Patented May 7, 1940 2,199,397

UNITED STATES PATENT OFFICE

2,199,397

SURFACE ACTIVE MATERIAL

Max Engelmann, Wilmington, Del., assignor to E. I. du Pont de Nemours & Company, Wilmington, Del., a corporation of Delaware

No Drawing. Application September 22, 1937, Serial No. 165,078

16 Claims. (Cl. 260—501)

This invention relates to new and useful surface active materials and more particularly refers to new pentavalent nitrogen compounds which are superior in many respects to soap and soap substitutes, as well as processes for their production. It is an object of this invention to produce new and useful surface active materials which may be substituted for or used in admixture with the various soaps and soap substitutes of the prior art. A further object is to produce new products which overcome many of the disadvantages of soap and soap substitutes. A still further object is to produce pentavalent nitrogen compounds which are of particular value as wetting, dispersing, penetrating, emulsifying and detergent agents. A still further object is to produce a class of compounds which may be used either alone or in admixture with one another and/or in admixture with soap and soap substitutes of the prior art for the numerous purposes wherein soap and soap substitutes of the prior art have previously been used or are capable of use. Additional objects will become apparent from a consideration of the following description and claims.

These objects are attained in accordance with the herein described invention wherein a trisubstituted amine is alkylated, the reactants being so chosen that one of them has substituted thereon at least one oxygen-containing acid group, one of them has substituted thereon a plurality of halogen atoms, and one of them contains an aliphatic hydrocarbon radical of at least six carbon atoms. The aforementioned groupings may all be substituted on one of the reactants or one of them may be substituted on a single reactant and the others substituted on the other reactant.

In a more restricted sense this invention is concerned with the products produced by reacting a tertiary amine with a mixture of halogenated fatty acids containing at least six carbon atoms, wherein a portion of this fatty acid mixture has substituted thereon more than one bromine atom.

In its preferred embodiment this invention is directed to the products produced by reacting a tertiary amine with a mixture of alpha-brominated fatty acids containing from twelve to eighteen carbon atoms, a portion of the aforesaid fatty acid mixture having substituted thereon more than one bromine atom. In this process the aliphatic amine should preferably have substituted thereon alkyl groups or substituted alkyl groups which individually contain less than five carbon atoms. Substantially all of the fatty acid mixture should be brominated in the alpha position, and in addition a portion of this mixture should have one or more bromine atoms substituted on other carbon atoms of the fatty acid radical. Likewise, the fatty acid or the tertiary amine may be further substituted with non-hydrocarbon groupings such as other halogen atoms and/or alkoxy, hydroxy, ether, ester, ketone or the like groups.

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

Example 1

460 parts of palmitic acid (F. P. 62–63° C.) are placed in a round bottom flask equipped with agitation and surrounded with a boiling water bath, 20 parts of phosphorus trichloride are added and the reaction mixture heated for one hour. 454 parts of bromine are then added dropwise over a period of 24 hours at 95° C. After all the bromine is in the heating is continued for 6 more hours. The bromine colored reaction mixture was then stirred up with 250 parts of water for one-half hour and it was then treated with SO_2 gas until the dark bromine color was changed to a light yellow. On standing the mixture separates into two layers and the brominated palmitic acid floats on top of the aqueous hydrobromic acid solution. After cooling down the acid solidifies and can be easily separated as a solid cake. It is washed with water and air dried. The yield is 653 parts. A sample has after removing adhered HBr and moisture 28.22% bromine. Theory for alpha-bromo-palmitic acid is 23.88%. The melting point is not sharp and lower than for the pure alpha-bromo-palmitic acid.

The halogenated fatty acid produced in accordance with the above instructions may be reacted with a tertiary amine or mixture thereof, for example, in accordance with the following instructions:

100 parts of overbrominated alpha-bromo-palmitic acid with a bromine content of 28.22% (theory for alpha-brominated palmitic acid is 23.88%) are slowly added in molten form while stirring to 300 parts of a 25% aqueous trimethylamine solution at 30° C. during a period of 2 hours. After standing for 48 more hours the solution is diluted with 500 parts of water and evaporated on a boiling water bath to remove the excess of trimethylamine and the water. The crystalline residue is mainly a mixture of myristylbetaine and trimethylamine-hydrobromide. Yield 130 parts. The product is soluble in water and organic solvents such as ethyl alcohol, benzene, acetone, etc., and has all the characteristics of a very efficient surface active material.

Example 2

2500 parts of triple pressed stearic acid (acid number 207, iodine number 2.7) are placed in a suitable container, equipped with agitation and surrounded with a boiling water bath. After the

acid is melted 150 parts of PCl_3 is added and the mixture heated for one hour. 2000 parts of bromine are added dropwise over a period of 20 hours. After all the bromine is added, the reaction mixture is further heated for 5 hours. 1500 parts of water is then added and the mixture stirred up for 30 minutes and SO_2 gas is simultaneously introduced to convert the excess of bromine to hydrobromic acid. Soon after the agitation is stopped, two clear layers are formed. The top layer is the brominated triple pressed stearic acid. It solidifies when cooled down to room temperature. Yield 3250 parts of air dry material. Bromine content 24.86% bromine. The theoretical amount of bromine required for a commercial stearic acid with an acid number of 207 and an iodine number of 2.8 should be 23.87% Br. It has a melting range of 38–42° C. and a freezing point of 40.3° C.

The above product may be reacted with various tertiary amines. A representative few of the tertiary amines comprised within this category are set forth in Downing and Johnson Patent No. 2,129,264.

Example 3

3000 parts of coconut oil fatty acids (acid number 257.4 and iodine number 11.5) are converted with 220 parts of phosphorus trichloride partly into the acid chloride and brominated with 3375 parts of bromine as described in Example 2. The reaction mixture is treated with 2500 parts of water, the excess of bromine removed with SO_2 gas. The brominated mixed fatty acids is the bottom layer. It is separated from the aqueous HBr solution in a separating funnel, washed with H_2O and air dried. The acid is liquid at room temperature. Total weight 4380 parts. Bromine analysis 33.4%. Theory for an acid with an acid number of 257.4 and an iodine number of 11.5 is 30.64% Br.

Overbromination of long chain fatty acids or their mixtures can be obtained also in using other well known bromination methods such as the Zelinsky-Volhard method with red phosphorus and bromine or in brominating for instance the acid halides or the acid anhydrides.

Other fatty acids which may be used are double pressed or single pressed stearic acid, myristic acid, lauric acid or mixtures thereof; or, in general, fatty acids which occur in vegetable or animal oils and fats.

Halogenated fatty acids produced as above may be converted to pentavalent nitrogen compounds by reacting with, for example, a tertiary amine or mixture thereof. An illustrative reaction of this type is as follows:

100 parts of overbrominated coconut oil fatty acids analyzing 33.4% bromine (the theory for coconut oil fatty acids with an acid number of 257.4 and with an iodine number of 11.5 is 30.64%) are heated for 10 hours under a reflux condenser with a mixture of 76 parts of dimethylethanolamine and 100 parts of methyl alcohol. The alcohol is then evaporated. The residue is a liquid of high viscosity. It is soluble in water and in organic solvents. Addition of diluted acids to an aqueous solution causes only slight turbidity. It is mainly a mixture of the dimethyl ethanolbetaines of the coconut oil fatty acids.

Example 4

1100 parts of brominated triple pressed stearic acid (25.1% Br) was placed in a round bottom flask surrounded by a boiling salt water bath and heated to 102–103° C. A slow stream of chlorine gas was introduced until a weight increase of 60 parts was obtained. The chlorinated acid was washed with water and air dried. The product has 4.44% Cl. It has a lower melting point than the unchlorinated material. The betaine made from this acid and $(CH_3)_3N$ has a higher solubility than the corresponding product prepared from the unchlorinated acid.

Unsaturated fatty acids such as oleic acid or mixtures consisting of saturated and unsaturated fatty acids such as coconut oil fatty acids subjected to the bromination process add first bromine on the double linkage. Thereafter the alpha position is brominated. The bromine that is added on the double linkage can be substituted by chlorine. This is done by treating the unsaturated acid first with chlorine.

As in the case of the preceding examples, the halogenated fatty acid produced in accordance with the instructions of the present example is converted to a valuable surface active material by reacting it with a tertiary amine, such as trimethylamine, in accordance with the following instructions:

500 parts of chlorinated bromostearic acid made from triple pressed stearic acid, as described supra, are slowly added in molten form while stirring to 1000 parts of a 30% aqueous trimethylamine solution at a temperature of 25–30° C. After standing for 24 hours 60 parts of sodium hydroxide dissolved in 300 parts of water are added and the solution kept for 24 more hours at 30° C. The solution is then diluted with 1000 parts of water and evaporated on a boiling water bath to a total weight of 1800 parts which is equivalent to a solution of 25% active ingredient mainly cetyl- and myristyl-betaine. It contains also sodium-bromide. This betaine solution can be cooled down to 3–4° C. without the formation of a crystalline residue whereas the corresponding material made from a non-chlorinated product starts to crystallize at temperatures lower than 18° C.

A product of similar properties is obtained, when triple pressed stearic acid is at first chlorinated until a chlorine content of 4.5% is reached and then brominated in the usual way.

Example 5

In 564 parts of oleic acid placed in a round bottom flask is passed in at 0 to +3° C. a slow stream of chlorine gas until a weight increase of 142 parts is reached. The resulting dichlorostearic acid is then brominated as described in Example 2 with 454 parts of bromine. The bromination mixture is stirred up with 1000 parts of water and the excess of bromine is removed with SO_2 gas. The acid is then separated in a separating funnel from the aqueous HBr solution. The chloro-bromo-stearic acid is a liquid at room temperature. Chlorine=20.04%. Bromine=19.31%. It has all the characteristics of a fatty acid. It is soluble in alkali. The calcium salt is insoluble in water. The acid is very soluble in organic solvents. It reacts with tertiary amines forming the corresponding betaines. It also is possible to saturate the double linkage only partly with chlorine and the remaining part with bromine.

It is to be understood that the above examples are illustrative merely of a few of the many practical embodiments of this invention. They may be varied widely, both with respect to the reactant, the proportions thereof, and the oper-

ating conditions, without departing from the scope hereof.

For example, where a higher fatty acid is used, this acid should contain at least six carbon atoms, and preferably from twelve to eighteen carbon atoms. Among the acids falling within this category are caproic, caprylic, capric, lauric, myristic, palmitic, stearic, arachidic, and the like. These acids may be of saturated or unsaturated character and they may contain branched chains and/or may be further substituted with non-hydrocarbon radicals. Among the groups which are contemplated for substitution thereon are halogen, alkoxy, acyl, ether, ester, ketone, etc. As in the case of the fatty acid radical the aforesaid or related substituents may also be further substituted when they are of a nature which makes such further substitution possible. The carboxylic acid group may be present as such or may be esterified, amidated, or in the form of some other derivative such as the nitrile grouping, the aforesaid derivative ordinarily being capable of conversion to the carboxylic group upon treatment in accordance with well known procedures. Likewise, this carboxylic acid group, or derivative thereof, may be replaced by some other oxygen-containing acid group such as a sulfuric acid, a sulfonic acid, a phosphoric acid, a boric acid, or related grouping. These oxygen-containing acid groupings may be esterified, amidated, or otherwise treated, in the same manner as the carboxylic acid group per se.

In place of a single fatty acid group, as above, it is contemplated that a mixture of such acids may be used. These acids may be obtained from vegetable, animal or synthetic sources. For example, they may be obtained from coconut oil, sperm oil, palm kernel oil, waxes, fish oils and other natural sources. The acid so obtained may be used as such or may be treated in such manner as to increase the proportion therein of certain constituents. For instance, a mixture of acids containing from say eight to eighteen carbon atoms may be rectified and individual fractions thereof segregated. Such fractions which predominate in certain acids may then be treated in accordance with the herein described invention.

The above acids and those related thereto are halogenated in accordance with the instructions hereof. It is to be understood that no specific type of halogenation treatment is required, and in general it may be stated that the usual halogenation reactions may be relied upon for this purpose. In this connection care should be taken to conduct the halogenation reaction in such manner that a portion at least of the fatty acids contain a plurality of halogen atoms. Mention may here be made of the fact that where the acid is unsaturated the halogenation which takes place at the unsaturated linkage is not the additional halogenation which is herein contemplated. In other words, halogen atoms should be introduced on two or more carbon atoms of the fatty acid radical which formerly were of a saturated character. This halogenation should preferably take place on the alpha position of the fatty acid, and the overhalogenation should take place on one or more additional saturated carbon atoms. In order to obtain such overhalogenation it is in general sufficient to use an excess of halogenating material and/or to avoid evaporation loss and/or to extend the halogenation period for a longer time. It should also be pointed out that more than one halogenation material may be used for this purpose. For example, the acid or acids in question may be first chlorinated and subsequently brominated or vice versa. Likewise, any unsaturated groupings may be first saturated by halogenation with one halogenating material and then the alpha position of the aliphatic radical as well as one or more other positions halogenated with the same or a different halogenating material.

For optimum results it is to be understood that the preferred type of halogenation treatment comprises bromination of the fatty acid or acids in question, preferably higher fatty acids containing from twelve to eighteen carbon atoms. In other words, the fatty acid is first converted to an alpha-bromo derivative and all or a part of this derivative is further brominated in order to obtain overbromination thereof. In place of bromination however it is to be understood that chlorination or other halogenation treatment, as well as mixtures of such treatments are contemplated.

Instead of overhalogenating, preferably overbrominating, a fatty acid containing six or more carbon atoms this treatment may be applied to fatty acids containing less than the aforesaid number of carbon atoms. Where the fatty acid in question contains less than six carbon atoms it is in general advisable that the aminating agent with which it is reacted should contain an aliphatic substituent of six or more carbon atoms. Likewise, instead of overhalogenating a fatty acid some other hydrocarbon or derivative thereof may be overhalogenated and subsequently treated with suitable reactants whereby a pentavalent nitrogen compound of the character under discussion is produced.

The halogenated fatty acids previously referred to, and/or those suggested thereby, are preferably reacted with a tertiary amine, or mixture thereof. Tertiary amines which are suitable for this purpose are well known in the chemical art and need not be described at length. Suffice it to say that amines such as trimethylamine, trialkylamines generally, cyclohexyl dialkylamines generally, dicyclohexyl-alkylamines, dialkyl alkylolamines, N-alkyl piperidines, N-alkylol piperidines and the like may be used. These amines may, as in the case of the compounds with which they are reacted, contain further substituents. For instance, those substituents which were referred to previously with respect to the fatty acids may be used. For optimum results it is in general advisable to use trialkylamines which contain less than five carbon atoms on the individual constituents thereof. Examples of such amines are trimethylamine, monomethyl diethylamine, monoethyl dimethylamine, dimethyl isopropylamine, etc.

The methods of alkylating the aforesaid amines with the fatty acid derivatives or other alkylating agents referred to herein are similar to the well known alkylation reactions of the chemical art. Since such reactions are well known, and have been illustrated herein by numerous representative but not mutually exclusive examples, no further mention thereof is considered to be necessary.

The products produced in accordance with the present invention have certain characteristics which are quite superior to those of the long chain betaine compounds previously known. This superiority is undoubtedly due to the fact that one of the reactants contains a plurality of halogen atoms.

The uses of the compounds embraced within the scope of this invention are legion and since they are of chief value because of their surface active properties no detailed description thereof is deemed essential. Suffice it to say that these products may be used in admixture with one another and/or in admixture with soap and/or soap substitutes of the prior art for the various purposes wherein soap and/or soap substitutes have previously been used or are capable of use. A representative few of these uses are set forth in Downing and Johnson Patent No. 2,129,264 and in Werntz Patent No. 2,178,353.

By means of the present invention an exceptionally valuable class of new surface active materials has been produced. These materials overcome many of the disadvantages of the soaps and soap substitutes of the prior art. In addition, they possess many of the advantages of such prior art soaps and soap substitutes. These products are quite ramified in their composition and may be produced from a wide range of raw materials.

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.

I claim:

1. A process for producing surface active products which comprises reacting a tertiary amine with a mixture of straight chain oxygen-containing aliphatic acids containing at least six carbon atoms in which the acid radicals are taken from the group consisting of carboxylic, sulfuric, sulfonic, phosphoric and boric, said acids having substituted thereon more than one halogen atom replacing hydrogen atoms per molecule of acid, one of said halogen atoms being located in alpha position with respect to the acid group of the acid.

2. A process for producing surface active products which comprises reacting a straight chain oxygen-containing aliphatic acid containing at least 6 carbon atoms in which the acid radical is taken from the class consisting of carboxylic, sulfuric, sulfonic, phosphoric and boric, with a halogenating agent until more than one hydrogen atom per each molecule of acid has been replaced by a halogen atom, one of said halogen atoms being located in alpha position with respect to the acid group of the acid, and then reacting the resulting halogenated acid with a tertiary amine.

3. A process for producing new surface active products which comprises reacting a tertiary amine with a mixture of halogenated straight chain fatty acids containing at least six carbon atoms, said halogenated fatty acids having substituted thereon more than one halogen atom replacing hydrogen atoms per molecule of acid, one of said halogen atoms being located in alpha position with respect to the carboxyl group of the fatty acid.

4. A process for producing new surface active products which comprises reacting a tertiary amine with a mixture of halogenated straight chain fatty acids containing at least six carbon atoms, said halogenated fatty acids having substituted thereon more than one bromine atom replacing hydrogen atoms per molecule of acid, one of said bromine atoms being located in alpha position with respect to the carboxyl group of the fatty acid.

5. A process for producing new surface active products which comprises reacting a tertiary aliphatic amine with a mixture of brominated straight chain fatty acids containing from twelve to eighteen carbon atoms, said brominated fatty acids having substituted thereon more than one bromine atom replacing hydrogen atoms per molecule of acid, one of said bromine atoms being located in alpha position with respect to the carboxyl group of the fatty acid.

6. The product produced in accordance with the process defined in claim 1.

7. The product produced in accordance with the process defined in claim 3.

8. The product produced in accordance with the process defined in claim 4.

9. The product produced in accordance with the process defined in claim 5.

10. A process for producing surface active products which comprises reacting a straight chain oxygen-containing aliphatic acid containing at least 6 carbon atoms in which the acid radical is taken from the class consisting of carboxylic, sulfuric, sulfonic, phosphoric and boric, with a brominating agent until more than one hydrogen atom per each molecule of acid has been replaced by a bromine atom, one of said bromine atoms being located in alpha position with respect to the acid group of the acid, and then reacting the resulting product with a trialkyl amine in which the alkyl radicals altogether contain less than 5 carbon atoms.

11. A process for producing surface active products which comprises reacting a straight chain fatty acid containing at least 6 carbon atoms with a halogenating agent until more than one hydrogen atom per each molecule of acid has been replaced by a halogen atom, one of said halogen atoms being located in alpha position with respect to the carboxyl group of the fatty acid, and then reacting the resulting halogenated fatty acid with a tertiary amine.

12. A process for producing surface active products which comprises reacting a straight chain fatty acid containing at least 6 carbon atoms with a brominating agent until more than one hydrogen atom per each molecule of acid has been replaced by a bromine atom, one of said bromine atoms being located in alpha position with respect to the carboxyl group of the fatty acid, and then reacting the resulting product with a trialkylamine in which the alkyl groups altogether contain less than 5 carbon atoms.

13. A process for producing new surface active products which comprises reacting trimethylamine with a polybrominated palmitic acid wherein one of the bromine atoms is located in alpha position with respect to the carboxyl group.

14. The product produced in accordance with the process defined in claim 13.

15. A process for producing new surface active products which comprises reacting trimethylamine with a polybrominated stearic acid wherein one of the bromine atoms is located in alpha position with respect to the carboxyl group.

16. The product produced in accordance with the process defined in claim 15.

MAX ENGELMANN.