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(54) Title: SOLVENT FREE LIQUID ALKYL BENZENE SULFONATE COMPOSITION AND ITS USE IN AGROCHEMICAL FORMULATIONS

(57) Abstract: A liquid alkylbenzene sulfonate composition comprising a salt of alkylbenzene sulfonate (preferably a calcium or DMAPA salt) and a liquid alcohol alkoxyate is disclosed. This composition is useful as an emulsifier. It is solvent-free and non-flammable and has low odor.

Solvent free liquid alkylbenzene sulfonate composition and its use in agrochemical formulations

Field of the Invention

- 5 The present invention is directed to a liquid alkylbenzene sulfonate composition comprising a salt of alkylbenzene sulfonate and a liquid alcohol alkoxyate. The invention also related to the use of said composition as an emulsifier.

Background of Invention

- 10 Almost all liquid pesticide formulations contain a package of emulsifiers when the pesticide is a hydrophobic substance. This is because the hydrophobic pesticide does not mix well with water and water is the most common carrier medium to dilute the pesticide formulations during application. The emulsifiers help bring together the hydrophobic pesticide and water to form kinetically stable emulsions or thermodynamically stable
15 microemulsions that can be sprayed. The phenomenon of forming the emulsions and microemulsions is called emulsification. Typical emulsifier blends comprise a blend of anionic surfactant, a nonionic surfactant, and a block copolymer, each is typically produced individually. In most formulations, the anionic surfactant in the blends of emulsifiers is a salt of alkylbenzene sulfonate. It is well known to the skilled in the art that when the salt is a
20 calcium salt, the alkylbenzene sulfonate is most effective in terms of emulsification power. Most popular calcium alkylbenzene sulfonate is calcium dodecylbenzene sulfonate (Ca-DDBS) and it can be made by neutralizing two moles of DDBS acid with one mole calcium oxide (or calcium hydroxide) in various inert solvents. Inert solvent is necessary to reduce the viscosity of Ca-DDBS. Without the solvent, Ca-DDBS is very difficult to handle due to its
25 high viscosity. The amount of solvent required to dilute Ca-DDBS into a handleable product is about 40-45 wt%. That is, the concentration of Ca-DDBS is about 55-60 wt%, which is the most common concentration used in the industry.

- Another less popular salt of alkylbenzene sulfonate is the dimethylamidopropylamine (DMAPA) salt. Similarly, DMAPA-DDBS requires ~ 40% solvents to reduce its viscosity to
30 make it easy to handle.

The solvents, or diluents, commonly used to dilute Ca-DDBS (or DMAPA-DDBS) emulsifier are listed in Table 1:

35

Table 1. Solvents commonly used to dilute Ca-DDBS emulsifier

Common Solvents used in Ca-DDBS	Flammability	Odor	Toxicity
Methanol	Flammable	Strong	May cause blindness if consumed
Isopropyl alcohol	Flammable	Strong	
Iso-butanol	Flammable	Strong	Potentially repro toxic
Hexanol	Flammable	Strong	
2-ethyhexanol		Strong	
Aromatic solvents	Some are flammable	Strong	Contains trace amount of naphthalene
Propylene glycol or other glycols	Non-flammable	None	None

As it is shown in the above table, all solvents except glycols have issues either with flammability, odor, and/or toxicity. In addition, all solvents, including glycols, serve only one function – to make the DDBS salts less viscous so that they can be handled easily.

Solvents are used in various pesticide formulations including emulsifiable concentrate (EC), microemulsion (ME), and suspoemulsion (SE). For example, EC formulations of 4 lbs/gallon 2,4-D ester containing solvents have been in the market for many years. The solvents may come from the DDBS salt or it may be added during preparation of the EC. Nowadays, use of solvents in pesticide formulations is becoming an issue due to environmental concerns. Because of that, 6 lb/gallon 2,4-D ester EC has appeared in the market place recently. Since 2,4-D ester itself is a liquid with quite low viscosity, this 6 lbs/gal 2,4-D EC can be formulated with only 2,4-D ester and emulsifiers without the need for additional solvents. However, the current 6 lbs/gal 2,4-D can't be claimed as solvent-free because some solvent is presented in the emulsifier blend which contains Ca-DDBS (or DMAPA-DDBS) with solvents. It would have market advantage for a manufacturer if a 6 lbs/gal 2,4-D EC can be claimed as solvent-free.

Therefore, there is a need to have a solvent-free, non-flammable, and low odor Ca-DDBS and DMAPA-DDBS in the market place.

The present inventors have addressed this need by introducing a liquid alkylbenzene sulfonate composition comprising a Ca (or DMAPA) alkylbenzene sulfonate and a liquid alcohol alkoxyate.

Berol[®] 9927, manufactured by AkzoNobel, contains Ca-DDBS, a solid alcohol alkoxyate, and butanol. However, the presence of butanol makes it flammable (flash point ~45°C).

US20070191229A1 discloses a so-called solventless herbicide composition, triclopyr butoxyethyl ester EC. Only one surfactant mixture is disclosed in this article as disclosed in example 1. The surfactant mixture of this article contains 50% Agnique ABS 60C, a 60% Ca-

DDBS in 2-Ethylhexanol solvent. Therefore, this so-called solventless herbicide composition claimed in this article is not truly solvent-free.

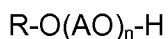
Similarly, WO 2007/095163, which relates to an emulsifying system and adjuvant for formulating water soluble or water emulsifiable pesticide formulations, does not disclose any blends that are solvent-free. WO 2007/095163 considers water and lower alcohol as non-solvents. Further, all of the examples in WO 2007/095163 contains significant amount of solvent because Agnique ABS 60C is 60% Ca-DDBS in 40% 2-ethylhexyl alcohol.

Summary of the Invention

10 The invention relates to a liquid alkylbenzene sulfonate composition comprising at least one alkylbenzene sulfonate salt selected from a calcium salt, a DMAPA salt, an ethanolamine salt, a diethanolamine salt, a triethanolamine salt, a diethylenetriamine salt, or an ethylenediamine salt of alkylbenzene sulfonate, and a liquid alcohol alkoxyate.

15 In one embodiment the alkyl group in the alkylbenzene sulfonate of the present invention comprises 10 – 20 carbon atoms; in another embodiment 12 – 14 carbon atoms, wherein said alkyl groups can be linear or branched, saturated or non-saturated, and optionally substituted. The concentration of alkylbenzene sulfonate salt in the liquid alkylbenzene sulfonate composition of the invention is, in one embodiment from about 40 – 70 wt%, in another embodiment from about 50 – 65 wt%, and yet another embodiment from
20 about 55 - 60 wt%.

The liquid alcohol alkoxyate in the novel liquid alkylbenzene sulfonate composition has the following general structure:



25 Wherein R is C6-C12, in another embodiment a C8-C10, linear or branched, hydrocarbon chain; A is an ethylene or branched propylene group, preferably an ethylene group; n is from 1 – 8, in another embodiment from 2 – 7, in another embodiment from 3 – 5. The concentration of the liquid alcohol alkoxyate in the liquid alkylbenzene sulfonate composition of the invention is from about 60 – 30 wt%, in another embodiment from about 50 – 35 wt%, and in yet another embodiment from about 45 – 40 wt%.

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Detailed Description

The present invention employs a method to turn a very viscous DDBS salt into a handlable liquid alkylbenzene sulfonate composition without using a solvent or a diluent. The liquid alkylbenzene sulfonate composition of the invention comprises at least one
35 alkylbenzene sulfonate salt selected from a calcium salt, a DMAPA salt, an ethanolamine salt, a diethanolamine salt, a triethanolamine salt, a diethylenetriamine salt, or an

ethylenediamine salt and a liquid alcohol alkoxylate. Preferably the alkylbenzene sulfonate salt is a calcium salt. The composition of the invention is useful as an emulsifier, or as part of an emulsifier blend. The composition is a liquid and it is solvent-free and non-flammable. It preferably is a clear liquid with reduced odor. A solvent-free product is herein defined as a product with less than about 3 wt% solvents, in one embodiment less than about 2 wt% solvents, in another embodiment less than about 1 wt% solvents, in yet another embodiment less than about 0.5 wt% solvents. As used herein, the term "solvents" means a low viscosity liquid substances, not including water. The term also does not include surfactants even though surfactants may be used to dissolve other chemicals, as disclosed herein. Examples of solvents are methanol, isopropyl alcohol, iso-butanol, hexanol, 2-ethylhexanol, aromatic solvents, propylene glycol or other glycols (such as polyethylene glycol), glycerine, ester of fatty acid, vegetable oil, alcohol, propylene carbonate, glycerine carbonate, mineral oil, hydrocarbons (e.g., octane), N-Methylpyrrolidone (NMP), amides (e.g. alkyl dimethyl amide), etc.

The alkyl chain in alkylbenzene sulfonate of the present invention is C10 – C20, in another embodiment C10 – C18, and in yet another embodiment a C12 – C14, linear or branched, saturated or non-saturated, hydrocarbon chain. In another embodiment of the invention the alkyl chain in alkylbenzene sulfonate is a dodecyl chain. The concentration of alkylbenzene sulfonate salt in the composition of the invention is generally from about 40 – 70 wt%, in another embodiment from about, 50 – 65 wt%, and still another embodiment from about 55 - 60 wt%. Preferably the rest of the component amounting to 100% is a liquid alcohol alkoxylate.

The liquid alcohol alkoxylate of the present invention has the following general structure:



Wherein R is C6-C12, linear or branched, hydro carbon chain; A is an ethylene or branched propylene group; n is from 1 – 8, in another embodiment from 2 – 7, and in yet another embodiment from 3 – 5. It is understood that n is the average degree of alkoxylation. The degree of alkoxylation reflects the moles of alkyleneoxide reacted with one mole of alcohol (the R-OH). The concentration of the liquid alcohol alkoxylate in the composition of the invention is from about 60 – 30 wt%, in another embodiment from about 50 – 35 wt%, and in another embodiment from about 45 – 40 wt%. In one embodiment R is a branched C8-10 alcohol alkoxylate. In yet another embodiment R is 2-ethylhexanol (2-EH) with 2 - 6 EO or 2-propylhapanol (2-PH) with 2- 6EO. In still another embodiment R is 2-EH with 3 - 5EO.

The liquid alkylbenzene sulfonate composition of the invention may contain a small amount of additives. The term additives used in the specification refer to additional chemicals which are not already present in the alkylbenzene sulfonate salt and liquid alcohol alkoxyate. These additives do not affect the handling of the composition according to the present invention. Such additives include, for example, methanol, butanol, isopropyl alcohol, ethanol, glycols, aromatic solvents, and water. The amount of the additives is preferably less than 5wt%, in another embodiment less than 3wt%, in another embodiment less than 2 wt%; in another embodiment less than 1 wt% and in another embodiment zero.

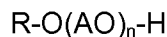
The liquid alkylbenzene sulfonate composition of the present invention may be used alone, though not common, in certain oily liquid pesticide formulations depending on the hydrophilic-lipophilic balance (HLB) characteristic of the medium. However, it is preferred to use the liquid alkylbenzene sulfonate composition together with a high HLB nonionic surfactant such as a castor oil ethoxylate with 36EO (example of castor oil ethoxylate is Emulpon[®] CO-360 manufactured by AkzoNobel)) and/or a high HLB EO-PO block copolymer (example of a EO-PO block copolymer is Ethylan[®] NS-500LQ manufactured by AkzoNobel). When it is used together with other emulsifiers, it is typically used at more than 20%, preferably more than 40%, and more preferably more than 50% in the total emulsifier package. The liquid alkylbenzene sulfonate composition of the present invention is useful for oily agro chemical formulations. Particularly useful oily agro chemical formulations are pesticide formulations. Particularly useful pesticides are (1) herbicides: 2,4-D ester, dicamba ester, MCPA ester, propanil, clethodim, cyhalofop, acetochlor, alachlor, and butochlor; and (2) insecticides: cyhalothrin, pyrethrins, methprene and pyrethroids such as bifenthrin, permethrin, and cypermethrin. Typically the total concentration of all emulsifiers in the oily agro chemical formulations is less than 20%, more commonly less than 10%.

The present inventors have discovered that not all liquid surfactants are suitable for this invention. In order to form a flowable and non-flammable liquid alkylbenzene sulfonate, the liquid surfactants must have a low viscosity, low melting point, and high flash point with reduced odor. As it is well known in the art that an alcohol is not a surfactant while an ethoxylated alcohol is a surfactant, depending on the chain length of the alcohol and the extent of the ethoxylation. For example, when carbon chain length is 4 or shorter, the alcohol ethoxylate is not a surfactant because it does not form microstructures such as micelle, microemulsion, or liquid crystal in water. When an odorous alcohol is turned into an alkoxyated alcohol, the odor is reduced significantly.

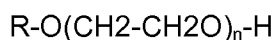
The present invention pertains to:

1. A solvent-free emulsifier composition comprising at least one liquid salt of alkylbenzene sulfonate and a liquid alcohol alkoxyate, wherein the alkyl group in the alkylbenzene sulfonate is C10 – C20, linear or branched, saturate or non-saturated, substituted or non-

substituted hydrocarbon group; and wherein the liquid alcohol alkoxyate has the following structure:



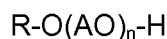
wherein R is C6-C12, linear or branched, hydrocarbon group, A is an ethylene or branched propylene group and n is from 1 – 8. The alkylbenzene sulfonate salt may be selected from a calcium salt, dimethylamidopropylamine salt, an ethanolamine salt, a diethanolamine salt, a triethanolamine salt, a diethylenetriamine salt, a ethylenediamine salt of alkylbenzene sulfonate. The alkyl group in the alkylbenzene sulfonate may be C12 – C14 linear or branched, saturate or non-saturated, substituted or non-substituted hydrocarbon group. In one embodiment, the liquid alcohol alkoxyate has the following structure:



wherein R is C6-C10, linear or branched, hydrocarbon chain, and n is from 1 – 8. In another embodiment, the R is a branched C8-C10 alkyl group and n is from 3-5. Additional additives in the composition are present in a concentration of less than 2% by weight. In one embodiment, the composition is essentially free of additional additives. The concentration of the alkylbenzene sulfonate salt is from about 40 – 70 wt%, in another embodiment, from about 50 – 65 wt%, in yet another embodiment, from about 55 – 60 wt%.

The concentration of the liquid alcohol alkoxyate in the composition is from about 60 – 30 wt%, in another embodiment, from about 50 – 35 wt%, in yet another embodiment, from about 45 – 40 wt%. In one embodiment, the composition comprises 55-65 wt% of calcium dodecylbenzene sulfonate and 35-45% of 2-ethylhexanol with 3- 5EO.

2. A solvent-free emulsifier composition comprising from about 55-65 wt% of a liquid salt of alkylbenzene sulfonate and 35-45% of liquid alcohol alkoxyate, wherein the alkyl group in the alkylbenzene sulfonate is a dodecyl group and wherein the liquid alcohol alkoxyate has the following structure:



wherein R is a 2-ethylhexyl group and the n is 3 – 5. In one embodiment, the liquid salt of alkylbenzene sulfonate in the composition is from about 55-60 wt% and the liquid alcohol alkoxyated in the composition is 40-45%.

3. An oily liquid agricultural formulation comprising at least one agrochemical active and an effective amount of the solvent free emulsifier composition of 1 (above). The solvent free emulsifier composition of 1 may be in the oily liquid agricultural formulation at an amount of 1 – 10 wt% based on total weight of agricultural formulation. The agrochemical active may be a pesticide, herbicide, fungicide or mixtures thereof, in one embodiment, the agrochemical active is a herbicide. The herbicide may be selected from 2,4-D ester, dicamba ester, MCPA

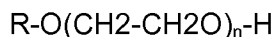
ester or a mixture thereof. The pesticide may be selected from permethrin, methoprin, or a mixture thereof.

4. A herbicidal formulation comprising at least one herbicidally active ingredient and an effective amount of the solvent free emulsifier composition comprising about 55-60 wt% of a liquid salt of alkylbenzene sulfonate and 40-45% of a liquid alcohol alkoxyate, wherein the alkyl group in the alkylbenzene sulfonate is a dodecyl group and wherein the liquid alcohol alkoxyate has the following structure:



- 10 wherein R is a 2-ethylhexyl group and the n is 3 – 5. The herbicidally active ingredient may be selected from 2,4-D ester, dicamba ester, MCPA ester or a mixture thereof.

5. A method of reducing the viscosity of a viscous alkylbenzene sulfonate salt in the absence of a solvent or a diluent wherein the method comprises mixing the alkylbenzene sulfonate salt with an effective amount of a liquid alcohol alkoxyate. In one embodiment, the liquid salt of alkylbenzene sulfonate is calcium or dimethylamidopropylamine salt of alkylbenzene sulfonate. In another embodiment, the alkyl group in the alkylbenzene sulfonate is C12 – C14 linear or branched, saturated or non-saturated, substituted or non-substituted hydrocarbon group. In yet another embodiment, the liquid alcohol alkoxyate has the following structure:



- wherein R is C6-C10, linear or branched, hydrocarbon chain, and n is from 1 – 8. R, in one embodiment, is a branched C8-C10 alkyl group and n is from 3-5. The composition may be essentially free of additional additives. In one embodiment, the concentration of the alkylbenzene sulfonate salt is from about 40 – 70 wt%, in another embodiment, from about 55 – 60 wt%, in yet another embodiment, from about 60 – 30 wt%.

The invention will now be illustrated by the following non-limiting examples.

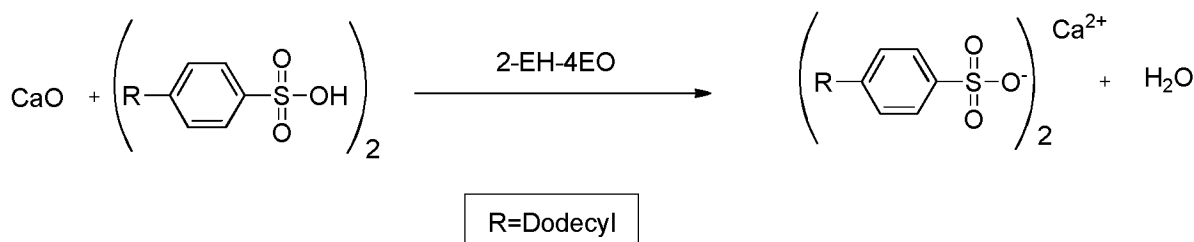
- 30 Example 1 - Making concentrated Ca-DDBS in a liquid alcohol alkoxyate, 2-ethylhexanol-4EO (2-EH-4EO) surfactant

- A. To a 1 L round bottom flask equipped with an over head stirrer, addition funnel, reflux condenser and thermocouple was added CaO (21.4 g) and methanol (100 g).
- 35 B. The Witconic 1298H branched DDBS acid (248 g) is dissolved in methanol (301 g) and then added to the addition funnel.

- C. The Witconic 1298H /methanol solution is added drop-wise to a vigorously stirred reaction slurry. The addition of the acid to the CaO/methanol reaction slurry is exothermic so cooling is applied to keep the temperature < 65°C (See reaction scheme 1).

5

Reaction Scheme 1.



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- D. Once all of the Witconic 1298H /methanol solution is added to the reaction mixture the temperature is maintained at 60°C for 1-2 hours to continue to digest.
- E. After an hour the mixture is cooled and the solids are allowed to settle by centrifuge. The Ca-DDBS/Methanol liquid mixture is then decanted (or filtered) away from the solids (mostly CaSO₂).
- F. The Ca-DDBS/Methanol liquid is mixed with the 2-EH-4EO surfactant in the proper ratio to give the desired activity (~57 wt% in this example) and then added to a flask for removal of the methanol.
- G. The methanol is then removed under a reduced atmosphere with the aid of a rotary evaporator until the methanol is completely gone. The sample is a clear, flowable liquid with a % active of ~ 57% Ca-DDBS and ~ 43% 2-EH-4EO surfactant. The pH of a 5% sample in 25% IPA aqueous solution is ~7.5.

15

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Example 2 - Emulsification performance of Ca-DDBS sample prepared in example 1 is compared with Witconate P-1220EH (~60% Ca-DDBS + ~ 40% 2-EH alcohol) in various hydrophobic substances. Since the % active of the main component, Ca-DDBS, is about the same, the difference between these two samples is in the other component, one with 2-EH-4EO (a surfactant with a reduced odor) and the other with 2-EH (not a surfactant and with a strong odor).

25

Procedure:

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- A. Prepare a sample of 90% hydrophobic substance + 10% Ca-DDBS blend. This is called sample A.

B. Add 5% sample A into 95% water with 1000 hardness. This is called sample B.

C. Shake sample B. This is called emulsion.

D. Observe emulsion appearance with eyes. Take a picture.

The results are tabulated in Table 2.

Table 2. Emulsion comparison between Ca-DDBS/2-EH-4EO and Witconate P-1220EH

Sample #	Emulsifier	Hydrophobic substance	Emulsion Comparison
1	Witconate P-1220EH	Soy methyl ester	
2	57% Ca-DDBS in 2-EH-4EO	Soy methyl ester	Milkier than Sample #1
3	Witconate P-1220EH	Exxsol 110	
4	57% Ca-DDBS in 2-EH-4EO	Exxsol 110	Milkier than Sample #3
5	Witconate P-1220EH	Isopar L	
6	57% Ca-DDBS in 2-EH-4EO	Isopar L	Milkier than Sample #5
7	Witconate P-1220EH	Aromatic 150	
8	57% Ca-DDBS in 2-EH-4EO	Aromatic 150	Milkier than Sample #7
9	Witconate P-1220EH	Soybean oil	
10	57% Ca-DDBS in 2-EH-4EO	Soybean oil	Milkier than Sample #9

In the emulsification test, a milkier emulsion signals a better emulsion. It can be seen from the result in Table 2 that in all the systems, Ca-DDBS with 2-EH-4EO is better than Ca-DDBS with 2-EH.

Example 3 - Solvent-free 2,4-D ester 6 lbs/gal EC

		EC #1, wt%	EC #2, wt%
2,4-D Octyl ester		93	93
57% Ca-DDBS in 2-EH-4EO			3.85
Emulpon NS-500LQ	Butyl alcohol EO-PO block copolymer	3.89	1.75
Emulpon CO-360	Castor oil ethoxylate (36EO)	3.11	1.4
Bloom		Poor	Excellent
Emulsion sediment after 2 hours		Crashed emulsion	Excellent (No sediment)

EC #1 doesn't contain the Ca-DDBS (57% in 43% 2-EH-4EO) and its performance is very poor.

5 EC #2 contains Ca-DDBS (57% in 43% 2-EH-4EO) and it has excellent emulsification performance (excellent bloom and no sediment) in soft water (34 ppm), 342 ppm, and 1000 ppm water.

Example 4 – Making concentrated DMAPA-DDBS in a liquid alcohol alkoxyate, 2-ethylhexanol-4EO (2-EH-4EO) surfactant

10 To make DMAPA-DDBS in 2-EH-4EO: Add 51.7% Witconic 1298H (branched DDBS acid) into a container, add 40% 2-EH-4EO, mix well. Then add 8.3% DMAPA (dimethylamidopropylamine), mix well. The system becomes warm due to acid-base neutralization. A clear, low viscosity sample is obtained.

15 Example 5 – Making concentrated ethylene diamine-DDBS (EDA-DBBS) in a liquid alcohol alkoxyate, 2-ethylhexanol-4EO (2-EH-4EO) surfactant

20 To make EDA-DDBS in 2-EH-4EO: Add 53.4% Witconic 1298H (branched DDBS acid) into a container, add 40% 2-EH-4EO, mix well. Then add 6.6% EDA (ethylene diamine), mix well. The system becomes warm due to acid-base neutralization. A clear, low viscosity sample is obtained.

Claims:

1. A solvent-free emulsifier composition comprising at least one liquid salt of alkylbenzene sulfonate and a liquid alcohol alkoxyate, wherein the alkyl group in the alkylbenzene sulfonate is C10 – C20, linear or branched, saturate or non-saturated, substituted or non-substituted hydrocarbon group; and wherein the liquid alcohol alkoxyate has the following structure:

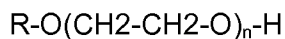


wherein R is C6-C12, linear or branched, hydrocarbon group, A is an ethylene or branched propylene group and n is from 1 – 8.

2. The composition of claim 1 wherein said alkylbenzene sulfonate salt is selected from a calcium salt, dimethylamidopropylamine salt, an ethanolamine salt, a diethanolamine salt, a triethanolamine salt, a diethylenetriamine salt, a ethylenediamine salt of alkylbenzene sulfonate.

3. The composition of claim 1 or 2 wherein the alkyl group in the alkylbenzene sulfonate is C12 – C14 linear or branched, saturate or non-saturated, substituted or non-substituted hydrocarbon group.

4. The composition of any one of the preceding claims wherein the liquid alcohol alkoxyate has the following structure:

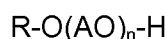


wherein R is C6-C10, linear or branched, hydrocarbon chain, for example, a branched C8-C10 alkyl group, and n is from 1 – 8, for example 3-5.

5. The composition of any one of the preceding claims wherein additives in said composition are present in a concentration of less than 2% by weight, for example, wherein the composition is essentially free of additives.

6. The composition of any one of the preceding claims wherein the concentration of the alkylbenzene sulfonate salt is from about 40 – 70 wt%, for example from about 50 – 65 wt% or from about 55 – 60 wt%, and/or wherein the concentration of the liquid alcohol alkoxyate in the composition is from about 60 – 30 wt%, for example from about 50 – 35 wt% or from about 45 – 40 wt%.

7. The composition of any one of the preceding claims wherein the concentration of the liquid salt of alkylbenzene sulfonate is from about 55-65 wt%, for example, from about 55-60 wt%, and the concentration of the liquid alcohol alkoxyate is 35-45%, for example 40-45%, the alkyl group in the alkylbenzene sulfonate is a dodecyl group, and the liquid alcohol alkoxyate has the following structure:



wherein R is a 2-ethylhexyl group and the n is 3 – 5.

8. The composition of any one of the preceding claims wherein the composition which comprises 55-65 wt% of calcium dodecylbenzene sulfonate and 35-45% of 2-ethylhexanol with 3- 5EO.

9. An oily liquid agricultural formulation comprising at least one agrochemical active, for example a pesticide, herbicide, fungicide or mixtures thereof, and an effective amount, for example 1 – 10 wt% based on total weight of agricultural formulation, of the solvent free emulsifier composition of any one of the preceding claims.

10. The formulation of claim 9 wherein said herbicide is selected from 2,4-D ester, dicamba ester, MCPA ester or a mixture thereof or wherein said pesticide is selected from permethrin, methoprin, or a mixture thereof.

11. A herbicidal formulation comprising at least one herbicidally active ingredient and an effective amount of the composition of any one of claims 1-8.

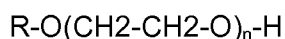
12. A method of reducing the viscosity of a viscous alkylbenzene sulfonate salt in the absence of a solvent or a diluent wherein the method comprises mixing the alkylbenzene sulfonate salt with an effective amount of a liquid alcohol alkoxyate.

13. The method of claim 12 wherein:

(a) the liquid salt of alkylbenzene sulfonate is calcium or dimethylamidopropylamine salt of alkylbenzene sulfonate; and/or

(b) the alkyl group in the alkylbenzene sulfonate is C12 – C14 linear or branched, saturate or non-saturated, substituted or non-substituted hydrocarbon group; and/or

(c) the liquid alcohol alkoxyate has the following structure:



wherein R is C6-C10, linear or branched, hydrocarbon chain, for example a branched C8-C10 alkyl group, and n is from 1 – 8, for example 3-5.

14. The method of claim 12 or 13 wherein said composition is essentially free of additives.

15. The method of any one of claims 12-14 wherein the concentration of the alkylbenzene
5 sulfonate salt is from about 40 – 70 wt%, for example from about 55 – 60 wt%, and/or
wherein the concentration of the liquid alcohol alkoxyate in the composition is from about 60
- 30 wt%.

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INTERNATIONAL SEARCH REPORT

International application No PCT/EP2014/066122

A. CLASSIFICATION OF SUBJECT MATTER
 INV. A01N25/04 A01N25/02 B01F17/00 A01N37/40 A01N39/04
 A01N53/00 A01N25/30
 ADD.
 According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED
 Minimum documentation searched (classification system followed by classification symbols)
 A01N B01F A61K A23L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
 EPO-Internal, BIOSIS, CHEM ABS Data, EMBASE, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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X	US 2013/165323 A1 (POMPEO MICHAEL [US] ET AL) 27 June 2013 (2013-06-27) examples -----	9,11
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Further documents are listed in the continuation of Box C.

See patent family annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier application or patent but published on or after the international filing date
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- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- "&" document member of the same patent family

Date of the actual completion of the international search 3 September 2014	Date of mailing of the international search report 11/09/2014
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Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Galley, Carl
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INTERNATIONAL SEARCH REPORT

International application No PCT/EP2014/066122

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
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