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ALKYL-ALKANOL AMINE SALTS OF ALKYL-
ATED ARYL SULFONIC ACIDS

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This invention relates to new amine salts of alkylated aryl sulfonic acids having excellent wetting, foam, and detergent characteristics, and relates more particularly to alkyl-alkanol amine salts of alkylated benzene sulfonic acids, the alkyl group of such acids containing from 9 to 15 carbon atoms and preferably an average of 12 carbon atoms. Such compounds have exceptional utility in dishwashing.

Recently a number of liquid detergents have been synthesized which are water-soluble and consequently useful in washing dishes and similar cleaning processes. While such materials have met with some commercial success, some are not entirely satisfactory because of their relatively low water solubility and poor cleaning power. In an effort to improve upon these heretofore known synthetic detergents, I produced alkanol-amine salts of alkylarylsulfonic acids such, for example, as the tri-ethanolamine salts of alkylated benzene sulfonic acids. Such compounds are of particular value for household liquid detergents because of their high water solubility and rinsability.

I have discovered that if at least one of the alkanol groups on the trialkanol amine salts of alkyl aryl sulfonic acids is replaced by an alkyl group, new compositions are obtained which are less soluble in water but, surprisingly, markedly better detergents for proteinaceous and fatty soils and mixtures thereof.

They are less irritating to the skin than the corresponding inorganic soaps. These new compounds have exceptional utility in washing dishes, not only because of their improved detergency, but likewise because of their superior foaming power and foam stability. The latter is particularly important in the economical use of such detergents, since it furnishes the user with a measure of the residual detergent available in the wash solution, e. g., a dishpan, throughout the cleansing operation.

In accordance with the present invention, the new amine salts may be produced simply by neutralizing, or reacting a theoretical stoichiometric amount of, an alkyl benzenesulfonic acid or acid mixture with an alkylalkanol amine.

The amines used in the production of the new compounds include the alkyl dialkanol amines and the dialkylalkanol amines in which the alkyl group or groups contain from 1 to 6 carbon atoms and the alkanol group or groups are the lower alkanols containing 2 or 3 carbons atoms such, for example, as ethanol, n-propanol, or isopropanol. Such alkylalkanol amines can be pre-

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pared by various methods, as for example, by the reaction of an alkylene oxide with an alkyl amine, and many of these materials are commercially available. Specific examples of the alkylalkanol amines herein contemplated as suitable for the preparation of the new compounds of the present invention are methyldiethanol amine, ethyldiethanol amine, n-propyldiethanol amine, n-butyldiethanol amine, isopropyldiethanol amine, isobutyldiethanol amine, amyldiethanol amine, hexyldiethanol amine, dimethylethanol amine, diethylethanol amine, dipropylethanol amine, dibutylethanol amine, diamylethanol amine, methyldipropanol amine, ethyldipropanol amine, propyldipropanol amine, butyldipropanol amine, amyldipropanol amine, hexyldipropanol amine, dimethyl-n-propanol amine, dimethylisopropanol amine, diamyl-n-propanol amine, diamylisopropanol amine, methyl-ethylethanol amine, amylethylethanol amine, ethylpropyl-n-propanol amine, and ethylpropylisopropanol amine. It is to be understood that the alkyl groups in the case of a dialkylalkanol amine may be similar or dissimilar, as desired. The same is true of the alkanol groups in an alkylalkanol amine.

The alkylarylsulfonic acids or acid mixtures which are neutralized, in accordance with this invention, to produce the new amine salts having exceptional utility in dishwashing are those obtained by sulfonation of alkylated benzenes or benzene mixtures having from 9 to 15 carbon atoms in the alkyl group, and preferably averaging about 12 carbon atoms in the alkyl group. In addition to the long chain alkyl group, other nuclear hydrogen atoms of the aromatic may be substituted by alkyl groups having from 1 to 3 carbon atoms. These sulfonic acids may be readily prepared by sulfonating appropriate alkylated benzene hydrocarbons or hydrocarbon mixtures using sulfuric acid of about 98% to 99% concentration or higher and then separating the spent sludge containing free sulfuric acid from the desired sulfonic acid by settling and decanting or other suitable methods. The resulting sulfonic acid preferably is further purified by dissolving the same in benzene, octane, or other convenient solvent and decanting or otherwise removing the additional sludge which is thereby separated. The solvent may be removed from the sulfonic acid by evaporation or other methods either prior or subsequent to neutralization or reaction of the sulfonic acid with the alkylalkanol amine.

As previously stated, the alkyl benzene hydro-

carbon or hydrocarbon mixtures which are sulfonated to provide the necessary sulfonic acids for neutralization have an alkyl group containing from 9 to 15 carbon atoms and the remaining nuclear substituents of the benzene radical are selected from the group consisting of hydrogen and lower alkyl groups having from 1 to 3 carbon atoms. In all cases, however, the aryl hydrocarbon may be one or a mixture of two or more hydrocarbons such as benzene, toluene, xylene, ethyl benzene, propyl benzene, and isopropyl benzene.

Specific examples of the alkyl aromatic hydrocarbons herein contemplated as suitable for the invention are nonyl benzene, nonyl toluene, nonyl ethyl benzene, nonyl propyl benzene, nonyl dimethyl benzene, nonyl diethyl benzene, nonyl methyl ethyl benzene, nonyl methyl propyl benzene, nonyl ethyl propyl benzene, nonyl dipropyl benzene, decyl benzene, decyl toluene, decyl ethyl benzene, decyl propyl benzene, decyl dimethyl benzene, decyl diethyl benzene, decyl methyl ethyl benzene, decyl methyl propyl benzene, decyl ethyl propyl benzene, decyl dipropyl benzene, undecyl benzene, undecyl toluene, undecyl ethyl benzene, undecyl dimethyl benzene, undecyl diethyl benzene, undecyl methyl ethyl benzene, undecyl methyl propyl benzene, undecyl dipropyl benzene, dodecyl benzene, dodecyl toluene, dodecyl ethyl benzene, dodecyl propyl benzene, dodecyl dimethyl benzene, dodecyl diethyl benzene, dodecyl methyl ethyl benzene, dodecyl methyl propyl benzene, dodecyl dipropyl benzene, tridecyl benzene, tridecyl toluene, tridecyl ethyl benzene, tridecyl propyl benzene, tridecyl dimethyl benzene, tridecyl diethyl benzene, tridecyl methyl ethyl benzene, tridecyl methyl propyl benzene, tridecyl dipropyl benzene, tetradecyl benzene, tetradecyl toluene, tetradecyl ethyl benzene, tetradecyl propyl benzene, tetradecyl dimethyl benzene, tetradecyl diethyl benzene, tetradecyl methyl ethyl benzene, tetradecyl methyl propyl benzene, tetradecyl dipropyl benzene, pentadecyl benzene, pentadecyl toluene, pentadecyl ethyl benzene, pentadecyl propyl benzene, pentadecyl dimethyl benzene, pentadecyl diethyl benzene, pentadecyl methyl ethyl benzene, pentadecyl methyl propyl benzene, and pentadecyl dipropyl benzene, or mixtures thereof.

The production of the alkylated benzene hydrocarbons or hydrocarbon mixtures may be accomplished by various methods such, for example, as by reacting a chlorinated alkyl hydrocarbon or hydrocarbon mixture having 9 to 15 carbon atoms with the aromatic hydrocarbon in the presence of a Friedel-Crafts catalyst such as $AlCl_3$. The alkyl halide may be obtained by chlorinating the proper petroleum fraction such as a kerosene fraction. The aromatic hydrocarbon may be benzene, toluene, xylene, ethyl benzene, propyl benzene, and isopropyl benzene.

Preferably, however, the benzene hydrocarbon may be alkylated with a mono-olefin polymer or mixture of polymers containing from 9 to 15 carbon atoms in the presence of a suitable catalyst such as sulfuric acid, $AlCl_3$, $SnCl_4$, $ZnCl_2$, BF_3 , or HF . The olefin polymer or polymer mixture is most suitably derived by subjecting a lower olefin to polymerizing conditions in the presence of a catalyst such as phosphoric acid impregnated on a carrier such as kieselguhr. Propylene or gaseous mixtures containing substantial amounts of propylene is preferred. Mixtures of propylene and propylene dimers or trimers may also be used. It is desirable, however, that readily polymeriz-

able olefins such as isobutylene be absent inasmuch as the resulting polymers easily depolymerize under alkylating conditions, and produce alkylated aryl hydrocarbons in which the alkyl group or groups are of short chain length. Most convenient and economic for use are petroleum refinery gas streams which have been fractionated to remove all or substantially all of the butane, butenes, and heavier hydrocarbons. For example, a refinery gas stream comprising 4.6 mol per cent methane, 5.2 mol per cent ethylene, 19.5 mol per cent ethane, 26.2 mol per cent propylene, and 44.5 mol per cent propane may be contacted with a supported phosphoric acid catalyst at 300° F. to 600° F. under a pressure between 200 and 1800 p. s. i., employing a space velocity of 0.05 to 0.15 lb. mols of propylene per lb. of catalyst per hour. The resulting polymers will comprise a complex mixture of olefinic hydrocarbons containing from 6 to about 18 carbon atoms per molecule, and these polymers will not consist solely of dimers, trimers, pentamers, etc., but will include C_7 , C_8 , C_{10} , C_{11} , C_{13} , C_{14} , and slightly higher polymers due to the interpolymerization of propylene polymer degradation products as well as the presence, in most cases, of ethylene which may be interpolymerized. The polymer mixture may also contain minor amounts of paraffins of various molecular weights as by-products of the polymerization reaction. Preferred conditions for polymerization require temperatures between 300° F. and 500° F. under pressures of 300 to 1000 p. s. i. at a space velocity of about 0.004 lb. mols of propylene per lb. of phosphoric acid catalyst per hour. To obtain a preponderance of polymers averaging 9 carbon atoms, high pressures and high space velocities are desirable, i. e., 1000 to 1800 p. s. i. and 0.006 space velocity. On the other hand, to obtain high yields of polymers averaging 12 carbon atoms with minor amounts of polymers averaging 15 carbon atoms, somewhat lower pressures and space velocities should be used, for example, 200 to 800 p. s. i. and 0.002 to 0.004 space velocity. Depending upon the average chain length or molecular weight of the polymers desired for the alkylation of the aryl hydrocarbon, the crude propylene polymers may be fractionally distilled to obtain the necessary fraction or fractions, and these may be either distillates or distillation residues.

A polymer fraction may be mixed, for example, with 5 to 6 molar equivalents of benzene and 0.05 to 0.1 molar equivalents of a catalyst such as $AlCl_3$, and the alkylation carried out at 100° F. to 180° F. The catalyst then is separated from the alkylation mixture, the mixture is washed with dilute alkali solution, settled, and washed to remove alkali. The alkylation mixture is then fractionally distilled to remove excess benzene, low boiling alkylated benzene resulting as degradation by-products, and small amounts of low boiling olefins and paraffins.

An alkylated aryl hydrocarbon mixture which is particularly useful in the present invention may be obtained by reacting the above mentioned propylene polymer fraction containing from 9 to 15 carbon atoms with an aromatic hydrocarbon and subsequently fractionating the alkylated aryl hydrocarbon mixture to obtain a fraction consisting predominantly of alkyl aromatics having 12 carbon atoms in the alkyl group, or, alternatively, the propylene polymer fraction having 9 to 15 carbon atoms may be fractionated to separate a narrow boiling cut consisting of a major proportion of polymers having 12 carbon

atoms which may subsequently be reacted with the aromatic hydrocarbon to produce a mixture of alkylated aromatics having predominantly 12 carbon atoms in the alkyl group.

If desired, a combination of these two methods may be used, i. e., fractionation of the C₉ to C₁₅ propylene polymer mixture, alkylation with the C₁₂-cut, then fractionation of the alkylated aromatic mixture. In all cases, however, the alkylated aromatic hydrocarbon mixture which is particularly useful contains a major proportion of an alkylated aromatic hydrocarbon having 12 carbon atoms in the alkyl group with very minor amounts of alkylated aromatics having alkyl groups other than 12 carbons and within the range from 9 to 15 carbons.

The following examples are given for the purpose of further illustrating the present invention, but are not intended to be limiting on the scope thereof. The alkylalkanol amine salts produced in the examples in accordance with the present invention were subjected either to the York dishwashing test or to an accelerated dishwashing test, as indicated. By way of comparison, the same tests were performed on the unsubstituted alkanol amine salts, specifically triethanolamine salts, of the same alkylated benzene sulfonic acids to show the very marked and unexpected superiority of the alkylalkanol amine salts for dishwashing.

The York dishwashing test was made in accordance with the procedure described by Machlis and Michaels in Soap and Sanitary Chemicals, September 1948, pages 42-44. The results of such test are given in the table in terms of the percent detergency (by reflection).

The accelerated dishwashing test involves soiling 8-inch white china dishes by first applying to each dish 7 gms. of a blend of 71.5% fresh egg and 28.5% bacon grease mixed in a Waring Blendor and then drying the dishes in an oven, maintained at 150° F. for 15 minutes. After cooling to room temperature, the dishes are washed one by one in an oval 14" by 18" by 15" dishpan containing 2000 cc. of 100 p. p. m. hard water solution having 0.15% concentration of the detergent under investigation. Prior to placing any dishes in the water solution, it is agitated violently by hand for approximately 15 seconds to build a full head of foam.

As the dishes are washed, the foam breaks down and the end point is reached when no foam remains in the dishpan. Results of the test are reported as the number of dishes, each containing originally 7 gms. of soil, cleaned before all foam disappears.

This test has proven to have a high degree of reproducibility upon repeated testing with a given detergent and among a variety of operators as well.

EXAMPLE I

To a quantity of sulfonic acid prepared by sulfonation of a heart-cut alkylated benzene mixture containing an average of 12 carbon atoms in the alkyl group and produced as above described, pure amyldiethanol amine was added in sufficient quantity to substantially neutralize the acid. The resulting salt was subjected to the York dishwashing tests and the results thereof for 0.06% and 0.20% concentrations in 100 p. p. m. hard water are reported in Table I.

EXAMPLE II

To a quantity of the same sulfonic acid as used in Example I, n-butyl-diethanol amine in suffi-

cient quantity to substantially neutralize the acid was added. The percent detergency, as determined by the York test, is given in Table I for 0.06% and 0.20% concentrations in 100 p. p. m. hard water.

EXAMPLE III

A quantity of the same sulfonic acid as used in Example I was neutralized with pure triethanolamine. The resulting product was subjected to the York dishwashing test and the results thereof for 0.06% and 0.20% concentrations in 100 p. p. m. hard water are given in Table I.

Table I

Example No.	Percent Detergency (0.06% Solution)	Percent Detergency (0.20% Solution)
I.....	34	53
II.....	20	57
III.....	12	40

The above examples and data clearly show the marked and unexpected superiority, as dishwashing compounds, of the alkylalkanol amine salts of alkylated benzene sulfonic acids having 9 to 15 carbon atoms in the alkyl group over the unsubstituted alkanol amine salts of such acids. In addition, the alkylalkanol amine salts of alkyl benzene sulfonic acids have very satisfactory water solubility and cleaning power.

EXAMPLE IV

A quantity of the sulfonic acid of Example I was neutralized with amyldiethanol amine and the resulting product was subjected to the accelerated dishwashing test. The results of such test are reported in Table II.

EXAMPLE V

To a quantity of the sulfonic acid of Example I was added sufficient n-butyl-diethanol amine to neutralize the acid. The product was subjected to the accelerated dishwashing test and the results thereof are given in Table II.

EXAMPLE VI

Another quantity of the sulfonic acid was neutralized with isobutyldiethanol amine. The product was tested by the accelerated dishwashing procedure and the results are given in Table II.

EXAMPLE VII

In this case, triethanol amine was used to neutralize a quantity of the sulfonic acid. The product was tested by the accelerated method and the results are presented in Table II.

EXAMPLE VIII

A quantity of the sulfonic acid of Example I was neutralized with diethanol amine. The resulting product was subjected to the accelerated dishwashing test. The results of the test are presented in Table II.

Table II

Example	No. of Dishes Washed
IV.....	8
V.....	7
VI.....	6.5
VII.....	4.5
VIII.....	4

The above examples and resulting data further show that alkylalkanol amine salts of alkylated benzene sulfonic acids having an alkyl group of from 9 to 15 carbon atoms are vastly superior as dishwashing compounds to unsubstituted alkanol amine salts of such acids. The superiority of the alkyl alkanol amine is very marked and unexpected.

I claim:

1. A tertiary amine salt of an alkyl benzene sulfonic acid, the alkyl radical of said acid having from 9 to 15 carbon atoms, and the remaining nuclear substituents of the benzene radical being selected from the group consisting of hydrogen and lower alkyl groups having from 1 to 3 carbon atoms and the tertiary amine being selected from the group consisting of dialkyl alkanol amines and alkyl dialkanol amines, wherein the alkyl substituents have from 1 to 6 carbon atoms and the alkanol substituents have from 2 to 3 carbon atoms.

2. An alkyl dialkanol amine salt of an alkyl benzene sulfonic acid, the alkyl radical of said acid having from 9 to 15 carbon atoms and the remaining nuclear substituents of the benzene radical being selected from the group consisting of hydrogen and lower alkyl groups having from 1 to 3 carbon atoms, the alkyl substituents of the amine having from 1 to 6 carbon atoms, and the alkanol substituents of the amine having from 2 to 3 carbon atoms.

3. A dialkyl alkanol amine salt of an alkyl benzene sulfonic acid, the alkyl radical of said acid having from 9 to 15 carbon atoms and the remaining nuclear substituents of the benzene radical being selected from the group consisting of hydrogen and lower alkyl groups having from 1 to 3 carbon atoms, the alkyl substituents of the

amine having from 1 to 6 carbon atoms, and the alkanol substituents of the amine having from 2 to 3 carbon atoms.

4. An amyldiethanol amine salt of an alkylbenzene sulfonic acid, the alkyl group of said acid having from 9 to 15 carbon atoms.

5. An n-butyldiethanol amine salt of an alkylbenzenesulfonic acid, the alkyl group of said acid having from 9 to 15 carbon atoms.

6. An isobutyldiethanol amine salt of an alkylbenzenesulfonic acid, the alkyl group of said acid having from 9 to 15 carbon atoms.

7. An isopropyldiethanol amine salt of an alkylbenzenesulfonic acid, the alkyl group of said acid having from 9 to 15 carbon atoms.

8. An amyldiethanol amine salt of an alkylbenzenesulfonic acid in which the alkyl group averages 12 carbon atoms.

9. An n-butyldiethanol amine salt of an alkylbenzenesulfonic acid in which the alkyl group averages 12 carbon atoms.

10. An isobutyldiethanol amine salt of an alkylbenzenesulfonic acid in which the alkyl group averages 12 carbon atoms.

11. An isopropyldiethanol amine salt of an alkylbenzenesulfonic acid in which the alkyl group averages 12 carbon atoms.

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