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- [54] **LINEAR ALKYLPHENOL SULFATE-SULFONATE PHOSPHATE-FREE DETERGENT ACTIVES**
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- [51] **Int. Cl.**.....**C07c 141/00**
- [58] **Field of Search**.....**260/457**

- [56] **References Cited**
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- 2,106,716 2/1938 Bruson.....260/457 X

FOREIGN PATENTS OR APPLICATIONS

6,709,714 1/1968 Netherlands260/458

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[57] **ABSTRACT**

Heavy duty detergent active materials capable of heavy duty washing performance in the absence of phosphate builders are provided, the materials comprising alkylphenol sulfate-sulfonate compounds in which the alkyl groups are linear of 16–24 carbon atoms.

4 Claims, No Drawings

LINEAR ALKYLPHENOL SULFATE-SULFONATE PHOSPHATE-FREE DETERGENT ACTIVES

BACKGROUND OF THE INVENTION

This invention is concerned with novel linear alkylphenol sulfate-sulfonate compounds which are effective in detergent applications as detergent actives.

Increased concern over water pollution has produced significant changes in household detergents. Initially, major emphasis has been placed on producing biodegradable surface-active components for detergents. The shift to linear surface-active materials, including linear alkylbenzene sulfonate (LAS) and alpha-olefin sulfonates, etc., has reduced pollution attributed to nonbiodegradability.

However, the above-mentioned surface-active materials are inadequate in terms of soil removal in the absence of phosphate builders. Increasing evidence appears to indicate that phosphates contribute to the growth of algae in the nation's streams and lakes. This algae growth poses a serious pollution threat to the maintenance of clear, good domestic water supplies.

Consequently, there has developed a need for detergent active materials which will function successfully in the absence of phosphate builders. Recently, certain non-phosphate building materials have been proposed as replacements for the phosphates. Thus, materials such as the polysodium salts of nitrilotriacetic acid, ethylene diamine tetraacetic acid, copolymers of ethylene and maleic acid, and similar polycarboxylic materials have been proposed as builders. These materials, however, when employed with conventional detergent actives such as LAS, have, for one reason or another, not proved to be quite as effective as phosphates in detergent formulations. For example, some of the materials have proven to be insufficiently biodegradable to meet present and anticipated requirements.

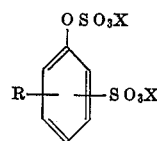
It is therefore desirable to provide compounds which are effective as detergent active materials in the absence of phosphate builders and are sufficiently biodegradable that their use does not contribute foam to the water supply.

In addition, in the past, with heavy duty detergents, it has been thought that to achieve good soil removal it was necessary to maintain a high pH in washing solutions. This concept, which began with the strongly alkaline laundry soaps, has continued to the present day LAS-phosphate combinations which are in widespread use in heavy duty detergent formulations. One apparent reason for this is that the alkylbenzene sulfonate detergents are not effective in heavy duty detergent formulations in the absence of a builder. The phosphate builders, for example, must be employed at a pH greater than 9 to be effective, and even the newer builders such as sodium nitriloacetate have a pH of about 9 in solution. The advantages to be gained with heavy duty detergents which may be employed at neutral pH are many. Deleterious effects from skin contact are lessened. Enzyme-type soil looseners may be more easily combined in neutral solutions. Injury to fabrics is minimized. It is, therefore, desirable to provide detergent active materials which, in addition to the previously mentioned non-polluting characteristics, achieve their maximum detergency at or near neutral pH.

The formulation of liquid heavy duty detergent compositions achieves many desirable results. They are easy to package and measure, and their use opens the possibility of automatic dispensing in washing machines. However, in the past it has been impracticable to formulate heavy duty detergents in liquid form because of the insufficient solubility of the inorganic ingredients (phosphate builders, etc.) required for heavy duty applications and the high cost of organic substitutes for such inorganic ingredients. It is therefore highly desirable to provide detergent active materials having good water solubility and which, because of their excellent detergency without builders, can be formulated into effective, reasonably priced, heavy duty liquid detergent formulations.

SUMMARY OF THE INVENTION

Heavy duty detergent materials are provided which comprise alkylphenol sulfate-sulfonates of the formula



in which R is a substantially linear alkyl group of from about 16 to 24 carbon atoms and X is H or a water soluble salt-forming cation.

The compounds of this invention do not require the presence of a builder to achieve good heavy duty detergency, and while they are effective over a broad pH range, reach their maximum effectiveness at a pH near neutral in detergent solutions. Thus washing at a pH of 6.5 to 8.0, preferably 6.5 to 7.5, will give maximum soil removal while securing the previously mentioned advantages which inhere in the use of neutral washing solutions. Further, the compounds may be easily compounded into effective liquid heavy duty formulations because of the substantial solubility of the compounds in water and because of the lack of need for large adjunctive portions of inorganic materials such as builders.

DESCRIPTION OF PREFERRED EMBODIMENTS

The salt-forming cation X may be any of numerous materials such as alkali metal, alkaline earth metal, ammonium, or various organic cations. Examples of suitable organic cations include nitrogen-containing organic cations such as diethanolammonium and triethanolammonium cations. The alkali metal cations are preferred, and sodium ions are particularly preferred.

The alkyl groups represented by R are, as previously noted, substantially linear, although the presence of a random methyl radical upon the linear chain, for example, may not adversely affect the performance of the compounds. Alkyl radicals representative of R include hexadecyl, heptadecyl, octadecyl, nonadecyl, eicosyl, heneicosyl, docosyl, tricosyl, and tetracosyl. The preferred compounds will have as alkyl substituents octadecyl, nonadecyl, and eicosyl groups.

The alkylphenols which are suitable for the preparation of the compounds of this invention are prepared by conventional techniques. Such techniques include thermal and catalytic alkylation of phenol with olefins, al-

cohols and haloparaffins. Catalytic methods include the use of Friedel-Crafts catalysts such as aluminum chloride, zinc chloride, etc., and various acid catalysts and clay catalysts.

The alkyl groups are generally derived from alcohols, olefins, or haloparaffins. The position of the attachment of the aromatic nucleus on the alkyl chain may be at any point. With alpha olefins the predominant point of attachment of the alkylation product will be end group attachment—that is, either at the 1 or 2 but principally at the 2 position of the chain. On the other hand, with an isomerized mixture of olefins or olefins derived from haloparaffins which have, in turn, been produced by halogenation of paraffins, the position of the double bond will be generally completely random on the chain, and thus the corresponding aromatic nucleus attachment will be random.

The sulfonation and sulfation of the alkylphenols to produce the compounds of this invention is accomplished by reacting the alkylphenol with a sulfonating agent capable of (1) converting the aromatic hydroxyl radical to a sulfate and (2) forming a ring-substituted $-\text{SO}_3\text{H}$ under conditions such that the reaction product contains both an $-\text{OSO}_3\text{H}$ and an $-\text{SO}_3\text{H}$ radical attached to the aromatic nucleus. The preferred sulfonating agent satisfying these reaction prerequisites is sulfur trioxide. The sulfur trioxide may be employed in mixtures with an appropriate liquid solvent such as a chlorinated hydrocarbon or liquid SO_2 . Complexed SO_3 may also be used to effect the reaction. Typical complexing agents are dioxane and dimethylaniline, triethylamine, etc.

In contrast, the reaction of the alkylphenol with sulfuric acid, oleum, or chlorosulfonic acid under conventional sulfonation conditions does not result in any appreciable yields of the corresponding sulfate-sulfonate.

The alkylphenol sulfate-sulfonate compounds of this invention thus are suitably prepared by the reaction of an alkyl-phenol with sulfur trioxide. The reaction is carried out in an anhydrous inert solvent such as the chlorinated hydrocarbons, e.g., dichloroethane. The quantity of sulfur trioxide to be used should equal or exceed 2 moles per mole of alkylphenol for 100% conversion of the latter. Mole ratios of SO_3 to alkylphenol as high as 10:1 may be employed, but preferably the ratio is in the range of 3:1 to 5:1. At mole ratios below 2:1, some of the desired alkylphenol sulfate-sulfonate will be formed, but depending on the mole ratio used, substantial amounts of mono sulfonated material will be formed. Reaction temperatures are generally in the range of -10° to 10°C , preferably about -5° to 0°C . Alkylphenol, dissolved in the solvent is cooled to the reaction temperature and then SO_3 dissolved in the same solvent is added. The reaction is exothermic, and cooling means must be employed to keep the temperature within the desired range. The rate of addition of SO_3 is such that the cooling means can hold this temperature. Thus the time required for reaction varies as to efficiency of cooling, size of reaction mass, etc., but generally the addition will be complete within 10 to 120 minutes for small sized batches. Continuous procedure is preferred for large batches. In continuous processing, the reactants, dissolved in an appropriate solvent and cooled to reaction temperature, are charged to a cooled tubular reactor, wherein the average residence time is only a few minutes or less.

After sulfonation, the reaction product may be neutralized with a water-soluble, salt-forming cationic neutralizing agent, usually a metal oxide or hydroxide, and more preferably an alkaline earth metal or alkali metal hydroxide. The alkali metal hydroxides are preferred, and sodium hydroxide is most preferred. In addition to the inorganic bases described above, the neutralizing agent may be any of various organic bases. Sufficient base is added to neutralize both acid sites, that is about two moles. The final pH of the neutralized mixture should be about 7, but pH values within the range of 6 to 8 are satisfactory.

Following neutralization, the inert organic solvent is removed for reuse. This may be done by phase separation, or preferably by distillation. The organic solvent free material comprises an aqueous solution of the organic surface active materials and any inorganic salt, such as sodium sulfate. The neutralized product, which will contain a substantial quantity of water and from 1 to 4 parts of a normally inorganic sulfate from the neutralization of excess SO_3 (e.g., Na_2SO_4), may be used, as is, in combination with conventional detergent additives to formulate liquid heavy duty detergents. Alternatively, water may be removed in any quantity to complete dryness by conventional concentration techniques such as evaporation, distillation, drum drying, etc., to yield a concentrated solution, a slurry, or a dry particulate solid which may then be blended to form a heavy duty detergent.

The solid product isolated as described above may be desalted by the usual procedures as used in the alkylbenzene sulfonate art. In this method the solid material is mixed with about a 70/30 alcohol/water solution. The insoluble inorganic sulfate is removed by filtration, and the organic surfactant may be used as such or isolated by evaporation of the solvent. The liquid concentrates and slurries may be treated in similar fashion with allowance made for the quantity of water already present. These desalting procedures give a detergent product that is essentially free of inorganic salt.

The following examples describe the preparation of the compounds of this invention.

Example 1 — Preparation of Octadecylphenol Sulfate-Sulfonate

To a 20 ml. reaction vessel fitted with a septum, drying tube, thermometer, and a magnetic stirring bar, was charged 1.0 g. (0.00289 mols) of a C_{18} alkylphenol which had been prepared by thermal alkylation of phenol with a linear C_{18} alpha olefin according to the procedure of U.S. Pat. No. 3,423,474. A 10 ml. portion of dry 1,2-dichloroethane was charged to the reaction flask. The solution was flushed with nitrogen and stirring was begun. The solution was cooled to -10°C in an ice-acetone bath.

A solution of 1.0 ml anhydrous sulfur trioxide (1.9 g, 0.0237 mols) in 5 ml. of dry 1,2-dichloroethane was cooled to about 0°C . The solution was injected into the reaction solution with a syringe at such a rate as to maintain the reaction temperature at about 0°C . After the addition was complete, the cooling bath was removed, and the reaction mixture was allowed to warm to room temperature over a period of about 15 minutes. It was then added to 50 ml. of 0.5 N NaOH solution and titrated to a pH of about 10 with additional 0.5 N NaOH. The mixture was then placed upon a rotary evaporator, and the organic solvent was

removed under vacuum at 25°–30° C. The remaining water solution was diluted to 500 ml. and titrated by a standard Hyamine procedure giving about a 90% yield of octadecylphenol sulfate-sulfonate. Dilute acid hydrolysis followed by titration showed that the primary product contained both sulfate and sulfonate groups in substantially equal amounts; that is, it was an alkylphenol sulfate-sulfonate.

An infrared spectrum of the product showed strong adsorption in the 1,020–1,070 cm^{-1} and in the 1,200–1,280 cm^{-1} regions.

Example 2 — Preparation of Additional Linear Alkylphenol Sulfate-Sulfonates.

Following the general procedure of Example 1, materials were prepared by employing as precursors a series of alkylphenols in which the alkyl groups were linear and the major ring attachment was at the two carbon atom of the alkyl group. Additionally, alkylphenols were used in which the attachment of the aromatic nucleus was random on the alkyl chain. Alkylphenols having alkyl groups of 14, 16, 20, and 22 carbon atoms and mixtures of alkylphenols containing 18, 19, 20 alkyl carbons and 18, 20, and 22 alkyl carbons were reacted with sulfur trioxide. Analysis was by the method shown in Example 1.

Example 3 — Drying of Aqueous Alkylphenol Sulfate-Sulfonate Solution

An aqueous solution of octadecylphenol sulfate-sulfonate prepared as described in Example 1 was neutralized with sufficient sodium hydroxide to give a pH of 7. The dichloroethane was removed by heating under vacuum at about 25°–30° C. The temperature was then raised, and all of the water was removed to leave a particulate solid mass weighing 5.15 g. Analysis showed that this material contained 31 percent octadecylphenol sulfate-sulfonate, a small amount of water, and the remainder sodium sulfate. The above isolated solid was a free-flowing powder.

The compounds of this invention are useful as heavy duty detergent actives. In the past, heavy duty detergent formulations useful for removing soil from textiles have comprised an organic surfactant (detergent) and an inorganic phosphate builder; the phosphate being present by weight, in an amount of from one to four times that of the detergent. The compounds of the present invention are excellent soil removers without the aid of any phosphate builder. That is, the compounds of this invention satisfy all need for both organic surfactant and builder in the final heavy duty detergent formulation. One way that this may be accomplished is by preparing a mixture of the sulfate-sulfonate materials of the instant invention and an inert material, e.g. water, sodium sulfate, sodium carbonate, etc. Such mixtures may contain any amount of sulfate-sulfonate in excess of about 10 percent, preferably 15 percent or more. One useful composition comprises from 30 to 50 percent sulfate-sulfonate and the remainder, sodium sulfate. Many other combinations make useful formulations and may be either liquid solutions or particulate solids.

As heavy duty detergents, it is contemplated that the sulfate-sulfonate compounds will be used in wash water at concentrations of about 0.01 percent to about 0.10 percent. This is within the same range of concentrations as are employed with the present day commercial

detergents. In other words, the soil removal properties of the present compounds are essentially equivalent to the soil removal properties of an equal amount of the current commercial surfactant combined with at least an equal amount of phosphate.

Detergency of the compounds of the present invention is measured by their ability to remove natural sebum soil from cotton cloth. By this method, small swatches of cloth, soiled by rubbing over face and neck, are washed with test solutions of detergents in a miniature laboratory washer. The quantity of soil removed by this washing procedure is determined by measuring the reflectances of the new cloth, the soiled cloth, and the washed cloth, the results being expressed as per cent soil removal. Because of variations in degree and type of soiling, in water and in cloth, and other unknown variables, the absolute value of per cent soil removal is not an accurate measure of detergent effectiveness and cannot be used to compare various detergents. Therefore, the art has developed the method of using relative detergency ratings for comparing detergent effectiveness.

The relative detergency ratings are obtained by comparing and correlating the per cent soil removal results from solutions containing the detergents being tested with the results from two defined standard solutions. The two standard solutions are selected to represent a detergent system exhibiting relatively high deterative characteristics and a system exhibiting relatively low deterative characteristics. The systems are assigned detergency ratings of 6.3 and 2.2, respectively.

By washing portions of each soiled cloth with the standardized solutions, as well as with two test solutions, the results can be accurately correlated. The two standard solutions are identical in formulation but are employed at different hardnesses.

Standard Solution Formulation Ingredient	Weight %
Linear Alkylbenzene sulfonate (LAS)	25
Sodium triphosphate	40
Water	8
Sodium sulfate	19
Sodium silicate	7
Carboxymethylcellulose	1

The standard exhibiting high deterative characteristics (Control B) is prepared by dissolving the above formulation (1.0 g.) in 1 liter of 50 ppm hard water (calculated as two-thirds calcium carbonate and one-third magnesium carbonate). The low deterative standard (Control A) contained the formulation (1.0 g.) dissolved in one liter of 180 ppm water (same basis).

A miniature laboratory washer is so constructed that four different solutions can be used to wash different parts of the same swatch. This arrangement ensures that all four solutions are working on identical soil (natural facial soil). Relative detergency ratings (RDRs) are calculated from soil removals (SRs) according to the equation:

$$RDR = 2.2 + 4.1 \frac{\%SR_{\text{Test}} - \%SR_{\text{Control A}}}{\%SR_{\text{Control B}} - \%SR_{\text{Control A}}}$$

Detergency results obtained on a variety of the subject compounds are given in the following table. Each value shown is the average of at least four tests. For comparison, the detergency rating is given for a linear alkylbenzene sulfonate (LAS) (having from 11 to 14 carbon straight chain alkyl groups) both with and without phosphate builder.

Each formulation tested comprised 25 weight percent of the test material along with 1 percent carboxymethylcellulose, 7 percent sodium silicate, 8 percent water, and 59 percent sodium sulfate. The LAS comparison formulations were prepared in the same way except that in Test 2 40 percent of the sodium sulfate was replaced by an equal amount of sodium tripolyphosphate and only 20 percent of LAS was used. The formulations were tested at several concentrations in water ranging from 0.1 to 0.2 weight percent. These concentrations were chosen in order to bracket the 0.15 percent concentration typical of household use. The test results were obtained at a pH of 7, except for the two LAS examples, which were run at a pH of 9 (without phosphate) and 10 (with phosphate).

TABLE

Detergent Effectiveness of Linear Alkylphenol Sulfate-Sulfonates

Test No.	Compounds Tested	Relative Detergency Ratings (at indicated formulation concentrations)			
		50 ppm H ₂ O	180 ppm H ₂ O	0.10	0.15
1	Linear Alkylbenzene Sulfonate (11-14 carbon atoms in the alkyl chain) (LAS)	2.2	3.2	4.1	1.4
2	LAS (20%)/Sodium Tripolyphosphate (40%)	5.3	5.7	6.0	3.7
3	Octadecylphenol Sulfate-Sulfonate	4.9	5.3	5.6	4.4
4	Hexadecylphenol Sulfate-Sulfonate	3.3	-	4.8	3.9
5	Tetradecylphenol Sulfate-Sulfonate	3.6	-	-	2.4
6	Eicosylphenol Sulfate-Sulfonate	4.9	5.7	5.9	4.7
7	Docosylphenol Sulfate-Sulfonate	5.0	-	5.4	4.2

These data show that the alkylphenol sulfate-sulfonates of this invention are greatly superior to phosphate-free LAS and are substantially equivalent to phosphate-built LAS in detergency. More particularly, it may be noted that the compounds are very effective non-phosphate detergents and are particularly effective in hard water.

It will be understood that the effective compositions of this invention include those materials which comprise a mixture of the alkylphenol sulfate-sulfonates in which the alkyl groups vary in their carbon chain length between 16 and 24. Thus in most instances a single species in this respect will not be practical commercially and generally most effective compositions will comprise mixtures wherein at least 10 and preferably at

least 15 percent by weight of at least two species of the alkylphenol sulfate-sulfonates are present in which R is an alkyl radical of 16, 17, 18, 19, 20, 21, 22, 23 or 24 carbon atoms. The preferred range of carbon atoms in the mixtures will be from about 18 to 22 and most preferably from about 18 to 20 carbon atoms.

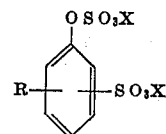
The alkylphenol sulfate-sulfonates may be employed in combination with other detergent active materials. They are particularly effective with other dianionic materials, examples of which include linear alkyl and alkenyl disulfates and disulfonates. A particularly useful class of materials for use in detergent active combinations is that of linear 2-alkenyl or linear 2-alkyl 1,4-butane diol disulfates in which the alkenyl or alkyl groups contain from 15 to 20 carbon atoms. Another particularly effective class of materials are the alkylphenol disulfonates described in our previously mentioned copending patent application.

In employing the detergent active materials of this invention in detergent compositions, they may be formulated with additional compatible ingredients being optionally incorporated to enhance the detergent properties. Such materials may include but are not limited to anticorrosion, antiredeposition, bleaching and sequestering agents, and certain organic and inorganic alkali metal and alkaline earth metal salts such as inorganic sulfates, carbonates, or borates. Also nonphosphate builders may be included in the composition. Examples of these builders include the sodium salts of nitrilotriacetic acid, ethylene diamine tetraacetic acid, and ethylene-maleic acid copolymers, etc. Also small quantities of phosphate builders may be included in the compositions, although, of course, they are not necessary for effective detergency.

While the character of this invention has been described in detail with numerous examples, this has been done by way of illustration only and without limitation of the invention. It will be apparent to those skilled in the art that modifications and variations of the illustrative examples may be made in the practice of the invention within the scope of the following claims.

We claim:

1. A compound of the formula:



in which R is a linear alkyl radical of 16 to 24 carbon atoms and X is hydrogen or a cation selected from the group consisting of alkali metal, alkaline earth metal, ammonium, diethanolammonium and triethanolammonium cations.

2. The compound of claim 1 in which R is an alkyl radical of 18 to 20 carbon atoms.

3. The compound of claim 1 in which X is an alkali metal cation.

4. The compound of claim 3 in which X is Na.

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