

[54] METHOD OF WASHING FABRICS USING
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3,766,254.

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[51] Int. Cl. C11d 1/22

[58] Field of Search 252/539, 558; 260/505,
260/512

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[57]

ABSTRACT

Method of washing fabrics by contacting said fabrics with an aqueous solution containing as the detergent active material from about 0.01 to 0.10 percent by weight of polysulfonated alkylphenols produced by sulfonating C16–22 monoalkylphenols of not more than 20 mol percent para alkyl content with a sulfonating agent to incorporate an average of at least 1.5 sulfonic acid groups into molecule and neutralizing the product.

3 Claims, No Drawings

METHOD OF WASHING FABRICS USING POLYSULFONATED ALKYLPHENOLS

CROSS-REFERENCE TO RELATED APPLICATION

This application is a division of copending application Ser. No. 34,886, filed May 5, 1970 now U.S. Pat. No. 3,766,254.

BACKGROUND OF THE INVENTION

This invention is concerned with certain alkylphenol disulfonates which are effective as heavy duty 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 also sufficiently biodegradable that their use results in contributing neither foam producers nor phosphates 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.

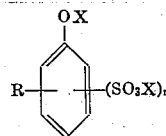
The formulation of liquid heavy duty detergent compositions achieves many desirable results. They are easy to package and measure, and their use opens the possibility of automatic dispensing in washing machines. However, in the past it has been impracticable to formulate heavy duty detergents in liquid 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.

DESCRIPTION OF THE PRIOR ART

U.S. Pat. No. 2,249,757 discloses as surface active agents a broad class of sulfonated, branched and linear, alkylphenols. The proposed sulfonated alkylphenols include both mono and disulfonates. The patent claims compounds of a general formula including alkylphenol disulfonates having from 12 to 18 carbon atoms in the alkyl group. By way of example, the alkylphenols are prepared by reacting phenol and olefins of 14 to 15 carbon atoms obtained by caustic soda treatment of monochlorinated petroleum distillate. The olefin and phenol are reacted in the presence of zinc chloride. Such alkylphenols have a high content of para alkylphenol isomers, usually about 35 to 40 percent. The alkylphenol is then sulfonated with sulfuric acid, oleum, or chlorosulfonic acid. The disclosures of this patent precede both the nonbiodegradability problem and the more recent phosphate water pollution problem.

SUMMARY OF THE INVENTION

It has now been found that effective heavy-duty detergent compositions may be formulated without the necessity of phosphate builders by employing as the detergent active materials polysulfonated alkylphenols of the formula:



in which R is linear alkyl of 16 to 22 carbon atoms, X is H or a water-soluble salt-forming cation, n is at least 1.5, and not more than 25 mol percent of the sulfonated alkylphenols have R attached on the aromatic nucleus in a position para to -OX.

It has been discovered that the materials which degrade the detergent performance of the compounds in these phosphate-free formulations are those compounds in which the alkyl group R is substituted para to the hydroxyl group, these compounds possessing minimal detergent activity. The explanation of this phenomenon is unclear.

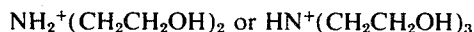
Thus the effective materials are primarily either ortho or meta alkyl substituted. Preferably, the major portion of the alkyl groups will be substituted ortho to

the phenolic hydroxyl group on the ring. The meta alkyl materials are effective as phosphate-free detergents; however, the difficulty and consequent expense of making the high meta alkyl materials limits their use at this time in commercial formulations.

The compounds of this invention do not require the presence of a builder to achieve good 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 adjunctive inorganic additives 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 amino materials such as those of the following structure:



The alkali metal cations are preferred, and sodium ions are particularly preferred.

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

The compounds of the invention are preferably prepared by sulfonation of a suitable alkylphenol.

The alkylphenols which are suitable as precursors for the compounds of this invention are prepared by methods which provide low para-content isomer products. Such methods include thermal alkylation of phenol with an alpha olefin, thermal alkylation of phenol with an internal monoolefin, and those catalytic methods which result in production of a high ortho-content alkylphenol. Examples of alkylation catalysts which have been employed to produce high ortho-content alkylphenols include various metal phenoxides, particularly those of aluminum and magnesium; hydrogen fluoride-treated aluminum silicate; alkyl sulfonic acids; dimethyl sulfate; benzene sulfonic acid; naphthalene sulfonic acid; transitional alumina; and gallium and indium oxides.

Employing any of these alkylation techniques, it is, as previously noted, important that the alkylphenol mixture must not have a para alkylphenol content of more than 24 and preferably not more than 20 mol percent. This may be achieved by the noted thermal or catalytic methods with the direct product of the process having no more than the prescribed content or it may be achieved by conventional acid catalyzed alkylation followed by distillation or by separation of the components by various extractive techniques such as water solubilization, etc. This separation may be accomplished either with the alkylphenol mixtures or with the sulfonated products.

The alkyl groups represented by R are generally derived from either 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 either at the 1 or 2 and 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 alkyl chain-nucleus attachment will be random.

The sulfonation of the alkylphenols to produce the compounds of this invention may be accomplished by any suitable method. Thus, materials which may be reacted with the alkylphenol include chlorosulfonic acid, oleum, or sulfuric acid. It is only important that enough sulfonating agent be employed to incorporate an average of at least 1.5, preferably 1.6 atoms of sulfur (in the form of sulfonate groups) into each molecule. Each sulfonate group incorporated into these alkylphenols can be measured as a surface active site by titration. This number is referred to as active group incorporation (AGI). Sulfonation with oleum is preferred.

The sulfonation is usually accomplished with a ratio of at least 2 and preferably from 4 to 10 mols of available SO_3 from the sulfonating agent to one mol of the alkylphenol. The use of a solvent is ordinarily not required in carrying out the sulfonation. The alkylphenol and the sulfonating agent are simply mixed and the reaction is allowed to proceed, maintaining the temperature of the reaction mixture within the desired limits. The time required for disulfonation will be dependent upon the reaction temperature, the sulfonating agent, the ratio of sulfonating agent to alkylphenol, and the total quantity of reactants present. The reaction is usually effected at a temperature in the range of 0° to 150°C , preferably 25° to 100°C .

After sulfonation, the product may be neutralized with a water-soluble, salt-forming cationic neutralizing agent, usually a metal oxide or hydroxide, and preferably an alkaline earth metal or alkali metal hydroxide.

The alkali metal hydroxides are preferred, and most preferred is sodium hydroxide.

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 ortho Heptadecylphenol Disulfonate

To a small glass sulfonator (100 ml.) equipped with a mechanical stirrer was added 16.8 g. (0.05 mol) of ortho heptadecylphenol (prepared by thermal alkylation of phenol with 1-heptadecene). To a small dropping funnel was added 25.74 g. of 21.5 percent fuming sulfuric acid. The acid was added to the alkylphenol over a period of 15 minutes. The sulfonator was then heated to 75°C in an oil bath, and stirring was continued for a period of 25 minutes. The product was then neutralized to pH 7 with 2.5 N NaOH in an ice bath. Analysis by Hyamine titration* (*See method of House and Darragh, Anal. Chem., 26, 1492 (1954).) and dilute acid hydrolysis indicated that the product was approximately a 50/50 mixture of heptadecylphenol disulfonate and sodium sulfate. The yield was 91 percent based upon alkylphenol.

Example 2

Preparation of Heneicosylphenol Disulfonate

Following the general procedure of Example 1, 25.74 g. of 21.5 percent fuming sulfuric acid was reached with 19.2 g. of heneicosylphenol (prepared by an acid-clay catalyzed alkylation of phenol with a mixture of heneicosenes and having a 62/38 ortho/para isomer distribution). The product was analyzed as in Example 1 and showed a 91 percent yield of heneicosylphenol disulfate.

Following the general procedure of Example 1 a variety of materials were prepared employing as precursors alkylphenols in which the alkyl groups were linear and had aromatic nucleus attachment at all positions on the alkyl group and with varying proportions of ortho and para alkyl isomers. Mixtures of these materials were also prepared.

Example 3

Preparation of a Mixture of Octadecyl-, Nonadecyl-, and Eicosylphenol Disulfonates

A mixture of about equal amounts of octadecenes, nonadecenes, and eicosenes was prepared by isomerization of the corresponding mixture of 1-isomers. This mixture was employed to alkylate the phenol. The crude alkylphenol was distilled, and the fraction having a boiling range of 444° to 472°F at 5 mm/Hg was taken as the product. Analysis of this product showed it to contain over 96 percent ortho alkyl isomers.

A 360 g. portion of the distilled alkylphenol mixture was charged to an 800 ml. sulfonator equipped with a thermometer, dropping funnel, reflux condenser, and mechanical stirrer. While the material was being strongly agitated, 514 g. of 21.5 percent fuming sulfuric acid was added through the dropping funnel over a period of 36 minutes while the temperature was maintained at from 5° to 10°C. The temperature was then raised to 75°C for 30 minutes. The reaction was then quenched by dropping the product onto ice, cooling it to a temperature of 0°-5°C. The product was then neutralized with 490 ml. of 50 percent NaOH. The final volume was adjusted to 2700 ml. Analysis by the previ-

ously described method showed a 95 percent yield of alkylphenol disulfonate.

Example 4

5 Drying of Alkylphenol Disulfonate

A 500 ml. portion of the product of Example 3 was dried in a conventional small-scale drum drier in which the drums were operated under a pressure of 30 psi of steam. In this manner there was recovered about 150 g. of dry particulate solid which analyzed 52.5 percent of the mixture alkylphenol disulfonate, 44.0 percent sodium sulfate, with the balance being water.

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 disulfonate materials of the instant invention and an inert material, e.g., water, sodium sulfate, sodium carbonate, etc. Such mixtures may contain any amount of disulfonate in excess of about 10 percent, preferably 15 percent or more. One useful composition comprises from 30 to 50 percent disulfonate 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 disulfonate 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

detergent characteristics. The systems are assigned detergent 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 detergent characteristics (Control B) is prepared by dissolving the above formulation (1.0 g.) in one liter of 50 ppm hard water (calculated as 2/3 calcium carbonate and 1/3 magnesium carbonate). The low detergent 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 detergent ratings (RDRs) are calculated from soil removals (SRs) according to the equation:

$$RDR = 2.2 + 4.1 \left[\frac{(\% SR_{Test} - \% SR_{Control A})}{(\% SR_{Control B} - \% SR_{Control A})} \right]$$

A further refinement in the determination of relative detergent ratings was developed. In this method, instead of employing two standard formulations, one of the formulations used in preparing the four test solutions had a known relative detergent rating (RDR) which had been determined by the above formula. Relative detergent ratings of the other three formulations were then determined by comparing the percent soil removal (SR) of these formulations with that of the known formulation.

Table I presents the detergent data on a group of representative alkylphenol disulfonates, all having at least 95 percent ortho alkyl attachment. For comparison, the detergent rating is given for a linear alkylbenzene sulfonate (LAS) (having from 11 to 14 carbon atom straight chain alkyl groups) both with and without a 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 Example 2 40 percent of sodium triphosphate, and only 20 percent of LAS was used. 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 I

Effect of Molecular Weight on the Detergency of Alkylphenol Disulfonates

Test	Relative Detergency Rating (at 0.15% concentration)
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No.	Compounds Tested	50 ppm water	180 ppm water
1	Linear alkylbenzene sulfonate (LAS)	3.2	1.4
2	LAS (20%) sodium triphosphate (40%)	5.7	3.7
3	Tetradecylphenol disulfonate	3.6	—
4	Hexadecylphenol disulfonate	5.9	4.4
5	Heptadecylphenol disulfonate	5.7	4.7
6	Octadecylphenol disulfonate	5.4	4.2
7	Eicosylphenol disulfonate	6.3	4.7
8	A blend of approximately equal amounts of octadecyl-, nonadecyl-, and eicosylphenol disulfonates	6.0	4.3
9	A blend of approximately equal amounts of hexadecyl-, heptadecyl-, octadecyl-, nonadecyl-, and eicosylphenol disulfonates	5.4	4.5

All of the above compounds were prepared by disulfonating an alkylphenol in which the aromatic nucleus is attached predominately to the number two carbon of the alkyl group (end chain attachment). Essentially the same detergent results are obtained from alkylphenol disulfonates in which the aromatic nucleus is not attached predominately to any one carbon atom of the alkyl group, but is at all possible positions (random attachment). For example, a blend of approximately equal amounts of octadecyl-, nonadecyl-, and eicosylphenol disulfonates having random attachment, gave relative detergent ratings of 5.6 and 4.2 in 50 ppm and 180 ppm water, respectively (compare with test 8 above).

These examples show that the alkylphenol disulfonates having an alkyl group chain length in excess of 14 carbon atoms are extremely efficient detergents. The alkylphenol disulfonates of this invention remove soil as effectively as the presently commercial LAS-phosphate combinations do in soft water, and they are more effective in hard water.

In order to show the effect of ring positional isomers, two blends of octadecyl-, nonadecyl-, and eicosylphenol disulfonates having random attachment were prepared. One blend had a para isomer content of 4 percent and the other 40 percent. These two blends were then further combined to give a series of blends in which the para isomer content varied between these two values. Table II shows the detergent effectiveness of these various blends.

TABLE II

Effect of para Isomer Content on the Detergency of Alkylphenol Disulfonates

Test No.	Isomer Distribution of the Alkylphenol Disulfonate Test Compound ¹		Relative Detergency Rating (at 0.15% concentration) 180 ppm water
	% ortho	% para	
10	96	94	4.2
11	90	10	3.6
12	80	20	2.6
13	70	30	1.9
14	60	40	0.0

¹The test compound comprised a blend of approximately equal amounts of octadecyl-, nonadecyl-, and eicosylphenol disulfonates having random attachment.

In addition to the above, essentially 100 percent para-octadecylphenol disulfonates were synthesized and found to have no soil removal properties. The detergent depressing effect of the para isomer was also

observed in soft water, but to a somewhat lesser degree.

The above tests show that the para-alkylphenol disulfonate has little, if any, detergency. In mixtures with the highly effective ortho-alkylphenol disulfonate, the para isomer compound depresses the soil removal properties to such an extent that a 70% ortho - 30% para mixture is only about as good as linear alkylbenzene sulfonate without phosphate (see Table I, test 1). This is unsatisfactory performance and is not acceptable for a heavy duty phosphate-free detergent.

Alkylphenol monosulfonates are known detergents and constitute the main by-product occurring in the preparation of alkylphenol disulfonates. The amount of monosulfonate in the product is determined by analyzing for the average number of surface active groups incorporated (AGI) into the alkylphenol molecule. Table III presents the detergency of several mixtures of mono- and di-sulfonated alkylphenols prepared from a blend of approximately equal amounts of octadecyl-, nonadecyl-, and eicosylphenols.

TABLE III

Effect of Alkylphenol Monosulfonate Content on the Detergency of Alkylphenol Disulfonates

Test No.	A.G.I.	Sulfonate Mono-	Content Di-	Relative Detergency Rating (at 0.15% concentration)	
				50 ppm	180 ppm
15	1.87	13	87	5.6	4.2
16	1.59	41	59	4.8	2.9
17	0.98	100	0	3.1	1.5

These data show that the monosulfonated alkylphenol (Test 17) is about equivalent to linear alkylbenzene sulfonate without phosphate in both hard and soft water (see Table I, test 1). For satisfactory phosphate-free detergent performance, it is necessary that the amount of mono sulfonated alkylphenol be less than 50 percent, i.e., the AGI must be greater than 1.5.

It will be understood that the effective compositions of this invention include those materials which comprise a mixture of the sulfonated alkylphenols in which the alkyl groups vary in their carbon chain length between 16 and 24. Thus, in most instances, a single molecular weight species will not be as practical commercially as the mixtures, 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 sulfonated alkylphenols are present in which R is an alkyl radical of 16, 17, 18, 19, 20, 21, or 22 carbon atoms. The preferred range of carbon atoms will be from about 17 to 21 and most preferably from about 18 to 20 carbon atoms.

The alkylphenol disulfonates may be employed in combination with other detergent active materials.

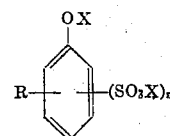
They are particularly effective with other dianionic materials, examples of which include linear alkyl and alkenyl disulfates and disulfonates. A particularly useful class of materials for use in detergent active combinations is that of linear 2-alkenyl or linear 2-alkyl 1,4-butane diol disulfates in which the alkenyl or alkyl groups contain from 15 to 20 carbon atoms.

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 are 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 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. In a method of washing fabric by contacting said fabric with an aqueous solution containing a detergent amount of detergent active material under conditions of time and temperature to effect substantial soil removal from the fabric, the improvement which comprises carrying out the washing at substantially neutral pH and in the absence of phosphate builders and employing as detergent active material from about 0.01 percent to about 0.10 percent by weight of polysulfonated alkylphenols of the formula



in which R is linear alkyl of 16 to 22 carbon atoms, X is H or an alkali metal, alkaline earth metal, ammonium, or a tertiary lower hydroxy alkyl amino cation, n is an average of 1.5 to 2, and not more than 20 mol percent of the sulfonated alkylphenols have R attached on the aromatic nucleus in a position para to -OX.

2. The method of claim 1 in which R is linear alkyl of 17 to 21 carbon atoms.

3. The method of claim 1 in which n is at least 1.6.

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