

1

2,744,874

DETERGENT COMPOSITIONS

Elmer A. Fike and William H. Seaton, Nitro, W. Va., assignors to Monsanto Chemical Company, St. Louis, Mo., a corporation of Delaware

No Drawing. Application May 24, 1952,
Serial No. 289,910

5 Claims. (Cl. 252—161)

The present invention relates to improved detergent compositions. The problems involved in the preparation and use of synthetic detergents include the difficulty of preparing concentrated aqueous solutions which do not separate solids in transit or after standing. In addition the dry particulate forms are often dusty and cause serious irritation and discomfort. The addition of various materials has been suggested for overcoming both of these defects but they have proved objectionable or unsatisfactory for one reason or another. The present invention is directed to an improved class of additives for synthetic organic detergent compositions.

The synthetic anionic detergents and surface active agents and more particularly those having a sulfur-acid group in the molecule are valued for the copious foaming of their aqueous solutions. On the other hand the nonionics, as for example poly alkylene ethers, are particularly useful where foaming is objectionable, as for example in automatic washers. The addition of small amounts of these nonionics to the former class has been proposed as a means for abating dustiness but as might be expected, this results in a serious diminution of foam.

In accordance with the present invention a class of poly alkylene ethers has been discovered which in combination with anionic detergents having a sulfur-acid group in the molecule provide compositions having very strong foaming properties. In addition the solubility in aqueous solution is considerably enhanced over solubility in the absence of the poly alkylene ether. Furthermore, the dustiness of the dry particulate composition is reduced by a remarkable degree.

The general formula of poly alkylene ethers employed is $RO-(R_1O)_nH$ where RO is the residue remaining after removal of hydrogen from a carbinol substituted heterocyclic radical containing a hetero atom from the group consisting of oxygen and sulfur, R_1 is an alkylene group and n is an integer. These poly ethers may be prepared by condensation of an alkylene oxide as for example ethylene oxide, propylene oxide, butylene oxide or glycidol, with the carbinol. Suitable examples of the latter include alpha-furyl methyl carbinol, 5-chloro-2-thenyl alcohol, 2-(alpha-hydroxy ethyl) diphenylene oxide, 2-hydroxy-5-methyl thiophene, 5-methyl-2-thenyl alcohol, furfuryl alcohol, tetrahydrofurfuryl alcohol, tetrahydro-thenyl alcohol, methyl thienyl carbinol and tetrahydropyran-2-methanol. While short chain alkyl groups may be present in the heterocyclic radical represented by R in the above general formula, it is believed that long chain substituents are undesirable since the evidence indicates that foaming may then be retarded in spite of the hetero atom. Methods for preparing hydroxyalkoxy tetrahydrofurfuryl ethers are described in Dickey U. S. Patent 2,196,748.

The substances alone or in combination which may be improved by the aforesaid class of reagents include salts of aromatic sulfonates and particularly the alkylated derivatives thereof, such as the water soluble salts of alkyl benzene sulfonates in which the alkyl group con-

2

tains 9 to 16 carbon atoms. The invention may be applied with advantage to particulate solid detergent compositions as described in Samaras and Harris Patents U. S. 2,298,650 and U. S. 2,298,651 and in Harris Patent U. S. 2,298,696. These compositions contain from 35 to 65 parts by weight of a water soluble salt of a mono alkyl aromatic hydrocarbon sulfonic acid the alkyl group of which contains 9 to 16 carbon atoms, and 65 to 35 parts by weight of sodium sulfate, part of which may be substituted by magnesium sulfate, sodium carbonate, tetra sodium pyrophosphate, borax and the like. Other detergents include salts of long chain alkyl primary and secondary sulfates, phosphates and borates, salts of diphenyl and alkylated diphenyl mono and poly sulfonic acids, salts of long chain alkyl esters and long chain alkyl amides of sulfoacetic acids, the salts of mono ethers and mono carboxylic acid esters of isethionic acid, the salts of mono carboxylic acid amides of taurine, the sodium salt of sulfated fatty alcohols obtained by hydrogenation of cocoanut oil and the sodium salt of a sulfonic acid produced by sulfonating a fraction of a liquid sulfur dioxide extract of petroleum with fuming sulfuric acid.

For abating dust the preferred method of application is to spray the poly ether onto the dry particles of the detergent while tumbling. The tumbling or mixing operation should not be prolonged beyond the point required for proper mixing since it has been observed that dustiness then increases after continued mixing. Of course for the purpose of preparing aqueous concentrates the poly ether is added to an aqueous solution. In this connection it is entirely feasible to add the poly ether to the aqueous solution before drying in order to produce a particulate detergent having little tendency to dust but when this procedure is used more of the additive is required. It has been found that roughly twice as much is required to obtain the same dust value exhibited by an identical composition in which the poly ether is applied to the dry particles. The mixing may be done at ordinary or elevated temperatures.

Since some of these poly ethers, particularly those containing the higher ratios of ether groups, are viscous syrups or even waxy solids, it is convenient either to melt them or apply them as solutions.

In general quantities in the range of 0.5 to 5.0% based on the dry weight of the detergent include the practical limits for dust abatement. A slight effect has been observed with amounts as low as 0.1% but the improvement is not considered significant. For application to a dry particulate form, 1.25% is about optimum.

The number of poly ether groups as represented by n in the general formula will in general fall within the range of 5 to 15 although compositions having poly ether groups outside this range can be used if desired. The effectiveness rises very rapidly as the number of ether groups is increased and then levels off so that little or no advantage is observed from increasing the number. Furthermore, compositions containing an excessive number of ether groups are more difficult to apply.

A convenient method for evaluating the dustiness of the detergent composition is to measure the light transmitted through the dust cloud raised by the falling detergent composition. The dust value which is reported as microampere seconds (m. a. s.) is determined as follows: A light source is adjusted so that the light coming through the test chamber gives an output of 100 microamperes from a photoelectric cell. A sample of the detergent is dropped into the test chamber and the dust cloud reduces the light received by the cell with a corresponding amperage output decrease. The microampere readings from the cell during the test is plotted. The area between this plot and the plot that would be obtained if no dust were present (a straight line at 100 microamperes) is a

3

measure of the dustiness. Therefore, a high m. a. s. value indicates a dusty product. In carrying out the test a 100 gram sample of the detergent is fed into the chamber through a funnel in approximately 3 seconds and the microampere output of the cell recorded every 5 seconds, readings being taken for 100 seconds.

By the foregoing procedure a particulate detergent composition comprising 40 parts by weight of dodecyl benzene sodium sulfonate and 60 parts by weight of sodium sulfate was evaluated both before and after treating with various amounts of the condensation product of one mole of tetrahydrofurfuryl alcohol and fifteen moles of ethylene oxide. The additive was applied to the dry particles by spraying. About 3 minutes was consumed in spraying a 30 pound charge. The results are summarized below:

Table I

Amount of additive (wt. percent):	Dust value (m. a. s.)
0.5	1875
1.0	210
1.25	195
2.0	165
None	3516

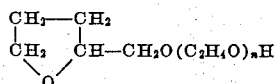
Similar tests were carried out on compositions prepared by adding the condensation product of tetrahydrofurfuryl alcohol and ethylene oxide to an aqueous slurry of the detergent before drying. The composition was then dried on the rolls of a drum drier and the dust values obtained as described.

Table II

Amount of additive (wt. percent):	Dust value (m. a. s.)
2.5	1160
5.0	803
None	4290

It will be noted that the dustiness of the product was very markedly retarded by the addition of a poly ether although the effect is less pronounced than when the dry particles were treated.

Further tests were carried out employing products in which the number of ether groups varied. Thus the condensation of tetrahydrofurfuryl alcohol and ethylene oxide results in a product which may be assigned the general formula



where the value of n depends upon the ratio of ethylene oxide condensed. n should be at least 5 but not more than 20. The compositions were applied by spraying the dry particles of the particulate detergent while tumbling as has already been described. The value of n in the aforesaid general formula is indicated in the table below together with the amount of additive applied and dust values obtained. Also recorded is the dust value for one of the compositions after three months storage.

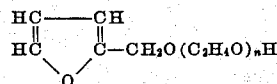
Table III

Value of n	Amount Applied, Percent by Wt.	Dust Value, m. a. s.
5.0	1.0	365
5.0	1.5	185
10.0	1.25	265
15.0	1.3	367
15.0	1.3	1400
	none	3,516

¹ Value after three months' storage.

Similar tests were carried out by applying a composition of the general formula

4



to the dry particulate detergent. The detergent composition was the same as that employed in the foregoing tests and the additive was applied by spraying and tumbling in the manner described.

Table IV

Value of n	Amount Applied, Percent by Wt.	Dust Value, m. a. s.
10.0	1.25	255
15.0	1.25	1,053
	none	3,525

Foaming of the treated and untreated compositions was compared employing the test devised by John Ross and Miles described in Oil and Soap, vol. 18, page 99 (1941). This test gives astonishingly reproducible results. The apparatus comprises a jacketed measuring cylinder in which a portion of the test solution is placed. A second portion of the solution is allowed to stream in from a fixed height through a standard orifice. The height of the foam is measured in centimeters. The latter tests described below were obtained with 0.1% aqueous solutions of the detergent compositions in water of hardness 300 p. p. m. The height of the foam is recorded immediately and after 5 minutes. The base for the preparation of the detergent compositions was the mixture of sodium dodecyl benzene sulfonate and sodium sulfate employed in the foregoing tests. To this was added a commercial non-ionic detergent which is the condensation product of tall oil and ethylene oxide. Other compositions contained the condensation product of tetrahydrofurfuryl alcohol and ethylene oxide. The data are set forth in the table below:

Table V

Composition added to Base	Amount, Percent by wt.	Foaming (cc.)	
		At Once	5 Mins.
None		12.5	12.5
Tall oil-ethylene oxide	2.0	4.0	3.7
	4.0	4.3	4.3
None		15.6	15.5
Tetrahydrofurfuryl alcohol-ethylene oxide ($n=15$)	1.0	15.8	15.8
	2.5	16.1	16.1
	5.0	15.6	15.5
None		15.6	15.5
Tetrahydrofurfuryl alcohol-ethylene oxide ($n=5$)	1.0	15.6	15.6

Other tests were carried out employing a foam test which consists in bubbling air through 500 cc. of the solution to be tested and measuring the loss of solution due to foaming. The concentration of the test solutions was 0.1%. They were made up from tap water having an average hardness of 65 p. p. m. The results were reported on the basis of the control as 100 or in other words as percent of control, high values indicating high foaming tendencies. The control or untreated detergent was a 0.1% solution of a mixture of 40 parts dodecyl benzene sodium sulfonate and 60 parts sodium sulfate.

Table VI

Additive	Amount (Percent) On dry Detergent	Foaming
None		100
Tall oil-ethylene oxide (1:11)	1.0	87
	2.0	61.4
Tetrahydrofurfuryl alcohol-ethylene oxide (1:15)	2.5	119
	5.0	127

These data show that the additives of this invention permit the preparation of detergent compositions having little or no dust but which at the same time have excellent foaming characteristics. The foaming is if anything improved by the addition of the small amount of poly alkylene ether. Although the condensation product of tall oil and ethylene oxide has been selected to illustrate the fact that the properties are not shared by poly alkylene ethers generally because this is the well known commercial product, it will be appreciated that a large number of poly alkylene ethers have been evaluated. These in general have seriously reduced foaming in hard water. Another serious shortcoming of many additives heretofore suggested for the purpose of abating dust is that they result in caking of the detergent composition. Initially the caking tendency of the new detergent compositions is increased somewhat as compared to the untreated materials but surprisingly the tendency decreases with aging. Caking may be evaluated by determining the force required to rupture the mass produced by subjecting the detergent to a force approximating that to which it is subjected at the bottom of a 200 pound drum. It was found that after three months storage the values approached those of the untreated controls. Detergent compositions treated with the poly alkylene ethers of the present invention have remained in crumbly particulate condition after long periods of storage.

Compositions containing synthetic organic detergents are admixed with dichromates in certain applications and the additives of this invention cause no discoloration of these compositions. For example an admixture of dodecyl benzene sodium sulfonate, sodium sulfate and a small quantity of the condensation product of tetrahydrofurfuryl alcohol and ethylene oxide is color stable in the presence of dichromate whereas replacement of the tetrahydrofurfuryl alcohol by tall oil in the ethylene oxide condensate results in darkening in the presence of dichromate.

As illustrative of the solubilizing effect of the additives, a composition was prepared as follows:

	Parts by weight
Dodecyl benzene sodium sulfonate	35.19
Sodium sulfate	5.38
Sodium chloride	0.83
Water	58.60

This composition having a total solids content of 41.4% was found to possess a cloud point of 52° C. Thereto was added a condensation product of tetrahydrofurfuryl alcohol and ethylene oxide, the particular additive being indicated by designating the value of n in the general formula as heretofore explained. The concentrations are expressed as percent of the total solution weight.

Table VII

Value of n	Cloud Point, ° C. at Concentrations of—		
	1%	3%	10%
5	40	22	-2
10	39	20	-7

Further tests were carried out employing solutions of decyl benzene sodium sulfonate having concentrations in the range of 29–31%. The cloud points of the untreated solutions averaged 5° C. However, the cloud point was reduced to 0° C. by the addition of the condensation product of one mole of tetrahydrofurfuryl alcohol and ten

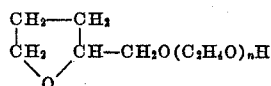
moles of ethylene oxide, the concentration of the additive being 2% based on the total weight of the solution. Raising the concentration to 3% reduced the cloud point to -2.5° C. From this data it is evident that the additives of this invention are important solubilizers for synthetic organic detergents.

It is intended to cover all changes and modifications of the examples of the invention herein chosen for purposes of disclosure which do not constitute departures from the spirit and scope of the invention.

What is claimed is:

1. A detergent composition comprising an alkyl benzene sodium sulfonate wherein the alkyl group contains from 9 to 16 carbon atoms and an amount within the range of 0.5 to 5% of an oxy alkylene ether of the structure $R-CH_2O(C_2H_4O)_nH$ where R is a five membered heterocyclic radical containing four carbon atoms and an oxygen atom and n is an integer at least five but not more than fifteen.

2. A detergent composition comprising an alkyl benzene sodium sulfonate wherein the alkyl group contains from 9 to 16 carbon atoms and an amount within the range of 0.5 to 5% of an oxy alkylene ether of the structure



where n is an integer at least five but not more than twenty.

3. A detergent composition in particle form comprising dodecyl benzene sodium sulfonate and sodium sulfate in the ratio of 35–65 parts of the former to 65–35 parts of the latter having incorporated therein 0.5–5.0% based on the total detergent composition of an oxy alkylene ether of the structure $R-CH_2O(C_2H_4O)_nH$ where R is a five membered heterocyclic radical containing four carbon atoms and an oxygen atom and n is an integer at least five but not more than fifteen.

4. An aqueous detergent preparation comprising a solution of an alkyl benzene sodium sulfonate wherein the alkyl group contains from 9 to 16 carbon atoms and having a small but effective amount within the range of 1–10% based on the total solution, sufficient to lower the cloud point, of an oxy alkylene ether of the structure $RO(R_1O)_nH$ where RO is the residue after removal of hydrogen from a carbinol substituted by a five membered heterocyclic radical containing four carbon atoms and an oxygen atom, R_1 is an alkylene group containing at least 2 but not more than 4 carbon atoms and n is an integer at least five but not more than fifteen.

5. A detergent composition comprising as an essential active ingredient an alkyl benzene sodium sulfonate wherein the alkyl group contains from 9 to 16 carbon atoms and an effective amount within the range of 0.5%–5% thereof of an oxy alkylene ether of the structure $RO(R_1O)_nH$ where RO is the residue after removal of hydrogen from a carbinol substituted by a five membered heterocyclic radical containing four carbon atoms and an oxygen atom, R_1 is an alkylene group containing at least 2 but not more than 4 carbon atoms and n is an integer at least 5 but not more than 20.

References Cited in the file of this patent

UNITED STATES PATENTS

1,970,578	Schoeller	Aug. 21, 1934
2,489,955	Colgate	Nov. 29, 1949
2,477,383	Lewis	May 24, 1952