finished detergent product.

This product, too, is an excellent laundry detergent. The other water-soluble vicinal acylamido and N-substituted acylamido sulfonates and sulfates, including, for example, sodium 2-(beta-arylsulfonyl) propionamidom-n-hexadecane sulfonate can be utilized advantageously as in Examples IV and V, above, by merely substituting in the formulation the desired vicinal sulfonate or sulfate compound, or mixtures thereof.

Throughout the foregoing discussion and examples, the vicinal acylamido and N-substituted acylamido sulfonate compounds of the present invention have been described as though they were and are relatively "pure" materials, in terms of the number of carbon atoms contained therein, for example. It will be understood, however, that although these materials can be made and utilized in the "pure" (single compound) form; for example, when the sulfonates are made starting with organic raw materials (e.g., olefins in one of the preferred processes described above) that are relatively "pure," as a general rule, the hydrophobic "organic radical" back-bone of the valuable surfactants of this invention are not "pure" in this respect at all. Rather, since they are generally most economically prepared from commercial olefins, for example (which in turn are generally blends of hydrocarbons of varying carbon chain lengths and structures having similar boiling points or distillation ranges), most of the surfactant materials of the present invention will, in reality, contain a mixture or blend of compounds which vary one from another in the number of carbon atoms contained therein. Generally, the number of carbon atoms in the hydrophobic "back-bone" of the vicinal acylamido and N-substituted acylamido sulfonic compounds of the present invention will vary from about 8 to about 24, while the average number of carbon atoms in the hydrophobic "back-bones" (i.e., R plus R'−2, in the foregoing formulae) should preferably be from about 12 to about 18. Those containing an alkyl "back-bone" having an average of about 16 carbon atoms are particularly preferred materials.

What is claimed is:

1. A compound of the formula:

   \[
   \begin{align*}
   A & \quad \text{SO}_{3}M \\
   R & \quad C & O & C & R' \\
   R_2 & \quad N & B \\
   C & \quad O \\
   R'' & 
   \end{align*}
   \]

   wherein R and R' contain a combined total of from 8 to 22 carbon atoms and in each instance are selected from the group consisting of hydrogen, alkyl radicals, mono-olefinic aliphatic hydrocarbon radicals, and substituted alkyl and mono-olefinic aliphatic hydrocarbon radicals having substituents selected from the group consisting of fluoride, chloride, bromide, and iodide substituents; R'' is selected from the group consisting of hydrogen, lower alkyl radicals, and substituted lower alkyl radicals having substituents selected from the group consisting of fluoride, chloride, bromide, and iodide substituents; A and B are selected from the group consisting of hydrogen and lower alkyl radicals; M is selected from the group consisting of hydrogen, alkali metal, ammonium and alkaline earth metal; and R_2 is selected from the group consisting of hydrogen, phenyl, and alkyl radicals containing at most about 8 carbon atoms, the combined total number of carbon atoms in R'' plus R_2 being at most about 10.

2. A compound of the formula:

   \[
   \begin{align*}
   A & \quad \text{SO}_{3}M \\
   R & \quad C & O & C & R' \\
   H & \quad N & B \\
   C & \quad O \\
   R'' & 
   \end{align*}
   \]

   wherein R and R' contain a combined total of from 8 to 22 carbon atoms and in each instance are selected from the group consisting of hydrogen, alkyl radicals, mono-olefinic aliphatic hydrocarbon radicals, and substituted alkyl and mono-olefinic aliphatic hydrocarbon radicals having substituents selected from the group consisting of fluoride, chloride, bromide, and iodide substituents; R'' is selected from the group consisting of hydrogen, lower alkyl radicals, and substituted lower alkyl radicals having substituents selected from the group consisting of fluoride, chloride, bromide, and iodide substituents; A and B are selected from the group consisting of hydrogen and lower alkyl radicals; M is selected from the group consisting of hydrogen, alkali metal, ammonium and alkaline earth metal; and R_2 is selected from the group consisting of hydrogen, phenyl, and alkyl radicals containing at most about 8 carbon atoms, the combined total number of carbon atoms in R'' plus R_2 being at most about 10.

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