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3,634,271

LIQUID DETERGENT COMPOSITIONS

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4 Claims

ABSTRACT OF THE DISCLOSURE

Detergent compositions of linear alkylbenzene sulfonates containing a mixture of sodium and ethanolamine salts of said sulfonates and polyethylene glycol. The compositions are characterized by having improved low temperature storage stability.

Detergents such as the alkylbenzene sulfonates are commonly marketed in the form of liquid, aqueous compositions. These liquid detergent compositions offer the advantage of convenience in consumer use in the cleansing of dishes and fabrics. One of the most commonly employed detergents in such formulations is sodium alkylbenzene sulfonate wherein the alkyl substituent is from about 9 to 15 carbon atoms and may be either branched-chain or linear. In recent years the emphasis on biodegradable products has resulted in the increasing importance of the linear type of alkylbenzene sulfonates since the linear or straight-chain type is readily degraded by microorganisms found in sewage. A disadvantage encountered generally in the production of aqueous solutions of detergents has been the problem of producing liquid detergent compositions having low clear points, i.e. solutions which do not become turbid or clouded from layers of precipitated matter at relatively low temperature. Such has been the case with aqueous solutions of sodium alkylbenzene sulfonates when after storage at low temperatures they tend to become cloudy and may thicken to a gel-like stat or even undergo a phase separation. While the occurrence of such phenomena does not adversely affect the cleansing properties, it does present problems with respect to appearance and pourability of the composition and is undesirable from a marketing standpoint. It is a particularly troublesome problem when handling sulfonate solutions in bulk, i.e. transportation in tank cars or storage in unheated tanks especially in cold weather.

It has been found that in the case of the branched-chain type of sodium alkylbenzene sulfonates the problem could be solved by the addition of certain modifiers including a lower alkylbenzene sulfonate such as a toluene sulfonate or a glycol such as ethylene glycol. With aqueous formulations of the linear type, however, the problem is considerably more acute and even with addition of such modifiers the problem still exists when these modified linear type formulations are stored at low temperatures.

It has now been discovered that aqueous liquid compositions of linear alkylbenzene sulfonates can be prepared which have the specific advantage of remaining clear and fluid even after extended periods of storage at low temperatures.

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In accordance with the present invention there is provided an aqueous liquid detergent composition having substantially improved low temperature stability containing:

(A) as solutes therein between about 30 and 50% of sodium and ethanolamine salts of a mixture containing a major proportion of linear higher alkylbenzene sulfonates wherein the alkyl constituent is a straight chain hydrocarbon of 9 to 15 carbon atoms, preferably 10 to 13 carbon atoms, and a minor proportion of lower alkylbenzene sulfonates containing between 1 and 6, preferably 2 to 4 non-aromatic carbon atoms, and

(B) between about 0.5% and 5%, preferably between 1 and 2% of a polyethylene glycol having an average molecular weight of between about 200 and 1250, preferably 400-800, the higher and lower alkylbenzene sulfonates being present predominantly as sodium salts with a solubilizing amount of monoethanolamine salts thereof. Substantially improved low temperature stability is achieved in compositions wherein the ratio of monoethanolamine to sodium cations is between about 0.1 and 1.0 preferably 0.3 to 0.7.

The higher linear alkylbenzene sulfonates of the present compositions can be prepared by any one of a number of well-known methods such as sulfonation of the corresponding linear alkylbenzene, for example, by reaction with 100 percent sulfuric acid and neutralization of resultant alkylbenzene sulfonic acid with sodium hydroxide and monoethanolamine. The higher linear alkylbenzenes are commercially available compounds, commonly prepared by condensation of the partially halogenated product of a normal paraffin of 9 to 15 carbon atoms, or mixtures thereof, with benzene in the presence of a Friedel-Crafts catalyst such as aluminum chloride. Processes of this type are described in U.S. Pats. Nos. 2,314,255, 2,364,767 and 2,387,572. Representative of the linear alkyl substituent on the benzene nucleus are such groups as decyl, dodecyl, keryl, pentadecyl, etc. and mixture thereof.

The lower alkylbenzene sulfonates function as solubilizing agents in the compositions of the present invention. They are employed in amounts sufficient to provide a mol ratio from about 4.0 to about 2.5, preferably 3.0 to 3.5, of higher to lower alkylbenzene sulfonate. These compounds are prepared as described above by sulfonating the corresponding alkylbenzene and neutralizing the resultant sulfonic acid with sodium hydroxide and ethanolamine. Suitable compounds include the homologs of benzene sulfonate containing from 1 to 6 non-aromatic carbon atoms, for example the sulfonates of toluene, xylene, cumene, cymene, butylbenzene, amylbenzene, hexylbenzene, butylxylene and the like. Because of its availability, relatively low cost and freedom from undesirable coloration effects, toluene sulfonate is preferred. The lower alkylbenzene sulfonate may be added to the composition prior to sulfonation (as the alkylbenzene), or prior to neutralization (as the sulfonic acid) or after neutralization of the higher alkylbenzene sulfonic acid. In the latter case the lower alkylbenzene sulfonate is added in the form of a mixture of sodium and monoethanolamine salts wherein the mol ratio of monoethanolamine to sodium cations is between about 0.1 and 1.0.

The polyethylene glycols, which also serve as solubilizing agents in the compositions of the present invention,

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are commercially available high molecular weight compositions of the general formula



wherein n is an integer from about 2 to about 10. They are commonly prepared by the reaction of ethylene glycol with varying amounts of ethylene oxide. The polyethylene glycols are commercially available in a wide range of molecular weights. For the purpose of the present invention those having an average molecular weight of between about 200 and 1250 have been found most suitable. Thus, they include triethylene glycol, tetraethylene glycol and higher polyethylene glycols having molecular weights within this range. They may be employed in the form of the individual polyglycol or in the form of mixtures such as are obtained commercially by the reaction of a glycol with ethylene oxide. The glycols may be employed in amounts ranging from 0.5% to 5%, preferably 1% to 2% of the weight of the final solution. The glycols can be incorporated into the detergent solution at any stage of the manufacture thereof subsequent to the formation of the sulfonic acid, and in any order with respect to the other components of the solution. An advantageous procedure for the manufacture of the solution involves carrying out the neutralization of the higher alkylbenzene sulfonic acid in an aqueous medium containing the glycol.

In a preferred method of preparing the compositions of the present invention, toluene and a higher linear alkylbenzene are combined in the proportions stated hereinabove and the mixture is sulfonated by reaction with 100 percent sulfuric acid in a known manner. The reaction mass is then allowed to settle and a phase separation occurs. The lower layer of spent sulfonating acid is withdrawn. The upper layer, comprising a mixture of higher linear alkylbenzene sulfonic acid and toluene sulfonic acid is charged into a mixture of water and a polyethylene glycol having an average molecular weight between 200 and 1250. Simultaneously with the charging of the sulfonic acid mixture to the water-glycol mixture, a stream of monoethanol amine is added in sufficient quantity to neutralize the desired amount of the alkylbenzene sulfonic acid mixture. The remaining unreacted sulfonic acid mixture is then neutralized by addition of aqueous sodium hydroxide.

Various other modifiers such as are commonly employed in detergent compositions may be added. Such additional modifiers may be present in amounts up to about 10 percent by weight based on the final weight of the detergent solution. Typical additives which may be employed are sodium tripolyphosphate which serves as a sequestering agent for iron, sodium hypochlorite, which functions as a purifying agent (as described in U.S. Pat. 2,333,830), sodium bisulfite, which serves to decompose any residual sodium hypochlorite in the treated solution, and others. Water may be added to the composition during the preparation or after to provide the degree of concentration desired. The concentration may vary considerably, the usual being between about 30 and 50 percent solids in the final aqueous composition.

To further illustrate the present invention and the manner in which it may be practiced, the following specific examples are set forth. In the examples, unless otherwise indicated all parts are by weight and all temperatures are in centigrade degrees.

EXAMPLE 1

Ten parts of toluene was mixed with 90 parts of a linear alkylbenzene consisting predominantly of C_{10} - C_{13} paraffin hydrocarbon substituents and having an average molecular weight of about 241 (available commercially as Phillip's linear detergent alkylate Type-1, Phillip's Petroleum Co.). To the mixture, 146 parts of 100 percent

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sulfuric acid were added and the reaction mixture was agitated at 55 to 58 degrees for about one hour. Next, 29.5 parts of water were added, with cooling to maintain the temperature of the reaction mass below 70 degrees.

Following the addition of water, the reaction mass was allowed to settle while the temperature was maintained at 65 to 70 degrees. A phase separation occurred over a period of about one hour and the lower layer of spent sulfonating acid was withdrawn. The upper layer of alkylbenzene sulfonic acids was neutralized in the following manner: Separate streams of the alkylbenzene sulfonic acid and of monoethanolamine (12.3 parts) were charged simultaneously to a mixture of 90 parts of water and 5.6 parts of a commercial polyethylene glycol having an average molecular weight of about 400 ("Polyglycol E-400," Dow Chemical Co.). Next, 18.5 parts of sodium hydroxide were added (as a 30% aqueous solution) to neutralize the remaining sulfonic acid. Near the end of the neutralization procedure the batch was treated successively with the addition of a solution of 1.67 parts of sodium tripolyphosphate in water, 1 part of a 10 percent sodium hypochlorite solution and 0.49 parts of sodium bisulfite in water.

The final acidity of the solution was adjusted to a grass-green color on Nitrazine Yellow test paper (a pH of 6.3 to 6.7). Sufficient water was added to adjust the total solids content to 41.0 percent. The detergent solution thus prepared was stored at a temperature of 2 to 4 degrees for a period of several months. The solution remained clear and fluid.

EXAMPLE 2

To a mixture of 100 parts of toluene and 1000 parts of sulfuric acid-washed linear alkylbenzene consisting predominantly of C_{10} - C_{13} paraffin hydrocarbons having an average molecular weight of about 241 (available commercially as "ARLA-4," Atlantic Refining Co.), was added 767 parts of 100 percent sulfuric acid and the reaction mixture was agitated for about 1 hour at 55 to 58 degrees. Next, 300 parts of water were added and the temperature was maintained at 65 to 70 degrees for about one hour while the reaction mixture settled and separated into two layers. The lower layer comprising spent acid was withdrawn. The remaining mixture of alkylbenzene sulfonic acids was combined with 340 parts of water and 26.7 parts of polyethylene glycol having an average molecular weight of 400 ("Polyglycol E-400," Dow Chemical Co.) and neutralized with 28.2 parts of monoethanolamine and 48.7 parts of sodium hydroxide (as a 30% aqueous solution). To the neutralized mixture were added 8.0 parts of sodium tripolyphosphate in 26.8 parts of water, 1.5 parts of a 10 percent sodium hypochlorite solution, and 1.9 parts of sodium bisulfite in 5.3 parts of water. Sufficient water was added to adjust the total solids content to 41.0 percent. The detergent solution thus prepared was stored at a temperature of 2 to 4 degrees for a period of several months. The solution remained clear and fluid.

EXAMPLE 3

The procedure of Example 1 was repeated except that monoethanolamine was omitted and the amount of sodium hydroxide was increased accordingly to 25.6 parts to neutralize the acids. The resultant detergent solution was stored at a temperature of 2-4 degrees. At the end of the third day in storage the solution appeared cloudy and by the end of the fourth day was a gel-like solid.

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The procedure of Example 1 was repeated except that the amounts of monoethanolamine and sodium hydroxide were varied as shown in Table 1 below. The solutions, thus prepared, were stored at 2-4 degrees for a period

of 8 days and the appearance of the solutions observed daily with the results as shown.

polyethylene glycols having an average molecular weight of between 200 and 1250.

TABLE I

Ex.	Monoethanolamine (parts)	NaOH (parts)	DAYS							
			1	2	3	4	5	6	7	8
			Condition of samples after storage at 2-4 degrees							
4-----	0	25.8	Semi-solid ¹	-----	-----	Gel-like solid. ²	Gel-like solid. ²	Gel-like solid. ²	Gel-like solid. ²	Gel-like solid. ²
5-----	0	25.4	Milky and fluid.	-----	-----	do. ²	do. ²	do. ²	do. ²	Do. ²
6-----	0	26.2	Clear and fluid.	Hazy and fluid.	-----	do. ²	do. ²	do. ²	do. ²	Do. ²
7-----	11.8	18.6	do.	Clear and fluid.	Clear and fluid.	Clear and fluid.	Clear and fluid.	Clear and fluid.	Clear and fluid.	Clear and fluid.
8-----	14.3	16.0	do.	do.	do.	do.	do.	do.	do.	Do.
9-----	16.4	14.9	do.	do.	do.	do.	do.	do.	do.	Do.
10-----	18.4	12.4	do.	do.	do.	do.	do.	do.	do.	Do.
11-----	10.2	19.4	do.	do.	do.	do.	do.	do.	do.	Do.

¹ Difficultly pourable.

² Non-pourable.

As will be apparent from the foregoing examples, the compositions of the present invention containing a selected mixture of sodium and monoethanolamine salts of linear alkylbenzene sulfonic acids exhibit substantially improved low temperature stability, remaining clear and fluid even after storage for 8 days at temperatures of 2-4 degrees centigrade.

It will be apparent to those skilled in the art that many variations and modifications of the invention as hereinabove set forth, may be made without departing from the spirit and scope of the invention. The invention is not limited to those details and applications described except as set forth in the appended claims.

We claim:

1. An aqueous detergent composition having improved low temperature stability consisting essentially of as solutes therein, in percent by weight of the aqueous composition, (A) between about 30 and 50 percent of sodium and monoethanolamine salts of a mixture of linear higher alkylbenzene sulfonic acid wherein the alkyl substituent is a straight chain hydrocarbon of 9 to 15 carbon atoms, inclusive, and a lower alkylbenzene sulfonic acid containing 1 to 6 non-aromatic carbon atoms, inclusive, the mol ratio of higher to lower alkylbenzene sulfonic acids being between about 4.0 and 2.5 and the mol ratio of monoethanolamine to sodium cations being between about 0.1 and 1.0, and (B) between about 0.5 and 5 percent of a polyethylene glycol or mixture of

2. An aqueous detergent composition as claimed in claim 1 wherein the linear higher alkyl substituent is a mixture of straight chain hydrocarbons containing 10 to 13 carbon atoms and the lower alkyl substituent is methyl.

3. An aqueous detergent composition as claimed in claim 1 wherein the mol ratio of higher to lower alkylbenzene sulfonic acids is between about 3.0 and 3.5 and the mol ratio of ethanolamine to sodium cations is between about 0.3 to 0.7.

4. An aqueous detergent composition according to claim 2 wherein the lower alkylbenzene sulfonic acid is toluene-benzenesulfonate and the polyethylene glycol has an average molecular weight of about 400.

References Cited

UNITED STATES PATENTS

3,140,261	7/1964	Noad	-----	252-161
3,174,935	3/1965	Eccles et al.	-----	252-161
3,282,852	11/1966	Trusler et al.	-----	252-152
3,303,138	2/1967	Dewitt et al.	-----	252-137
3,440,171	3/1969	Warren	-----	252-152

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