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3,175,978

LIGHT DUTY LIQUID DETERGENT

Luther H. Smithson, Jr., Berkeley, Calif., assignor to California Research Corporation, San Francisco, Calif., a corporation of Delaware

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This invention relates to the preparation of an aqueous detergent composition. More particularly, the invention has to do with the preparation of a light-duty liquid detergent solution having good detergency and sudsing properties. Liquid detergent solutions of alkylbenzene sulfonates which are useful in the washing of lightly soiled fabrics and dishes have been proposed. However, in order to produce a solution of sufficiently low clear point, an alkylbenzene sulfonate material is selected which is sufficiently soluble to produce the desired results. These materials having the proper solubility characteristics have a relatively low molecular weight.

Alkylbenzene sulfonates of higher molecular weight give superior detergency as compared with the lower molecular weight alkylbenzene sulfonates. It would be desirable, therefore, to utilize this property of superior detergency in liquid detergent compositions, but the lower solubility of the higher molecular materials presents a problem in producing liquid detergent compositions which have low clear points, i.e., solutions which do not become turbid or clouded from form layers of precipitated matter at relatively low temperatures.

In addition, it is desirable to be able to use those alkylbenzene sulfonates having associated with them connate inorganic sulfate, such as sodium or ammonium sulfate. As is known in the art, a convenient way of preparing the sulfonates is to sulfonate the alkylbenzene stock with fuming sulfuric acid (22% oleum), after which the sulfonation reaction product mixture is diluted with water in order to secure an adequate separation of the organic sulfonic acid phase from the inorganic phase of unreacted sulfuric acid. Invariably, some sulfuric acid remains admixed with the sulfonic acid in the organic phase, and, upon neutralization with suitable base, e.g., sodium hydroxide or ammonium hydroxide, the final product will ordinarily contain from about 8 to 15%, by weight, of inorganic sulfate, based on organic sulfonate. The presence of this inorganic sulfate as part of the alkylbenzene sulfonate component has a deleterious effect on clear point. Of course, it is possible to remove the inorganic sulfate, as by repeated water washings of the neutralized sulfonate product, but such procedure is expensive.

As the alkylbenzene intermediate in making the sodium or ammonium alkylbenzene sulfonates, it is preferred to use those in which the alkyl groups are derived from propylene polymer, the alkylbenzenes having an average molecular weight between about 250 and 300. The production of these detergent sulfonates is described in detail in the literature, e.g., U.S. Patent 2,477,383.

In accordance with the present invention it is possible not only to use alkylbenzene sulfonates of high molecular weight but also those having associated therewith an inorganic sulfate content of 8 to 15% by weight of the alkyl sulfonate component.

Recent market research has indicated that liquid detergent solutions should have clear points not exceeding 40° F. Light-duty liquid detergents currently on the market have clear points of 41-50° F. The formulations herein contemplated have clear points in the range 32-40° F. The clear point is simply determined by slowly cooling and stirring the solution, or heating gently, and observing the temperature at which the solution turns cloudy or clear, respectively. However, the method is accurate and reproducible to within less than 0.5 degree.

In accordance with the present invention there is provided a liquid detergent solution, the solute of which comprises a unique combination of alkylbenzene sulfonates, the ammonium salt of the sulfate ester of an alkyl phenoxy polyoxyethylene ethanol and optionally a sudsing agent, such as lauric diethanolamide. The alkylbenzene sulfonate component material is a mixture of sodium and ammonium sulfonates of alkylbenzenes having an average molecular weight between about 250 and 300, and having associated therewith 8 to 15% inorganic sodium and/or ammonium sulfate, the weight ratio of the sodium alkylbenzene sulfonate to the ammonium alkylbenzene sulfonate ranging from about 25:75 to 75:25, preferably 50:50 to 75:25.

As a solvent agent for the solute there is used a mixture of urea, low molecular weight alcohol, and water. As examples of suitable alcohols there can be mentioned methyl, ethyl, propyl, and isopropyl alcohols. Formula 3A alcohol is preferred alcohol. By volume it is comprised of 90.48% ethyl alcohol, 4.76 methyl alcohol, and 4.76 water.

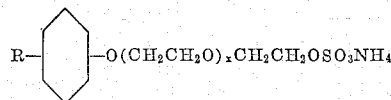
More specifically, satisfactory light-duty detergent solutions of the present invention will contain the foregoing ingredients in about the following percentages, by weight, based on the solution:

Alkylbenzene sulfonate component	15 to 20
Inorganic sulfate	1.2 to 3
Ammonium salt of the sulfate ester of alkyl phenoxy polyoxyethylene ethanol	5 to 10
Lauric diethanolamide	0 to 3
Urea	2 to 4
Lower molecular weight alcohol	15 to 16
Water, quantity sufficient to make 100%.	

In addition to the foregoing ingredients the final composition can contain other components. These include perfumes in illustrative amounts based on the foregoing compositions, of 0.05 to 0.5%, and 0.05 to 0.5% dyestuff.

In place of the lauric diethanolamide above-mentioned, other foam-boosting agents can be employed, such as lauric-myristic diethanolamide fatty acid monoethanolamides and other fatty acid alkylolamides, such as lauric isopropanolamide. As aforesaid, while no foam-boosting agent is required, it is preferred to use at least 1% of it, up to about 3%.

The ammonium salt of the sulfate ester of alkyl phenoxy polyoxyethylene ethanol can be one in which the alkyl group attached to the benzene nucleus may contain 8 to 18 carbon atoms of branched chain or straight chain structure, saturated or unsaturated. Moreover, the number of oxyethylene groups can range from 4 to 20. A preferred material is one in which the alkyl group is a branched chain C₉ radical derived from polypropylene and has four oxyethylene groups. In general, this material may be represented by the formula:



wherein R is an alkyl group of the type specified containing 8 to 18 carbon atoms, and x is a number from 4 to 20.

The following examples illustrate the practice of the invention.

EXAMPLE 1

Preparation of liquid detergent solution

A 50 gallon kettle equipped with a mechanical stirrer, inlet port, and cooling coils is charged with 40.6 parts of water. During the processing, the temperature is maintained at 100-110° F. by the proper adjustment of the cooling water flow rate. Stirring is commenced and 6.4

parts of concentrated sodium hydroxide (45% by weight in water) is added. Then 4.3 parts of aqueous ammonia (10% by weight); powdered urea, 3 parts; ammonium salt of sulfate ester of C₉ polypropylene phenoxy polyoxyethylene ethanol (4 oxyethylene groups, 58% active, in water and Formula 3A alcohol), 10.0 parts; lauric diethanolamide, 2.0 parts; and 14.0 parts of Formula 3A alcohol are added through the port, and the resulting slurry is stirred until only one phase is present. Finally, there is added a mixture of sulfonic acid and sulfuric acid, containing 18.9 and 2.1 parts of acid, respectively, and prepared by the oleum sulfonation of polypropylene benzenes, having an average molecular weight of 267. The pH of the solution is 7.0-7.5 after the addition of these acids. As a result, there is obtained a mixture having the following composition in percent by weight:

Sodium polypropylene benzene sulfonate	15.0
Ammonium polypropylene benzene sulfonate	5.0
Ammonium salt of sulfate ester of the alkyl phenoxy polyoxyethylene ethanol	6.0
Urea	3.0
Lauric diethanolamide	2.0
Sodium sulfate	2.25
Ammonium sulfate	.75
Formula 3A alcohol	15.00
Water	51.00
	100.00

This liquid detergent has a viscosity of 25.3 centistokes at 77° F. and a clear point of 37° F.

EXAMPLES 2-17

In these examples various liquid detergent solutions are examined for clear point. These solutions are prepared by mixing the appropriate quantities in parts by weight, of sodium and/or ammonium polypropylene benzene sulfonate; sodium and/or ammonium sulfate; sulfate ester; water; Formula 3A alcohol; and where indicated urea and amide foaming agent. The resulting mixture is stirred at a gradually decreasing temperature until a cloudy solution is obtained. Then the clear point is determined by warming slightly and observing the temperature at which the solution clears. The results are given in Table I.

TABLE I

Example	Na ABS ¹	NH ₄ ABS ¹	Na ₂ SO ₄	(NH ₄) ₂ SO ₄	Sulfate Ester ²	Foaming Agent ³	Urea	Formula 3A Alcohol	Water	Clear Point, ° F.
2	20	0	3.0	0	6	2	0	15	54	46
3	20	0	3.0	0	6	2	0	16	53	57
4	20	0	3.0	0	6	2	3	15	51	59
5	15	5	2.25	0.75	6	2	0	15	54	46
6	15	5	2.25	0.75	6	2	0	16	53	50
7	15	5	2.25	0.75	6	2	0	14	55	54
1	15	5	2.25	0.75	6	2	3	15	51	37
8	15	5	2.25	0.75	6	2	3	14	52	45
9	0	20	0	3.0	6	2	3	15	51	43
10	15	5	1.67	0.55	6	2	3	16	50.8	29
11	15	5	1.67	0.55	6	0	3	16	52.8	32
12	10	10	1.11	1.11	6	2	3	16	50.8	29
13	10	10	1.11	1.11	6	0	3	16	52.8	32
14	5	15	0.55	1.67	6	2	3	16	50.8	34
15	5	15	0.55	1.67	6	0	3	16	52.8	36
16	15	5	2.25	0.75	6	0	3	15	53	38
17	20	0	.62	0	6	2	3	14	54.4	37

¹ ABS=Alkylbenzene sulfonate detergents prepared from a polypropylene benzene having an average MW of 267.

² Ammonium salt of sulfate ester of C₉ polypropylene phenoxy polyoxyethylene ethanol containing four oxyethylene groups.

³ Lauric diethanolamide.

Review of the data in Table I indicates the following.

Example 2, based on sodium sulfonate alone, and containing 15 parts of alcohol but no urea has a clear point of 46° F. When alcohol content is increased, Example 5, the clear point further rises to 57° F. Addition of urea, Example 4, does not improve the clear point, and indeed raises it to 59° F.

The effect of replacing the sodium sulfonate with a 75/25 mixture of sodium/ammonium sulfonate is shown by comparing Examples 2 and 5. In this case there is no change in the clear point, indicating little effect due to mixing the sulfonates.

It will be noted that thus far in spite of changing conditions in a direction that the prior art would indicate to lead to improved clear points, has instead caused an increase in clear point or no change.

Replacing inorganic salt and sodium organic sulfonate with a mixture of sodium and ammonium inorganic salts and organic sulfonates, gives a clear point of 50° F. Example 6, as compared with a clear point of 46° F., Example 2, even though more alcohol is used in Example 6. The effect of mixed inorganic and sulfonic salts and less alcohol is shown in Example 7. Here the clear point is raised to 54° F.

Proper correlation of alcohol, mixed sulfonates, and urea gives a solution having a clear point of 37° F., Example 1. That proportion of alcohol is important as shown by a comparison of Example 1 with Example 8.

Replacing all of the sodium sulfonate with ammonium sulfonate does not give a solution of sufficiently low clear point, as shown in Example 9.

Examples 10 through 15 illustrate various ratios of sodium and ammonium sulfonates and sulfates. In general within the range 75/25-25/75 sodium/ammonium ratios, satisfactory solutions are obtained. These same experiments indicate about a 2° F. lowering of clear point upon the addition of 2 parts of the foaming agent, as can be seen by a comparison of Experiments 10, 12, and 14 with 11, 13 and 15. Example 16 as compared with Example 1 also shows an improvement in clear point in the presence of the foaming agent.

Example 17 is a formulation having a low inorganic content. This formulation has only 13 parts alcohol and yet the clear point is 37° F. A composition of this type having a high inorganic salt content would have a clear point in excess of 45° F. (see Example 8).

A comparison of the formulation of Example I with four commercially available liquid detergents indicated that the present compositions are equal or superior to the commercially available liquid detergents. The test employed in this evaluation is described in Journal of American Oil Chemists' Soc., 34, 361-363 (1957), by L. O.

Leenerts and H. J. Meyers, and is entitled "Qualitative Foam Stability Evaluation of Hand Dishwashing Detergents."

The deterative property of the present compositions was determined by the following dishwashing test:

To six liters of water of predetermined hardness at a temperature of 115° F. or 80° F. was added 150 g. of a

6 percent solution in water of the test detergent formulation. Plates soiled with 2.2 cc. of molten fat shortening evenly applied to the surface were then washed by hand. When the suds disappear from the surface of the wash solution the test is deemed complete, and the number of washed plates is counted. Using the indicated formulations of the present invention, and a well-known commercially available liquid detergent, hereinbelow identified as "X," the following tabulated results were obtained.

TABLE II.—DISHWASHING TEST

Water Hardness	Number of Plates Washed		
	"X"	Example 1	Example 16
At 80° F.:			
10 p.p.m.-----	15	14	14
50 p.p.m.-----	22	22	22
180 p.p.m.-----	22	25	25
300 p.p.m.-----	22	27	28
At 115° F.:			
10 p.p.m.-----	19	22	20
50 p.p.m.-----	27	27	27
180 p.p.m.-----	28	28	28
300 p.p.m.-----	28	30	32

The foregoing data indicate that the present compositions are equal to or superior to the commercially available liquid detergent. At a water hardness of 300 p.p.m. the present compositions are superior. This is so whether or not a foam-boosting agent is present (Example 1) or is absent (Example 16). Of course, as shown previously, the presence of the foam-boosting agent has an unexpected desirable effect on clear point.

I claim:

1. A detergent solution having a clear point below about 40° F., consisting essentially of by weight, based on the solution, of the following ingredients in the indicated proportions, sufficient water being present to give 100%:

(a) 15 to 20 percent of a mixture of sodium and ammonium sulfonates of alkyl benzenes having an average molecular weight between about 250 and

300, the weight ratio of the sodium alkyl benzene sulfonate to ammonium alkyl benzene sulfonate ranging from about 25:75 to 75:25;

(b) 5 to 10 percent of ammonium salt of the sulfate ester of alkyl phenoxy polyoxyethylene ethanol having 8 to 18 carbon atoms in the alkyl group, and 4 to 20 oxyethylene groups;

(c) 1.2 to 3 percent of inorganic sulfate selected from the group consisting of sodium and ammonium sulfate;

(d) 0 to 3 percent of an alkylolamide foam-improving agent selected from the group consisting of lauric diethanolamide and lauric isopropanolamide;

(e) 15 to 16 percent of low-molecular weight alcohol; and

(f) 2 to 4 percent of urea.

2. A detergent solution according to claim 1, wherein the weight ratio of the sodium alkyl benzene sulfonate to ammonium alkyl benzene sulfonate ranges from about 75:25 to 50:50.

3. A detergent solution according to claim 1 wherein the ammonium salt of the sulfate ester of the alkyl phenoxy polyoxyethylene ethanol has a C₉ polypropylene as the alkyl group and four oxyethylene groups in the molecule.

4. A detergent solution according to claim 3 wherein a foam boosting agent is present in an amount of 1 to 3 percent.

5. A detergent solution according to claim 4 wherein the foam-boosting agent is lauric diethanolamide.

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JULIUS GREENWALD, *Primary Examiner*.