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Barbera

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[54] **UNSATURATED ZWITTERIONIC SURFACE ACTIVE COMPOSITION**

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Related U.S. Application Data

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[52] **U.S. Cl.** **252/526,** 252/545, 252/536, 252/555

[51] **Int. Cl.** **C11d 1/84,** C11d 3/06

[58] **Field of Search** ..... 252/545, 526, 533, 252/552; 260/512.12, 513 R

[56] **References Cited**

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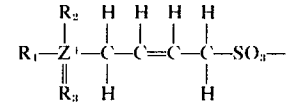
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[57] **ABSTRACT**

Zwitterionic surface active compounds are provided having the following formula:



wherein R_1 represents an unsaturated or saturated aliphatic group having six to 24 carbon atoms, R_2 and R_3 each represent an alkyl group having one to six carbon atoms, and Z represents nitrogen or phosphorus.

These compounds have valuable surface active properties that make them especially useful as detergent compounds.

2 Claims, No Drawings

UNSATURATED ZWITTERIONIC SURFACE ACTIVE COMPOSITION

This is a division of application Ser. No. 024,330, filed Mar. 31, 1970, now U.S. Pat. No. 3,668,240.

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to zwitterionic surface active compounds which are useful as detergents. The zwitterionic surface active compounds are characterized by having an unsaturated double bond located in the molecule between the anionic and cationic groups.

2. Prior Art

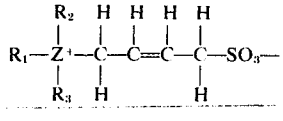
Zwitterionic or internally neutralized surface active compounds having both anionic and cationic groups are known. They are usually depicted as having a formula $R_1R_2R_3N^+R_4X^-$ in which the R's are alkyl or alkylene groups (R_4 always being saturated aliphatic) and X is COO^- or SO_3^-. No previous disclosure has been found of a surface active compound having R_4 representing a group

$$-CH_2-CH=CH-CH_2-.$$

It is this unique molecular arrangement which distinguishes the compounds of the present invention from prior art zwitterionic surface active compounds. It has been surprisingly discovered that the presence of the double bond contributes unexpectedly to the detergent properties of this molecule.

SUMMARY OF THE INVENTION

The compounds of the present invention have the formula



in which R_1 represents an unsaturated or saturated aliphatic group having six to 24 carbon atoms, preferably a saturated group having eight to 18 carbon atoms, R_2 and R_3 each represent an alkyl group having one to six carbon atoms, preferably one to three carbon atoms, and Z is selected from nitrogen or phosphorus, preferably nitrogen.

This class of compounds is illustrated by the following specific examples:

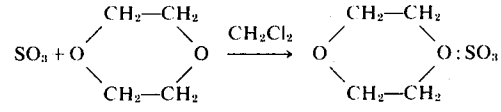
4-(N,N-dimethyl-N-hexadecyl-ammonio)-2-butene-1-sulfonate; 4-(N,N-dimethyl-N-alkylammonio)-2-butene-1-sulfonate, the alkyl group drived from tallow fatty alcohol; 4-(N,N-diethyl-N-hexadecylammonio)-2-butene-1-sulfonate; 4-(N,N-diethyl-N-tetradecylammonio)-2-butene-1-sulfonate; 4-(N,N-dimethyl-N-alkylammonio)-2-butene-1-sulfonate, the alkyl group being derived from the middle cut of coconut fatty alcohol; 4-(N,N-dimethyl-N-octadecylammonio)-2-butene-1-sulfonate; 4-(N-2-hydroxyethyl, N-methyl, N-tetradecylammonio)-2-butene-1-sulfonate; 4-(N,N-dimethyl-N-dodecylammonio)-2-butene-1-sulfonate; 4-(N,N-dimethyl-N-hexadecylphosphonio)-2-butene-1-sulfonate; 4-(N,N-dimethyl-N-alkylphophonio)-2-butene-1-sulfonate, the alkyl group derived from the middle cut of coconut fatty alcohol; and 4-(N,N-diethyl-N-hexadecylphosphonio)-2-butene-1-sulfonate. Specific reference to the above compounds is given only for the purpose of illustration, and it will

be appreciated that many other similar variations may be used in this invention so long as the general formula requirements are observed.

The preferred compounds of this invention are 4-(N,N-dimethyl-N-hexadecyl-ammonio)-2-butene-1-sulfonate; 4-(N,N-dimethyl-N-alkylammonio)-2-butene-1-sulfonate in which the alkyl group is tallow alkyl which approximately consists of a mixture of 66 percent C_{18}, 30 percent C_{16}, 4 percent C_{14}, or in which the alkyl group is middle cut coconut fatty alkyl which approximately consists of a mixture of 2 percent C_{10}, 66 percent C_{12}, 23 percent C_{14} and 9 percent C_{16}. It is preferred that that R_1 and R_2 be selected from methyl, ethyl, propyl, isopropyl, butyl and ethanol.

The unsaturated zwitterionic compounds of the present invention can be made by any convenient method or process. For example, they can be prepared by reacting tertiary amines or phosphines with butene sultones. The butene sultone can be from any source but a ready source is by a sulfonation reaction betwen 1,3-butadiene and an SO_3–dioxane complex.

An SO_3–dioxane complex can be prepared by the following procedure:



The complex readily precipitates out, and is then filtered and washed with dioxane. The filter cake is then ordinarily slurried in dioxane, and butadiene is bubbled through the slurry until all of the solids have disappeared. To the reaction product containing a butene sultone compound and a sulfonated butene polymer is added either a tertiary amine or phosphine compound, e.g., dodecyl dimethyl amine. The reaction proceeds at reflux and a reaction product is formed containing the desired 4-(N,N-dialkyl-N-alkyl)-2-butene-1-sulfonate in substantial yield. NMR and IR analyses have confirmed the desired reaction product.

EXAMPLE

160 g. SO_3 were added to a mixture of 212 g. dioxane and 588 g. ethylene dichloride. A white solid precipitate which formed was removed by filtering. The precipitate was added to 650 g. dioxane, the mixture was heated to 60°C. and butadiene was bubbled in until the solids were reacted. A two phase liquid resulted. The bottom phase, a yellow oil, was added slowly to 474 g. dimethyldodecylamine and 1308 g. acetone. This mixture was refluxed at 59°C. and amine values were taken to follow the reaction. Time "0" minutes on amine values is after addition; theoretical value is 56.

Time	Amine Value
0 minutes	43
30 minutes	40
90 minutes	42.4
180 minutes	41.9
300 minutes	42.5

The material was then chilled in a 0°F. box overnight and the white solids removed by filtering and washed with acetone. The solids were dissolved in a 50 percent 3 A alcohol in water solution to 20 percent solids level. The pH was raised to about 9 with 50 percent NaOH in order to free the amine from the salt form. This was then filtered to remove the soldium salts and washed with petroleum ether then dried to a solids form. The

material was then redissolved to a 62 percent volatiles — 38 percent solids level with water. Analysis confirmed a reaction product of 4-(N-dodecyl-N,N-dimethyl)-2-butene-1-sulfonate.

The discovery that the introduction of one double bond into the radical between cation and anion groups of a zwitterion as described herein produces a compound having surface active performance superior to that of its saturated four carbon counterpart was totally unexpected. The double bond, belived to be the cis-stereoisomer, apparently allows positioning of the charged zwitterionic groupings in such a manner as to enhance the surface activity of the unsaturated compounds beyond that of their saturated counterparts.

In preparing detergent compositions, especially valuable as laundering compositions, it is desirable to use the unsaturated zwitterionic surface active compounds of this invention in admixture with detergency builder compouds. Excellent compositions consist of an unsaturated zwitterionic detergent compound of this invention and at least one detergency builder selected from inorganic or organic alkaline builders in a proportion by weight of detergent to builder of 10:1 to 1:20 and preferably from 5:1 to 1:10. These compositions provide best overall laundering results including soil removal and whiteness maintenance results when used in washing solutions having a pH 6.5 to 11.5, preferably 7 to 11, optionally 8.5 –11.

Water soluble inorganic alkaline builder salts which can be used in this invention alone or in admixture are alkali metal carbonates, borates, phosphates, polyphosphates, bicarbonates and silicates. Ammonium or substituted ammonium, e.g., triethanol ammonium, salts of these materials can also be used. Specific examples of suitable salts are sodium tripolyphosphate, sodium carbonate, sodium tetraborate, sodium and potassium pyrophosphate, sodium and ammonium bicarbonate, potassium tripolyphosphate, sodium hexametaphosphate, sodium sesquicarbonate, sodium orthophosphate and potassium bicarbonate. The preferred inorganic alkaline builders according to this invention are alkali metal tripolyphosphates for built granular compositions.

Examples of suitable organic alkaline sequestrant builder salts used in this invention alone or in admixture are alkali metal, ammonium or substituted ammonium, aminocarboxylates, e.g., sodium and potassium ethylenediaminetetraacetate, sodium and potassium N-(2-hydroxyethyl)-ethylenediaminetriacetates, sodium and potassium nitrilotriacetates and sodium, potassium and triethanolammonium N-(2-hydroxyethyl)-nitrilodiacetates. Mixed salts of these polycarboxylates are also suitable. The alkali metal salts of phytic acid, e.g., sodium phytate are also suitable as organic alkaline sequestrant builder salts (see U.S. Pat. No. 2,739,942). Sodium ethane-1-hydroxy, 1-diphosphonate, and sodium citrate cam also be used as builders either alone or in mixtures with other builder compounds. Other suitable builders include methylene and ethylene diphosphonates and their derivatives, ethane-1-hydroxy-1,1,2-triphosphonate, sodium itaconate, and sodium polymaleate and the like.

The unsaturated zwitterionic surface active compounds of the present invention can also be used in combination with other detergent materials selected from anionic synthetic detergents, nonionic synthetic detergents and ampholytic and zwitterionic synthetic detergents.

A laundering method incorporating the discovery of the present invention can be practiced in a number of different ways. Preferably the washing step is followed by rinsing and drying the fabrics. The washing solution can be prepared by adding the granular, tablet or liquid detergent composition prepared according to this invention to any container which contains water at a temperature ranging from about 40°F. to about 200°F., usually about 80°F. – 160°F. The detergent composition concentration in solution can range from about 0.05 percent to 10.50 percent by total weight, and should be added in sufficient amount to provide a concentration of at least 0.005 percent of the zwitterionic detergent compounds. The fabrics can be added to the container or washer before or after the washing solution is added. As is usual in a washing step, the fabrics are then agitated in the detergent solution. While the period of time may vary, an automatic agitator type washer, generally employs a washing cycle which ranges from 8 to 15 minutes.

After the washing step, the washing liquor is drained off or the fabrics are separated from the liquor and thereafter the fabrics are rinsed in clean water. The fabrics can be rinsed as many times as desired in order to insure that washing liquor is removed. Using an automatic washer, it has been found that about four spray rinses and one deep rinse are usually sufficient for this purpose. Between and after rinsing steps, the bulk of the rinse water is usually drawn from, or spun out of the fabrics. After rinsing, the fabrics are dried. Although rinsing and drying are usual and desirable steps, the important advantage of the invention is achieved in the washing step.

The following compositions will illustrate the manner in which the zwitterionic surface active detergent compounds of this invention can be used. Included are both liquid and granular formulations. It will be understood, however, that the examples are not to be construed or limiting the scope of conditions claimed hereinafter. These compositions are useful in automatic washers and conventional type washers as well as hand washing operations.

EXAMPLE OF GRANULAR BUILT DETERGENT COMPOSITION

7% — 4-(N,N-dimethyl-N-hexadecylammonio)-2-butene-1-sulfonate
50% — sodium nitrilotriacetate
5% — sodium xylene sulfontae
7% — sodium silicate ($Na_2O:SiO_2$=1:2.5)
0.16% — fluorescent dye
0.2% — perfume
0.02% — benzotriazole
20.62% — sodium sulfate
10% — water and minor amounts of miscellaneous material

EXAMPLE OF BUILT LIQUID DETERGENT COMPOSITION

12% — 4-(N,N-dimethyl-N-alkylammonio*)-2-butene-1-sulfonate
20% — tetrapotassium pyrophosphate
3.8% — sodium silicate ($Na_2O:SiO_2$=1:1.6
8.5% — potassium toluene sulfonate
0.3% — sodium carboxymethyl hydroxy ethyl cellulose
0.12% — fluorescent dye

0.15% — perfume
0.02% — benzotriazole
55.11% — water
*alkyl referring to the R_1 group derived from the middle cut of coconut fatty alcohol (2% C_{10}, 66% C_{12}, 23% C_{14}, 9% C_{16})

EXAMPLE OF BUILT LIQUID DETERGENT COMPOSITION

22% — 4-(N,N-dimethyl-N-tetradecylammonio)-2-butene-1-sulfonate
19% — tetrapotassium pyrophosphate
3.8% — sodium silicate ($Na_2O:SiO_2$=1:16)
8.5% — potassium toluene sulfonate
0.3% — sodium carboxy methyl hydroxy ethyl cellulose
0.2% — perfume
0.02% — benzotriazole
46.18% — water and minor amounts of miscellaneous

EXAMPLE OF BUILT LIQUID DETERGENT COMPOSITION

12% — 4-(N,N-dimethyl-N-alkylammonio*)-2-butene-1-sulfonate
19% — tetrapotassium pyrophosphonate
3.8% — sodium silicate ($Na_2O:SiO_2$=1:1.6)
*alkyl referring to the R_1 group obtained from tallow fatty alcohol (66% C_{18}, 30% C_{16}, 4% C_{14})
8.5% — potassium toluene sulfonate
0.3% — sodium carboxy methyl cellulose
0.2% — perfume
56.20% — water

EXAMPLE OF GRANULAR BUILT DETERGENT COMPOSITION

17% — 4-(N,N-dimethyl-N-alkylammonio*)-2-butene-1-sulfonate
28% — sodium citrate
25% — sodium tripolyphosphate
6% — sodium silicate ($Na_2O:SiO_2$=1:2.5)
2% — sodium toluene sulfonate
0.3% — sodium carboxy methyl cellulose
13% — sodium sulfate
0.16% — fluorescent dye
8% — water
0.54% — protease enzyme
*alkyl referring to the R_1 group obtained from tallow fatty alcohol (66% C_{18}, 30% C_{16}, 4% C_{14}) and others.

EXAMPLE OF LIQUID BUILT DETERGENT COMPOSITION

10% — 4-(N,N-dimethyl-N-alkylammonio*)-2-butene-1-sulfonate
60% — sodium pyrophosphate
6% — sodium silicate ($Na_2O:SiO_2$=1:2.5)
2% — sodium toluene sulfonate
0.3% — sodium carboxy methyl cellulose
11.3% — water
Balance — miscellaneous (fluorescers, perfume, antitarnish agents, sodium sulfate, etc.)
*alkyl referring to the R_1 group obtained from tallow fatty alcohol (66% C_{18}, 30% C_{16}, 4% C_{14}) and others.

EXAMPLE OF GRANULAR BUILT DETERGENT COMPOSITION

17% — 4-(N,N-diethyl-N-alkylammonio*)-2-butene-1-sulfonate
45% — sodium citrate
6% — sodium silicate ($Na_2O:SiO_2$=1:2.5)
0.5% — sodium carboxy methyl cellulose
28% — sodium sulfate
3.5% — water
*alkyl referring to the R_1 group derived from the middle cut of coconut fatty alcohol (2% C_{10}, 66% C_{12}, 23% C_{14}, 9% C_{16})

EXAMPLE OF LIQUID BUILT DETERGENT COMPOSITION

12% — 4-(N,N-diethyl-N-hexadecylammonio)-2-butene-1-sulfonate
19% — sodium nitrilotriacetate
3.8% — sodium silicate ($Na_2O:SiO_2$=1:1.6)
0.3% — sodium carboxy methyl cellulose
63% — water
Balance — miscellaneous

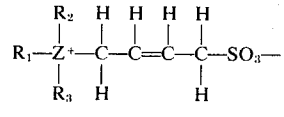
It will be appreciated that the unsaturated zwitterionic compounds used in the present invention can be incorporated into liquid or granular detergent compositions with suitable adjustments being made in the other components.

Materials which are considered normal and desirable additives in liquid or granule detergent compositions can also be added to the compositions of this invention without substantially modifying the basic characteristics of the unsaturated zwitterionic detergent surfactants. For example, a tarnish inhibitor such as benzotriazole or ethylene thio-urea may be added in amounts up to about 1 percent. Fluorescers, perfume, color, enzymes, antiredeposition agents, thickening agents, opacifiers, other detergent compounds, and blending or viscosity control agents, while not essential in the compositions of this invention, may also be added.

The zwitterionic surface active compounds of the present invention are especially valuable because of their excellent overall soil removing properties. In addition, these compounds possess excellent whiteness maintenance properties when used in combination with the builder compounds described above. Detergency tests have demonstrated that the unsaturated zwitterionic compounds of the present invention provide overall detergency at least equivalent to such an excellent detergent at sodium tallow alkyl sulfate and 3-(coconut alkyl dimethyl ammonio)-2-hydroxy-1-sulfonate.

What is claimed is:

1. A detergent composition consisting essentially of an unsaturated zwitterionic surface active compound having the formula



in which R_1 represents an unsaturated or saturated aliphatic hydrocarbon group having six to 24 carbon atoms, and R_2 and R_3 each represent an alkyl group having one to six carbon atoms, and Z is selected from nitrogen or phosphorus, and at least one detergency builder which is a water soluble organic or inorganic builder salt wherein the proportion of said surface active compound to said builder is in the proportion by weight of 10:1 to 1:20.

2. A detergent composition of claim **1** in which the proportion by weight of said surface active compound to said builder is 5:1 to 1:10.

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