

UNITED STATES PATENT OFFICE

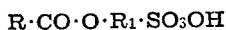
2,289,391

PROCESS OF PREPARING WETTING, SUDS-
ING, AND DETERGENT AGENTSNathaniel Beverley Tucker, Glendale, Ohio, as-
signor to The Procter & Gamble Company,
Cincinnati, Ohio, a corporation of OhioNo Drawing. Application April 10, 1941,
Serial No. 387,985

17 Claims. (Cl. 260-400)

This invention relates to a process for produc-
ing highly efficient sudsing, emulsifying and de-
tergent agents.

More specifically the present case relates to an
improved process for the preparation of water-
soluble salts of compounds of the following type



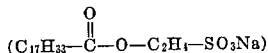
wherein $R \cdot CO$ is an acyl radical having eight to
twenty-two carbon atoms and R_1 is an aliphatic
hydrocarbon residue having two to four carbon
atoms. These salts possess wetting, sudsing and
detergent power in hard water and in accord-
ance with my invention are produced by the
condensation of a salt of a higher fatty acid
with a low molecular weight halogen substituted
alkyl sulfonate in the presence of amides or sub-
stituted amides as more fully hereinafter set
forth.

It is an object of my invention to provide an
improved method for the preparation of the
above compounds so that the resulting reaction
product is freer of products of side reactions,
contains a higher proportion of the desired prod-
uct, and under some conditions as described be-
low may be used directly without purification as
a washing agent of high efficiency in hard water.

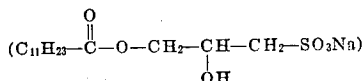
It is a further object of my invention to pro-
vide a means whereby the above compounds can
be manufactured economically and in good yields
from soap and a halo-alkyl metal sulfonate, thus
making unnecessary the use of the more costly
fatty acid halides as starting materials.

Other objects of my invention will be apparent
from the following description.

It is known that compounds coming within the
classification above given, such as the sodium
salt of the oleic acid ester of isethionic acid



and the sodium salt of the coconut oil fatty acid
ester of 1,2-dihydroxy propane sulfonic acid



may be prepared by heating a soap of the fatty
acid with a salt of the appropriate halogen sub-
stituted sulfonate, by heating the free fatty acid
with the hydroxy-alkyl sulfonate, or by reacting
the chloride of the fatty acid with the hydroxy-
alkyl sulfonate. Since both soap and fatty acids
are cheaper reagents than the relatively costly
acid chlorides, it is obviously advantageous to use
these in preference to the acid chloride. How-
ever, ordinarily such reactions as that of soap
with halo-alkyl sulfonates or the reaction of fat-
ty acids with hydroxy-alkyl sulfonates progress
slowly even at temperatures in the neighborhood
of 200° C. Consequently in prior methods for

producing detergent and sudsing agents of the
type here under consideration from soap or free
fatty acid, purification of the resulting product
of the condensation by crystallization from sol-
vents has been necessary for one of two reasons.
Either the product contains unreacted harmful
soap because of too short a time of reaction or
too low a reaction temperature, or the product
contains harmful by-products including decom-
position products and dark colored materials be-
cause of too long a reaction time or too high a
reaction temperature. In either case the impur-
ity is detrimental to the performance of the
product as a cleansing agent and as far as I am
aware there is no happy medium in which to op-
erate and obtain an active product resistant to
hard water and acids without subjecting the re-
action product to expensive and time consuming
purification including crystallization from a suit-
able solvent.

In accordance with the present invention, the
reaction between the soap and the halogen sub-
stituted sulfonate is brought nearer theoretical
completion by the use of a reaction medium con-
sisting essentially of certain amides or substi-
tuted amides, or mixture of same, derived from
monocarboxylic acids, which reaction medium is
volatilizable at a temperature below that at
which harmful decomposition products are
formed, such as for example temperatures not
substantially higher than 175° C. The products
of my invention at most contain only inconse-
quential quantities of unreacted soap. In addi-
tion the use of the amide or substituted amide
reaction medium materially reduces the time and
temperature of reaction to bring about suitable
formation of the desired product and this also
gives an improved result since reduction in re-
action time and temperature reduces decompo-
sition and the formation of by-products which
are detrimental to the performance of the ma-
terial as a washing agent in hard water. Thus
in the practice of my invention a product is ob-
tained which may be used in washing operations
directly without purification with excellent re-
sults provided the presence of the amide or sub-
stituted amide is not objectionable from an odor,
appearance or consistency standpoint and pro-
vided further that it is not harmful to the per-
formance of the detergent in aqueous solution.
As a rule those amides and substituted amides
which are water soluble are not detrimental and
need not be removed from the reaction product
unless other properties make separation essen-
tial or advisable.

Purification of the products of my invention is
necessary therefore only in case the presence of
the amide or substituted amide is undesirable.
If such is the case removal of this reaction medi-
um may be easily and readily accomplished mere-
ly by volatilizing at atmospheric or subatmos-

phoric pressure and separating the same by methods known in the art. Crystallization from a solvent is unnecessary and attendant disadvantages such as loss of yield and costly operation are therefore avoided.

The highly advantageous action of the reaction medium in the preparation of detergents of the type herein referred to is not due solely to any solvent action which the amide may have, because I have found that ethylene glycol, which is an excellent solvent for both reactants, does not function in the same manner as the amide or substituted amide but, in contrast thereto, results in a lower yield of a reaction product which is contaminated so highly with unreacted soap and other detrimental impurities that purification by crystallization from a solvent is essential in order to obtain an efficient wetting, sudsing and detergent agent. Apparently the amide or substituted amide possesses a characteristic or combination of characteristics, such as a catalytic effect in combination with a solvent effect, making this type of compound especially suitable for the purpose at hand because as far as I am aware there is no other compound which functions in the same manner as the amides and substituted amides covered herein to give the highly advantageous result of the present invention.

In the preferred practice of my invention, the fatty acid soap is heated with the halogen substituted sulfonate in the presence of a sufficient amount of amide or substituted amide as the reaction medium to allow the formation of a fluid reaction mix at elevated temperature. Under such conditions a substantial part of the reactants is in solution. After the reaction has reached substantial completion, as may be determined by the discontinuance of the precipitation of neutral salt or the complete solution of the product in hard water, the reaction medium may be removed by distillation from the mixture at atmospheric pressure or subatmospheric pressure but at a temperature below that at which the reactants or products decompose. The residue consists predominantly of the desired detergent product and is sufficiently active in sudsing and detergent power that it may be used directly without further purification in washing or laundering operations. Of course purification from a solvent may be effected if desired.

My invention will be more clearly understood from the following examples in which specific conditions of operation are set forth. However, the invention is not limited to those specific conditions as more particularly pointed out herein-after.

Example 1.—115 parts of sodium soap derived from coconut oil are mixed with 100 parts of sodium monochlorhydrin sulfonate and 150 parts of acetamide in a reaction vessel which is not attacked by the reactants, such as a glass-lined vessel for example. The mixture is heated with stirring at 145° C. for two hours, after which most of the acetamide is removed by distillation under vacuum at 140° C. A product so prepared possessed excellent sudsing and detergent characteristics in hard water containing the equivalent of 21 grains CaCO_3 per U. S. gallon.

Example 2.—5 parts sodium monochlorhydrin sulfonate and 6 parts sodium coconut oil soap were heated at 150° C. for two hours in the presence of 5 parts benzamide. The unpurified product dissolved completely in warm water and was unaffected by hardness and acid.

Example 3.—6 parts of the potassium salt of

beta methyl monochlorhydrin sulfonate and 7 parts potassium-oleate were heated at 145° C. for 3 hours in the presence of 8 parts acetanilide. The unpurified product dissolved completely in hard water to yield a solution which possessed excellent sudsing, detergent and wetting power.

Example 4.—42 parts magnesium laurate, 39 parts of sodium monochlorhydrin sulfonate and 80 parts acetamide were mixed and heated with agitation at about 145° C. for two hours. The reaction product was purified by a single crystallization from alcohol. The purified material was obtained in good yield and an aqueous solution thereof was clear and foamed profusely in the presence of acids and of hardness imparting constituents.

Example 5.—23 parts of coconut oil sodium soap, 21 parts of the potassium salt of beta methyl monochlorhydrin sulfonate and 20 parts of diethyl lauramide are mixed and heated together in a reaction vessel for four hours at about 150° C. The product thus obtained has excellent wetting, sudsing and detergent power in hard water.

In the above examples I have shown how my invention may be practiced with commonly occurring materials. However, while these examples express probably the most practical way of carrying out my process, other materials may be employed. For example, while I have shown the use of coconut oil soap, oleic acid soap and lauric acid soap in the examples, soaps of other fatty acids, individually and in admixture, having eight to twenty-two carbon atoms may be employed. Thus if desired, the stearates, palmitates, or myristates, or soaps from any of the naturally occurring vegetable and animal fats and oils may be used. Also, it should be noted that in addition to alkali metal soaps, alkaline earth metal soaps such as calcium and magnesium soaps, or even some heavy metal soaps, may be used provided the metal is such that it readily combines with the halogen of the halogen substituted sulfonate to produce a neutral salt.

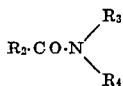
In the examples, I have shown throughout the use of chlorine substituted sulfonates merely because these derivatives are readily available or easily prepared. However, a sulfonate substituted with any other halogen, such as bromine, may be employed with equal ease without departing from the spirit of the invention.

The kind of metal ion in the halogen substituted sulfonate salt is relatively unimportant as long as the ultimate detergent agent, that is the condensation product, is water-soluble. Thus, for example, the alkali metals sodium and potassium and the alkaline earth metals calcium and magnesium may be employed since they form salts which are soluble in hard water. For obvious reasons I prefer to employ the same metal as that of the soap used in the reaction.

The intermediate sulfonates, that is the halogen substituted sulfonates, coming within the scope of the present invention are those aliphatic compounds having, as above stated, two to four carbon atoms. Thus the following compounds in addition to those given in the examples may be employed: potassium monochlorhydrin sulfonate, sodium beta methyl monochlorhydrin sulfonate, sodium chlorethyl sulfonate, chloro olefin sulfonic acids such as 2-chloromethyl propene sodium sulfonate and others which will be readily apparent to those versed in the art.

It has been stated above that the amides or substituted amides which may be employed in my

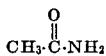
invention are those which do not take part in the reaction here involved and which may be volatilized at a temperature below that at which harmful decomposition products are formed in the reaction mix, such as for example a temperature not substantially higher than 175° C. In addition to these limitations the amides and substituted amides of monocarboxylic acids which I use are those having the formula



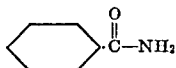
in which R_2 is alkyl, aryl or hydroxy alkyl and R_3 and R_4 are radicals selected from the group consisting of hydrogen, alkyl, aryl, hydroxy alkyl and alkylene joined through an oxygen atom ($-R_3 \cdot O \cdot R_4-$).

Specific examples of amides and substituted amides which may be employed in accordance with my invention are the following:

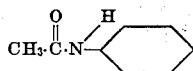
Acetamide



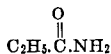
Benzamide



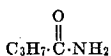
Acetanilide



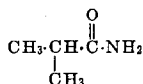
Propionamide



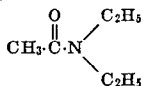
Butyramide



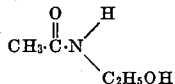
Isobutyramide



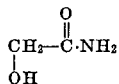
Diethyl acetamide



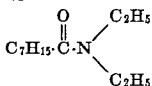
Ethanolacetamide



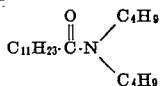
Hydroxy acetamide



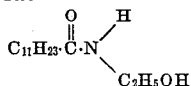
Diethyl caprylamide



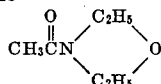
Dibutyl lauramide



Ethanol lauramide



Acetyl morpholine



The preferred temperature range within which to carry out the condensation reaction is 140 to 150° C., but of course the condensation may be carried out at temperatures outside of these limits. For example, some reaction is evident at temperatures as low as 130° C. and such low temperatures may be fully sufficient in some instances. Of course temperatures higher than 150° C. may also be employed, but temperatures substantially above 175° C. are usually unnecessary and may even be harmful since such high temperatures favor decomposition and the production of undesirable byproducts.

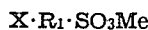
The amount of amide or substituted amide which should be employed is not very critical. In my work I have found that the minimum amount of reaction medium is about one half the weight of the mixture of soap and halogen substituted alkyl sulfonate. Ordinarily I employ an amount of reaction medium which is equal to the combined weights of soap and sulfonate, but of course the amount employed may be much larger, even four to six times the weight if such usage is desired. An excess is not harmful.

Having thus described my invention, what I claim and desire to secure by Letters Patent is:

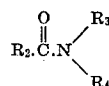
1. In the process of producing a wetting, sudsing and detergent agent of the general formula



wherein $R \cdot CO$ is the acyl radical of a fatty acid having eight to twenty-two carbon atoms, R_1 is a radical selected from the group consisting of alkylene and hydroxy alkylene radicals having two to four carbon atoms and Me is a metal forming a water-soluble salt, the step which consists in condensing a metal salt of a fatty acid having eight to twenty-two carbon atoms with a halogen substituted sulfonate of the general formula



wherein X is halogen, and R_1 and Me are as above indicated, in the presence of a reaction medium of the group consisting of amides and substituted amides of the formula



wherein R_2 is a radical of the group consisting of alkyl, aryl, and hydroxy alkyl and R_3 and R_4 are selected from the group consisting of hydrogen, alkyl, aryl, hydroxy alkyl and alkylene joined through an oxygen atom, the said reaction medium being one which does not enter into the reaction and being volatilizable at a temperature below that at which harmful decomposition products are formed in the reaction mix.

2. The process of claim 1 in which the reaction medium is an unsubstituted amide.

3. The process of claim 1 in which the reaction medium is acetamide.

4. The process of claim 1 in which the fatty acid salt is sodium coconut oil soap and the halogen substituted sulfonate is monochlorhydrin sodium sulfonate.

5. The process of claim 1 in which the fatty acid salt is sodium coconut oil soap; the halogen substituted sulfonate is monochlorhydrin sodium sulfonate, and the reaction medium is acetamide.

6. The process of claim 1 in which the reaction medium is an N-mono substituted amide.

7. The process of claim 1 in which the reaction medium is an N-mono substitute acetamide.

8. The process of claim 1 in which the reaction medium is N-ethyl acetamide.

9. The process of claim 1 in which the fatty acid salt is sodium oleate and the halogen substituted sulfonate is monochlorhydrin sodium sulfonate.

10. The process of claim 1 in which the fatty acid salt is sodium oleate, the halogen substituted sulfonate is monochlorhydrin sodium sulfonate and the reaction medium is N-ethyl acetamide.

11. The process of claim 1 in which the reaction medium is an N,N-disubstituted amide.

12. The process of claim 1 in which the reaction medium is a disubstituted acetamide.

13. The process of claim 1 in which the reaction medium is diethyl acetamide.

14. The process of claim 1 in which the fatty acid salt is sodium coconut oil soap and the halogen substituted sulfonate is beta methyl monochlorhydrin sodium sulfonate.

15. The process of claim 1 in which the fatty acid salt is sodium coconut oil soap, the halogen substituted sulfonate is beta methyl monochlorhydrin sodium sulfonate and the reaction medium is diethyl acetamide.

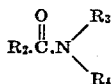
16. In the process of producing a wetting, sudsing and detergent agent of the general formula



where R·CO is the acyl radical of a fatty acid having eight to twenty-two carbon atoms, R₁ is a radical selected from the group consisting of alkylene and hydroxy alkylene radicals having two to four carbon atoms and Me is a metal forming a water soluble salt, the step which consists in condensing a metal salt of a fatty acid having eight to twenty-two carbon atoms with a halogen substituted sulfonate of the general formula



where X is halogen and R₁ and Me are as above indicated, in the presence of about fifty per cent to about one hundred per cent, based on the mixture of fatty acid salt and halogen substituted sulfonate, of a reaction medium of the group consisting of amides and substituted amides of the formula

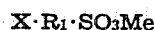


where R₂ is a radical of the group consisting of alkyl, aryl and hydroxy alkyl, and R₃ and R₄ are selected from the group consisting of hydrogen, alkyl, aryl, hydroxy alkyl and alkylene joined through an oxygen atom, the said reaction medium being one which does not enter into the reaction and being volatilizable at a temperature below that at which harmful decomposition products are formed in the reaction mix.

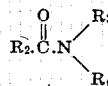
17. In the process of producing a wetting, sudsing and detergent agent of the general formula



where R·CO is the acyl radical of a fatty acid having eight to twenty-two carbon atoms, R₁ is a radical selected from the group consisting of alkylene and hydroxy alkylene radicals having two to four carbon atoms and Me is a metal forming a water soluble salt, the steps which consist in condensing a metal salt of a fatty acid having eight to twenty-two carbon atoms with a halogen substituted sulfonate of the general formula



where X is halogen and R₁ and Me are as above indicated, in the presence of about fifty per cent to about one hundred per cent, based on the mixture of fatty acid salt and halogen substituted sulfonate, of a reaction medium of the group consisting of amides and substituted amides of the formula



where R₂ is a radical of the group consisting of alkyl, aryl and hydroxy alkyl, and R₃ and R₄ are selected from the group consisting of hydrogen, alkyl, aryl, hydroxy alkyl and alkylene joined through an oxygen atom, and distilling off the reaction medium, the said reaction medium being one which does not enter into the reaction and being volatilizable at a temperature below that at which harmful decomposition products are formed in the reaction mix.

NATHANIEL BEVERLEY TUCKER.