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3,660,470
LIME SOAP DISPERSANTS AND COMPOSITIONS
CONTAINING THEM
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No Drawing. Filed Sept. 22, 1970, Ser. No. 74,496
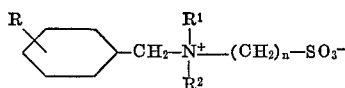Claims priority, application Great Britain, Oct. 1, 1969,
48,278/69
Int. Cl. C07c 143/14
U.S. Cl. 260—501.12                    6 Claims

## ABSTRACT OF THE DISCLOSURE

Alkylbenzyl di-lower alkylammonio alkane-1 sulfonates
having the formula

$$R\text{-}\langle C_6H_4\rangle\text{-}CH_2\text{-}\overset{R^1}{\underset{R^2}{N^\pm}}\text{-}(CH_2)_n\text{-}SO_3^-$$

wherein R is a straight or branched chain alkyl group
having 8 to 24, preferably 10 to 18, carbon atoms; $R^1$
is an alkyl group having 1 to 6 carbon atoms; $R^2$ is an
alkyl group having 1 to 6 carbon atoms; and $n$ is an integer
of from 1 to 4, preferably 2 or 3. These compounds have
excellent scum-dispersant properties and are effective in
solid, granular, bar, or liquid soap compositions to reduce
lime-scum formation. Compositions comprising higher
fatty acid soaps and the alkylbenzyl di-lower alkylam-
monio alkane-1 sulfonates are described. Desirable results
are obtained when the ratio of soap to zwitterionic, by
weight, is from 3:1 to 100:1.

This invention relates to alkylbenzyl di-lower alkyl
ammonio alkane sulfonates, and to soap-based detergent
compositions containing them.

Detergent compositions based on conventional water-
soluble soaps have many desirable properties, which
render them at least highly competitive with detergent
compositions based on other organic detergents. However,
they have the well known failing that in hard water in-
soluble soaps are formed, and these tend to flocculate,
especially in the conditions of the rinse, to form what is
often known as "lime scum." This tends to be deposited
either on fabrics which have been washed, where in effect
it constitutes "dirt," or on the vessels in which the wash-
ing and rinsing is carried out, for example as deposits on
washing machines, or as "bath tub ring." In the develop-
ment of washing products, this failing has generally been
countered either by making compositions based on syn-
thetic detergents and containing no soap or only minor
amounts of soap, or by adding agents, often known as
"lime soap dispersants," to soap compositions. These
agents either prevent the formation of insoluble lime
soaps, or prevent such soaps from flocculating, so that they
are flushed away with the washing or rinsing liquid and do
not adhere to fabrics or to the surfaces of the washing
vessels.

It has now been found that certain novel zwitterionic
compounds, derived from alkylbenzenes such as the so-
called detergent alkylates, have excellent scum dispersant
properties when combined, even in small proportions,
with soap. They also improve the sudsing of soap prod-
ucts, by lowering the concentration required just to form
suds in hard water, such a concentration being the con-
centration when soap first becomes available for clean-
ing articles.

The new compounds are alkylbenzyl di-lower alkylam-
monio alkane-1 sulfonates and have the formula:
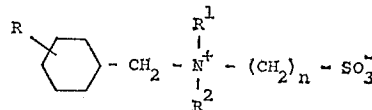
$$R\text{-}\langle C_6H_4\rangle\text{-}CH_2\text{-}\overset{R^1}{\underset{R^2}{N^+}}\text{-}(CH_2)_n\text{-}SO_3^-$$

wherein R is a straight or branched chain alkyl group
having 8 to 24, preferably 10 to 18 carbon atoms; $R^1$ is an
alkyl group having 1 to 6 carbon atoms; $R^2$ is an alkyl
group having 1 to 6 carbon atoms; and $n$ is an integer of
from 1 to 4, preferably 2 or 3.

The invention also embraces detergent compositions
comprising water-soluble soap and a compound as defined
above.

Preferably, the zwitterionic compounds are those where
$R^1$ and $R^2$ are each methyl or ethyl radicals. It is pre-
ferred to use those compounds wherein R is straight-
chained. The zwitterionic compounds can be based on
alkylbenzene mixtures, such as most commercial detergent
alkylates, which contain a mixture of alkyl benzenes of
mean chain length within the above ranges.

The zwitterionic compounds of the invention can be
conveniently made. One method is to form the alkyl-
benzyl chloride, e.g., by reaction in acetic acid of an
alkylbenzene with formaldehyde and hydrogen chloride
in the presence of zinc chloride, and to treat this com-
pound with the appropriate dialkylamine to form the
alkylbenzyl dialkylamine.

The resulting tertiary amine can be reacted for instance
with a halo-alkane sulfonate, typically Cl $(CH_2)_n$ $SO_3Na$
where $n$ has the meaning defined above, or, for the com-
pounds where $n$ is 3 or 4, with propane- or butane sultone.
Other preparative routes will occur to those skilled in the
art and may be selected on grounds of convenience or eco-
nomic advantage. For instance, it may be preferred to
attach the alkane sulfonate group to the amino nitrogen
and thereafter attach the alkylbenzyl radical.

The water-soluble soaps which can be used in the de-
tergent compositions of the invention are the higher fatty
acid soaps normally used for washing, for instance the
alkali metal, especially sodium or potassium, salts of fatty
acids having from 8 to 24, especially 10 to 18 carbon
atoms. The soaps can be made by direct saponification of
natural oils and fats, such as tallow, palm oil, lard, greases,
coconut or palm kernel oils and many others, or they can
be made by neutralization of fatty acids derived from
such oils and fats or from those made synthetically or de-
rived from petroleum and like sources. Soaps from natural
oils and fats, or from fatty acids derived from them, will
be predominantly straight-chained. The synthetic fatty
acids or those from petroleum sources can be straight- or
branch-chained. Preferred soaps are those made from mix-
tures of tallow, grease or palm oils to provide the longer
chain, e.g., $C_{16-18}$, fatty acid residues and coconut or palm
kernel oil to provide shorter chain, e.g., $C_{10-14}$, fatty acid
residues.

The zwitterionic compounds of the invention can be
present in any proportion relative to soap effective to pro-
vide lime soap-dispersing properties, but are normally
present in relatively small proportions. Desirable results
are obtained when the ratio of soap to zwitterionic, by
weight, is from 3:1 to 100:1, especially from 10:1 to 20:1.

The lime soap-dispersing properties of the zwitterionic
compounds of the invention can be employed to advantage
by adding the compounds to a wash liquor, before or
when the soap is added or before the washing process is
begun. Ordinarily, the zwitterionic compounds are incor-
porated into a soap composition, which can be a solid,
granular, in bar form or a liquid. Mixtures of the zwitter-
ionic compounds of the invention can be suitably em-
ployed. An alkaline builder salt can be included. The new

compounds are particularly valuable as a component of granular soap products, especially built soap powders intended primarily for washing clothes. Such products can contain, in addition to the soap and zwitterionic compound, water-soluble alkaline builder salts. Suitable builder salts include alkali metal silicates, carbonates, phosphates and polyphosphates, borax, organic sequestering agents such as sodium nitrilotriacetate, ethane-1-hydroxy-1, 1-diphosphonates, and the like. Bleaching agents such as sodium perborate or percarbonate can be present. Minor components such as dyes, perfumes, soil-suspending agents such as carboxymethyl cellulose, enzymes, tarnish inhibitors, dust-suppressing agents, stabilizers for the bleaching agents and/or the enzymes and the like can also be employed.

The invention is illustrated by the following examples.

### EXAMPLE I

Preparation of 3-(dodecylbenzyl dimethylammonio) propane-1-sulfonate

111 gms. of p-chloromethyl dodecylbenzene

$$(C_{12}H_{25}C_6H_4CH_2Cl)$$
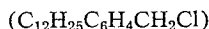
and 170 gms. of dimethylamine were charged into an autoclave provided with heating and stirring means. The mixture was heated in the closed autoclave, with stirring so that the temperature reached 155° C. over a period of 2 hours. After cooling, the reaction mix separated into two layers. The upper layer was separated, washed with water and dried, and yielded 69 gms. of dodecylbenzyl dimethyl amine of purity about 98%.

30.3 gms. of this tertiary amine, 12.2 gms. propane sultone and 168 gms. of acetone were heated, with stirring, under reflux for 3½ hours. Solid which separated was filtered and washed with acetone and dried at 60° C. The filtrate was treated with a further 1.2 gms. of propane sultone and the solid which formed was filtered etc. as above. This was repeated. The total yield was 35.7 gms. of the desired compound, 3 - (dodecylbenzyl dimethylammonio) propane-1-sulfonate.

### EXAMPLE II

Scum dispersant effect

A 1½% solution of soap in soft water was prepared, and arrangements provided so that air could be bubbled through it to form foam, which was carried over by the air current into a vessel containing hard (515 parts per million as $CaCO_3$) water, wherein the foam was quenched. By this treatment, lime soap was formed in flocculated form in the hard water. The water was poured through a 100 mesh BSS sieve and the collected flocculated lime soap dried and weighed. Addition of scum dispersants to the soap solution reduced the weight of flocculated lime soap formed.

In the test, soap alone gave 0.27 gm. flocculated lime soap. Soap with 10% by weight of the soap of 3-(dodecylbenzyl dimethylammonio) propane-1-sulfonate, prepared according to Example I, gave 0.01 gm. of flocculated lime soap indicating almost complete scum dispersion.

### EXAMPLE III

1.9% solutions of soap in de-ionized water were prepared, containing in addition quantities of 3-(dodecyl benzyl dimethylammonio) propane-1-sulfonate ($C_{12}$ sultaine) and of 3 (nonylbenzyl dimethylammonio) propane-1-sulfonate ($C_9$ sultaine). Each solution was placed in a water bath to maintain its temperautre at 55° C. and nitrogen was bubbled through at a fixed rate. The foam formed was carried over for a set time into a vessel containing hard (515 parts per million as $CaCO_3$) water, wherein the foam was quenched. The water was

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poured through a weighed 200 mesh BSS sieve, and the flocculated lime soaps retained determined, after drying, by re-weighing the sieve. Results obtained were:

| Weight ratio, soap:sultaine | Weight of flocculated lime soap retained, g. | |
| --- | --- | --- |
| | $C_{12}$ sultaine | $C_9$ sultaine |
| 50:1 | 0.0037 | 0.0054 |
| 20:1 | 0.0019 | 0.0054 |
| 10:1 | 0.0005 | 0.0027 |
| 6:1 | 0.0007 | 0.0016 |
| 3:1 | 0.0018 | 0.0012 |
| No sultaine | 0.024 | 0.025 |

### EXAMPLE IV

A Composition B consisted of 95.2 parts of Composipared consisting of:

| | Percent |
| --- | --- |
| Real soap (90% tallow; 10% coconut) | 50 |
| Sodium silicate | 9 |
| Sodium tripolyphosphate | 10 |
| Fatty acyl monoethanolamide | 4 |
| Carboxymethylcellulose | 0.3 |
| Sodium perborate | 16.5 |
| Miscellaneous | 1.2 |
| Moisture | 9.0 |
| | 100.0 |

A composition B consisted of 95.2 parts of Composition A and 4.8 parts of 3-(dodecylbenzyl dimethylammonio) propane-1-sulfonate, derived from commerical linear dodecylbenzene. Solutions of these compositions of concentration 0.25% by weight, were made up in hard water (256 parts per million hardness as $CaCO_3$) in a Hoover Mark III washing machine and agitated for 30 seconds at 54° C. The agitator was stopped and after 30 seconds a black perspex plate was dipped into the solution for 5 seconds and withdrawn through any scum present on the surface of the liquid. The plate was examined visually for adherent scum. The solutions of Composition A left visible scum on the black plates, while those of Composition B left no scum.

Similar results are obtained when the sodium tripolyphosphate of Composition B is replaced in whole or in part by sodium carbonate; borax; trisodium nitriloacetate or sodium ethane-1-hydroxy-1,1-diphosphonate in that scum formation is minimized.

### EXAMPLE V

When increments of the compositions of Example IV were added to 39 litres of water in the same washing machine it was found that 105 gms. of Composition A were required just to form stable suds, compared with 42 gms. of Composition B.

What is claimed is:

1. A zwitterionic surface active compound having the formula:
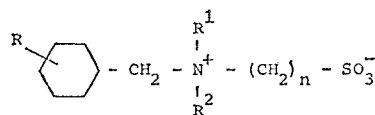


wherein R is an alkyl group of from 8 to 24 carbon atoms; $R^1$ and $R^2$ are each alkyl of from 1 to 6 carbon atoms; and $n$ is an integer of from 1 to 4.

2. The compound of claim 1 wherein $n$ is 2 or 3.

3. The compound of claim 1 wherein R is an alkyl group of from 10 to 18 carbon atoms.

4. The compound of claim 1 wherein R is a straight-chained alkyl.

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5. The compound of claim 1 wherein R$^1$ and R$^2$ are each methyl or ethyl.

6. The compound of claim 1 wherein R is a straight-chained alkyl having 12 carbon atoms; R$^1$ and R$^2$ are each methyl; and $n$ is 3.

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LEON ZITVER, Primary Examiner

M. W. GLYNN, Assistant Examiner

#### U.S. Cl. X.R.

252—117

# UNITED STATES PATENT OFFICE
## CERTIFICATE OF CORRECTION

Patent No. _____3,660,470_____      Dated_____May 2, 1972_____

Inventor(s)___David Graham Spencer Hirst_____

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 4, lines 19 and 20, "A Composition B consisted of 95.2 parts of Composi- pared consisting of:" should read -- A heavy duty household soap Composition A was prepared consisting of: --.

Signed and sealed this 24th day of October 1972.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.                     ROBERT GOTTSCHALK
Attesting Officer                         Commissioner of Patents