This invention relates to processes for the production of long chain alkyl derivatives, and more particularly refers to processes for the production of long chain thetine compounds and the products thereof.

It is an object of this invention to produce hydrocarbon derivatives which are of particular value in the many processes wherein surface active materials are required. A further object is to produce long chain alkyl derivatives of sulphur. A still further object is to produce a new class of surface active agents which possess satisfactory wetting, penetrating, dispersing and detergent properties. A still further object is to produce long chain alkyl thetines which are useful in place of or in conjunction with soap and soap substitutes. A still further object is to produce a new class of soap substitutes which may be used for all the purposes wherein soap and soap substitutes have been used or are capable of use. Additional objects will become apparent from a consideration of the following description and claims.

This invention is directed to tetravalent sulphur compounds having the following general formula:

\[
R_1 R_2 X
\]

wherein \( R \) and \( R_1 \) represent aliphatic radicals, \( R_2 \) represents hydrogen or an aliphatic radical, the carboxyl group is separated from \( S \) by no more than four carbon atoms, \( X \) represents an anion, and one of the aliphatic radicals contains from twelve to eighteen carbon atoms. These products may be produced in accordance with various processes which will hereafter be described in detail. One illustration of these processes is the reaction of a dialkyl sulphide with a halogenated fatty acid or ester or salt of such acid. One of the aliphatic radicals, represented by \( R_1 \) and \( R_2 \), should considerably contain from twelve to eighteen carbon atoms, although when \( R_1 \) is the long chain aliphatic radical it may contain a smaller number of carbon atoms than in the case of \( R \) and \( R_2 \). For instance, \( R_2 \) might contain from ten to sixteen carbon atoms. The remaining aliphatic radicals are preferably of relatively low molecular weight such as methyl, ethyl, propyl, isopropyl, and the like.

The invention may be more readily understood by a consideration of the following illustrative examples in which the quantities are stated in parts by weight:

**Example 1**

Chloride of dodecyl methyl thetine. 21.6 parts by weight of dodecyl methyl sulphide and 9.5 parts by weight of chloroacetic acid were heated at 60°C, with stirring for one hour. The two layers which were present at first have now become compatible and after cooling the product crystallized. After recrystallizing twice from acetone, the crystals softened at 67°C. and melted finally at 105°C. Analysis indicated the product to contain 10.6% sulphur, the theoretical value being 10.3% sulphur. The crystals are very hygroscopic and dissolve in water to give clear solutions which foam. Aqueous solutions are not precipitated by calcium chloride solution and when a strip of soiled felt was stirred around in the hard water solution the felt was cleansed. This compound, when tested in a Launderometer in hard, alkaline, soft and acid water, cleansed soiled felt as well as an alcohol sulphate detergent.

**Example 2**

Dodecyl methyl thetine. 11 parts by weight of dodecyl methyl sulphonium carboxy methyl chloride was dissolved in 39 parts by weight of absolute alcohol and titrated with 16 parts by weight of an alcohol solution containing 2.2 parts by weight of potassium hydroxide. A precipitate
formed at once which was filtered off and the alcohol solution allowed to evaporate slowly. A white crystalline mass soluble in water remained. This is dissolved in 240 parts by weight of hot water and filtered. On cooling, needles separated from the acetone solution but the needles soon formed a gum. The acetone solution was allowed to evaporate and the gummy mass dried over sulphuric acid in a vacuum desiccator. It did not contain chlorine and analyzed 12% sulphur, the calculated value being 11.7% sulphur. The product weighed 6 parts by weight. This material dissolves readily in water to form solutions which foam. It is exceptionally effective as an assistant in the mercerizing of cotton cloth.

**Example 3**

Bromide of benzyl octadeyl thentine. 33.3 parts by weight of octadeyl bromide and 18.3 parts by weight of benzyl thioglycollic acid were warmed together at about 80° C. with occasional shaking for seven days. The bromide of benzyl octadeyl thentine was only slightly soluble in water, but the solubility was increased when treated with alcoholic sodium hydroxide solution due to formation of benzyl octadeyl thentine. The solution foamed.

**Example 6**

Chloride of octadeyl benzyl thentine. 7.5 parts by weight of benzyl octadeyl sulphide and 1.5 parts by weight of chloroacetic acid were heated on the steam bath for two hours at the end of which time the solution was homogeneous. On cooling, the product crystallized and was only slightly soluble in water. When the chloride of octadeyl benzyl thentine was heated one hour with an alcoholic solution containing sodium hydroxide, the octadeyl benzyl thentine which formed was soluble in water and the solution foamed.

**Example 5**

Bromide of octadeyl ethyl alpha lauroyl thentine. 3.1 parts by weight of octadeyl ethyl sulphide and 2.8 parts by weight of alpha bromo-lauryl acid were heated at 70-80° C. After 1½ hours heating the product was a clear liquid which solidified on cooling. After warming eight hours, the bromide of octadeyl ethyl alpha lauroyl thentine dissolved readily in cold dilute sodium hydroxide and the solution formed a persistent foam. On acidification the product continued to foam. The product was refluxed one hour with 10 parts by weight of alcohol containing 0.44 part by weight of sodium hydroxide and a precipitate of sodium bromide separated from the solution. The alcohol solution was decanted, the alcohol evaporated and the residue which is octadeyl ethyl alpha lauroyl thentine was found to be sparingly soluble in dilute alkali and dilute acid solutions.

**Example 6**

Bromide of octadeyl ethyl alpha propionyl thentine. 3.1 parts by weight of octadeyl ethyl sulphide and 1.5 parts by weight of alpha bromo-propionic acid were warmed together at 70-80° C. for 1½ hours at the end of which time the two materials formed a homogeneous mixture. The bromide of octadeyl ethyl alpha propionyl thentine was refluxed one hour with 10 parts by weight of alcohol containing 0.44 part by weight of sodium hydroxide and a precipitate of sodium bromide separated from the solution. The alcohol solution containing octadeyl ethyl alpha propionyl thentine was decanted and poured into water. It was sparingly soluble in dilute alkaline and dilute acid solutions and the solutions foamed very much.

**Example 7**

Bromide of dodecyl methyl alpha lauroyl thentine. 2.2 parts by weight of dodecyl methyl sulphide and 2.8 parts by weight of alpha bromo-lauryl acid were heated at 70-80° C. for eight hours. The product, the bromide of dodecyl methyl alpha lauroyl thentine, was soluble in cold dilute sodium hydroxide solution and formed a persistent foam. The product was next heated one hour at the reflux temperature with 10 parts by weight of alcohol containing 0.44 part by weight of sodium hydroxide and a precipitate of sodium bromide separated from the solution. The alcohol solution containing dodecyl methyl alpha lauroyl thentine was decanted and poured into water. It was very soluble in both acid and alkaline solutions and the solutions produced a persistent foam when shaken.

**Example 8**

Bromide of dodecyl methyl thentine. 2.2 parts by weight of dodecyl methyl sulphide and 1.5 parts by weight of alpha bromo-acetic acid were heated eight hours at 70-80° C. At the end of which time the mixture was homogeneous. The product, the bromide of dodecyl methyl thentine, was soluble in dilute sodium hydroxide solution and foamed. When the product was heated one hour at the reflux temperature with 10 parts by weight of alcohol containing 0.44 part by weight of sodium hydroxide a precipitate of sodium bromide separated from the solution. The alcohol solution containing dodecyl methyl thentine was decanted and poured into water. It was very soluble in alkaline solutions which gave persistent foams when shaken.

**Example 9**

Bromide of dodecyl methyl alpha propionyl thentine. 2.2 parts by weight of dodecyl methyl sulphide and 1.5 parts by weight of alpha bromo-propionic acid were heated together two hours at 70-80° C. After which time the reactants were compatible and the product was soluble in water to give foaming solutions. The product, the bromide of dodecyl methyl alpha propionyl thentine, was heated one hour with 10 parts by weight of alcohol containing 0.44 part by weight of sodium hydroxide and a precipitate of sodium bromide separated from the solution. The alcohol solution containing dodecyl methyl alpha propionyl thentine was decanted and poured into water. It gave perfectly clear solutions in both acid and alkaline solutions which foamed persistently.

**Example 10**

Bromide of dodecyl methyl beta propionyl thentine. 2.2 parts by weight of dodecyl methyl sulphide and 1.5 parts by weight of beta bromo-propionic acid were heated together at 70-80° C. After warming three hours the product was soluble in water, in dilute sodium hydroxide solution and in dilute hydrochloric acid solution, and was foamed in each case. The product was refluxed for one hour with 10 parts by weight of alcohol containing 0.44 part by weight of sodium hydroxide and a precipitate of sodium bromide separated from the solution. The alcohol solution containing dodecyl methyl beta propionyl thentine was decanted and poured into water. It was very soluble in alkaline solutions which foamed when shaken.
Example 11
Bromide of benzyl octadecyl alpha lauroyl thentine, 3.5 parts by weight of benzyl octadecyl sulphide and 2.8 parts of alpha bromolaurolic acid were warmed together at 70-80°C. After heating eight hours the product, the bromide of benzyl octadecyl alpha lauroyl thentine, was soluble in dilute sodium hydroxide, fats and waxes by saponification or by catalytic or sodium reduction, or they may correspond to the radicals of alcohols isolated from the reaction of water and carbon oxides in the presence of catalysts employed in the methanol synthesis. The alkyl groups may be the same or dissimilar and they may have substituted thereon the same or dissimilar non-hydrocarbon groups. Also, it is contemplated that these radicals may be of cyclic nature, either carbocyclic or heterocyclic. In other words, one or both alkyl groups may be of aryl, heterocyclic, cycloaliphatic or aralkyl derivation, such as for example, phenyl, cyclohexyl, naphthenyl, benzyl, etc.

The aforesaid and related sulphides may be reacted with hydrocarbon derivatives to substituted thereon an oxygen-containing acid group or derivative thereof and an anion, in order to produce the desired tetravalent sulphur compounds. The hydrocarbon radical of this reactant may contain from one to twenty carbon atoms, as in the case of the alkyl or other carbon radicals of the sulphur containing reactant. This hydrocarbon group may also be a straight chain alkyl group or it may contain branched chains, it may be saturated or unsaturated, or may be further substituted with one or more non-hydrocarbon groups which do not interfere with the resulting reaction, and it may be or may have substituted thereon aryl, heterocyclic, cycloalkyl, aralkyl and the like groups. This hydrocarbon group should have substituted thereon, as previously stated, an oxygen-containing acid group or derivative thereof. Among the groups coming within this category mention may be made of carboxyl, sulphonlic acid, sulphuric acid, phosphoric acid, and their salts, esters, amides, ureas, thioureas, nitriles and related derivatives. It is to be understood that the carboxyl acid group is preferred for this purpose. The hydrocarbon group of the reactant under consideration should also have substituted thereon an anion such as bromine, chlorine, sulphuric acid, hydroxyl, sulphuric acid ester, sulphonic acid, sulphonic acid ester, etc. In this connection it might be mentioned that the preferred anion substituents are chlorine and bromine.

In accordance with the aforesaid instructions, the reactions set out may be, for example, between a cyclic sulphide such as diethylene disulphide, thiophene, or tetrahydrothiophene and a halogenated fatty acid containing from one to twenty carbon atoms. A mercaptan such as mercaptobenzothiazole may be reacted with a long chain halogen compound such as dodecyl bromide to obtain a sulphide for further reaction with bromoacetic acid to form a thione bromide which may be ring closed with an alkaline condensing agent such as sodium carbonate or with sodium hydroxide to form the thione. Thioglycolic acid may be reacted with a long chain halide such as octadecyl bromide to form octadecyl thioglycolic acid which, upon treatment with dimethyl sulphate will form the methyl sulphate of methyl octadecyl thentine, and this compound upon treatment with an alkaline condensing agent will cause ring closure to form methyl octadecyl thentine.
chain mercaptans such as hexadecyl mercaptan may be reacted with chloroacetic acid in the presence of alkaline condensing agents to produce hexadecyl thiglycollic acid, which may be further condensed with an additional quantity of chloroacetic acid or with dimethyl sulphate. A halide of a long chain ether such as the bromide of lauryl ethyl ether may be reacted with ethyl mercaptan to obtain the sulphide, which may be further condensed with bromoacetic acid to form a thione bromide. Likewise, a sulphide such as \( \text{C}_2\text{H}_5\text{CHCONHCH}_2\text{CH}_2\text{SH} \) may be reacted with chloroacetic acid. An alternative process involves the treatment of thiglycollic acid with di- or octadecyl sulphate to obtain the octadecyl sulphate of di- or octadecyl thione, which on treatment with sodium carbonate or sodium hydroxide forms a mixture of di- or octadecyl thione and sodium octadecyl sulphate. Another illustration of the many reactions contemplated herein concerns the condensation of methyl thiglycollic acid with dodecyl para toluene sulphonate to obtain the para toluene sulphonate of dodecyl methyl thione.

It is clear from the preceding description, the present embodiment of this invention pertains to tetravalent sulphur compounds which contain an aliphatic radical of between twelve and eighteen carbon atoms, two allyl groups of lower molecular weight, an anion such as chloride or bromide, and a carboxyl group. These compounds may be used in the production of materials which are superior to those used in the kier boilng of cotton goods. They may also be used in the production of cationic dyes for dyestuff applications. They are also useful in the production of insoluble dyes for dyestuff applications.
are useful in softening and treating baths for hides and skins, particularly in baths used for fat-liquoring leather and in processes of water-proofing leather. Solutions of these compounds are useful for pretreating leather prior to dyeing.

The dispersing and emulsifying powers of these novel compositions give rise to many interesting uses. They may be utilized for converting liquid or solid substances normally insoluble in water, such as hydrocarbons, higher alcohols, pitches and pitch substances into clear solutions or stable emulsions or dispersions. They are useful in preparing emulsions of wax, wax-like compositions which are used as leather dressings or floor polishes. They may be employed to prepare artificial dispersions of crude, vulcanized, or reclaimed rubber. They may be used as emulsifiers in the manufacture of cosmetic preparations such as cold creams and lipsticks. They may be employed for preparing emulsions of the water-in-oil type such as emulsions of water in such organic solvents as are used in the dry cleaning industry. They are also of value in the breaking of petroleum emulsions, such as those naturally occurring in nature or produced during the refining of petroleum.

These compositions may also be used alone as bactericides and contact insecticides and for enhancing the spreading power of other parasiticides. They may be employed in agricultural sprays in combination with the ordinary parasiticides and fungicides. They are useful for promoting the penetrating power of wood preservatives.

In the paper industry these products may be used as penetrants in the liquors used for cooking rags and pulp, and as assistants in paper softening, filling, and processes to increase absorbency.

These compositions may be employed as detergents in several different relations. They may be used in the washing of fruits and vegetables for spray residue removal. They may be used in combination with metal cleaning compounds in neutral, acid, or alkaline liquors. They may be used for paint, varnish, and lacquer cleaners. They may advantageously be employed as cleaning agents in hard water and where a fatty or oily film resists the ordinary cleansing media. They may be added to soap in acid or hard water baths, since these compositions do not form precipitates so readily in hard and acid waters as soaps and Turkey red oils.

These compositions may be used as aids in various chemical reactions. They may be used to control particle size and shape during precipitation or crystallization of compounds from reaction mixtures. They may be used to decrease the particle size of insoluble amine hydrochlorides just before these amines are to be diazotized.

These compositions also have several miscellaneous uses. They may be employed as foam stabilizing agents, especially for use in air-foam fire extinguishing compositions. They may be used to stabilize rubber latex. They may also be used as frothing and collecting agents in ore flotation processes, and in other processes such as the recovery of fixed oil from the oil sands. The uses mentioned will suggest many similar ones.

By means of the present invention a large class of new and commercially feasible surface active materials has been rendered available for use. These compounds possess satisfactory foaming properties and are of particular value for use in place of or in combination with soap and soap substitutes. This invention is of considerable interest in that the reactants which enter into it are for the most part readily available at a relatively low cost. The large variety of reactions which may be relied upon permit considerable latitude in the selection of reactants and the conditions of reaction. Likewise, the large number of compounds embraced within this category permits the selection of individual members thereof for a wide variety of purposes. In other words, where high wetting and dispersing properties are of paramount importance the molecular weight of these compounds may be lowered. On the other hand, where detergent properties are of primary interest the molecular weight of the compounds may be increased.

As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that the invention is not limited to the specific embodiments thereof except as defined in the appended claims.

1. A process for producing tetravalent sulphur compounds which comprises reacting a dialkyl sulphide with a halogenated fatty acid, one of the aforesaid reactants containing an alkyl group of from twelve to eighteen carbon atoms.

2. A process for producing tetravalent sulphur compounds which comprises reacting a diaalkyl sulphide with an alpha brom fatty acid, one of the aforesaid reactants containing an alkyl group of from twelve to eighteen carbon atoms.

3. A process for producing tetravalent sulphur compounds which comprises reacting a dodecyl methyl sulphide with chloroacetic acid.

4. Compounds having in their uncondensed form the following general formula:

\[ R \quad X \quad R_1 \quad CH_2 \quad Y \]

wherein \( R \) and \( R_1 \) represent hydrocarbon radicals which may be externally joined, \( R_2 \) represents a member of the group consisting of hydrogen and a hydrocarbon radical, \( X \) represents an anion, \( Y \) represents an oxygen-containing acid group, and one of the hydrocarbon radicals is an aliphatic radical of at least twelve carbon atoms.

5. Compounds having in their uncondensed form the following general formula:

\[ R \quad X \quad S \quad CH_2 \quad COOH \]

wherein \( R \) and \( R_1 \) represent aliphatic radicals, \( R_2 \) represents a member of the group consisting of hydrogen and an aliphatic radical, \( X \) represents an anion, and one of the aliphatic radicals contains from twelve to eighteen carbon atoms.

6. Compounds having in their uncondensed form the following general formula:

\[ R \quad X \quad CH_2 \quad COOH \]

wherein \( R \) and \( R_1 \) represent aliphatic radicals, \( R_2 \) represents an aliphatic radical containing from ten to sixteen carbon atoms, the carboxyl group being substituted in such manner that it is not separated from the sulphur nucleus by more than four carbon atoms, and \( X \) repre-
sents a member of the group consisting of chlorine and bromine.

7. Compounds having in their uncondensed form the following general formula:

\[
\begin{align*}
R & \quad S \\
R_1 & \quad CH_3COOH
\end{align*}
\]

wherein \( R \) and \( R_1 \) represent aliphatic radicals at least one of which contains from twelve to eighteen carbon atoms, \( R_2 \) represents a member of the group consisting of hydrogen and an aliphatic radical containing less than four carbon atoms, and \( X \) represents a member of the group consisting of chlorine and bromine.

8. A compound having in its uncondensed form the following formula:

\[
\begin{align*}
CH_3 & \quad Cl \\
CH_3(CH)_n & \quad CH_3COOH
\end{align*}
\]

9. The product defined in claim 8 after condensation having the following formula:

\[
\begin{align*}
CH_3 & \quad S \\
CH_3(CH)_n & \quad CH_3=O
\end{align*}
\]

10. The compounds taken from the class consisting of the open chain and inner onium salts of the free acids of the following general formula:

\[
\begin{align*}
R & \quad S \\
R_1 & \quad CH_3YO
\end{align*}
\]

wherein \( R \) and \( R_1 \) represent hydrocarbon radicals which may be externally joined, \( R_2 \) represents a member of the group consisting of hydrogen and a hydrocarbon radical, \( X \) represents an anion, \( Y \) represents an oxygen-containing acid group, and one of the hydrocarbon radicals is an aliphatic radical of at least twelve carbon atoms.

11. Tetravalent sulphur compounds selected from the class consisting of the open chain free acids of the following general formula and the inner onium salts of the free acids of the following general formula:

\[
\begin{align*}
R & \quad S \\
R_1 & \quad CH_3COOH
\end{align*}
\]

wherein \( R \) and \( R_1 \) represent aliphatic radicals at least one of which contains from twelve to eighteen carbon atoms, \( R_2 \) represents a member of the group consisting of hydrogen and an aliphatic radical containing less than four carbon atoms, and \( X \) represents a member of the group consisting of chlorine and bromine.


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