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2,766,212

DETERGENTS

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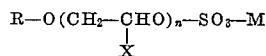
No Drawing. Application September 16, 1952,
Serial No. 309,953

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This invention relates to detergent compositions, and more particularly to detergent compositions of the polyoxyalkylene type, and processes for employing same.

It is an object of this invention to provide detergent compositions of the aforementioned type having improved foaming, foam stable and detergent properties. It is another object to provide a washing process employing such improved compositions. Other objects and advantages will appear as the description proceeds.

The aforementioned objects are obtained by the instant invention which involves the provision of a detergent composition comprising a water soluble salt of a polyvalent metal and a compound of the formula



in which R is a hydrocarbon radical containing at least 10 carbon atoms selected from the group consisting of alkyl radicals containing a plurality of branched chains, and alkylaryl radicals, X is selected from the group consisting of H and CH₃, M is a monovalent water solubilizing cation, and n is from 1 to 8.

The compositions of this invention have been found to have improved foaming and foam-stable properties in addition to increased rates of detergency and detergent efficiencies with respect to compositions containing the same polyoxyalkylene compounds but without the polyvalent metal salts. The mechanism whereby the improved results are obtained is not thoroughly understood, but it is apparent that some synergistic effect is involved. This should be apparent from the fact that the water soluble salts of polyvalent metals do not per se have any foaming or detergent properties. It is, therefore, indeed surprising that the addition of these water soluble salts of polyvalent metals to polyoxyalkylene compounds of the aforementioned type improves the foaming and detergent properties of such compounds to the remarkable extent described herein.

Polyoxyalkylene compounds of the above-mentioned type in which R is an alkyl radical containing a plurality of branched chains, and their process of manufacture, are disclosed and claimed in the copending application of Chiddix and Enyeart, Serial No. 263,002 filed December 22, 1951. In general, such compounds may be derived from branched chain primary aliphatic alcohols such as: 2,4,5,5,7-pentamethyl-1-octanol, 2,3,5,7-tetramethyl-1-nonanol, 3,5-diethyl-1-octanol, 2,4,7-trimethyl-1-nonanol, 2,4,5,6,8-pentamethyl-1-nonanol, 2,6,7-trimethyl-3-ethyl-1-octanol, 2,4,6,8-tetramethyl-1-nonanol, 2,3,5-trimethyl-4,7-diethyl-1-octanol, 2,3,5,6-tetramethyl-5,7-diethyl-1-octanol, 3,5-dimethyl-4,6-diethyl-1-heptanol, 3,4,5-trimethyl-4,6-diethyl-1-heptanol, 2-ethyl-3,5,7-trimethyl-1-octanol, 2-ethyl-4,6-dimethyl-1-octanol, 4-butyl-2-methyl-1-octanol, 2,5,7-tetramethyl-1-octanol, 3,5,7,7-tetramethyl-1-octanol, 2,5-diethyl-3,7-dimethyl-1-octanol, and 2,5,7,9-tetramethyl-1-decanol. Preferably alcohols may be used which are prepared by the catalytic reaction of an olefin such as tripropylene, tetrapropylene, penta-

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propylene, triisobutylene, tetraisobutylene, tributene, 4,6,8-trimethyl-1-nonene, 4,6,8-trimethyl-2-nonene, mixed propene-butene polymers, 5,7,7-trimethyl-1-octene, 3,5,7-trimethyl-1-heptene, and 2,4,6,6,8-pentamethyl-1-nonene, with carbon monoxide and hydrogen to form an aldehyde followed by catalytic reduction of this aldehyde to an alcohol. This two-stage process is known as the oxo process. Alcohols produced by the oxo process may be designated as oxo alcohols. Thus the oxo tridecyl alcohol mentioned hereinafter and in the claims is the C₁₃H₂₇OH polybranched chain primary aliphatic alcohol prepared from tetrapropylene by the oxo process.

The above-mentioned polyoxyalkylene compounds of the type in which R is an alkylaryl radical and their process of manufacture are disclosed in United States Patent 2,203,883. Such compounds may be derived from alkylated aromatic hydroxy compounds such as p-n-butylphenol, amycresol, diisobutylphenol, diamylphenol, isoheptylphenol, oleylphenol, isododecylphenol, isoctylresorcinol, nonylphenol, dinonylphenol, isoctylphenol, isoctyl-β-naphthol, isoheptylxylenol, n-octadecylphenol, and the like.

The above-mentioned alcohols and phenols are, in general, condensed under proper conditions with the required number of moles of ethylene oxide or propylene oxide, the condensation products thus obtained esterified with the requisite acids or acid derivatives, and the resulting esters neutralized to produce the monovalent water soluble salts thereof. General methods for carrying out the oxyalkylation reaction, the esterification and the salt formation in producing the polyoxyalkylene compounds employed in this invention are illustrated in United States Patents 1,970,578, 2,174,761 and 2,167,326.

The invention is particularly effective when employing the ammonium, sodium, potassium, alkylammonium or hydroxyalkylammonium, salts of the sulfuric acid esters of polyoxyalkylene compounds of the above-mentioned type containing from about 1 to 8, and preferably 1 to 6 polyoxyalkylene groups. Compounds containing 2-4 polyoxyalkylene groups are particularly preferred. Outstanding results are obtained when the compound is derived from oxotridecyl alcohol and ethylene oxide.

The water soluble salts of polyvalent metals which may be employed are, for example, the chlorides, sulphates, nitrates, bromides and acetates of magnesium, calcium, aluminum and iron or mixtures thereof. In some cases, it is preferable to use the hydrates of the aforementioned salts. Because of the required water solubility and other characteristics, the magnesium and calcium chlorides are preferred. These salts or mixtures thereof are employed in proportions of about 5 to 50% and preferably from about 10 to 45% by weight of the polyoxyalkylene compound.

When employed for detergent purposes, relatively small amounts of the composition of this invention are required to be dissolved in aqueous solution. Thus a solution containing .05% of the active polyoxyalkylene compound is sufficient to provide improved detergent and foam producing properties, although larger or smaller amounts may be employed when desired. The optimum amount in any particular instance will, of course, be readily determinable by a worker skilled in the art. Concentrates may be prepared for market in liquid or powdered form, or the like. The outstanding properties of the compositions of this invention are especially noticeable when employed in deionized, distilled or very soft water.

The examples set forth in the tables hereinafter are illustrative of the instant invention and are not to be regarded as limitative.

In Table 1 the hand dishwashing test consists essentially of washing dishes of 9" diameter, spread with

3 g. of a melted mixture of 80 parts Crisco, 20 parts ordinary bread flour, and 0.5 parts Oildag (graphite in oil). The number of dishes washed before the foam disappears is considered to be the end point for this test. The time required to wash 8 dishes is also an important criterion of effectiveness in this test.

The foam stability test of Table 2 is carried out by preparing a detergent solution in a jar and then adding clean water through a funnel into the solution and measuring the foam height at definite time intervals.

The examples of compositions which do not contain polyvalent metal salts are included in the tables merely for comparative purposes to illustrate the improvements attained by the instant invention.

TABLE 1
Hand dishwashing test

Example	Product (0.05% active material in distilled water)	No. of Soiled Dishes To Break Foam	Time to Wash 8 Dishes (Min.)
1.....	Iso-octylphenol+4 moles E. O. (sulfate, Na^+ salt).	6	5.7.
2.....	90% Iso-octylphenol+4 moles E. O. (sulfate, Na^+ salt), 6% CaCl_2 , 4% MgCl_2 .	10	4.0.
3.....	70% Iso-octylphenol+4 moles E. O. (sulfate, Na^+ salt), 18% CaCl_2 , 12% MgCl_2 .	18	
4.....	Nonylphenol+4 moles E. O. (sulfate, NH^+ salt).	5	8'+*
5.....	90% Nonylphenol+4 moles E. O. (sulfate, NH^+ salt), 6% CaCl_2 , 4% MgCl_2 .	18	3.4.
6.....	80% Nonylphenol+4 moles E. O. (sulfate, NH^+ salt), 20% MgCl_2 , 6 H_2O .	18	
7.....	70% Nonylphenol+4 moles E. O. (sulfate, NH^+ salt), 18% CaCl_2 , 12% MgCl_2 .	18	
8.....	Oxo tridecyl alc.+2 moles E. O. (sulfate, NH^+ salt).	1	6'+ for 5 dishes**.
9.....	90% Oxo tridecyl alc.+2 moles E. O. (sulfate, NH^+ salt), 6% CaCl_2 , 4% MgCl_2 .	24	4.0.
10.....	70% Oxo tridecyl alc.+2 moles E. O. (sulfate, NH^+ salt), 18% CaCl_2 , 12% MgCl_2 .	34	
11.....	80% oxotridecyl alc.+2 moles E. O. (sulfate, NH^+ salt), 20% MgCl_2 , 6 H_2O .	25	
12.....	70% Nonylphenol+4 Pr. O. (sulfate, NH^+ salt).	3	
13.....	70% Nonylphenol+4 Pr. O. (sulfate, NH^+ salt), 18% CaCl_2 , 12% MgCl_2 .	6	

*8th dish not clean.

**5th dish not clean.

E. O.=ethylene oxide.

Pr. O.=propylene oxide.

TABLE 2
Foam stability test

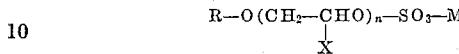
Product (0.05% active material in distilled water)	Ht. of Foam, Cm. at the end of—		
	0 Min.	2 Min.	5 Min.
14..... Oxo tridecyl alc. + 2 moles E. O. (sulfate, NH^+ salt)	10.5	4.0	2.0
15..... 80% Oxo tridecyl alc. + 2 moles E. O. (sulfate, NH^+ salt) plus 20% of:			
16..... Calcium chloride	11.5	9.5	9.0
17..... Magnesium sulfate	11.5	8.5	8.0
18..... Calcium acetate	11.5	10.0	9.5
19..... Aluminum sulfate	12.0	10.0	9.0
20..... Ferrous sulfate	13.0	10.0	7.5
21..... Sodium sulfate	10.5	4.0	2.0
22..... Sodium chloride	10.0	4.0	2.0
23..... Sodium tripolyphosphate	12.0	5.0	2.0
24..... Lauryl ethanolamide	12.5	3.0	2.0
25..... Nonylphenol + 4 moles E. O. (sulfate, NH^+ salt)	11.0	6.5	4.0
..... 90% Nonylphenol + 4 moles E. O. (sulfate, NH^+ salt), 6% CaCl_2 , 4% MgCl_2	10.0	3.5	7.5

The results summarized in Tables 1 and 2 clearly illustrate the unusual degree of improvement in foaming, foam stability and detergency obtained by the use of the instant invention.

Various modifications and variations of this invention will be obvious to a person skilled in the art and such variations and modifications are to be regarded as within the purview of this application and the spirit and scope of the appended claims.

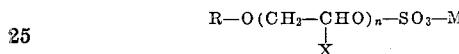
I claim:

1. A composition consisting essentially of a compound of the formula:



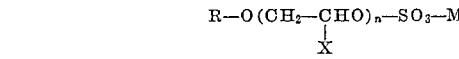
in which R is a hydrocarbon radical containing from about 10 to 24 carbon atoms selected from the group consisting of alkyl radicals containing a plurality of branched chains, and alkylaryl radicals, X is selected from the group consisting of H and CH_3 , M is a monovalent water-solubilizing cation, and n is from 1 to 8, and about 5 to 50% by weight thereof of a water soluble salt of a polyvalent metal wherein said metal is selected from the group consisting of magnesium, calcium, iron and aluminum.

2. A composition consisting essentially of a compound of the formula:



in which R is a hydrocarbon radical containing from about 10 to 24 carbon atoms selected from the group consisting of alkyl radicals containing a plurality of branched chains, and alkylaryl radicals, X is selected from the group consisting of H and CH_3 , M is a monovalent water-solubilizing cation, and n is from 1 to 8, and about 5 to 50% by weight thereof of magnesium chloride.

3. A composition consisting essentially of a compound of the formula:



40 in which R is a hydrocarbon radical containing from about 10 to 24 carbon atoms selected from the group consisting of alkyl radicals containing a plurality of branched chains, and alkylaryl radicals, X is selected from the group consisting of H and CH_3 , M is a monovalent water-solubilizing cation, and n is from 1 to 8, and about 5 to 50% by weight thereof of a mixture of magnesium chloride and calcium chloride.

4. A composition consisting essentially of about 80% by weight of the ammonium salt of the sulfuric acid ester of the condensation product of one mole of oxotridecyl alcohol with two moles of ethylene oxide and about 20% by weight of magnesium chloride.

5. A composition consisting essentially of about 70% by weight of the ammonium salt of the sulfuric acid ester of the condensation product of one mole of oxotridecyl alcohol with two moles of ethylene oxide, about 12% by weight of magnesium chloride and about 18% by weight of calcium chloride.

6. A composition consisting essentially of about 70% by weight of the sodium salt of the sulfuric acid ester of the condensation product of one mole of isoocetylphenol with four moles of ethylene oxide, about 12% by weight of magnesium chloride and about 18% by weight of calcium chloride.

7. A composition consisting essentially of about 70% by weight of the ammonium salt of the sulfuric acid ester of the condensation product of one mole of nonylphenol with four moles of ethylene oxide, about 12% by weight of magnesium chloride and about 18% by weight of calcium chloride.

8. A composition consisting essentially of about 80% by weight of the ammonium salt of the sulfuric acid ester of the condensation product of one mole of nonylphenol with 4 moles of ethylene oxide, and about 20% by weight of magnesium chloride.

9. A composition consisting essentially of a monovalent water soluble salt of the sulfuric acid ester of a condensation product of about 1 to 8 moles of ethylene oxide with 1 mole of a primary aliphatic alcohol of about 10 to 20 carbon atoms containing a plurality of branched chains, and about 5 to 50% by weight thereof, of a water soluble salt of a polyvalent metal wherein said metal is selected from the group consisting of magnesium, calcium, iron and aluminum.

10. A composition consisting essentially of a monovalent water soluble salt of the sulfuric acid ester of a condensation product of about 1 to 8 moles of ethylene oxide with 1 mole of a primary aliphatic alcohol of about 10 to 20 carbon atoms containing a plurality of branched chains, and about 10 to 45% by weight thereof of magnesium chloride.

11. A composition consisting essentially of a monovalent water soluble salt of the sulfuric acid ester of a condensation product of about 1 to 8 moles of ethylene oxide with 1 mole of a phenol substituted by an alkyl group of at least four carbon atoms, and about 5 to 50% by weight thereof of a water soluble salt of a polyvalent metal wherein said metal is selected from the group consisting of magnesium, calcium, iron and aluminum.

12. A composition consisting essentially of a monovalent water soluble salt of the sulfuric acid ester of a condensation product of about 1 to 8 moles of ethylene oxide with 1 mole of a phenol substituted by an alkyl group of at least four carbon atoms, and about 5 to 50% by weight thereof of magnesium chloride.

13. A composition consisting essentially of a monovalent water soluble salt of the sulfuric acid ester of the condensation product of about 1 to 8 moles of ethylene oxide with 1 mole of isoctylphenol and about 5 to 50% by weight thereof of a water soluble salt of a polyvalent metal wherein said metal is selected from the group consisting of magnesium, calcium, iron and aluminum.

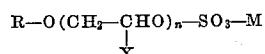
14. A composition consisting essentially of a monovalent water soluble salt of the sulfuric acid ester of the condensation product of about 1 to 8 moles of ethylene oxide with 1 mole of isoctylphenol and about 5 to 50% by weight thereof of magnesium chloride.

15. A composition consisting essentially of a monovalent water soluble salt of the sulfuric acid ester of the condensation product of about 1 to 8 moles of ethylene oxide with 1 mole of nonylphenol and about 5 to 50%

by weight thereof of a water soluble salt of a polyvalent metal wherein said metal is selected from the group consisting of magnesium, calcium, iron and aluminum.

16. A composition consisting essentially of a monovalent water soluble salt of the sulfuric acid ester of the condensation product of about 1 to 8 moles of ethylene oxide with 1 mole of nonylphenol and about 5 to 50% by weight thereof of magnesium chloride.

17. A washing process comprising contacting soiled objects with a composition consisting essentially of a compound of the formula:



15 in which R is a hydrocarbon radical containing from about 10 to 24 carbon atoms selected from the group consisting of alkyl radicals containing a plurality of branched chains, and alkylaryl radicals, X is selected from the group consisting of H and CH₃, M is a monovalent water-solubilizing cation, and n is from 1 to 8 and about 5 to 50% by weight thereof of a water-soluble salt of a polyvalent metal, said metal selected from the group consisting of magnesium, calcium, iron and aluminum.

18. A composition as defined in claim 1 wherein said salt is selected from the group consisting of the sulfates, chlorides, bromides, nitrates and acetates of said polyvalent metal.

19. A process as defined in claim 17 wherein said salt is selected from the group consisting of the sulfates, chlorides, bromides, nitrates and acetates of said polyvalent metal.

20. A composition as defined in claim 9 wherein said alcohol is oxotridecyl alcohol.

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