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[54] LIQUID DETERGENT COMPOSITIONS

[75] Inventors: **Marvin L. Mausner**, Teaneck;
Arnold H. Dater, Fair Lawn, both of
N.J.

[73] Assignee: **Witco Chemical Corporation**, New
York, N.Y.

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1970, Pat. No. 3,709,838, which is a
continuation-in-part of Ser. No. 777,143, Nov. 19,
1968, abandoned, which is a continuation-in-part of
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[58] Field of Search 252/545, 548, 529

[56] References Cited

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3,232,880 2/1966 Mausner 252/529

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cation No. T 903,009.

Primary Examiner—Mayer Weinblatt

Assistant Examiner—Edith L. Rollins

Attorney, Agent, or Firm—Morton Friedman; Jordan
J. Driks; Albert L. Gazzola

[57]

ABSTRACT

Polyfunctional low-foaming essentially 100% active
stable liquid detergent compositions consisting essen-
tially of (a) from 30 to 90% of an ethanolamine salt of
a C₈ to C₁₈ alkyl benzene- or alkyl toluene-sulfonic
acid, (b) from 5 to 35% of a nonionic normally liquid,
water-soluble polyoxyethylene-polyoxypropylene gly-
col condensation product surfactant, and (c) from 5
to 35% of a C₁₀ to C₁₈ fatty acid monoethanolamide,
diethanolamide or monoisopropanolamide.

19 Claims, No Drawings

LIQUID DETERGENT COMPOSITIONS

This application is a continuation-in-part of application Ser. No. 91,153, filed Nov. 19, 1970, issued as U.S. Pat. No. 3,709,838 which is a continuation-in-part of application Ser. No. 777,143, filed Nov. 19, 1968, now abandoned which is a continuation-in-part of application Ser. No. 510,358, filed Nov. 29, 1965, now abandoned.

This invention is directed to new and useful anhydrous or essentially anhydrous low foaming liquid surfactant compositions, and more particularly to polyfunctional liquid detergent compositions that comprise essentially 100% active organic surfactants and to a method of making them.

The production and marketing of polyfunctional detergent compositions has been known for a number of years and numerous formulations have been evolved. Various combinations of surfactant materials have been prepared in a wide range of concentrations to modify the properties of the detergent compositions in a desired manner. These combinations are disclosed in numerous U.S. Patents, illustrative of which are Nos. 2,383,737; 2,733,213; 2,733,214; 2,746,931; 2,826,596; 2,831,815; 2,846,402; 3,075,922; and 3,239,468.

It is known in the detergent art to prepare polyfunctional detergent compositions in powdered or flake form, such as obtained by the spray-drying or drum-drying of a slurry of a detergent composition, that contain a high concentration of active organic surfactant materials, i.e., as high as 90% of active surfactant material. It has also been suggested, as disclosed in the aforementioned U.S. Pat. No. 3,239,468, to prepare detergent compositions comprising certain proportions of alkyl aryl sulfonates, nonionic polyoxyethylene alkylphenol condensates and fatty acid-diethanolamine condensates without any added water or other vehicle, such as a liquid medium, and subsequently diluted to use concentrations, or subsequently admixed with a liquid medium. In point of fact, in the actual working example disclosures of said Pat. No. 3,239,468, aqueous slurries of the alkyl aryl sulfonates are utilized and, in Example 1 of said patent, which describes a detergent composition produced in the absence of either a liquid medium or water as added diluent, a very considerable amount of water is actually present, namely, about 16% of the total composition. Furthermore, as there disclosed, the alkyl aryl sulfonates, such as dodecylbenzene sulfonate, can be utilized in the form of their alkali metal, ammonium or alkanolamine salts. When the procedures described in said patent, utilizing the proportions of the various ingredients disclosed therein, are, however, sought to be applied to the production of essentially 100% active stable liquid detergent compositions, such compositions are, in fact, characterized by poor clarity and substantially instability, separating into layers after even quite short periods of standing. So far as we are aware, the preparation of polyfunctional organic detergent compositions in the form of stable, homogeneous liquids, which advantageously are also low-foaming, generally speaking, has been limited to solutions having a concentration of active organic surfactant materials of the order of 50 to 70%. While it is highly desirable from an economy standpoint to prepare polyfunctional detergent compositions in liquid form which are stable over prolonged periods of time, and in which the content of the active organic surfac-

tants approaches 100%, when attempts are made to produce such compositions, various problems arise.

One such problem in the production of essentially 100% active, stable polyfunctional liquid low foaming detergent compositions is the matter of instability. This instability may be evidenced by the formation of two or more immiscible phases either during the preparation of the detergent composition or on standing over short periods of time. Another of such problems is the production of such a detergent composition which will, upon dilution with water in certain concentrations, where such dilution may be desired, dissolve readily and operate to perform effectively its desired detergent functions.

In accordance with the present invention, it has been found that a 100% active, or essentially 100% active, of essentially anhydrous polyfunctional organic detergent composition in the form of a clear, homogeneous, stable liquid having low foaming properties can be prepared by a certain balancing of a number of essential ingredients, and advantageously employing a particular mixing or blending procedure.

The essentially anhydrous liquid polyfunctional organic detergent compositions of the present invention contain as essential ingredients, in the ranges of proportions set forth hereafter, (1) ethanolamine (i.e., monoethanolamine, diethanolamine and triethanolamine or mixtures of two or more thereof) salts of alkyl benzene sulfonic acids or alkyl toluene sulfonic acids, particularly the diethanolamine or triethanolamine salts of said sulfonic acids (2) certain ethanolamides or isopropanolamides, and (3) certain water-soluble non-ionic organic surfactants which are normally liquid or, in other words, liquid at usual room temperatures.

The alkyl benzene sulfonic acids and the alkyl toluene sulfonic acids, which are utilized in the form of their ethanolamine salts as stated above, are those in which the alkyl radical, which may be linear or branched chain, contains predominately from 8 to 16 carbon atoms and, better still, from 11 to 15 carbon atoms. Especially satisfactory are dodecyl benzene sulfonic acid and tridecyl benzene sulfonic acid, as well as mixtures thereof or mixtures in which one or the other or both predominate, in which the dodecyl and tridecyl radicals are essentially normal or straight chain. The alkyl benzene or alkyl toluene sulfonic acids are well known in the art and are conventionally made by alkylating benzene or toluene with normal or straight chain chloroparaffins, polypropylene, or olefins, although other sources of alkyl radicals can, of course, be utilized. The ethanolamine salts of the aforesaid sulfonic acids are formed and incorporated in the manner described below. It may be noted that it is important to the achievement of the results of the present invention, taken in conjunction with the other essential aspects of the invention, not only to utilize ethanolamine salts of the aforesaid sulfonic acids, because the alkali metal salts are not operative, but, in addition, that said ethanolamine salts be formed in situ. It may also here be noted that many alkanolamines are unsatisfactory for the purposes of our present invention. Furthermore, to achieve the optimum advantages of the present invention, said in situ formation should be carried out in the manner hereafter described as a part of the overall method of blending the ingredients to form the final liquid detergent compositions of the present invention. It may be stated that, in itself, in situ formation, broadly,

of ethanolamine salts of alkyl benzene sulfonic acids as a part of a procedure for producing liquid detergent compositions is known to the art and no claim is made generally thereto. However, in such cases, the in situ formation of ethanolamine salts of alkyl benzene sulfonic acids has occurred in connection with the production of liquid detergent compositions containing substantial quantities of water, for instance, about 35 to 50%, as an essential part of the liquid detergent compositions, as shown, for example, in U.S. Pat. No. 3,232,880 and in Australian Pat. No. 164,644. In any event, and as pointed out above, our present invention and our polyfunctional essentially 100% active stable liquid detergent compositions are sharply distinguishable therefrom.

The normally liquid water-soluble non-ionic surfactants which are utilized in the liquid detergent compositions of the present invention serve as primary surfactants and defoamers as well as liquid carriers. They are the normally liquid water-soluble polyoxyethylene-polyoxypropylene glycol condensation products described in U.S. Pat. No. 2,674,619, and sold by Wyandotte-BASF under the tradename PLURONIC. The normally liquid water-soluble PLURONICS generally have a molecular weight of less than about 7500, and are generally prepared by reacting ethylene oxide with a polyoxypropylene glycol having a molecular weight of 950, or higher, until a sufficient degree of water solubility has been attained. The preparation and characteristics of this class of surfactants are well known and require no further discussion herein. These normally liquid water-soluble polyoxyethylene-polyoxypropylene glycol surfactants, besides being essential ingredients to produce the present stable 100% active essentially anhydrous polyfunctional organic detergent compositions, are advantageously effective as foam reducing agents.

The ethanolamides and/or isopropanolamides, which serve as viscosity builders in the liquid detergent compositions of the present invention, are the fatty acid monoethanolamides, diethanolamides and isopropanolamides in which the fatty acid acyl radical contains from 10 to 16 carbon atoms. Said amides should be either normally liquid or have melting points not higher than about 60° C. Especially satisfactory are the diethanolamides derived from coconut oil mixed fatty acids or special fractions containing, for instance, very predominately C₁₂ or C₁₄ fatty acids, and wherein the mol ratio of the diethanolamine to the higher fatty acid is about 1:1.

The proportions of the ingredients, in terms of weight %, comprising the liquid detergent compositions of the present invention are (A) from 30 to 90%, better still 45 to 75%, of the aforementioned ethanolamine salts of the alkyl benzene- or alkyl toluene-sulfonic acids (B) from 5 to 35%, better still 15 to 30%, of the aforementioned non-ionic normally liquid, water-soluble polyoxyethylene-polyoxypropylene glycol surfactants, and (C) from 5 to 35%, better still 12 to 25%, of the aforementioned fatty acid amides of monoethanolamine, diethanolamine or isopropanolamine. Particularly desirable are liquid detergent compositions made pursuant to the present invention wherein the aforesaid ethanolamine salts of the alkyl benzene- or alkyl toluene-sulfonic acid constitute from 52 to 64%, the aforesaid non-ionic surfactant constitutes from 22 to 30%, and the aforesaid fatty acid mono- or diethanolamides or

isopropanolamides constitute from 14 to 18% of the compositions.

In the preparation of the polyfunctional essentially 100% active stable liquid detergent compositions of the present invention, it is particularly advantageous first to form a substantially homogeneous solution of the non-ionic normally liquid water-soluble surfactant with an ethanolamine and then gradually add thereto, under conditions of agitation, the alkyl benzene sulfonic acid and/or alkyl toluene sulfonic acid in an amount essentially to be neutralized by said ethanolamine thereby to form the ethanolamine salt of said sulfonic acid, the temperature of the mixture being controlled so as not to exceed about 100°C and preferably not to substantially exceed 50°C, and then add the ethanolamide and/or isopropanolamide, under conditions of agitation, until a clear, homogeneous liquid is obtained. An alternative procedure is first to form a mixture of the non-ionic surfactant and the sulfonic acid and then gradually add thereto the ethanolamine under conditions of agitation. Still other procedures can be used but the non-ionic surfactant must comprise the vehicle in which in situ formation of the ethanolamine salt of the sulfonic acid is effected. Thus, for instance, stable compositions cannot be formed if the ethanolamine salt of the sulfonic acid is sought to be formed in situ in the ethanolamide and/or isopropanolamide per se. As indicated, nonionic surfactant must be present during the in situ formation of the ethanolamine salt of the sulfonic acid.

It may also be noted that the polyfunctional essentially 100% active stable liquid detergent compositions of the present invention cannot be made by initially preparing an aqueous solution of the active ingredients and then evaporating off the water because, among other things, at a concentration of about 60% of the active ingredients, breakdown of the composition occurs and instability results.

The following examples include illustrative or particularly preferred embodiments of the present invention, but they are not to be construed as in any way limitative of the invention since numerous other embodiments can readily be evolved in the light of the guiding principles and teachings provided herein. All parts recited are by weight.

EXAMPLE I

To 26 parts of liquid water soluble polyoxyethylene-polyoxypropylene glycol sold under the trade name of PLURONIC L-64, by Wyandotte - BASF, there was added 20 parts of diethanolamine. Then 40 parts of dodecyl benzene sulfonic acid (88% minimum activity) was slowly added, under conditions of agitation, the temperature of the reactants and the reaction mixture being maintained below 50°C and, better still, between about 20 and 30°C. The aforementioned amount of diethanolamine is the stoichiometric quantity required to neutralize the dodecyl benzene sulfonic acid. When the neutralization was complete, 14 parts of a superamide (made from 1 mol of coconut oil fatty acids and 1 mol of diethanolamine) was added, under conditions of agitation, until a clear, homogeneous low foaming liquid was obtained.

The properties of said low foaming liquid detergent composition, hereinabove prepared, were as follows:

Appearance	Clear amber liquid
Water content	Less than 2%
Cloud point	Less than 0°C
Clear point	Less than 0°C
pH	7.9

The stability of said liquid detergent compositions was excellent, no separation of ingredients occurring after several months of aging at ambient temperatures and also at 0°C.

The above procedure, when conducted at temperatures of as high as 100°C, or even higher, results in detergent compositions which are progressively slightly darker as the temperature of the reaction increases. The darker compositions, prepared according to the present invention, are utilized when the end use thereof is not affected by the darker colors or wherein darker colored compositions are preferred. The efficacy and utility of the detergent compositions is, however, not affected by such color considerations.

The following table illustrates the slight degree of darkening of the final liquid detergent compositions as the temperature is increased. Readings were made on a Klett-Summerson Photoelectric Colorimeter. Readings were made immediately after neutralization and one hour after neutralization at the temperature indicated, to simulate conditions in the processing of large batches which would be difficult to cool rapidly.

	Klett Color After Addition	Klett Color After One Hour
at 50°C.	475	500
at 65°C.	520	550
at 80°C.	540	580
at 95°C.	570	620

It is apparent from the above table that the temperature of the reaction may be increased considerably over 95°C. if it is desired to produce a darker product.

The final liquid detergent composition is pourable. However, when diluted to up to about 50 percent with water, gelling occurs. This "pourable" characteristic of the substantially anhydrous final liquid detergent, which gells when water is added illustrates the importance and criticality of excluding water during the preparation of the compositions of the present invention, and the unexpectedness of our invention since it would have been assumed that any effort by those skilled in the art to make compositions such as ours would have resulted in gels. We found, however, surprisingly, that polyfunctional essentially 100% active liquid detergent compositions of the type here involved could be made which are stable and readily pourable.

EXAMPLE 1a

In sharp contrast to the results obtained in Example 1, when a detergent composition was sought to be made by simply mixing together 26 parts of the same PLURONIC L-64 used in Example 1, 14 parts of the same superamide used in Example 1, and 60 parts of the sodium salt of dodecyl benzene sulfonic acid (100% active, or in the form of an aqueous slurry as in the aforesaid Pat. No. 3,239,468), the resulting composition was unclear and unstable and quickly formed separate layers, including undissolved material.

EXAMPLE 1b

Again, when an essentially anhydrous detergent composition was sought to be made by simply admixing together 26 parts of the same PLURONIC L-64 used in Example 1, 14 parts of the same superamide used in Example 1, and 60 parts of a preformed diethanolamine salt of dodecyl benzene sulfonic acid made by admixing 20 parts of diethanolamine with 40 parts of dodecyl benzene sulfonic acid (88% minimum activity), an extremely non-homogeneous, unclear composition resulted in which solids readily separated out. Indeed, a usable preformed diethanolamine salt of dodecyl benzene sulfonic acid could not be made because an unmanageable gel resulted on mixing diethanolamine with dodecyl benzene sulfonic acid.

EXAMPLE 1c

A detergent composition was sought to be made by simply admixing together 30 parts of a PLURONIC L-44, a liquid water soluble polyoxyethylene-polyoxypropylene glycol condensation product, 50 parts of a coconut fatty acid-diethanolamine condensate (mol ratio of coconut fatty acids: diethanolamine being 1:1) and 20 parts of the sodium salt of dodecyl benzene sulfonic acid (100% active or in the form of an aqueous slurry as in the aforesaid Pat. No. 3,239,648). The resulting composition was unclear and unstable, readily separating out into layers.

EXAMPLE 1d

A detergent composition was sought to be made by simply admixing together 30 parts of PLURONIC L-44, a liquid water soluble polyoxyethylene-polyoxypropylene glycol condensation product, 50 parts of a coconut fatty acid-diethanolamine condensate (mol ratio of coconut fatty acids: diethanolamine being 1:1), and 20 parts of a preformed diethanolamine salt of dodecyl benzene sulfonic acid. The resulting composition was extremely non-homogeneous and unclear from which solids readily separated out. (Note the observations made in Example 1(b) regarding the matter of seeking to prepare the preformed diethanolamine salt of dodecyl benzene sulfonic acid).

Examples 1(c) and 1(d) are illustrative of compositions falling within the ranges of proportions of the stated ingredients disclosed in the aforesaid Pat. No. 3,239,468 sought to be made simply by mixing together said ingredients. These examples, as well as Examples 1(a) and 1(b), show that our polyfunctional essentially 100% active stable liquid detergent compositions are not obtainable by following the procedures described in said Examples 1(a), 1(b), 1(c) and 1(d).

EXAMPLE 2

	Parts
Diethanolamine	20
Linear Dodecyl Benzene Sulfonic Acid (88% Active)	40
PLURONIC L-44	18
Coconut Oil Fatty Acid	22
Diethanolamide (1:1 Mol Ratio)	

EXAMPLE 3

	Parts
Triethanolamine	25
Linear Dodecyl Benzene	35
Sulfonic Acid (88% Active)	
PLURONIC L-44	22
Lauric Acid Diethanolamide (1:1 Mol Ratio)	18

EXAMPLE 4

	Parts
Diethanolamine	14
Alkyl Benzene Sulfonic Acid (98% Active - Branched Chain Alkyl Radical Containing Pre- dominately 11 Carbon Atoms)	41
PLURONIC L-64	30
Coconut Oil Fatty Acid Diethanolamide (1:1 Mol Ratio)	15

EXAMPLE 5

	Parts
Diethanolamine	20
Linear Tridecyl Benzene	40
Sulfonic Acid	
PLURONIC L-64	24
Lauric Acid Diethanolamide (1:1 Mol Ratio)	16

The compositions of Examples 2-5 are made in the manner described in Example 1. They are all clear stable low foaming liquids under ambient conditions as well as at 0°C.

The liquid detergent compositions of the present invention, as pointed out above, are 100% active or essentially 100% active. In the preparation of said compositions, it is advisable, for optimum results, that no water be deliberately added during such preparation. However, some water may enter into the final liquid detergent compositions by reason of its presence in small proportions in one or more of the ingredients utilized in the preparation of said compositions. In any event, the method of preparation and the selection of ingredients should so be controlled that the water content of the final liquid detergent compositions does not exceed 2% of the total weight of said liquid detergent compositions. Where reference is made in the claims to "essentially 100% active stable liquid detergent composition", it will be understood that said compositions may contain up to 2% water.

The liquid detergent compositions of the present invention, in addition to exhibiting excellent cleaning power for many commercial and consumer requirements including hard surface cleaning, have the important advantages of providing essentially 100% organic surfactant activity with the accompanying economic advantages in shipping and storing, and outstanding stability over prolonged periods of time over a wide temperature range. Said liquid detergent compositions are readily pourable or pumpable, and they can be diluted with water to various commercially acceptable concentrations, forming aqueous solutions which are

also stable over a wide temperature range and for extended periods of time.

We claim:

1. In a method of making a polyfunctional essentially 100% active stable liquid detergent composition consisting essentially of the following ingredients in the following percentages by weight:

	%
A. An ethanolamine salt of a member selected from the group consisting of alkyl benzene- and alkyl toluene-sulfonic acids in which the alkyl radical contains from 8 to 18 carbon atoms.	30 to 90
B. A non-ionic normally liquid, water soluble surfactant comprising a polyoxyethylene-polyoxypropylene glycol condensation product	5 to 35
C. Fatty acid amides selected from the group consisting of mono-ethanolamide, diethanolamide and isopropanolamide in which the fatty acid acyl radical contains from 10 to 16 carbon atoms.	5 to 35

the steps which comprise forming a substantially homogeneous solution of the B ingredient with an ethanolamine, then gradually adding thereto, under conditions of agitation, a member selected from the group consisting of alkyl benzene and alkyl toluene-sulfonic acids in which the alkyl radical contains from 8 to 18 carbon atoms, said sulfonic acid being added in an amount essentially to be neutralized by said ethanolamine thereby to form the ethanolamine salt of said sulfonic acid, the temperature of the above mixture being maintained so as not to exceed about 100°C., and then adding under conditions of agitation, said C ingredient until a clear, homogeneous liquid is obtained.

2. In a method of making a polyfunctional essentially 100% active stable liquid detergent composition consisting essentially of the following ingredients in the following percentages by weight:

	%
A. An ethanolamine salt of a member selected from the group consisting of alkyl benzene- and alkyl toluene-sulfonic acids in which the alkyl radical contains from 8 to 18 carbon atoms.	30-90
B. A non-ionic normally liquid, water soluble surfactant comprising polyoxyethylene-polyoxypropylene glycol condensation product.	5 to 35
C. Fatty acid amides selected from the group consisting of mono-ethanolamide, diethanolamide and isopropanolamide in which the fatty acid acyl radical contains from 10 to 16 carbon atoms.	5 to 35

the steps which comprise forming a substantially homogeneous solution of the B ingredient with a member selected from the group consisting of alkyl benzene- and alkyl toluene- sulfonic acids in which the alkyl radical contains from 8 to 18 carbon atoms, then gradually adding thereto, under conditions of agitation, an ethanolamine, said ethanolamine being added in an amount essentially to be neutralized by said sulfonic acid thereby to form the ethanolamine salt of said sulfonic acid, the temperature of the above mixture being maintained so as not to exceed about 100°C., and then add-

ing, under conditions of agitation, said C ingredient until a clear homogeneous liquid is obtained.

3. A method according to claim 1, wherein the temperature is maintained at below 50°C.

4. A method according to claim 1, wherein the alkyl radical of said sulfonic acid contains predominantly from 11 to 15 carbon atoms.

5. A method according to claim 1, wherein the sulfonic acid is a member selected from the group consisting of dodecyl- and tridecyl-benzene sulfonic acid.

6. A method according to claim 5, wherein the B ingredient constitutes from 22 to 30%, the C ingredient constitutes from 14 to 18%, and the ethanolamine salt of the sulfonic acid constitutes from 52 to 64% of the finished liquid detergent composition.

7. A method according to claim 1, wherein the A ingredient constitutes 45 to 75%, the B ingredient constitutes 15 to 30%, and the C ingredient constitutes 12 to 25%.

8. A method according to claim 4, wherein the A ingredient constitutes 45 to 75%, the B ingredient constitutes 15 to 30%, and the C ingredient constitutes 12 to 25%.

9. A method according to claim 1, wherein the A ingredient is an ethanolamine salt of a member selected from the group consisting of dodecyl- and tridecyl-benzene sulfonic acid, and the C ingredient is a C₁₂-C₁₄ fatty acid diethanolamide.

10. A method according to claim 9, wherein the A ingredient constitutes from 52-64%, the B ingredient

constitutes from 22 to 30%, and the C ingredient constitutes from 14 to 18%.

11. A method according to claim 9, wherein the A ingredient is a diethanolamine salt of a linear tridecyl benzene sulfonic acid.

12. A method according to claim 9, wherein the A ingredient is a diethanolamine salt of a linear dodecyl benzene sulfonic acid.

13. A method according to claim 2, wherein the temperature is maintained at below 50°C.

14. A method according to claim 2, wherein the alkyl radical of said sulfonic acid contains predominately from 11 to 15 carbon atoms.

15. A method according to claim 14, wherein the B ingredient constitutes from 22 to 30%, the C ingredient constitutes from 14 to 18%, and the ethanolamine salt of the sulfonic acid constitutes from 52 to 64% of the finished liquid detergent composition.

16. A method according to claim 2, wherein the A ingredient constitutes 45 to 75%, the B ingredient constitutes 15 to 30%, and the C ingredient constitutes 12 to 25%.

17. A method according to claim 14, wherein the A ingredient constitutes 45 to 75%, the B ingredient constitutes 15 to 30%, and the C ingredient constitutes 12 to 25%.

18. The product by the method of claim 1.

19. The product by the method of claim 2.

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