

UNITED STATES PATENT OFFICE

2,342,563

PREPARATION OF WETTING, SUDSING, AND
DETERGENT AGENTSNathaniel Beverley Tucker, Glendale, Ohio, as-
signor to The Procter & Gamble Company, Cin-
cinnati, Ohio, a corporation of OhioNo. Drawing. Application December 29, 1941,
Serial No. 424,796

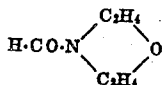
8 Claims. (Cl. 260-400)

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



where $R \cdot CO$ is an acyl radical having eight to
twenty-two carbon atoms and R_1 is an alkylene
or hydroxyalkylene radical having two to four
carbon atoms. These salts possess wetting,
sudsing and detergent power in hard water and,
in accordance with my invention, are produced
by the condensation of a salt of a higher fatty
acid with a low molecular weight halogen sub-
stituted alkyl sulfonate in the presence of formyl
morpholine, an amide of formic acid and mor-
pholine having the formula



The present application is related to but dis-
tinguishes from my copending application Serial
Number 387,985, now U. S. Patent 2,289,391,
which concerns a method for the preparation of
wetting, sudsing and detergent agents accord-
ing to which the above condensation reaction is
conducted in the presence of amides volatiliz-
able at a temperature below that at which harm-
ful decomposition products are formed and
which have the formula



where R_2 is alkyl, aryl or hydroxyalkyl, and R_3
and R_4 are radicals selected from the group con-
sisting of hydrogen, alkyl, aryl, hydroxyalkyl and
alkylene joined through an oxygen atom ($R_3 \cdot O \cdot R_4$).

As in the case of my application Serial No.
387,985, it is an object of the present invention
to provide an improved method for the prepara-
tion of the above wetting, sudsing and detergent
compounds so that the resulting reaction prod-
uct is freer of products of side reactions, con-
tains a higher proportion of the desired prod-
uct and may be used directly without purifica-
tion as a washing agent of high efficiency in hard
water if desired.

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 halo-alkyl metal sulfonates,

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
($\text{C}_{17}\text{H}_{33} \cdot \text{CO} \cdot \text{OC}_2\text{H}_4 \cdot \text{SO}_3\text{Na}$) and the sodium salt
of coconut oil fatty acid (predominantly lauric
acid) ester of 1,2-dihydroxy propane 3-sulfonic
acid ($\text{C}_{11}\text{H}_{23} \cdot \text{CO} \cdot \text{OCH}_2 \cdot \text{CHOH} \cdot \text{CH}_2 \cdot \text{SO}_3\text{Na}$) may
be prepared by heating a soap of the fatty acid
with a salt of the appropriate halogen substituted
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 chloride. However,
ordinarily such reactions as that of soap with
halo-alkyl sulfonate or the reaction of fatty
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
by 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 im-
purity 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
operate and obtain an active product resistant
to hard water and acids without subjecting the
reaction product to expensive and time consum-
ing purification, including crystallization from a
suitable 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 formyl morpholine, there-
by producing a product containing only incon-
sequential quantities of unreacted soap. In ad-
dition, the use of the formyl morpholine reaction
medium materially reduces the time and tem-
perature of reaction necessary to bring about

suitable formation of the desired product and this also gives an improved result since reduction in reaction time and temperature reduces decomposition and the formation of by-products which are detrimental to the performance of the material as a washing agent in hard water.

For some purposes the formyl morpholine need not be removed from the product before use. If, however, purification is desired, it may be accomplished easily and readily merely by volatilizing the formyl morpholine under pressure conditions such that temperatures substantially above 175° C. are not required, and separating the formyl morpholine 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 formyl morpholine in the preparation of detergents of the type herein referred to is not due solely to any solvent action which the formyl morpholine 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 used herein, 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 formyl morpholine possesses a characteristic or combination of characteristics such as a catalytic effect in combination with a solvent effect, making this compound especially suitable for the purpose at hand.

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 formyl morpholine to effect 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 for example by titration of a sample of the mix for ionic halogen, the reaction medium may be removed by distillation from the mixture under pressure conditions that permit the use of 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 example in which specific conditions of operation are set forth. However, the invention is not limited to these specific conditions, as more particularly pointed out herein-after.

Example.—45 parts of dry sodium soap derived from coconut oil are mixed with 39.3 parts monochlorhydrin sulfonate and 100 parts formyl morpholine 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 140 to 150° C. for two hours, after which most of the formyl morpholine is removed by distillation at 145° C. under vacuum. The product dissolves to a perfectly clear solution in hot or cold hard water and possesses excellent sudsing and detergent characteristics.

In the above example, I have shown how my invention may be practiced with commonly occurring materials. However, while this example may express probably the most practical way of carrying out my process, other materials may be employed. For example, other soaps than coconut oil soap such as oleic acid soap and 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 natural 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, and provided that the metal does not form an insoluble salt with the condensation product.

In the example I have shown the use of a chlorine substituted sulfonate because this derivative is 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 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.

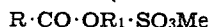
The intermediate sulfonates, that is, the halogen substituted sulfonates coming within the scope of the present invention, are those aliphatic compounds having two to four carbon atoms as above stated. Thus the following compounds, in addition to the monochlorhydrin sodium sulfonate given in the example,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

The preferred temperature range for conducting the condensation reaction is 140 to 150° C., but of course the condensation may be carried out at temperatures outside of these limitations. 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 by-products.

The amount of formyl morpholine which should be employed is not very critical. In my work I have found that amounts as small as one half the weight of the mixture of soap and halogen substituted sulfonate may be employed, but ordinarily I prefer to use an amount of reaction medium which is at least equal to the combined weights of the soap and sulfonate. Of course the amount employed may be much larger, even four to six times the weight of the reactants, 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



where $R \cdot CO$ 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 formyl morpholine.

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



where $R \cdot CO$ 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, at a temperature not substantially above $175^\circ C.$ and in the presence of formyl morpholine.

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



5 where $R \cdot CO$ 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 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



10 where X is halogen and R_1 and Me are as above indicated, in the presence of formyl morpholine, and distilling off the formyl morpholine at a temperature not substantially higher than $175^\circ C.$

4. The process of claim 1 in which the halogen substituted sulfonate is a monochlorhydrin sulfonate.

25 5. 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.

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

7. The process of claim 1 in which the halogen substituted sulfonate is a beta methyl monochlorhydrin sulfonate.

8. 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.

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