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Anderson

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[54] **DETERGENT COMPOSITION WITH
DISULFONATED CATECHOL AS
DETERGENT BUILDER**

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252/540

[51] Int. Cl..... **C11d 1/12**

[58] Field of Search 252/550, 551, 554, 555,
252/558, 559, 539, 540

[56] **References Cited**

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[57] **ABSTRACT**

Phosphate-free detergent compositions comprise an organic water soluble anionic, nonionic, ampholytic, or zwitterionic detergent-active material in combination with from one-eighth to 8 parts of catechol disulfonate.

11 Claims, No Drawings

DETERGENT COMPOSITION WITH DISULFONATED CATECHOL AS DETERGENT BUILDER

BACKGROUND OF THE INVENTION

Field of the Invention

This invention is concerned with novel detergent compositions containing builder materials which provide good heavy-duty detergency in combination with conventional detergent actives and, more particularly, in combination with recently developed dianionic detergent actives.

The function of a "builder" in detergent compositions has not been in the past clearly defined except in terms of the enhancement of detergent activity of soaps and detergents when builders are employed in combination. It, however, is known that the presence of builders particularly enhances detergency when the detergent compositions are employed in hard water, so it has been conjectured that some large amount of the effectiveness of the builder results from the ability to tie up the so-called hardness ions in the water, i.e., calcium and magnesium ions. Builders have been therefore regularly employed in washing compositions designed for use in heavy-duty applications—that is, cleansing of washable fabrics, particularly cotton, in powered washing machines.

Increased concern over water pollution has caused a great demand for substitutes for the components of conventional heavy-duty detergent compositions. Thus branched chain alkylbenzene sulfonates, which were used for many years as the active components of most heavy-duty detergent compositions, have been replaced in the United States as well as many foreign countries with linear alkylbenzene sulfonates, which possess the advantage of being biodegradable and thus do not contribute to the foam situation which had begun to become serious in rivers, streams and lakes.

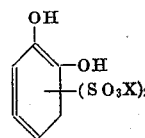
A more recent, and one believed by many to be a more significant problem, lies in the phenomenon of eutrophication, which has contributed to the destruction of water bodies. This phenomenon, which involves the greatly increased growth of algae in the water bodies, results in removal of dissolved oxygen from the water bodies resulting in eventual death of almost all present living organisms. It is believed by many, and increasing evidence appears to indicate, that the presence of phosphates, largely derived from heavy-duty detergents, accounts for eutrophication.

Attempts to eliminate the phosphate builders have been made using one of two approaches. First, efforts have been made to provide new detergent active materials which do not require the presence of any builder for heavy-duty washing, and secondly, efforts have been made to simply replace the phosphate builders with builder materials which lack the nutrient potential of phosphate. The second approach has resulted in the introduction of various materials as builders, none of which has been completely successful in replacing phosphates because of other problems encountered. For example, the salts of nitrogen-containing polycarboxylic acids have been proposed, the most widely used—the polysodium salt of nitrilotriacetic acid—encountering extreme difficulty from findings that this compound, when in the presence of certain heavy metals, possesses possibly dangerous teratogenic activity. Other materials, such as various metal carbonates and

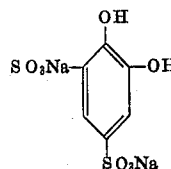
silicates, etc., have been used but have been found to leave substantial deposits on clothes and in many cases are dangerously corrosive to human skin. Polyelectrolyte builders such as copolymers of ethylene and maleic acid are believed to be incapable of bacterial degradation and thus possess some disadvantages in use.

SUMMARY OF THE INVENTION

Heavy-duty detergent compositions are provided which comprise (1) an organic water-soluble anionic, nonionic, ampholytic or zwitterionic detergent-active material and (2) as a nonpolluting builder in an amount sufficient to enhance the detergency of the composition, a compound of the formula:



in which X is a water-soluble, salt-forming cation. The preferred materials have the formula



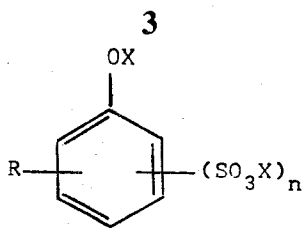
This compound which can be named 4,5-dihydroxy-m-benzene-1,3-di-sulfonic acid disodium salt has been used as a colorimetric agent for various metals.

The formulations may be employed in which the builder is used in combination with any conventional heavy-duty detergent active. These materials, of course, include anionic, ampholytic, zwitterionic, and nonionic materials.

The anionic materials which may be used include soaps, not strictly detergents, which are the salts, usually the sodium, potassium, ammonium, etc., salts of higher fatty acids. Another representative class of suitable anionic detergents are the olefin sulfonates which are produced by the sulfonation of olefins generally of about 10 to 24 carbon atoms with sulfur trioxide followed by hydrolysis and neutralization of the reaction mixture. Another class of suitable anionic materials are those produced by the hydrogenation of the olefin sulfonates to the extent that at least 50% of the ethylenic double bonds in the mixture are hydrogenated.

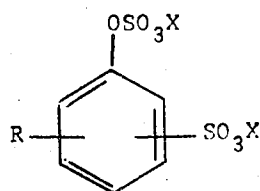
Another particularly valuable class of materials are the polysulfonated alkylphenols of the formula disclosed in U.S. Pat. application Ser. No. 34,886 filed May 5, 1970. These materials, which have good detergent activity in the absence of any builder, benefit particularly when used in combination with the builder materials of this application. The enhancement of multicycle detergency is of great significance and duplicates the conditions which are encountered in home use wherein the retention of brightness and cleanliness of clothes after repeated washings is highly desirable.

The particularly useful alkylphenols are polysulfonated materials 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 polysulfonated alkylphenols have R attached on the aromatic nucleus in a position para to $-OX$. The preferred materials contain from 17 to 20 carbon atoms. Other useful polysulfonated alkylphenols comprise materials of similar structure wherein X on the nuclear oxygen is alkyl of one to six carbon atoms and there is no limitation on the para alkyl content.

Another class of useful anionic detergent-active materials comprise alkylphenol sulfate sulfonates of the formula



in which R is a linear alkyl radical of 16 to 24 carbon atoms and X is hydrogen or a water-soluble salt-forming cation.

Another useful class of materials is that described in U.S. Pat. application Ser. No. 259,924. These materials comprise sulfated glycol or polyglycol half esters of alkyl or alkenyl succinic acids, or water-soluble salts thereof, wherein the alkyl or alkenyl group contains from about 14 to about 22 carbon atoms, the glycol moiety of the ester contains from one to four units of two to four carbon atoms, and the sulfate group is terminally attached to the glycol or polyglycol chain.

Another representative group of anionic materials are the straight chain alkyl or alkenyl butanediol disulfates in which the alkyl groups contain from 10 to 24 carbon atoms. Other useful sulfuric esters include the sulfate derivatives of straight chain alcohols of from 10 to 24 carbon atoms.

Another useful class of anionic materials are the alkyl aryl sulfonates, particularly the straight chain materials, which are usually monosulfonates of alkylbenzene in which the alkyl chain contains from about 10 to 15 carbon atoms. These materials are known as linear alkylbenzene sulfonates and have in recent years accounted for the bulk of heavy-duty detergent materials. Also included are the corresponding alkyl aromatic hydrocarbons in which a polyethylene side chain has been introduced. These materials are prepared by reacting ethylene with a lower alkylated benzene such as toluene or cumene followed by sulfonation.

Examples of the nonionic materials include various ethoxylated or polyethoxy compounds which may be prepared by treating an alcohol, a phenol, or a carboxy acid with ethylene oxide. The most widely used of these materials are the condensation products of alkylphenol with ethylene oxide—for example, the product obtained by condensing from 6 to 20 or more moles of ethylene oxide with para tertiary alkylphenol. The corresponding polyethyleneoxy ethers of straight chain al-

cohols and mercaptans may be employed. Particularly useful materials are the polyethoxy derivatives of straight chain primary alcohols of 10 to 18 carbons in which about five to 30 ethyleneoxy groups are present.

5 The polyethoxy esters are exemplified by those compounds made by condensing ethylene oxide with oxidized paraffin wax. Other materials which have been oxyated to form nonionic surface-active esters include alkyl cyclohexene carboxylic acids, rosin acids, acids of various modified rosins, and long chain ethyl ethers of thioglycolic acid. In all of these cases it is possible to substitute propylene oxide and even higher alkylene oxides for the ethylene oxide although, in general, the ethylene oxide derivatives are preferred.

15 Another class of suitable nonionic surfactants are the polyhydroxy derivatives such as those produced by esterification of sugar alcohols such as sorbitol and mannitol. Similar materials may be prepared from the glucose derivatives including the fatty acid esters of hydroxypropyl glucoside.

Suitable zwitterionic detergent actives are derived from aliphatic quaternary ammonium compounds having straight or branched chain aliphatic radicals, at least one of which contains about eight to 20 carbon atoms and also contains an anionic hydrophilic group such as a sulfate or sulfonate group, etc.

The ampholytic surfactants which may be included in the composition are those materials which contain both acidic and basic functions in their structures. Examples of these materials include compounds having either carboxy or phosphoric esters as the acidic group and non-quaternary nitrogen as the basic group. Another example of a typical ampholytic detergent-active material is the water-soluble salt of dodecyl- β -alanine.

The concentration of surface-active material in the detergent formulations will generally be from about 10 to 30%, preferably 15 to 25% by weight. The ratio of the builder material to the detergent-active will generally be in the range of from about 8:1 to 1:8, preferably 5:1 to 1:5.

The formulations may be employed in dry form as either powdered or granulated materials or as liquid materials. The builder component of this invention is particularly suitable for use as builders in liquid formulations, as it is significantly more soluble than any of the other proposed or currently employed builders.

In addition to the detergent-active materials and builder of the composition there may be optionally present additional ingredients which enhance the detergent properties of the composition. Such materials may include but are not limited to anticorrosion, antiredeposition, bleaching, and sequestering agents, as well as various filler materials such as the inorganic alkali metal and alkaline earth metal salts such as the sulfates, carbonates, silicates or borates, etc. Typically, sodium sulfate will be present in the compositions because it is in many cases and particularly with sulfuric acid-derived anionic actives, a by-product of the detergent preparation.

The cations which may be employed with the anionic detergent active materials as well as those cations which are employed in conjunction with the builder material (as X in the formula) are, as previously noted, water-soluble salt-forming materials. Representative of these cations are those of the alkaline earth metals and the alkali metals and ammonium. The alkali metal cat-

ions are preferred, and, particularly preferred, is sodium.

The builder is prepared by sulfonating catechol with conventional sulfonating agents such as sulfuric acid, oleum, chlorosulfonic acid, etc., using a sufficient quantity of the sulfonating agent to ensure that approximately two sulfonic acid groups are substituted on the nucleus. Sulfonation is usually carried out at elevated temperatures, i.e., from about 20° to 150° C., preferably from about 50° to 100° C.

The effectiveness of the compositions of this invention is demonstrated in a miniature Terg-O-Tometer test. In this test, the effectiveness of the compositions is measured by their ability to remove natural sebum soil from cotton cloth. 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. The procedure employed is so designed that two standard solutions and two test formulations can be used to wash different parts of the same soiled swatch. This arrangement ensures that all formulations are working on identical soil.

The two standard solutions are identical in formulation, but are employed at different hardnesses.

Standard Solution Formulation	
Ingredient	Weight %
Linear alkylbenzene sulfonate (LAS)	20
Sodium triphosphate	40
Water	8
Sodium sulfate	24
Sodium silicate	7
Carboxymethylcellulose	1

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

Relative detergency (RD) values were calculated from soil removals (SR), according to the equation:

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

In a variation of the above-described test, a refinement in the determination of the relative detergency rating was developed. In this method, instead of employing two standard formulations, one of the formulations used in preparing one of the four test solutions had a known relative detergency rating (RDR) which had been determined by the above formula. Relative detergency 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 detergency data derived by the above-described test on detergent formulations containing a disodium linear alkylphenol disulfonate (LAPS) having an average 18 carbon atoms in the alkyl group. Tests were performed with the compound as the only active ingredient and further tests with different concentrations of the catechol disulfonate (CDS) which was the disodium salt of 4,5-dihydroxybenzene-1,3-disulfonate. Each formulation contained the indicated weight percent of each detergent and builder. Also in the formulation were 1% carboxymethylcellulose, 7% sodium silicate, 8% water, and sufficient sodium sulfate to total 100%. For comparison purposes, detergency data from linear alkylbenzene sulfonate (LAS) having from 11 to 14 carbon atom straight chain alkyl groups is provided both with and without a phosphate builder and with the CDS. The LAS formulation contained 25% by weight of the active material. The LAS-phosphate formulation contained 20 weight percent LAS and 40% of sodium triphosphate. These formulations were prepared in the same manner as the alkylphenol polysulfonate formulations. The pH at which the tests were run is indicated in the Table. Each test was performed at a pH of 10 and 12. The pH was adjusted with NaOH.

TABLE I

EFFECT OF CATECHOL DISULFONATE ON
DETERGENCY OF LAS AND LAPS
MODIFIED MINIATURE TERG-O-TOMETER TEST

Test No.	Compounds Tested	Wt. % in Composition	Relative Detergency Rating			
			50 ppm water (9.1% Concentration)		180 ppm water (0.15% Concentration)	
			pH10	pH12	pH10	pH12
1	LAS	25	3.9	6.4	1.6	4.0
2	LAS	20	6.4	5.9	5.8	6.0
	Sodium triphosphate (STP)	40				
3	LAS	25	5.0	5.8	2.6	5.5
	CDS	30				
4	LAPS	25	—	5.3	—	5.3
5	LAPS	35	—	5.3	—	5.7
	CDS	30				

These data show the effectiveness of the catechol disulfonate of this invention in increasing the detergency of various detergent-active materials. The effect is particularly significant at the higher pH, the LAS/CDS combination being only slightly inferior to the LAS/STP combination in hard water.

As significant as the improvement in detergency shown above is the effect observed after several soilings and washings of the same cloth. The multicycle test employed to determine this effect is as follows: The test equipment and basic procedure is the same as that described above in the Terg-O-Tometer test. However, rather than the results being expressed in terms of relative detergency, they are more conveniently expressed in percent reflectance. (Clean unsoiled cloth has a reflectance of 92.2%). In this test 16 sebum soiled swatches are washed with each subject detergent composition, they are dried and their reflectances measured. The cloth is then resoiled, rewashed, and the reflectance remeasured four additional times.

In the test a detergent formulation concentration of 0.10% was employed at 50 ppm hardness water and a concentration of 0.15% in 180 ppm hardness water. Formulations of the alkylphenol polysulfonate had the same composition as before. The alkylphenol polysulfonate was the same as previously tested (17 to 20 carbon atom alkyl groups) and was tested in the presence of 20% of the sodium salt of the catechol disulfonate. The results of the test may be found in the following Table II. The results are reported for the average of the fourth and fifth washings.

TABLE II

MULTICYCLE DETERGENCE TEST

Test No.	Compound Tested	Reflectance, Percent		pH
		Average of 4th an 5th Cycle		
		50 PPM Water 0.1% Conc.	180 PPM Water 0.15% Conc.	
6	LAS	79.6	—	9.5
7	LAS 20%, Polyphosphate 40%	85.3	80.0 ¹	10.0
8	LAS 20% CDS 20%	82.8	75.8	10.5
9	LAPS	84.0	81.8	9.5
10	LAPS 20% CDS 12%	84.7	81.4	9.5
11	LAPS 20% CDS 12%	84.6	82.4	10.5

¹Estimated from 77.4% at 0.10 and 83.3% at 0.18% Conc.

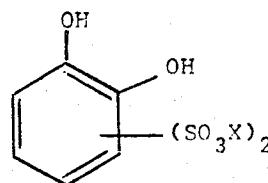
As may be seen from these data, the reflectance of the cloth after five washings is significantly higher in the case of the combination of the catechol disulfonate and LAS as compared to LAS alone. The data also shows that catechol disulfonate has building action with linear alkylphenol disulfonates. These data indicate that after numerous washings the brightness of fabrics will be higher in the case of formulations using the detergent-builder combination than with formula-

tions using the detergent active alone.

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.

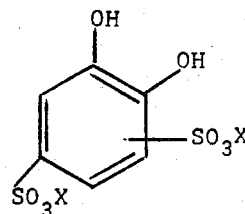
I claim:

1. A heavy-duty detergent composition comprising an organic water-soluble anionic, nonionic, ampholytic or zwitterionic detergent-active material and as a builder in an amount sufficient to enhance the detergency of the composition, a salt of a catechol disulfonate having the following formula:



in which X is a water-soluble salt-forming cation, the weight ratio of said detergent-active material to said builder being from about 8 to 1 to 1 to 8.

2. The composition of claim 1 in which the catechol disulfonate has the structure:



3. The composition of claim 1 in which the detergent-active material is anionic.

4. The composition of claim 3 in which the detergent-active material is a linear alkylphenol polysulfonate.

5. The composition of claim 4 in which the linear alkylphenol polysulfonate has from 16 to 24 carbons in the alkyl group and not more than 25 mol percent of the alkyl groups are attached in a position para to the phenolic hydroxyl groups.

6. The composition of claim 1 in which the detergent-active material is nonionic.

7. The composition of claim 6 in which the detergent-active material is an ethoxylated linear primary aliphatic alcohol.

8. The composition of claim 1 in which the detergent-active material is linear alkylbenzene sulfonate in which the alkyl groups contain from 10 to 15 carbon atoms.

9. The composition of claim 8 in which the alkyl groups of the linear alkylbenzene sulfonates contain from 11 to 14 carbon atoms.

10. The composition of claim 1 in which X is alkali metal.

11. The composition of claim 8 in which X is sodium.

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