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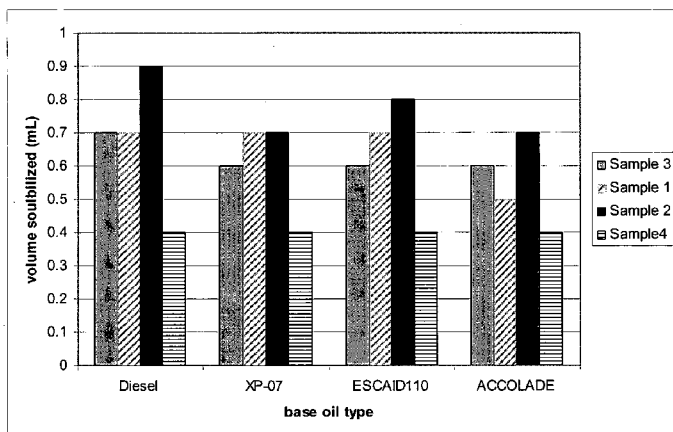


FIG. 1

(57) Abstract: A method comprising contacting a zwitterionic surfactant, co-surfactant, and water to form a microemulsifier, and contacting the microemulsifier with an oleaginous fluid under low shear conditions to form a microemulsion. A method comprising introducing a first wellbore servicing fluid comprising at least one oleaginous fluid into a wellbore, wherein the first wellbore servicing fluid forms oil-wet solids and/or oil-wet surfaces in the wellbore, and contacting the oil-wet solids and/or oil-wet surfaces in the wellbore with a second wellbore servicing fluid comprising a zwitterionic surfactant, a co-surfactant, and a brine to form a microemulsion.

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## MICROEMULSIFIERS AND METHODS OF MAKING AND USING SAME

### BACKGROUND

[0001] The present disclosure generally relates to wellbore servicing fluids. More particularly, this disclosure relates to microemulsifiers and methods of making and using same.

[0002] Natural resources such as gas, oil, and water residing in a subterranean formation or zone are usually recovered by drilling a wellbore down to the subterranean formation while circulating a drilling fluid in the wellbore. After terminating the circulation of the drilling fluid, a string of pipe, e.g., casing, is run in the wellbore. The drilling fluid is then usually circulated downward through the interior of the pipe and upward through the annulus, which is located between the exterior of the casing and the walls of the wellbore.

[0003] During drilling and as the drilling fluid is circulated upward through the annulus, a thin layer of residue is deposited on the annulus between the exterior of the drill string and/or the casing and the walls of the wellbore. The thin layer of residue is referred to as a filtercake and aids in controlling drilling fluid from leaking-off into the subterranean formation. After drilling and casing the wellbore, the well has to be emptied of drilling mud before it can be completed. Additionally, prior to production, the casing may be cleaned (e.g., removal of oleaginous fluid contaminants) and/or the filtercake removed. Cleaning of the casing may improve adherence of the casing to the cement composition used to seal the annulus and removal of the filtercake may be advantageous as its presence would restrict the inflow of hydrocarbons into the wellbore. The completion fluid used to displace the drilling mud is typically a brine composed of water and a suitable salt (e.g., sodium chloride, zinc bromide, calcium chloride) and may contain additional components that

facilitate the cleaning of the casing and/or the removal of the filtercake. Such additional components should promote the efficient cleaning of the casing and/or removal of the filtercake while in contact with the high salinity solution (e.g., brine). For example, the completion fluid may contain one or more surfactants such as cationic, anionic, and non-ionic surfactants. A non-ionic surfactant may be considered for use in high salinity solutions (e.g., brines) due to their increased salt tolerance and indifference to multivalent ions. However, drawbacks to the use of non-ionic surfactants in a completion fluid include the presence of an upper temperature limit for stability of microemulsions comprising the non-ionic surfactants. Without wishing to be limited by theory, this thermal instability may be attributable to dehydration of ethoxylate groups of the non-ionic surfactant as the temperature is increased. This phenomenon is referred to as the cloud point and it is where the non-ionic surfactant has a drastic reduction in its solubility causing it to phase separate. Additionally, a specific non-ionic surfactant may have to be chosen for a removal of a specific oleaginous fluid and as such may display a reduced versatility when compared to other types of surfactants.

**[0004]** A cationic or anionic surfactant while displaying increased stability and versatility when compared to a non-ionic surfactant may also have drawbacks associated with its use. For example, anionic surfactants may exhibit reduced effectiveness in brines composed of multivalent ions (e.g.  $\text{Ca}^{2+}$  or  $\text{Zn}^{2+}$ ) while cationic surfactants which are compatible with most completion brines typically have toxicity issues associated with their use. Thus, it would be desirable to develop compositions and methods for cleaning a casing and/or removing a filtercake from a subterranean formation that are compatible with brines.

## SUMMARY

[0005] Disclosed herein is a method comprising contacting a zwitterionic surfactant, co-surfactant, and water to form a microemulsifier, and contacting the microemulsifier with an oleaginous fluid under low shear conditions to form a microemulsion.

[0006] Also disclosed herein is a method comprising introducing a first wellbore servicing fluid comprising at least one oleaginous fluid into a wellbore, wherein the first wellbore servicing fluid forms oil-wet solids and/or oil-wet surfaces in the wellbore, and contacting the oil-wet solids and/or oil-wet surfaces in the wellbore with a second wellbore servicing fluid comprising a zwitterionic surfactant, a co-surfactant, and a brine to form a microemulsion.

## BRIEF DESCRIPTION OF THE DRAWINGS

[0007] For a more complete understanding of the present disclosure and the advantages thereof, reference is now made to the following brief description, taken in connection with the accompanying drawings and detailed description:

[0008] Figure 1 is a plot of volume of oil solubilized as a function of base oil type for the samples from Example 1.

[0009] Figure 2 is a plot of percentage oil cleaned as a function of cleaning fluid for the samples from Example 3.

[0010] Figure 3 is a plot of percentage oil cleaned as a function of cleaning fluid for the samples from Example 4.

## DETAILED DESCRIPTION

[0011] It should be understood at the outset that although an illustrative implementation of one or more embodiments are provided below, the disclosed systems and/or methods may be implemented using any number of techniques, whether currently known or in existence. The

disclosure should in no way be limited to the illustrative implementations, drawings, and techniques illustrated below, including the exemplary designs and implementations illustrated and described herein, but may be modified within the scope of the appended claims along with their full scope of equivalents.

**[0012]** Disclosed herein are compositions comprising a surfactant and a co-surfactant. In an embodiment the surfactant is zwitterionic and the composition comprising the zwitterionic surfactant and co-surfactant is termed a surfactant package (SP). The SP may act as a microemulsifier that when contacted with one or more oils form an oil-in-water emulsion. Also disclosed herein are oilfield servicing fluids (OSF) comprising the SP and a brine. In an embodiment, the OSFs are placed downhole and contacted with an oleaginous fluid (i.e., an oil-containing fluid) to form a microemulsion. The oleaginous fluid may be oil-based residue on one or more components of a wellbore, oil-wet solids such as those found in an oil-based filtercake and the like. In some embodiments, the OSF may be used for removing oil-based residue from a casing such as in a cased completion and may also be referred to as a cleaning fluid. In other embodiments, the OSF may be used for the removing the oil-wet components of a filtercake such as in an open-hole completion. The components of the OSFs as well as methods of making and using same will be described in more detail later herein.

**[0013]** In an embodiment, the SP comprises a zwitterionic surfactant. Surfactants in general are wetting agents that lower the surface tension of a liquid in which they are dissolved, allowing easier spreading and decreasing the interfacial tension between two liquids. Zwitterionic surfactants are electrically neutral surfactants that carry both a formal positive and a formal negative charge on different atoms in the same molecule. Such surfactants are characterized by a

high solubility in water, low solubility in organic solvents, and increased stability at higher temperatures when compared to other types of surfactants (e.g., non-ionic surfactants).

**[0014]** For the purposes of this disclosure a zwitterionic surfactant will be used in conjunction with a co-surfactant to form a microemulsion. Zwitterionic surfactants may provide the most universal behavior across all brine types and are essentially non-toxic. Examples of zwitterionic surfactants suitable for use in this disclosure include without limitation alkyl amine oxides, alkyl betaines, alkyl amidopropyl betaine, alkyl sulfobetaines, alkyl sultaines, dihydroxyl alkyl glycinate, alkyl amphi acetate, phospholipids, alkyl aminopropionic acids, alkyl imino monopropionic acids, alkyl imino dipropionic acids, or combinations thereof.

**[0015]** In an embodiment, the zwitterionic surfactant comprises an amine oxide. Amine oxides, also termed amine N-oxides or N-oxides, are chemical compounds that comprise the functional group  $R_3N^+-O^-$  where R may be an alkyl moiety having from 1 to 20 carbon atoms. The term amine oxide herein is meant to comprise oxides of tertiary amines including nitrogen containing aromatic compounds, analogous primary or secondary amines, derivatives thereof, or combinations thereof. Examples of amine oxides suitable for use in this disclosure include without limitation decylamine oxide, dodecylamine oxide, tetradecylamine oxide, or combinations thereof.

**[0016]** In an embodiment, the zwitterionic surfactant comprises a betaine. Betaines are neutral chemical compounds comprising a positively charged cationic functional group and no hydrogen atom and a negatively charged functional group that may not be adjacent to the cationic site. For example, a betaine may comprise an onium ion (e.g., ammonium, phosphonium) and a carboxylate group. Examples of betaines suitable for use in this disclosure include without limitation laurylamidopropyl betaine, decyl betaine, dodecyl betaine, or combinations thereof.

[0017] In an embodiment, the zwitterionic surfactant comprises a phospholipid. Phospholipids are similar in structure to tri-glycerides with the exception that the first hydroxyl of the glycerine molecule has a polar phosphate containing group in place of the fatty acid. The hydrocarbon chain of the phospholipid is hydrophobic while the charges on the phosphate groups make that portion of the molecule hydrophilic resulting in an amphiphilic molecule. Examples of phospholipids suitable for use in this disclosure include without limitation lecithin, phosphatidyl choline, derivatives thereof, or combinations thereof.

[0018] In an embodiment, the zwitterionic surfactant may be present in the SP in an amount of from about 10 weight percent (wt.%) to about 90 wt.% based on the total weight percentage of the SP, alternatively from about 20 wt.% to about 80 wt.%, alternatively from about 30 wt.% to about 70 wt.%.

[0019] In an embodiment, the SP comprises a co-surfactant. Generally, co-surfactants are hydrophobic materials that synergistically act with the surfactant to reduce the interfacial tension between two liquids. In an embodiment, the co-surfactant comprises any hydrophobic material compatible with the other components of the SP that does not self-assemble or self-aggregate. Examples of co-surfactants suitable for use in this disclosure include without limitation alkyl alcohols (e.g., methanol, ethanol, propanol, butanol, etc.), alkyl acetate, alkyl pyrrolidone (e.g., n-octyl-2-pyrrolidone, n-methyl pyrrolidone, etc.), alkyl ketone, acryl amide, or combinations thereof. In an embodiment, the co-surfactant comprises butanol. In another embodiment, the co-surfactant comprises n-octyl-2-pyrrolidone.

[0020] In an embodiment, the co-surfactant may be present in the SP in an amount of from about 10 wt.% to about 90 wt.% based on the total weight percentage of the SP, alternatively from about 20 wt.% to about 80 wt.%, alternatively from about 30 wt.% to about 70 wt.%.

**[0021]** In an embodiment, the SP may be contacted with fresh water to form a microemulsifier. In an alternative embodiment, the SP is contacted with a brine to form an OSF. Brines are aqueous fluids that are typically saturated or nearly saturated with salt. In an embodiment, the OSF comprises a brine that comprises a salt at a concentration below saturation such that the brine contains some amount of free water. In an embodiment, OSFs of the type described herein may comprise any brine solution compatible with the other components of the OSF and the intended function of the OSF.

**[0022]** Examples of brines suitable for use in this disclosure include without limitation saturated or partially saturated aqueous solutions comprising halide-containing salts, alkali metal salts, alkaline metal salts, formate-containing compounds, sodium bromide (NaBr), calcium chloride (CaCl<sub>2</sub>), calcium bromide (CaBr<sub>2</sub>), sodium chloride (NaCl), zinc bromide (ZnBr<sub>2</sub>), ethyl formate, sodium formate, cesium formate, potassium formate, methyl formate, methyl chloroformate, triethyl orthoformate, trimethyl orthoformate, derivatives thereof, or combinations thereof. In some embodiments, the SP is contacted with a brine prepared from a mixture of two or more salts. In such embodiments, the brine mixture may be formed by contacting the constituent brines in any ratio compatible with their intended use.

**[0023]** The choice of brine may be dictated by a variety of factors such as the formation condition and the desired density of the resulting solution. In an embodiment, the brine comprises a saturated or partially saturated aqueous solution containing NaBr, alternatively CaCl<sub>2</sub>, alternatively a mixture of CaCl<sub>2</sub>/CaBr<sub>2</sub>. In an embodiment, the brine may have a density of from about 8.5 ppg to about 15.1 ppg, alternatively from about 8.5 ppg to about 12.5 ppg, alternatively from about 10.5 ppg to about 11.6 ppg.



[0024] In an embodiment, a method of preparing an OSF comprises preparing an SP by contacting a zwitterionic surfactant and a co-surfactant of the type described previously herein. In an embodiment, the SP may have a zwitterionic surfactant:co-surfactant mole ratio of from about 1:10 to about 10:1, alternatively from about 1:5 to about 5:1, alternatively from about 1:0.1 to about 0.1:1.

[0025] In an embodiment, the surfactant:co-surfactant ratio is chosen so as to prevent phase separation and provide a single phase microemulsifier when contacted with the brine. Further, the surfactant:co-surfactant mole ratio may be chosen so as prevent precipitation of one or both components of the SP when contacted with the brine. Contacting of the zwitterionic surfactant and the co-surfactant may be carried out using any suitable technique (e.g., mixing, blending, etc.) and under any suitable conditions.

[0026] In an embodiment, the SP comprises laurylamidopropyl betaine and butanol in a 1:4.8 mole ratio. Alternatively, the SP comprises dodecylamine oxide and butanol in a 1:2 mole ratio. Alternatively, the SP comprises decylamine oxide and n-octyl-2-pyrillidone in a 1:2 mole ratio. Alternatively, the SP comprises decylamine oxide and butanol in a 1:2 mole ratio.

[0027] The method may further comprise contacting the SP with a fluid comprising some amount of free water. In an embodiment, the fluid is an aqueous solution, alternatively a partially saturated brine. The fluid and SP may be contacted in any manner known to one of ordinary skill in the art with the benefits of this disclosure.

[0028] In an embodiment, the SP or OSF is able to form an oil-in-water emulsion (microemulsion) upon contacting with an oleaginous fluid. Microemulsions are thermodynamically stable mixtures of oil, water (e.g., brine), and surfactant (e.g., zwitterionic surfactant and co-surfactant). In contrast to conventional emulsions, microemulsions of this

disclosure form spontaneously or almost spontaneously upon contacting of the components under low shear conditions which are in contrast to the conditions generally used in the formation of conventional emulsions.

[0029] In order for an emulsion to form spontaneously or almost spontaneously upon contacting of the components, there has to be a reduction in the free energy of the system. This reduction in free energy is brought about by an increase in conformational entropy, a reduction in surface tension, and a decrease in curvature energy. The free energy change of a system is represented by the following equation 1 or 2:

$$\Delta G = \Delta H - T \Delta S \quad \text{Equation 1}$$

$$\Delta G = \Delta A \cdot \gamma_{ow} - T \Delta S \quad \text{Equation 2}$$

where G is the Gibbs free energy, T is the temperature, S is the entropy, A is the interfacial area, and  $\gamma$  is the interfacial tension at the oil-water interface. The entropy is increased by the creation of several small droplets, however, the creation of these droplets also causes a large increase in the oil/water interfacial area. The amount of surface area created is enormous and generating a large energy penalty from contacting oil/water. This energy penalty must be reduced by the addition of surfactants which lower the interfacial tension, thus reducing the amount of energy to form an interface. Generally emulsification is a non-spontaneous process such that  $\Delta A \cdot \gamma_{ow} \gg T \Delta S$ . However, the amount of thermodynamic energy required to create the new interface ( $\Delta A \cdot \gamma_{ow}$ ) is small when compared with the amount of energy that is required to form a conventional emulsion. The additional energy required is due to the interfacial curvature. The energy required to change the interfacial curvature can be represented by the following equation 3:

$$F = \int dA \cdot \left\{ \left( \frac{\hat{e}}{2} \right) (c_1 + c_2 - 2c_0)^2 - \bar{\kappa} c_1 c_2 \right\} + NkTf(\Phi) \quad \text{Equation 3}$$

where  $\kappa$  is the bending modulus,  $\bar{\kappa}$  is the Gaussian modulus,  $c_1$  and  $c_2$  are the radii of curvature,  $c_0$  is the spontaneous curvature and  $NkTf(\Phi)$  is the entropic in origin. The addition of a co-surfactant to the system reduces the  $\kappa$  term, thus reducing the energy required to produce a curved surfactant film at the oil/water interface.

[0030] In an embodiment, an SP and/or OSF of the type described herein when contacting an oleaginous fluid is able to form an oil-in-water emulsion in less than about 10 minutes, alternatively less than about 5 minutes, alternatively about instantaneously under low shear conditions. Herein low shear conditions refer to the ability of the SP and/or OSF when contacted with the oleaginous fluid to form an oil-in-water emulsion in the absence of substantial agitation.

[0031] In an embodiment, an SP and/or OSF of the type described herein when contacting an oleaginous fluid is able to form an oil-in-water emulsion spontaneously. Without wishing to be limited by theory, the spontaneous formation of oil-in-water may have a Gibbs free energy of equal to or less than about 0.

[0032] In an embodiment, the amount of oleaginous fluid solubilized by an OSF and/or SP of the type described herein is from about 0.01 ml to about 1.0 ml of oleaginous fluid per 1 ml of a 30 wt.% solution of OSF, alternatively from about 0.01 ml to about 0.5 ml of oleaginous fluid per 1 ml of a 15 wt.% solution of OSF, alternatively from about 0.01 ml to about 0.25 ml of oleaginous fluid per 1 ml of a 7.5wt.% solution of OSF, alternatively from about 0.01 ml to about 0.9 ml of oleaginous fluid per 1 ml of a 30 wt.% solution of OSF, alternatively from about 0.01 ml to about 0.8 ml of oleaginous fluid per 1 ml of a 30 wt.% solution of OSF.

[0033] OSFs of the type described herein may exhibit thermal stability as assessed by their ability to emulsify the oleaginous fluid after being contacted with brine and statically aged at a temperature of from about 65°F to about 350°F, alternatively from about 70°F to about 200°F,

alternatively from about 75°F to about 120°F for a period of from about 1 hours to about 240 hours, alternatively from about 1 hours to about 120 hours, alternatively from about 1 hours to about 24 hours.

**[0034]** In an embodiment, a method of servicing a wellbore comprises drilling a wellbore in a subterranean formation and introducing to the subterranean formation a wellbore servicing fluid that comprises at least one oleaginous fluid, wherein oil-coated/wet solids (e.g., filtercake, drill cuttings, etc.) and/or oil-coated wet surfaces (e.g., casing, drill string, etc.) are formed as a result. It is to be understood that “subterranean formation” encompasses both areas below exposed earth and areas below earth covered by water such as ocean or fresh water. Oleaginous fluids herein refer to oil-based drilling or servicing fluids, invert emulsions, servicing fluids comprising substantially no aqueous component, and the like. Examples of the oleaginous fluids suitable for use in this disclosure include without limitation olefins, internal olefin based oils, mineral oil, kerosene, diesel oil, fuel oil, synthetic oil, linear or branched paraffins, esters, acetals, mixtures of crude oil, derivatives thereof, or combinations thereof. In some embodiments, after drilling, the method further comprises running a casing in the wellbore and securing the casing into position against the subterranean formation using a sealant composition (e.g., cement).

**[0035]** After drilling and/or casing the wellbore, a completion operation is performed to prepare the wellbore to produce hydrocarbons. The completion operation includes first perforating the subterranean formation by introducing a perforating fluid into the wellbore and jetting the perforating fluid from the wellbore to the subterranean formation thereby forming perforation tunnels within the subterranean formation. In an embodiment, the introduction of an oleaginous fluid (e.g., drilling fluid, perforating fluid) may result in the formation of oil-wet solids and/or oil wet surfaces within the wellbore. The oil-wet solids and/or surfaces may be oil-based residue

located on the components of the wellbore, the walls of a casing, a formation face, a fracture face, a perforation, on a screen (e.g., a gravel pack screen) or another piece of equipment located in the wellbore or subterranean formation, an oil-based filtercake, or a water-based filtercake that has been contaminated with oil.

**[0036]** An OSF of the type described herein may be introduced to the wellbore and contacted with the oil-based fluid, oil-wet solids, and/or oil-wet surfaces resulting in the formation of an oil-in water emulsion. In an embodiment, the OSF introduced into the wellbore is a completion fluid comprising a brine, a surfactant (e.g., laurylamidopropyl betaine) and a co-surfactant (e.g., butanol). Herein, a completion fluid refers to a solids-free liquid used to "complete" an oil or gas well. This fluid is placed in the well to facilitate final operations prior to initiation of production, such as setting screens production liners, packers, downhole valves or shooting perforations into the producing zone. The fluid is meant to control a well should downhole hardware become functionally compromised, without damaging the producing formation or completion components.

**[0037]** In an embodiment where a casing is run in the wellbore (i.e., well-cased wellbore), the oil-based fluid and/or oil-wet solids and/or surface may be on walls of the casing. In such an embodiment, the OSF may contact the oil-based fluid on the sides or surfaces of the casing. Upon contact with the oil-based fluid, the OSF forms microemulsions that are subsequently removed from the wellbore.

**[0038]** In another embodiment (i.e., open-hole wellbore), the oil-based fluid and/or oil-wet solids and/or surface may be a filtercake formed along the walls of the wellbore. In such an embodiment, the OSF may form a microemulsion upon contacting the oil-wet components of the filtercake. As will be understood by one of ordinary skill in the art, removal of the oil-wet components may increase the susceptibility of the filtercake to degradation by other agents (e.g.,

acid). Methods of removing a filtercake comprising oil-wet components are described for example in U.S. Patent Application Serial No. 12/120,159 entitled "Compositions and Methods for the Removal of Oil-Based Filtercakes" filed May 13, 2008 and incorporated by reference herein in its entirety.

**[0039]** The method may further comprise fracturing the subterranean formation by injecting fracturing fluids into the perforation tunnels thereby propagating fractures from the perforation tunnels deeper into the subterranean formation. Production can then take place, if desired or appropriate, as for example in a hydrocarbon-producing well.

**[0040]** In an embodiment, the SP, OSF, or both are used to remove oleaginous fluid from one or more oil-wet solids and/or oil-wet surfaces located outside of a wellbore. For example, the SP may be contacted with the surface of one or more materials that have been contacted with an oleaginous fluid. In such embodiments, the SP may be contacted with drill cuttings, wellbore servicing equipment, and the like which have oleaginous fluid present on the surfaces of the materials. Contacting of the SP with these materials may result in the formation of microemulsions and the removal of the oleaginous fluid from the surfaces of these materials.

#### EXAMPLES

**[0041]** The disclosure having been generally described, the following examples are given as particular embodiments of the disclosure and to demonstrate the practice and advantages thereof. It is understood that the examples are given by way of illustration and are not intended to limit the specification or the claims in any manner.

#### EXAMPLE 1

**[0042]** The ability of OSFs of the type described herein to form microemulsions when contacted with various oils was investigated. The various oils used were diesel, ESCAID 110, XP-

07 and ACCOLADE. ESCAID 110 hydrocarbon fluid is a petroleum distillate commercially available from EXXON-MOBIL Corp; XP-07 is a paraffin base oil; and ACCOLADE is an olefin/ester blend both of which are commercially available from Halliburton Energy Services. Four OSF samples, designated Samples 1-4, were prepared. Sample 1 comprised laurylamidopropyl betaine and butanol in a mole ratio of 1:4.8. Sample 2 comprised dodecylamine oxide and butanol in a mole ratio of 1:4. Sample 3 comprised decylamine oxide and n-octyl-2-pyrrolidone in a mole ratio of 1:2. Sample 4 comprised decylamine oxide and butanol in a mole ratio of 1:2.

[0043] Sodium bromide brine was added to each of the zwitterionic surfactant/co-surfactant solution at a 1:1 volume ratio to form Samples 1-4 having 15 wt.% zwitterionic surfactant/co-surfactant in 10.5 ppg sodium bromide. The components of each sample are summarized in Table 1.

Table 1

Sample	Zwitterionic Surfactant	Co-surfactant	Zwitterionic Surfactant:Co-surfactant Mol Ratio	Brine	Brine Concentration in OSF
1	laurylamidopropyl betaine	butanol	1:4.8	NaBr	10.5 ppg
2	dodecyl amine oxide	butanol	1:4	NaBr	10.5 ppg
3	decyl amine oxide	n-octyl-2-pyrrolidone	1:2	NaBr	10.5 ppg
4	decyl amine oxide	butanol	1:2	NaBr	10.5 ppg

[0044] Between about 0.4 ml and about 0.9 ml of the oils were added to vials containing 4 ml of the OSF sample. The vials were rolled once or twice to provide low shearing. Microemulsions were observed to form in less than about 45 seconds after the vials were rolled. Figure 1 is a plot of volume of oil solubilized as a function of oil type for Samples 1-4. The results showed that the

OSF samples were able to form microemulsions when contacted with the oils under low shear conditions.

**[0045]** The ability of the OSFs to emulsify oil in the presence of solid particles was also investigated. Four samples were prepared; each sample contained 4 ml of either Samples 1, 2, 3, or 4 and 0.5 ml of ACCOLADE field mud. The samples were rolled once or twice to provide low shearing and formed a microemulsion. The ACCOLADE field mud was ACCOLADE base fluid with standard drilling fluid additives including barite as a weighting agent. It was observed that the base fluid was removed from the solid particles leaving them water wet. Further, Sample 1 was observed to effect the largest removal of ACCOLADE from solid particles. Without wishing to be limited by theory, the better performance of Sample 1 (which comprised a betaine as the zwitterionic surfactant) when compared to Samples 2-4 (which comprised an amine oxide as the zwitterionic surfactant) may be attributable to the fact that betaine formally has two full charges while amine oxides formally have two partial charges. The full charges on the betaine may increase the surface activity of the molecule, which could increase the ability of OSFs comprising the betaines to remove from the particle surface and solubilize oil when compared to OSFs comprising amine oxides.

#### EXAMPLE 2

**[0046]** The thermal stability of the OSFs was investigated. Three OSF samples, designated Samples 5-7, were prepared. Sample 5 comprised dodecylamine oxide and butanol in a 1:4 mole ratio and was contacted with a 10.5 ppg NaBr brine. Sample 6 comprised dodecylamine oxide and butanol in a 1:4 mole ratio and was contacted with a 11.0 ppg CaCl<sub>2</sub> brine. Sample 7 comprised dodecylamine oxide and butanol in a 1:4 mole ratio and was contacted with a 13.5 ppg mixture of



CaCl<sub>2</sub> and CaBr<sub>2</sub> brine. Table 2 tabulates the components, ratios and concentrations of Samples 5-7.

Table 2

Sample	Zwitterionic Surfactant	Co-surfactant	Zwitterionic Surfactant:Co-surfactant Mol Ratio	Brine	Brine Concentration in OSF
5	dodecyl amine oxide	butanol	1:4	NaBr	10.5 ppg
6	dodecyl amine oxide	butanol	1:4	CaCl <sub>2</sub>	11.0 ppg
7	dodecyl amine oxide	butanol	1:4	CaCl <sub>2</sub> /CaBr <sub>2</sub>	13.5 ppg

[0047] Static aging tests were performed on Samples 5-7 by heating each sample in an oven at 250°F for 16 hours. The aged OSF samples were then visually observed. Both Samples 5 and 6 showed slight yellowing while Sample 7 was clear. The capability of aged OSF samples to dissolve oil was investigated by adding base oils of the type described in Example 1 to samples 5-7. All the samples retained their capability to dissolve the various oils under low shear conditions.

EXAMPLE 3

[0048] The ability of OSFs, referred to also as cleaning fluids, to solubilize oil-based drilling muds was investigated and compared to conventional casing cleaners. The OSFs were Samples 1 and 2 from Example 1. The conventional cleaners were BARASCRUB, designated Sample 3, which is a casing wash that is commercially available from Halliburton Energy Services, Inc. and a casing wash that is commercially available, designated as Sample 4. BARASCRUB and Sample 4 are not compatible with any brine. The oil-based drilling mud was 15 ppg ACCOLADE. The cleaning tests were performed at 40°F, 75°F, and 120°F and the samples were heated to the cleaning test temperatures prior to use.

[0049] Cleaning tests were carried out by smearing ACCOLADE onto the inside of a 400 ml PYREX glass beaker between the 75 ml and 200 ml marks on the beaker. The beaker was also weighted prior to and after smearing the beaker with ACCOLADE to determine the mass of ACCOLADE used. 175 ml of sample was added to the beaker smeared with ACCOLADE. The beaker was then placed in a double walled circulation bath filled with water to maintain constant temperature during the cleaning tests. Each sample was mixed for 10 minutes with a FANN 35A rheometer, which is commercially available from Fann Instruments, Inc. The test speeds used were 600 rpm, 300 rpm, and 100 rpm. At the end of the cleaning tests, the beaker was removed from the circulation bath and the OSF poured out. The beaker was gently washed with 10-50 ml of deionized water and ethanol. If there was any ACCOLADE on the bottom of the beaker, the ACCOLADE was assumed to have been removed from the beaker walls.

[0050] The beaker was then either placed in a vacuum oven set to room temperature and dried out under vacuum for 30 minutes or dried in a vacuum oven at temperatures ranging from 120°F to 150°F for at least 4 hours. The beaker was then weighted to measure the remaining amount of ACCOLADE.

[0051] The results demonstrate that Sample 3 removed all traces of ACCOLADE; however, it had low density (about 7 ppg) and was not compatible with any brine. Figure 2 is a plot of percentage ACCOLADE cleaned as a function of sample type for the cleaning test performed at 75°F and the test speed of 300 rpm. The results demonstrated that Samples 1 and 2 were able to remove more than 90% of ACCOLADE from the beaker; however, Sample 4 was able to remove about 70% ACCOLADE. Sample 4 also had a low density (about 7.5 ppg) and was not compatible with any brine. When additional water was added to Sample 4, the sample was observed to become an opaque solution, which suggested that Sample 4 did not form a microemulsion with

water. Without wishing to be limited by theory, the opaque solution was a short lived kinetically stabilized emulsion. Sample 4 with the additional water solution would phase separate into two phases within an hour demonstrating this is a highly unstable emulsion.

#### EXAMPLE 4

**[0052]** The ability of OSFs of the type described herein, also referred to as cleaning fluid, to solubilize diesel field mud was investigated and compared to a conventional casing cleaner. The OSF used for in this example was Sample 2 from Example 1. The conventional casing cleaner was Sample 4 from Example 3. The diesel field mud had a high solids loading with a density of 17.1 ppg. Figure 3 is a plot of percentage diesel solubilized as a function of the sample type for the cleaning test performed at 75°F and the test speed of 300 rpm. The results demonstrated that Sample 2 was able to remove more than 30% of diesel field mud from the beaker while Sample 4 was able to remove about 10% of diesel field mud.

**[0053]** While embodiments of the disclosure have been shown and described, modifications thereof can be made by one skilled in the art without departing from the spirit and teachings of the disclosure. The embodiments described herein are exemplary only, and are not intended to be limiting. Many variations and modifications of the disclosure disclosed herein are possible and are within the scope of the disclosure. Where numerical ranges or limitations are expressly stated, such express ranges or limitations should be understood to include iterative ranges or limitations of like magnitude falling within the expressly stated ranges or limitations (e.g., from about 1 to about 10 includes, 2, 3, 4, etc.; greater than 0.10 includes 0.11, 0.12, 0.13, etc.). For example, whenever a numerical range with a lower limit,  $R_L$ , and an upper limit,  $R_U$ , is disclosed, any number falling within the range is specifically disclosed. In particular, the following numbers within the range are specifically disclosed:  $R=R_L+k*(R_U-R_L)$ , wherein  $k$  is a variable ranging

from 1 percent to 100 percent with a 1 percent increment, i.e., k is 1 percent, 2 percent, 3 percent, 4 percent, 5 percent, ...50 percent, 51 percent, 52 percent, ....., 95 percent, 96 percent, 97 percent, 98 percent, 99 percent, or 100 percent. Moreover, any numerical range defined by two R numbers as defined in the above is also specifically disclosed. Use of the term "optionally" with respect to any element of a claim is intended to mean that the subject element is required, or alternatively, is not required. Both alternatives are intended to be within the scope of the claim. Use of broader terms such as comprises, includes, having, etc. should be understood to provide support for narrower terms such as consisting of, consisting essentially of, comprised substantially of, etc.

**[0054]** Accordingly, the scope of protection is not limited by the description set out above but is only limited by the claims which follow, that scope including all equivalents of the subject matter of the claims. Each and every claim is incorporated into the specification as an embodiment of the present disclosure. Thus, the claims are a further description and are an addition to the embodiments of the present disclosure. The discussion of a reference is not an admission that it is prior art to the present disclosure, especially any reference that may have a publication date after the priority date of this application. The disclosures of all patents, patent applications, and publications cited herein are hereby incorporated by reference, to the extent that they provide exemplary, procedural, or other details supplementary to those set forth herein.

## CLAIMS

What is claimed is:

1. A method comprising:  
contacting a zwitterionic surfactant, co-surfactant, and water to form a microemulsifier; and  
contacting the microemulsifier with an oleaginous fluid under low shear conditions to form a microemulsion.
2. The method of claim 1 wherein the zwitterionic surfactant comprises alkyl amine oxides, alkyl betaines, alkyl amidopropyl betaine, alkyl sulfobetaines, alkyl sultaines, dihydroxyl alkyl glycinate, alkyl ampho acetate, phospholipids, alkyl aminopropionic acids, alkyl imino monopropionic acids, alkyl imino dipropionic acids, or combinations thereof.
3. The method of claim 2 wherein the alkyl betaine comprises laurylamidopropyl betaine, decyl betaine, dodecyl betaine, or combinations thereof.
4. The method of claim 2 wherein the alkyl amine oxide comprises decylamine oxide, dodecylamine oxide, tetradecylamine oxide, or combinations thereof.
5. The method of claim 2 wherein the phospholipid comprises lecithin, phosphatidyl choline, derivatives thereof, or combinations thereof.
6. The method of claim 1 wherein the co-surfactant comprises alkyl alcohols, alkyl acetate, alkyl pyrrolidone, alkyl ketone, acryl amide, or combinations thereof.
7. The method of claim 6 wherein the alkyl alcohol comprises methanol, ethanol, propanol, butanol, or combinations thereof.
8. The method of claim 6 wherein the alkyl pyrrolidone comprises n-octyl-2-pyrrolidone, n-methyl pyrrolidone, or combinations thereof.

9. The method of claim 1 wherein the zwitterionic surfactant and the co-surfactant are present in the microemulsifier in a mole ratio of from about 1:10 to about 10:1.
10. The method of claim 1 wherein the co-surfactant is hydrophobic and does not self-aggregate.
11. The method of claim 1 wherein oleaginous fluid comprises olefin, internal olefin based oil, mineral oil, kerosene, diesel oil, fuel oil, synthetic oil, linear or branched paraffin, ester, acetal, mixtures of crude oil, derivatives thereof, or combinations thereof.
12. The method of claim 1 wherein the amount of oleaginous fluid contacted by the microemulsifier is from about 0.01 ml to about 1.0 ml of oleaginous fluid per 1 ml of a 30 wt.% solution of the microemulsifier.
13. The method of claim 1 wherein the microemulsion forms in less than about 10 minutes.
14. The method of claim 1 wherein the microemulsifier when exposed to a temperature of from about 65°F to about 350°F for a period of from about 1 hour to about 240 hours retains its ability to form a microemulsion when contacted with a oleaginous fluid.
15. The method of claim 1 wherein the microemulsifier is a wellbore servicing fluid.
16. The method of claim 1 wherein the microemulsion is formed in a wellbore.
17. A method comprising:  
introducing a first wellbore servicing fluid comprising at least one oleaginous fluid into a wellbore, wherein the first wellbore servicing fluid forms oil-wet solids and/or oil-wet surfaces in the wellbore; and  
contacting the oil-wet solids and/or oil-wet surfaces in the wellbore with a second wellbore servicing fluid comprising a zwitterionic surfactant, a co-surfactant, and a brine to form a microemulsion.

18. The method of claim 17 wherein the brine comprises solutions comprising halide-containing salts, alkali metal salts, alkaline metal salts, formate-containing compounds, sodium bromide (NaBr), calcium chloride (CaCl<sub>2</sub>), calcium bromide (CaBr<sub>2</sub>), sodium chloride (NaCl), zinc bromide (ZnBr<sub>2</sub>), ethyl formate, sodium formate, cesium formate, potassium formate, methyl formate, methyl chloro formate, triethyl orthoformate, trimethyl orthoformate, derivatives thereof, or combinations thereof.
19. The method of claim 17 wherein the brine comprises sodium bromide, calcium chloride, calcium bromide, sodium chloride, zinc bromide, or combinations thereof.
20. The method of claim 17 wherein the brine has a density of from about 8.5 ppg to about 15.1 ppg
21. The method of claim 17 wherein the oleaginous fluid comprises olefin, internal olefin based oil, mineral oil, kerosene, diesel oil, fuel oil, synthetic oil, linear or branched paraffin, ester, acetal, mixtures of crude oil, derivatives thereof, or combinations thereof.
22. The method of claim 17 wherein the oil-wet solids and/or oil-wet surfaces comprise residuals on a casing, components of a filtercake, components of a formation face, components of a fracture face, components of a perforation, components on a screen, components on a gravel pack screen, or combinations thereof.
23. The method of claim 17 further comprising removing the microemulsion from the wellbore.
24. The method of claim 17 further comprising:  
providing a first composition comprising a zwitterionic surfactant and a co-surfactant;

contacting the first composition with a brine to form the second wellbore servicing fluid;  
and contacting the second wellbore servicing fluid with the oil-wet solids and/or oil-wet  
surfaces in the wellbore.



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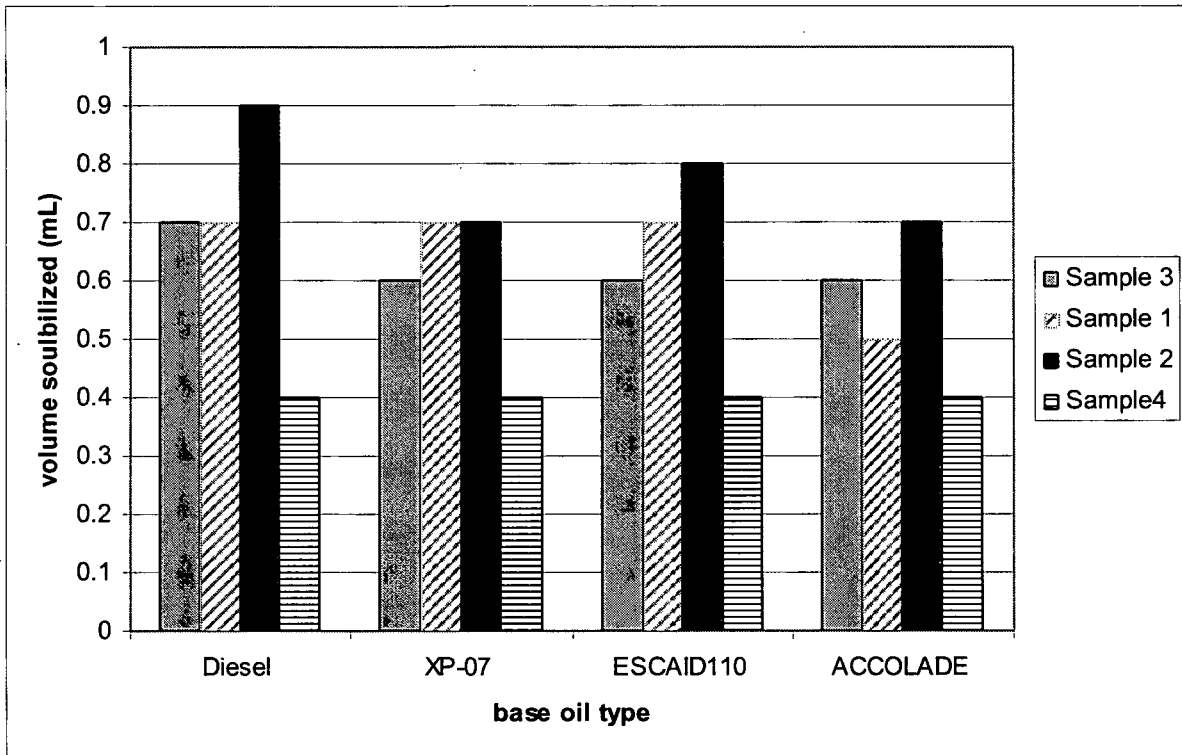


FIG. 1

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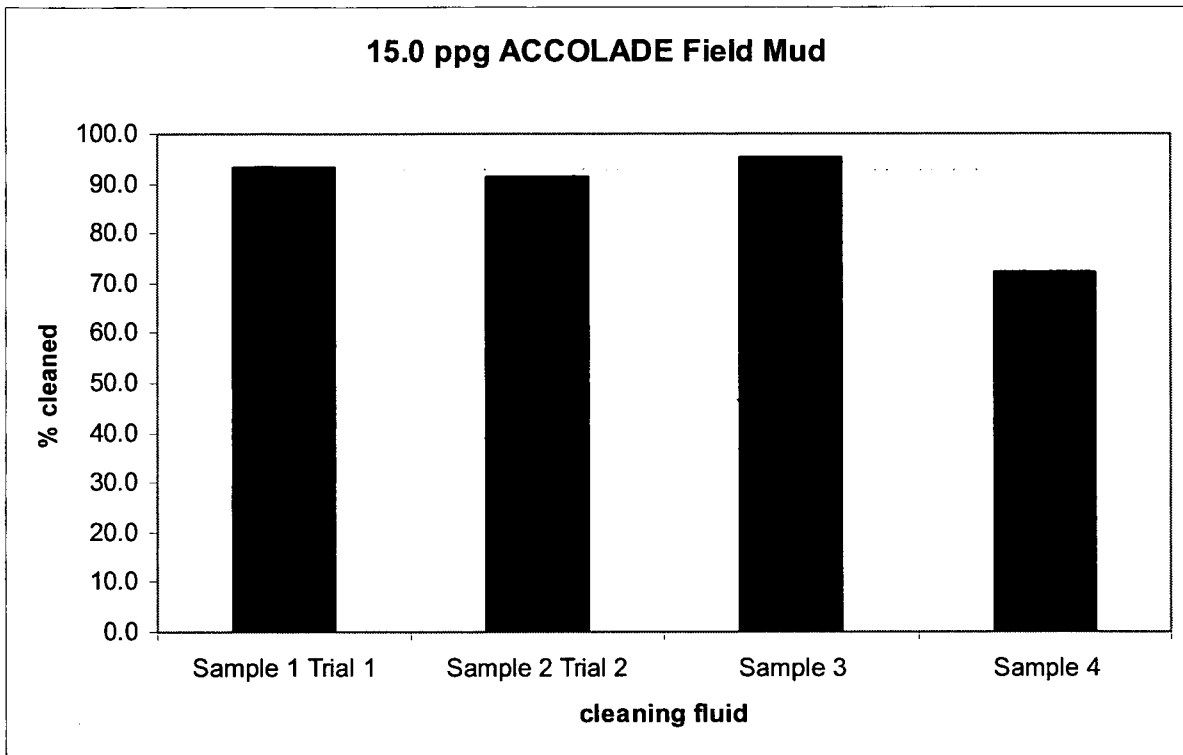


FIG. 2

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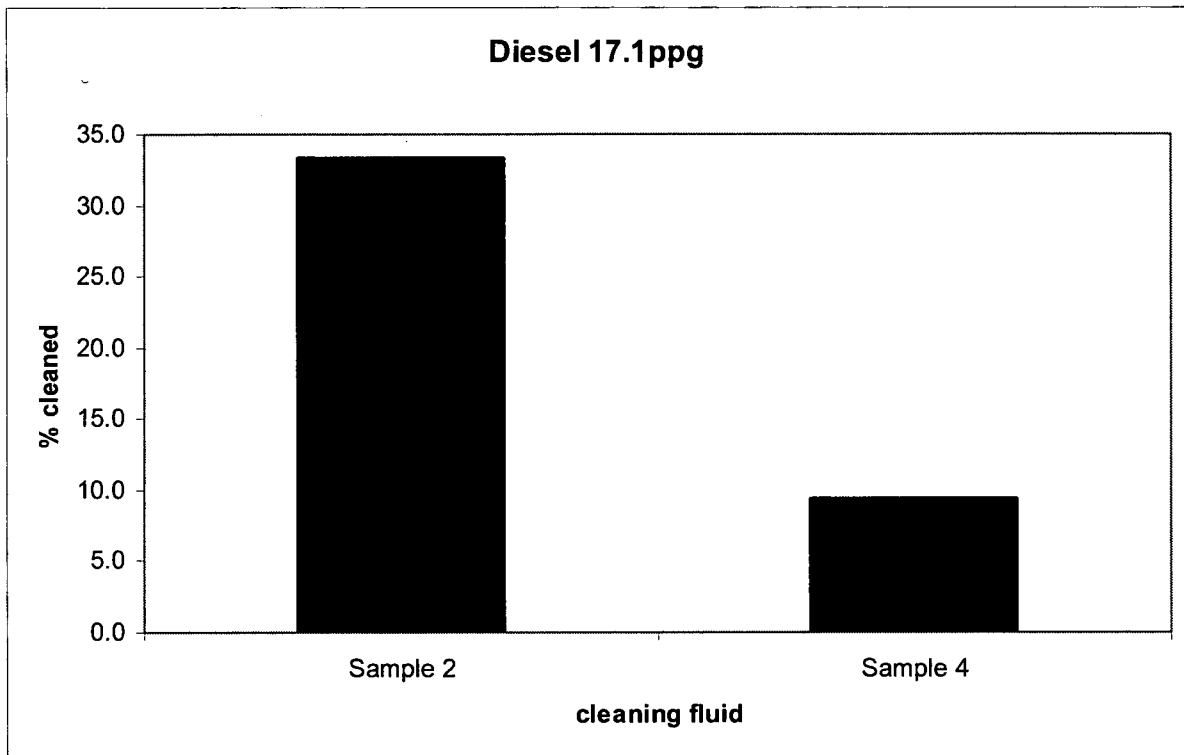


FIG. 3

# INTERNATIONAL SEARCH REPORT

International application No  
PCT/GB2009/002156

<b>A. CLASSIFICATION OF SUBJECT MATTER</b> INV. C09K8/32      C09K8/34      C09K8/36      C09K8/524				
According to International Patent Classification (IPC) or to both national classification and IPC				
<b>B. FIELDS SEARCHED</b>				
Minimum documentation searched (classification system followed by classification symbols) C09K				
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 practical, search terms used) EPO-Internal, WPI Data				
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>				
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.		
Y	US 2008/110618 A1 (QUINTERO LIRIO [US] ET AL) 15 May 2008 (2008-05-15) paragraph [0008] - paragraph [0012]; claims -----	1-16		
Y	US 2006/137879 A1 (CHAN ALBERT F [US]) 29 June 2006 (2006-06-29) paragraph [0009] - paragraph [0011]; claims -----	1-16		
Y	US 2002/010104 A1 (EWBANK ERIC [BE] ET AL) 24 January 2002 (2002-01-24) claim 1 -----	1-16		
A	GB 2 032 491 A (ELF AQUITAINE) 8 May 1980 (1980-05-08) claims -----	1-24		
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<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input checked="" type="checkbox"/> See patent family annex.				
* Special categories of cited documents :				
<table style="width: 100%; border: none;"> <tr> <td style="width: 50%; border: none; vertical-align: top;">                     "A" document defining the general state of the art which is not considered to be of particular relevance                      "E" earlier document but published on or after the international filing date                      "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)                      "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                 </td> <td style="width: 50%; border: none; vertical-align: top;">                     "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                      "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone                      "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.                      "&amp;" document member of the same patent family                 </td> </tr> </table>			"A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "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 "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "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
"A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "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 "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "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 <p style="text-align: center; font-size: 1.2em;">28 January 2010</p>		Date of mailing of the international search report <p style="text-align: center; font-size: 1.2em;">05/02/2010</p>		
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 <p style="text-align: center; font-size: 1.2em;">Grittern, Albert</p>		

# INTERNATIONAL SEARCH REPORT

International application No  
PCT/GB2009/002156

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2006/109016 A1 (SURFACTANT TECHNOLOGIES LTD [GB]; HARRISON JOHN [GB]; ZWINDERMAN MARK) 19 October 2006 (2006-10-19) page 10, line 27 - page 11, line 17; claims -----	1-24

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Information on patent family members

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