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EMULSIFIER COMPOSITIONS BASED ON MIXTURES OF AMINE SALTS OF LINEAR ALKYL ARYL SULFONIC ACIDS

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U.S. Cl. 252—153 19 Claims

ABSTRACT OF THE DISCLOSURE

An emulsifier composition consisting essentially of (a) at least one isopropylamine salt selected from the group consisting of C_{11} to C_{16} linear alkyl benzene and linear alkyl toluene monosulfonic acids, and (b) at least one amine salt selected from the group consisting of C_{11} to C_{16} linear alkyl benzene and linear alkyl toluene monosulfonic acids in which the amine is selected from the group consisting of n-butylamine, diisopropylamine, isobutylamine, tert-butylamine, cyclohexylamine and n-propylamine, said (b) compound or compounds constituting from about 15 to 35%, by weight, of the mixture of said (a) and (b) compounds, with the proviso that, in the case of n-propylamine salts of the (b) compounds, said n-propylamine salt or salts constitutes from about 40 to 60%, by weight, of the mixture of said (a) and (b) compounds.

This application is a continuation-in-part of my application Ser. No. 587,946, filed Oct. 20, 1966 and now abandoned.

This invention relates to novel emulsifiers and emulsion compositions containing the same, particularly for use in dry cleaning, degreasing, metal grinding coolants, paint brush cleaners, agricultural and pesticidal emulsions, aerosol compositions, and the like, wherein an oleaginous material is dispersed or emulsified in water.

Numerous emulsifying agents and emulsifier compositions are known and used commercially for a wide variety of emulsions. One of such types of emulsifying agents which has been utilized for certain types of emulsions is the amine salts of higher molecular weight alkyl benzene sulfonic acids, exemplified by n-propylamine, isopropylamine, n-butylamine, diethanolamine and triethanolamine salts of C_{12} to C_{15} alkyl benzene sulfonic acids, particularly dodecylbenzene sulfonic acid, wherein the C_{12} to C_{15} alkyl radical is derived from highly branched chain olefins, the production of such branched chain alkyl benzene sulfonic acids being shown, for instance, in U.S. Pat. No. 2,477,383. It has also been known to utilize the isopropylamine salt of dodecyl benzene sulfonic acid (isopropylammonium dodecyl benzene sulfonate) for the preparation of water-in-oil emulsions of 1,1,2-trichloro-1,2,2-trifluoroethane, as disclosed in Canadian Pat. No. 737,892.

Because of their resistance to biodegradability by bacteria, the aforementioned branched chain higher molecular weight alkyl benzene sulfonates have been sought to be replaced by higher molecular weight alkyl benzene sulfonates in which the alkyl radical is linear in character, since such linear alkyl benzene sulfonates are biodegradable. It has been found, however, that, for various purposes, the linear alkyl benzene sulfonates cannot be substituted for the branched chain alkyl benzene sulfonates because certain properties of the one are not shared by the other. Thus, for example, in certain emulsions, an amine salt of a branched chain dodecylbenzene sulfonic acid produces a relatively stable emulsion, whereas a generally corresponding amine salt of a linear

dodecyl benzene sulfonic acid does not. More specifically, but only by way of illustration, if one seeks to prepare an emulsion of 8 grams of a trichlorotrifluorethane, such as 1,1,2-trichloro-1,2,2-trifluoroethane, in 12 grams of water, the addition of 4 grams of the isopropyl amine salt of a branched chain dodecyl (propylene tetramer) benzene sulfonic acid produces a satisfactory, clear emulsion. However, if one seeks to use the isopropylamine salt of a linear dodecyl benzene sulfonic acid as the emulsifier in such an emulsion, then the emulsion which results is cloudy and unstable and rapidly separates.

I have discovered that if an isopropylamine salt of a C_{11} to C_{16} linear alkyl benzene or toluene sulfonic acid is used in admixture with a n-butylamine salt, or certain other amine salts referred to below, of a C_{11} to C_{16} linear alkyl benzene or toluene sulfonic acid, in certain proportions with respect to each other as stated below, a surprising and wholly unexpected coaction occurs with respect to the functioning thereof as an emulsifier. Thus, for instance, in the aforementioned emulsion of trichlorotrifluorethane in water, the use of a mixture of the isopropylamine and n-butylamine salts of the C_{11}–C_{12} linear alkyl benzene sulfonic acids, in a molar ratio of 82 of the former to 18 of the later, results in the production of a clear or transparent emulsion of excellent stability.

While it is particularly advantageous to use the n-butylamine salt of the C_{11} to C_{16} linear alkyl benzene or toluene sulfonic acid in conjunction with the isopropylamine salt of said sulfonic acids, there can be used, in place of said n-butylamine salts, the corresponding salts of diisopropylamine, isobutylamine, tert-butylamine and cyclohexylamine and, to a lesser extent, n-propylamine, and mixtures of two or more thereof.

The n-butylamine, or the diisopropylamine, the isobutylamine, the tert-butylamine, and cyclohexylamine salt of the C_{11} to C_{16} linear alkyl benzene or toluene sulfonic acid, in all cases, is used in amounts distinctly less than the amount of the isopropylamine salt of the C_{11} to C_{16} linear alkyl benzene or toluene sulfonic acid and, as a practical proposition, said n-butylamine or other aforementioned amine salt will constitute from about 15 to 35%, better still about 20 to 30%, by weight, of the total of, or the mixture of, the isopropylamine and n-butylamine or said other amine salts of the C_{11} to C_{16} linear alkyl benzene or toluene sulfonic acids. The optimum weight ratios of the isopropylamine and the other said amine salts to be used in any given emulsion will, of course, vary, depending, among other things, on the particular amine salt used in combination with the isopropylamine salt, on the particular C_{11} to C_{16} linear alkyl radical or radicals selected, and the particular emulsion into which said two salts are incorporated. Simple routine tests can be made in any given case to arrive at the substantially optimum weight ratios. In the case where the n-propylamine salt is used in conjunction with the isopropylamine salt, the proportions of said n-propylamine salt are materially greater than where the n-butylamine salt is used, being of the order of 40 to 60%, preferably about 50%, by weight of the mixture thereof of the isopropylamine salt.

The amount or proportions of the mixture of the aforesaid isopropylamine salt, and n-butylamine or said other amine salts, of the C_{11} to C_{16} linear alkyl benzene or toluene sulfonic acids, which are used in any given emulsion is variable, being dependent, for instance, upon the particular emulsion composition involved. In general, the percentage will range from 0.5 to 15%, by weight, of the oleaginous constituent of constituents of the emulsion. Based on the weight of the emulsion, the emulsifier composition will ordinarily fall within the range of about 0.2 to about 45%, more commonly about 2% to 20%.

The production of biodegradable C_{11} to C_{16} linear alkyl benzene and toluene sulfonic acids and the isopropylamine and n-butylamine salts thereof is well known to the art. The linear alkyl radical can be derived from various sources, a typical and preferred one of which is straight chain alkanes containing predominately 11 to 16 carbon atoms which may be obtained from petroleum distillates, by separating the straight chain alkanes from the branched chain alkanes by known means such as molecular sieves or by adduction with urea, but other sources of C_{11} to C_{16} linear alkyl radicals can be utilized to produce the biodegradable alkyl sulfonic acids which may then be neutralized to produce the isopropylamine and n-butylamine or said other amine salts. The linear alkyl benzene and toluene sulfonic acids which are employed will generally comprise primarily or mainly monoalkyl monosulfonic benzenes and toluene, but dialkyl monosulfonic acid derivatives can also be used. The isopropylamine salts and the n-butylamine or other said amine salts of the C_{11} to C_{16} linear alkyl benzene or toluene sulfonic acids can be separately produced and then admixed to form the emulsifier composition; or a C_{11} to C_{16} linear alkyl benzene or toluene sulfonic acid can be neutralized with isopropylamine and, say, n-butylamine, or a mixture of said amines, in proper proportions to produce the mixtures described above. It is, of course, most advantageous to utilize a composition comprising pre-mixture of the isopropylamine and n-butylamine, or said other amine salts of the C_{11} to C_{16} linear alkyl benzene or toluene sulfonic acids in the production of the emulsions. However, in making any given emulsion, the isopropylamine salt and the n-butylamine or said other amine salts can be added separately or together with the other ingredients of the emulsion, following, however, standard mixing procedures to produce any given emulsion which may be involved.

The oleaginous phase of the emulsions is most advantageously of mineral character and includes, for instance, liquid hydrocarbons such as mineral oils, kerosene, odorless mineral spirits, Stoddard solvent, naphtha; halogenated, notably chlorinated, hydrocarbons such as perchlorethylene and 1,1,1-trichlorethane; and such mixed halogenated, notably chlorinated-fluorinated, hydrocarbons such as trichlorofluoromethane, dichlorofluoromethane and dichlorotetrafluoroethane, particularly 1,1,2-trichloro-1,2,2-trifluoroethane. Such oleaginous materials are normally insoluble or essentially insoluble in water.

The emulsions produced pursuant to the present invention can be prepared in the form of finished compositions for use for the intended purpose or in the form of concentrates for dilution with oleaginous or aqueous materials, as the case may be, prior to use for the intended purpose. The emulsions can be of the oil-in-water type, or the water-in-oil type, the latter being particularly preferred. In such latter emulsions, particularly where the oleaginous, continuous phase is 1,1,2-trichloro-1,2,2-trifluoroethane, the water content may range from about 1 to 50%, the 1,1,2-trichloro-1,2,2-trifluoroethane content may range from about 30 to 98%, and the balance, from about 0.5 to 45%, the emulsifier composition.

The following examples are illustrative of compositions which fall within the scope of the present invention. It will be understood that said examples are not intended in any way to be limitative of the invention but, rather, illustrative typical compositions following the new and useful teachings provided herein. All parts stated are by weight.

EXAMPLE 1

	Parts
Isopropylamine salt of linear dodecyl benzene sulfonic acid	76
n-Butylamine salt of linear dodecyl benzene sulfonic acid	24

EXAMPLE 2

	Parts
Isopropylamine salt of linear tridecyl benzene sulfonic acid	78
n-Butylamine salt of linear tridecyl benzene sulfonic acid	22

EXAMPLE 3

	Parts
Isopropylamine salt of linear dodecyl toluene sulfonic acid	82
n-Butylamine salt of linear dodecyl benzene sulfonic acid	18

EXAMPLE 4

	Parts
Isopropylamine salt of linear dodecyl benzene sulfonic acid	75
n-Butylamine salt of linear tridecyl toluene sulfonic acid	25

EXAMPLE 5

	Parts
Isopropylamine salt of linear pentadecyl benzene sulfonic acid	73
n-Butylamine salt of linear pentadecyl benzene sulfonic acid	27

EXAMPLE 6

	Parts
Isopropylamine salt of linear dodecyl benzene sulfonic acid	72
n-Butylamine salt of linear dodecyl benzene sulfonic acid	28

EXAMPLE 7

	Parts
Isopropylamine salt of linear dodecyl benzene sulfonic acid	80
Isobutylamine salt of linear dodecyl benzene sulfonic acid	20

EXAMPLE 8

	Parts
Isopropylamine salt of linear dodecyl benzene sulfonic acid	78
Tert-butylamine salt of linear tridecyl benzene sulfonic acid	22

EXAMPLE 9

	Parts
Isopropylamine salt of linear dodecyl benzene sulfonic acid	81
Diisopropylamine salt of linear dodecyl benzene sulfonic acid	19

EXAMPLE 10

	Parts
Isopropylamine salt of linear dodecyl benzene sulfonic acid	78
Cyclohexylamine salt of linear dodecyl benzene sulfonic acid	22

EXAMPLE 11

	Parts
Isopropylamine salt of linear dodecyl benzene sulfonic acid	50
n-Propylamine salt of linear dodecyl benzene sulfonic acid	50

EXAMPLE 12

	Parts
Kerosene	9.5
Water	90
Composition of Example 1	0.5

EXAMPLE 13

	Parts
Naphtha	9.5
Water	90
Composition of Example 6	0.5

EXAMPLE 14

	Parts
Perchlorethylene	14
Water	85
Composition of Example 2	1

EXAMPLE 15

	Parts
Light mineral oil	60
Water	38
Composition of Example 1	2

EXAMPLE 16

	Parts
1,1,2-trichloro-1,2,2,-trifluoroethane	33.3
Water	50
Composition of Example 3	16.7

EXAMPLE 17

	Parts
1,1,2-trichloro-1,2,2-trifluoroethane	90
Water	7
Composition of Example 1	3

EXAMPLE 18

	Parts
1,1,2-trichloro-1,2,2-trifluoroethane	92
Water	6
Composition of Example 2	2

EXAMPLE 19

	Parts
1,1,2-trichloro-1,2,2-trifluoroethane	37
Ammonium hydroxide (28.5% NH_3)	21
Composition of Example 1	42

The compositions represented by Examples 16–19 are particularly useful for cleaning machinery and may be used in the manner and for the purposes described in the aforementioned Canadian Pat. No. 737,892 as such and admixed with ammonia or ammonium hydroxide.

Various additional or supplemental ingredients can be added for the purpose of obtaining special effects as, for instance, oil-soluble and water-soluble constituents such as lanolin or lanolin esters; high fatty alcohols such as cetyl alcohol; isopropyl myristate; polyvinyl pyrrolidone; ethoxylated lanolins; chelating agents such as ethylenediamine tetra-acetic acid and its salts, and the like.

I claim:

1. An emulsifier composition consisting essentially of (a) an isopropylamine salt selected from the group consisting of C_{11} to C_{16} linear alkyl benzene monosulfonic acids and linear alkyl toluene monosulfonic acids and mixtures thereof, and (b) an amine salt selected from the group consisting of C_{11} to C_{16} linear alkyl benzene monosulfonic acids and C_{11} to C_{16} linear alkyl toluene monosulfonic acids and mixtures thereof in which the amine is selected from the group consisting of n-butylamine, diisopropylamine, isobutylamine, tert-butylamine and cyclohexylamine, said (b) salt constituting from about 15 to 35%, by weight, of the mixture of said (a) and (b) salts.

2. A composition according to claim **1**, in which the linear alkyl benzene sulfonic acids are predominately monododecyl benzene monosulfonic acid.

3. A composition acording to claim **2**, in which the (b) salt is predominantly the n-butylamine salt.

4. A composition according to claim **3**, in which the n-butylamine salt constitutes from about 18 to 24%, by weight, of the mixture of said salts of said sulfonic acids.

5. A composition according to claim **1**, in the form of an aqueous emulsion in which the aqueous phase is the dispersed phase.

6. A composition according to claim **5**, in which the continuous phase of the emulsion is a liquid hydrocarbon.

7. A composition according to claim **1**, in which the halogenated compound is 1,1,2-trichloro-1,2,2-trifluoroethane.

8. A composition according to claim **7**, in which the linear alkyl benzene sulfonic acids are predominately monododecyl benzene monosulfonic acid, and wherein the (b) salt is the n-butylamine salt.

9. A composition according to claim **8**, in which the n-butylamine salt constitutes from about 18 to 24% by weight, of the mixture of said salts of said sulfonic acids.

10. A stable emulsion consisting essentially of at least about 30%, by weight, of 1,1,2-trichloro-1,2,2-trifluoroethane as the continuous phase, from about 0.5 to 50%, by weight, of water as the dispersed phase, and from about 0.2 to about 45%, by weight, of the emulsifier composition of claim **1**.

11. A stable emulsion consisting essentially of at least about 30%, by weight, of 1,1,2-trichloro-1,2,2-trifluoroethane as the continuous phase, from about 0.5 to 50% by weight, of water as the dispersed phase, and from about 0.2 to about 45%, by weight, of the emulsifier composition of claim **4**.

12. A composition according to claim **5**, in which the continuous phase of the emulsion is a member selected from the group consisting of perchlorethylene and liquid halogenated methanes and liquid halogenated ethanes.

13. An emulsifier composition consisting essentially of (a) an isopropylamine salt selected from the group consisting of C_{11} to C_{16} linear alkyl benzene monosulfonic acids and C_{11} to C_{16} linear alkyl toluene monosulfonic acids and mixtures thereof, and (b) an amine salt selected from the group consisting of C_{11} to C_{16} linear alkyl benzene monosulfonic acids and linear alkyl toluene monosulfonic acids and mixtures thereof in which the amine is n-propylamine, said (b) salt constituting from about 40 to 60%, by weight, of the mixture of said (a) and (b) salts.

14. A composition according to claim **13**, in which the linear alkyl benzene sulfonic acids are predominantly monododecyl benzene monosulfonic acid.

15. A composition acording to claim **13**, in the form of an aqueous emulsion in which the aqueous phase is the dispersed phase.

16. A composition according to claim **15**, in which the continuous phase of the emulsion is a liquid hydrocarbon.

17. A composition according to claim **16**, in which the continuous phase of the emulsion is a member selected from the group consisting of perchlorethylene and liquid halogenated methanes and liquid halogenated ethanes.

18. A composition according to claim **17**, in which the halogenated hydrocarbon is 1,1,2-trichloro-1,2,2-trifluoroethane.

19. A stable emulsion consisting essentially of at least about 30%, by weight, of 1,1,2-trichloro-1,2,2-trifluoroethane as the continuous phase, from about 0.5 to 50%, by weight, of water as the dispersed phase, and from about 0.2 to about 45%, by weight, of the emulsifier composition of claim **13**.

References Cited

UNITED STATES PATENTS

3,336,232 8/1967 Bauer et al.

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