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(54) Title: INVERT EMULSION SCREEN RUNNING FLUID STABILITY AND REVERSIBILITY CONTROL

(57) Abstract: A wellbore fluid is disclosed. The wellbore fluid has a non-oleaginous internal phase and an oleaginous external phase. A reversible emulsifier stabilizes the invert emulsion by pH. One or more alkanolamines are also included in the wellbore fluid.



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## INVERT EMULSION SCREEN RUNNING FLUID STABILITY AND REVERSIBILITY CONTROL

### BACKGROUND

- [0001]** This application claims priority to and the benefit of U.S. Provisional Application No. 62/687221, filed June 19, 2018, the entire disclosure of which is hereby incorporated herein by reference.
- [0002]** Many types of fluids have been used in the drilling of oil and gas wells. The selection of an oil-based drilling fluid, also known as oil-based mud, involves a careful balance of both the good and bad characteristics of such fluids in a particular application, the type of well to be drilled, and the characteristics of the oil or gas field in which the well is to be drilled. A surfactant capable of emulsifying incorporated water into the oil is an essential component of oil-based muds.
- [0003]** The primary benefits of selecting an oil-based drilling fluid include: superior hole stability, especially in shale formations; formation of a thinner filter cake than the filter cake achieved with a water-based mud; excellent lubrication of the drilling string and downhole tools; penetration of salt beds without sloughing or enlargement of the hole as well as other benefits that should be known to one of skill in the art.
- [0004]** An especially beneficial property of oil-based muds is their excellent lubrication qualities. These lubrication properties permit the drilling of wells having a significant vertical deviation, as is typical of off-shore or deep-water drilling operations or when a horizontal well is desired. In such highly deviated holes, torque and drag on the drill string are a significant problem because the drill pipe lies against the low side of the hole, and the risk of pipe sticking is high when water based-muds are used. In contrast oil-based muds provide a thin, slick filter cake which helps to prevent pipe sticking and thus the use of the oil-based mud can be justified.
- [0005]** Despite the many benefits of utilizing oil-based muds, they have disadvantages. In general, the use of oil-based drilling fluids and muds has high initial and operational costs. These costs can be significant depending on the depth of the hole to be drilled. However, often the higher costs can be justified if the oil-based drilling fluid prevents caving in or

hole enlargement within a well, which can greatly increase drilling time and costs. Oil-based fluids render the wellbore oil wet after use, but for cleaning up, completion, and well-stimulation the wellbore needs to be water wet. This can prolong the time required for a particular drilling operation. Increasing efficiency is especially vital in open-hole operations due to the risk of the hole collapsing unexpectedly. Additionally, oil-based fluids are generally much less dense than aqueous fluids, meaning that additional weighting agents need to be added to oleaginous formulations to make them suitable for certain applications.

### DETAILED DESCRIPTION

**[0006]** Embodiments disclosed herein generally relate to reversible invert emulsion oil-based fluids in which the oil-continuous phase fluid is converted to a water-wet fluid without the application of an external trigger. The timing of the reversible event is controlled by the composition of the fluid. Such reversible invert emulsion oil-based fluids may be useful in the completion of subterranean wells, particularly in screen running. As the fluid is sufficiently alkaline without the use of lime, it can be significantly solid-free and minimizes the risk of screen plugging, as compared to conventional drilling fluids.

**[0007]** Oil-in-water emulsions are typically stabilized by both electrostatic stabilization (through formation of an electric double layer between the two phases) and steric stabilization (through van der Waals repulsive forces), whereas invert emulsions (water-in-oil) are typically stabilized by only steric stabilization. Because there is only one mechanism of stabilization for invert emulsions, they are generally more difficult to stabilize. This is particularly true at high internal phase volumes. Suitable emulsifiers, however, enable the formation and stabilization of invert emulsions.

**[0008]** Some embodiments of the present disclosure relate to invert emulsion fluids having a high internal phase ratio (HIPR; <50/50 O/W), which are stabilized by an emulsifying agent. By virtue of the greater internal phase concentration, weight may be provided to the fluid primarily through the inherent density of the aqueous or other internal phase, thus minimizing the total solid content. One of skill in the art should appreciate that the

chemical properties of the emulsifiers are important in the selection of a suitable emulsifier to form stable invert emulsions.

**[0009]** Oil-based muds often contain water, be it unintentionally added during the drilling process (i.e. seepage from penetrated formations or residual water in the hole), or intentionally added water to affect the properties of the drilling fluid or mud. In such water-in-oil type emulsions, also known as invert emulsions, an emulsifier is utilized that will stabilize the emulsion. In general, the invert emulsion may contain both water soluble and oil soluble emulsifying agents. Conventional examples of emulsifiers include polyvalent metal soaps, fatty acids and fatty acid soaps, and other similar suitable compounds that should be known to one of skill in the art.

**[0010]** The use of traditional emulsifiers and surfactants in invert emulsion drilling fluid systems can complicate the clean-up process in open-hole completion operations. Drilling fluids using traditional surfactant and emulsifier materials may require the use of solvents and other surfactant washes to penetrate the filter cake and reverse the wettability of the filter cake particles. That is to say, washing with detergents should convert the oil-wet solids of the filter cake into water-wet solids. Water-wet solids in the filter cake are necessary so that the subsequent acid wash can attack the particles of the mud cake and destroy or remove them prior to production. The productivity of a well is somewhat dependent on effectively and efficiently removing the filter cake while minimizing the potential of water blocking, plugging or otherwise damaging the natural flow channels of the formation. The problems of efficient well clean-up, stimulation, and completion are a significant issue in all wells, and especially in open-hole horizontal well completions.

**[0011]** Some of these issues can be circumvented through the use of a reversible emulsifier which stabilizes the invert emulsion, but which may be reversed by a change in pH. In more alkaline environments, an invert emulsion may be formed in which the oleaginous liquid is the continuous phase and the non-oleaginous liquid is the discontinuous phase. That is to say, the emulsifier is able to stabilize an invert emulsion. Upon a decrease in fluid pH, the oleaginous liquid may become the discontinuous phase and the non-

oleaginous liquid may become the continuous phase. In other words, the invert emulsion may be converted to a regular emulsion upon acidification of the fluid.

**[0012]** Conventional reversible emulsions rely on lime to provide sufficient alkalinity to prevent premature reversion. However, high amounts of lime cannot be used in screen running completion fluids as the solid can pose the risk of screen plugging. Rather, in accordance with embodiments of the present disclosure, sufficient alkalinity to stabilize the emulsion can be provided through the use of a liquid alkanolamine, while allowing the fluid to be solid-free. Additionally, some alkanolamines, such as ethanolamine, decompose over time under the high temperatures found in wellbores. After sufficient time has passed, the amount of ethanolamine depleted can sufficiently lower the pH of the fluid to enable reversion to occur. The timing of this reversion can be predetermined by the amount of alkanolamine added to the wellbore fluid.

**[0013]** A typical horizontal well completion process includes one or more of the following: drilling the horizontal section utilizing an oil-based drilling fluid; smoothing directional corrections with a hole opener; displacing the open-hole section with an unused drill-in fluid to minimize solids exposed to the completion assembly; running the completion assembly into the horizontal well; displacing the drill-in fluid with a completion brine; washing the filter cake with solvents and surfactants to remove or wash away the oil-based drilling fluid; destroying the filter cake with an acid soak; and, commencing production. Extension of the time required to clean up the open-hole well can result in wellbore instability and possible collapse. The collapse of a well is generally considered a bad occurrence because the well will then have to be re-drilled or opened up if production from the formation is to occur. Thus, the stability of the open-hole well limits the number of steps performed before commencing production and there is a tradeoff between increased production due to the wellbore being fully cleaned up, and the potential of well collapse due to instability.

**[0014]** In view of the above, an oil-based wellbore fluid or mud emulsion that can be automatically broken after a pre-determined time would allow the number of steps involved in hole completion to decrease, while minimizing the risk of well collapse.

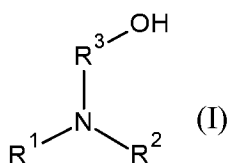
Solid-free drill-in fluids can be utilized for running completion assemblies, such as screens, by removing the risk of screen plugging. Thus, in one or more embodiments, the fluid may contain an alkanolamine and a reversible emulsifier that is sensitive to pH, providing an oil-based fluid that can be made water-wet after a certain time while remaining solid free.

**[0015]** The fluid may also possess internal aqueous phase that is stably emulsed within the external oleaginous phase. Specifically, upon application of an electric field to an invert emulsion fluid, the emulsified non-oleaginous phase, which possesses charge, will migrate to one of the electrodes used to generate the electric field. The incorporation of emulsifiers in the invert emulsion fluid stabilizes the emulsion and results in a slowing of the migration rate and/or increased voltage for breakage of the emulsion. Thus, an electrical stability (ES) test, specified by the American Petroleum Institute at API Recommended Practice 13B-2, Third Edition (February 1998), is often used to determine the stability of the emulsion. ES is determined by applying a voltage-ramped, sinusoidal electrical signal across a probe (consisting of a pair of parallel flat-plate electrodes) immersed in the mud. The resulting current remains low until a threshold voltage is reached, whereupon the current rises very rapidly. This threshold voltage is referred to as the ES (“the API ES”) of the mud and is defined as the voltage in peak volts-measured when the current reaches 61  $\mu$ A. The test is performed by inserting the ES probe into a cup of 120°F [48.9°C] mud applying an increasing voltage (from 0 to 2000 volts) across an electrode gap in the probe. The higher the ES voltage measured for the fluid, the stronger or harder to break would be the emulsion created with the fluid, and the more stable the emulsion is. Thus, the present disclosure relates to invert emulsion fluids having a high internal phase ratio but that also have an electrical stability of at least 10 V for a minimum of 15 hours, with the ES decreasing over time as the alkanolamine component of the fluid degrades. The electrical stability decreases to below 10 V within 7 days, reverting the emulsion to a water-wet fluid.

**[0016]** In one or more embodiments, an invert emulsion wellbore fluid may include an oleaginous fluid, a non-oleaginous fluid, a reversible emulsifier that stabilizes the invert by pH, and an alkanolamine.

**[0017]** Alkalinity is required to maintain the stability of an invert emulsion by preventing the premature conversion of the fluid from oil-wet to water-wet. This alkalinity is conventionally supplied to a reservoir drill-in fluid by lime, however its use is limited in screen-running applications due to the risk of solids causing screen plugging. In one or more embodiments, invert emulsion fluids include one or more alkanolamines. Alkanolamines add alkalinity, similarly to lime, but are generally liquid-phase and thus do not pose a risk of screen plugging. Additionally, alkanolamines degrade over time and so provide a means of automatically reverting the fluid from an invert emulsion without the application of an external acid.

**[0018]** The alkanolamine can be of many different forms, but must consist of at least one primary, secondary, or tertiary amine and one or more hydroxyl group. In some embodiments, the alkanolamine may consist of the structure shown in Formula I, below:



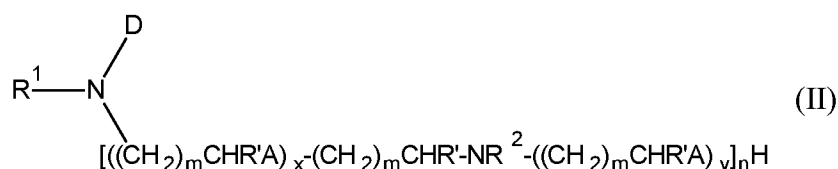
wherein  $\text{R}^1$  and  $\text{R}^2$  are independently selected from a hydrogen atom, a linear or branched alkyl group, alkenyl group, alkyl substituted cycloalkyl group, or mixtures thereof, and  $\text{R}^3$  is a linear or branched hydrocarbon chain consisting of at least one C atom. In some embodiments,  $\text{R}^1$  and  $\text{R}^2$  may include one or more further functional groups, such as esters, ethers, aldehydes, ketones, carboxylic acids, imines, sulfides, thiols, and amides.

**[0019]** In some embodiments, the alkanolamine will be a primary alkanolamine wherein both  $\text{R}^1$  and  $\text{R}^2$  are hydrogen atoms. In some more preferred embodiments, the alkanolamine will be ethanolamine, wherein  $\text{R}^1$  and  $\text{R}^2$  are hydrogen atoms, and  $\text{R}^3$  is  $-\text{CH}_2\text{CH}_2-$ . As discussed previously, the amount of alkanolamine present in the wellbore fluid directly influences the stability of the invert emulsion, and determines the time at which the fluid reverts from being oil-wet to water-wet. In some embodiments, the alkanolamine will be present in the wellbore fluid in a concentration of less than 15 lbm/bbl. In one or more preferred embodiments, the alkanolamine will have a

concentration of about 1–10 lbm/bbl. One of ordinary skill in the art will appreciate that the concentration of alkanolamine utilized will be determined by the specific application of said fluid.

**[0020]** In some embodiments, the electrical stability (ES) of the wellbore fluid should be greater than 10 V for more than 15 hours. As the alkanolamine degrades, the ES decreases over time. In one or more embodiments, the ES starts decreasing after a minimum of 15 hours. In other embodiments, the ES has started decreasing before 7 days.

**[0021]** In one or more embodiments, the reversible emulsifier may be an amine having a molecular weight (Mw) of greater than 700 daltons. In one or more particular embodiments, the amine emulsifier may have the structure shown in Formula (II) below:



**[0022]** wherein R<sup>1</sup> and R<sup>2</sup> are independently selected from a linear or branched C<sub>12</sub> to C<sub>22</sub> alkyl group, alkenyl group, alkyl substituted cycloalkyl group, or mixtures thereof; A is independently selected from a monoester group, a diester group, a triester group, an ether group, an amide group, or a CH-substituted by a hydroxyl group; R' is H, or a C<sub>1</sub> to C<sub>3</sub> alkyl; m is independently 1 or 2; x+y ≥ 2; n is 2 to 12; D is either another [((CH<sub>2</sub>)<sub>m</sub>CHR'A)<sub>x</sub>-(CH<sub>2</sub>)<sub>m</sub>CHR'-NR<sup>2</sup>-((CH<sub>2</sub>)<sub>m</sub>CHR'A)<sub>y</sub>]<sub>n</sub>H group with the same limitations on A, m, x, y and n as described above, or D is a ((CH<sub>2</sub>)<sub>m</sub>CHR'E)<sub>z</sub>H group, wherein m is independently 1 or 2; R' is H, or a C<sub>1</sub> to C<sub>3</sub> alkyl; E is NH or O; and z is 1, 2, or 3. In some embodiments, the Mw may be from about 700 daltons to 7000 daltons. In some embodiments, the R<sub>1</sub> group may be an aliphatic C<sub>12</sub> to C<sub>22</sub> hydrocarbon and more specifically in some embodiments a non-cyclic aliphatic hydrocarbon. In one or more embodiments, the R<sub>1</sub> group may contain at least one unsaturation, for example a carbon-carbon double bond. In some embodiments, the R<sub>1</sub> group may be a commercially recognized mixture of aliphatic hydrocarbons such as soya, which is a mixture of C<sub>14</sub> to

C20 hydrocarbons, or tallow which is a mixture of C16 to C20 hydrocarbons, or tall oil which is a mixture of C14 to C18 hydrocarbons.

**[0023]** When a majority of the amine(s) in the emulsifier of the present disclosure is in its unprotonated form, an invert emulsion may be formed in which the oleaginous liquid is the continuous phase and the non-oleaginous liquid is the discontinuous phase. That is to say, the unprotonated form of the amine emulsifier is able to stabilize an invert emulsion. Upon degradation of the alkanolamine, the pH of the fluid decreases, enabling a majority of the amine(s) in the emulsifier to become protonated. Subsequently, the oleaginous liquid may become the discontinuous phase and the non-oleaginous liquid may become the continuous phase. In other words, the invert emulsion may be converted to a regular emulsion upon the degradation of the alkanolamine component, and the protonation of the amine emulsifier. Further, upon addition of more alkanolamine or another deprotonating agent, herein referred to as a base capable of deprotonating a majority of the protonated amines in the emulsifier, an invert emulsion may be again formed; that is, the invert emulsion of the present disclosure is reversible to an oil-in-water emulsion, and back.

**[0024]** The amount of the reversible emulsifier present in the invert emulsion fluid, as noted above, should be sufficient to stabilize an invert emulsion so that, generally, the emulsion will last for more than about 1 minute after the halting of the agitation or shearing motion that forms the water-in-oil emulsion. While the concentration may vary depending on the desired application of, or the particular components in, the wellbore fluid or mud, generally the concentration is less than about 20 lbm/bbl by volume of the fluid. Thus, in one or more embodiments, the amine emulsifier is present in the invert emulsion fluid at a concentration of about 8 to 12 lbm/bbl.

**[0025]** In one or more embodiments, the oleaginous fluid is a liquid and more specifically may be a natural or synthetic oil. In one or more embodiments, the oleaginous fluid is selected from the group including diesel oil; mineral oil; a synthetic oil, such as polyolefins, polydiorganosiloxanes, siloxanes or organosiloxanes; and mixtures thereof. The concentration of the oleaginous fluid should be sufficient so that an invert emulsion

forms and may be less than about 99% by volume of the invert emulsion. In one or more embodiments, the amount of oleaginous fluid is from about 30% to about 95% by volume or from about 40% to about 90% by volume of the invert emulsion fluid. The oleaginous fluid in one or more embodiments may include at least 5% by volume of a material selected from the group including esters, ethers, acetals, dialkylcarbonates, hydrocarbons, and combinations thereof.

**[0026]** In one or more embodiments, the non-oleaginous fluid used in the formulation of the invert emulsion fluid of the present disclosure is a liquid, such as an aqueous liquid. For example, the non-oleaginous liquid may be selected from the group including sea water, a brine containing organic and/or inorganic dissolved salts, liquids containing water-miscible organic compounds and combinations thereof. For example, the aqueous fluid may be formulated with mixtures of desired salts in fresh water. Such salts may include, but are not limited to alkali metal chlorides, hydroxides, or carboxylates, for example. In various embodiments of the fluids disclosed herein, the brine may include seawater, aqueous solutions wherein the salt concentration is less than that of sea water, or aqueous solutions wherein the salt concentration is greater than that of sea water. Salts that may be found in seawater include, but are not limited to, sodium, calcium, aluminum, magnesium, potassium, strontium, and lithium, salts of chlorides, bromides, carbonates, iodides, chlorates, bromates, formates, nitrates, oxides, phosphates, sulfates, silicates, and fluorides. Salts that may be incorporated in a given brine include any one or more of those present in natural seawater or any other organic or inorganic dissolved salts. Additionally, brines that may be used in the drilling fluids disclosed herein may be natural or synthetic, with synthetic brines tending to be much simpler in constitution. In one embodiment, the density of the drilling fluid may be controlled by increasing the salt concentration in the brine (up to saturation). In a particular embodiment, a brine may include halide or carboxylate salts of mono- or divalent cations of metals, such as cesium, potassium, calcium, zinc, and/or sodium.

**[0027]** The amount of the non-oleaginous fluid is generally less than the theoretical limit needed for forming an invert emulsion. Thus, in one or more embodiments, the amount of non-oleaginous fluid is less than about 70% by volume and more specifically from

about 1 % to about 70% by volume. In some embodiments, the non-oleaginous fluid is from about 5% to about 60% by volume of the invert emulsion fluid. Due to the high internal phase ratio, the density of such fluids can be sufficiently high for wellbore applications even in the absence of additional weighting agents. In some embodiments, the total density of the wellbore fluid is about 9–21 lbm/gal. In other, more preferred embodiments the density of the fluid is of the range 10–13 lbm/gal.

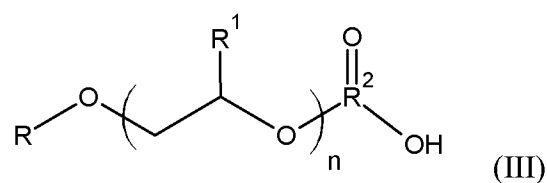
**[0028]** As noted previously, the success of a screen-running fluid is dependent upon it remaining substantially free of suspended solid materials, minimizing the risk of screen plugging occurring. To accomplish this, in one or more embodiments the wellbore fluid has a concentration of solids less than 1 lbm/bbl.

**[0029]** In one or more embodiments, the invert emulsion fluids may further contain additional chemicals depending upon the particular application of the invert emulsion, so long as they do not interfere with the reversibility of the invert emulsion fluids described herein and do keep the fluid substantially solid-free. For example, additional emulsifiers, organophilic clays, surfactants, viscosifiers, and weighting agents may be added to the fluid compositions to provide additional functional properties. The addition of such agents should be well known to one of skill in the art of formulating wellbore fluids and muds. However, it should be noted that the addition of such agents should not adversely interfere with the properties imparted by the ethanolamine and reversible emulsifier as described herein.

**[0030]** Some embodiments include, in addition to a pH-sensitive reversible emulsifier, one or more additional emulsifiers. Such emulsifiers will be selected so as to aid the formation of a stable invert emulsion. Given the large variety of invert emulsion emulsifiers available, one of ordinary skill in the art need only do a routine screen of emulsifiers by forming an invert emulsion to select an emulsifier suitable for use in the fluids disclosed herein. For example, in one or more embodiments, a fatty acid (one or more of a C<sub>10</sub>–C<sub>24</sub> fatty acid, for example, which may include linear and/or branched, and saturated and/or unsaturated fatty acids) may be reacted with one or more ethyleneamines (e.g., ethylenediamine, diethylenetriamine, triethylenetetraamine,

tetraethylenepentaamine) to produce an emulsifier selected from one or more of amides, polyamides, and/or amidoamines, depending, for example, on the mole ratio of the polyamine to the fatty acid. In one or more embodiments, the emulsifier may be a dimer poly-carboxylic C12 to C22 fatty acid, trimer poly-carboxylic C12 to C22 fatty acid, tetramer poly-carboxylic C12 to C22 fatty acid, mixtures of these acids, or a polyamide wherein the polyamide is the condensation reaction product of a C12–C22 fatty acid and a polyamine selected from the group consisting of diethylenetriamine, triethylenetetramine; and tetraethylenepentaamine. In one or more embodiments, the emulsifier may be a blend of C15–40 polyolefins, polyamides with a molecular weight greater than 1200, and amines. Emulsifiers of the present disclosure may have an amine number in the range of 25–50. The term “amine number” refers to the ratio of the mass of potassium hydroxide which consumes exactly as much acid on neutralization as does the sample being examined, to the mass of that sample. In one or more embodiments, the emulsifier may be a polyalkenyl succinimide compound.

**[0031]** In one or more embodiments, the emulsifier may be an alkoxyated ether acids. In one or more embodiments, an alkoxyated ether acid is an alkoxyated fatty alcohol terminated with a carboxylic acid, represented by the following formula (III):



**[0032]** where R is C<sub>6</sub>-C<sub>24</sub> or –C(O)R<sup>3</sup> (where R<sup>3</sup> is C<sub>10</sub>-C<sub>22</sub>), R<sup>1</sup> is H or C<sub>1</sub>-C<sub>4</sub>, R<sup>2</sup> is C<sub>1</sub>-C<sub>5</sub> and n may range from 0 to 20 in one or more embodiments (0 in some embodiments and 1-20 in other embodiments). Such compounds may be formed by the reaction of an alcohol with a polyether (such as poly(ethylene oxide), poly(propylene oxide), poly(butylene oxide), or copolymers of ethylene oxide, propylene oxide, and/or butylene oxide) to form an alkoxyated alcohol. The alkoxyated alcohol may then be reacted with an α-halocarboxylic acid (such as chloroacetic acid, chloropropionic acid, etc.) to form the alkoxyated ether acid. In a particular embodiment, the selection of n may be based on the lipophilicity of the compound and the type of polyether used in the alkoxylation.

In some particular embodiments, where  $R^1$  is H (formed from reaction with poly(ethylene oxide)),  $n$  may be 2 to 10 (between 2 and 5 in some embodiments and between 2 and 4 in more particular embodiments). In other particular embodiments, where  $R^1$  is  $-CH_3$ ,  $n$  may range up to 20 (and up to 15 in other embodiments). Further, selection of  $R$  (or  $R^3$ ) and  $R^2$  may also depend on based on the hydrophilicity of the compound due to the extent of polyetherification (*i.e.*, number of  $n$ ). In selecting each  $R$  (or  $R^3$ ),  $R^1$ ,  $R^2$ , and  $n$ , the relative hydrophilicity and lipophilicity contributed by each selection may be considered so that the desired HLB value may be achieved. Further, while this emulsifier may be particularly suitable for use in creating a fluid having a greater than 50% non-oleaginous internal phase, embodiments of the present disclosure may also include invert emulsion fluids formed with such emulsifier at lower internal phase amounts. In one or more embodiments, the emulsifier may be a tall oil fatty acid (TOFA) amide, such as TOFA diethanolamide. In one or more embodiments, the emulsifier may be a mono-ethanol amide, a di-ethanol amide, or an isopropanol amide. In one or more embodiments, the emulsifier may be an oleic-based amide, such as oleic acid diethanolamide or similar amides with different head groups (e.g., oleyl sarcosinate and oleyl taurate). In one or more embodiments, the emulsifier may be a polyisobutylenesuccinic anhydride.

**[0033]** In one embodiment, the additional emulsifier may be PRIMO-MUL, which is commercially available from M-I L.L.C., Houston, Tex. In one or more embodiments, an additional emulsifier may be present in a concentration of less than about 15 lbm/bbl. In preferable embodiments, the concentration of the additional emulsifier may be from about 2 to about 8 lbm/bbl

**[0034]** Organophilic clays, normally amine treated clays, may be useful as viscosifiers in one or more embodiments of the fluid compositions of the present disclosure. Such clays alter the rheology of the fluid and can enhance stability of the emulsion in addition to minimizing oil separation. Other viscosifiers, such as oil soluble polymers, polyamide resins, polycarboxylic acids and soaps can also be used. The amount of viscosifier used in the composition can vary depending upon the end use of the composition. However, in some embodiments about 0 to 1 lbm/bbl are sufficient for most applications. TRUVIS, VG69, VG-SUPREME and VG-PLUS are organoclay materials distributed by M-I

L.L.C. Houston, TX, and Versa-HRP is a polyamide resin material manufactured and distributed by M-I L.L.C. Houston TX, that may be used in fluids disclosed herein.

**[0035]** In one or more embodiments, surfactant compounds may be used in conjunction with the amine emulsifiers utilized herein. However, in such cases, it is relevant that the quantity and nature of these supplemental surfactants do not interfere in the ability and properties given the emulsion fluid by the amine emulsifier to act as described herein.

**[0036]** Wetting agents that may be suitable for use in the fluids disclosed herein include crude tall oil, oxidized crude tall oil, surfactants, organic phosphate esters, modified imidazolines and amidoamines, alkyl aromatic sulfates and sulfonates, and the like, and combinations or derivatives of these. However, the use of fatty acid wetting agents may be minimized so as to not adversely affect the reversibility of the invert emulsion disclosed herein. SUREWET®, VERSAWET® and FAZEWET® are examples of commercially available wetting agents manufactured and distributed by M-I L.L.C Houston, TX that may be used in fluids disclosed herein.

**[0037]** Weighting agents or density materials suitable for use in the fluids disclosed herein include galena, hematite, magnetite, iron oxides, ilmenite, barite, siderite, celestite, dolomite, calcite, and the like. The quantity of such material added, if any, depends upon the desired density of the final composition. In one or more embodiments, weight material is added to result in a drilling fluid density of up to about 24 pounds per gallon. For example, the weight material may be added to achieve a fluid with a weight of at least 9 pounds per gallon and up to 21 pounds per gallon. Further, it is also envisioned that the desired density may be achieved without solid weighting agents but instead through the internal aqueous phase present in the invert emulsion. Specifically, in particular embodiments, the use of a HIPR invert emulsion may allow the overall density of the fluid to increase by virtue of the salts present in the aqueous phase. Such salts are described above.

**[0038]** The method used in preparing the fluids described herein is not critical. Conventional methods can be used to prepare the wellbore fluids in a manner analogous to those normally used, to prepare conventional oil-based wellbore fluids. In one

representative procedure, a desired quantity of oleaginous fluid such as a base oil and a suitable amount of amine emulsifier are mixed together and the remaining components are added sequentially with continuous mixing. An invert emulsion of the present disclosure is formed by vigorously agitating, mixing or shearing the oleaginous fluid and the non-oleaginous fluid.

**[0039]** One advantageous aspect of drilling subterranean wells with the invert emulsion of the present disclosure is that well clean-up and completion are much easier and quicker to carry out, especially when the well penetrates or comes into contact with a producing formation. As described above, cleaning up and completing the well may include washing with detergents that convert the oil-wet solids of the filter cake into water-wet solids. If these operations are to be fully effective, a significant amount of aqueous fluid may penetrate the formation resulting in water blockages in the formation which adversely affect production. In addition, time is of the essence when open-hole operations are being conducted because the hole can collapse unexpectedly. Thus, in one or more embodiments, an invert emulsion fluid may be used in the drilling, completion and workover of a well. When the invert emulsion fluid comes into contact with a producing formation, a filter cake is formed in a conventional manner. When running screens into a hole, or performing one or more other completion operations, the present fluids may be particularly suitable due to the formulation with no or minimal solids. However, instead of washing the hole with a detergent solution and an acid breaker, the use of the invert emulsion drilling fluid of the present disclosure allows for the *automatic conversion* of the fluid from oil wet to water wet. This is achieved through the alkanolamine being consumed over time, causing the pH of the fluid to decrease. Once the fluid is sufficiently acidic, the reversible emulsifier switches the invert emulsion from water-wet to oil-wet without the addition of an external acid breaker. The timing of this automatic process can be controlled through the formulation of the fluid with the correct level of alkanolamine. This reduces the number of steps necessary for wellbore cleaning and completion, enabling the process to be accomplished more effectively and rapidly.

**[0040]** Another advantageous aspect of using the invert emulsion fluids of the present disclosure is the ability to use such fluids for completion processes such as screen

running. When using reversible emulsifiers that are pH sensitive, alkalinity is required to maintain the stability of the invert emulsion by preventing the premature conversion of the fluid from oil wet to water wet. This alkalinity is conventionally supplied by lime which, at high concentrations, can lead to high levels of suspended solids in the fluid. These solids limit the use of such formulations for screen running due to the risk of such solids causing screen plugging. Through the use of alkanolamines, which are generally liquid-phase, fluids can be formulated without lime and remain sufficiently solid-free for screen-running applications.

**[0041]**        **EXAMPLES**

**[0042]**        The following examples were used to demonstrate the electrical stability of solid-free invert emulsion screen running fluids that contain alkanolamines.

**[0043]**        Example 1

**[0044]**        The general formulation to prepare an invert emulsion screen running fluid is shown in Table 1. The type of base oil is determined by the operation and location. The type of brine and its density are determined by the final fluid density required for the application.

**Table 1:** General formulation for an invert emulsion screen running fluid

<b>Product</b>	<b>Concentration</b>	<b>Function</b>
Base oil	As required	Base fluid
Organophilic clay (optional)	0 – 1 lb/bbl	Rheology, Enhance stability, Minimize oil separation
Lime (optional)	0 – 1 lb/bbl	Alkalinity
PRIMO-MUL	2 – 8 lb/bbl	High internal phase ratio emulsifier
ECF-1867	8 – 12 lb/bbl	Reversible emulsifier
Brine	As required	Density

**[0045]**        The polymeric emulsifier, ECF-1867, was used in this example as a secondary emulsifier to create a reversible invert emulsion system. The fluid formulations and properties are shown in Table 2. All formulations were formulated using calcium bromide (CaBr<sub>2</sub>) brine with an oil-water ratio (OWR) of 30:70. Emulsion stability is determined by

the drop test of fluid in water where a stable invert emulsion fluid, i.e., oil-wet, would present a spherical bead in water. The electrical stability (ES, volts) provides relative emulsion stability from one fluid to another, i.e., the higher the ES, the more stable the invert emulsion. The duration of invert emulsion stability is determined and recorded in Table 2. Without clay, the fluid was less stable and lost its invert emulsion property in a day (Formulation 1). Adding clay did enhance fluid stability for a few extra days (Formulation 2); however, in many cases that may be inadequate for long term use during operation. Higher loading of lime was used to further enhance fluid emulsion stability, as shown in Formulation 3.

**Table 2:** 11.2 lb/gal solids-free formulations and their properties after heat ageing at 180°F

<b>Formulation:</b>	<b>#1</b>	<b>#2</b>	<b>#3</b>
<b>Product</b>	<b>Concentration (lb/bbl)</b>		
LVT 200	60.6	60.6	60.3
VG Plus	-	0.50	0.50
Lime	1.00	1.00	6.00
ECF-1867	12.00	12.00	12.00
PRIMO-MUL	4.00	4.00	4.00
Brine density, lb/gal	12.98	12.98	12.94
Mud density, lb/gal	11.2	11.2	11.2
Initial ES, volts	50	58	54
Drop test	Bead	Bead	Bead
Ageing time before invert emulsion breaks, days	1	< 4	> 21

**[0046]** Results in Table 2 demonstrate that the solids-free system requires high alkalinity to maintain emulsion stability. However, higher amount of lime (i.e., 200 mesh / 74 microns solid) has a high risk for screen plugging and must be avoided. Instead, a liquid organic amine, e.g., ethanolamine, was added to the formulation to provide alkalinity to the system. With adequate concentrations of ethanolamine, the long-term fluid stability can be achieved, as shown in Table 3.

**Table 3:** Solids-free formulations and their properties after heat ageing at 180°F and 250°F

<b>Formulation:</b>	<b>#4</b>		<b>#5</b>		<b>#6</b>	
<b>Product</b>	<b>Concentration (lbm/bbl)</b>					
LVT 200	60.3		59.4		58.1	
VG Plus	0.50		0.50		0.50	
ethanolamine	1.00		5.00		10.00	
ECF-1867	12.00		12.00		12.00	
PRIMO-MUL	4.00		4.00		4.00	
Brine density, lb/gal	13.37		13.42		13.48	
Mud density, lb/gal	11.5		11.5		11.5	
Initial ES, volts	364		237		223	
Drop test	Bead		Bead		Bead	
Ageing Temperature, °F	180	250	180	250	180	250
Ageing time before invert emulsion breaks, days	1	1	>14	>14	>19	>19

[0047] Example 2

[0048] Fluids were formulated as shown in Table 4 with different loadings of ethanolamine. Each fluid was static ageing at 225°F with 200 psi nitrogen overbalance. Formulation 7 reverted from oil-wet to water-wet the next day while Formulation 8 and 9 maintained stable invert emulsions. Formulation 8 gave an invert emulsion that became unstable and reverted after 5 days, while Formulation 9 was still stable after even 12 days of heat ageing. By varying the loading of liquid amine in the formulation, the fluid stability and reversibility can be controlled to meet the application for the duration required before the fluid would be cleaned out and removed from the well.

**Table 4:** Solids-free formulations and their properties after heat ageing at 225°F

<b>Formulation:</b>	<b>#7</b>	<b>#8</b>	<b>#9</b>
<b>Product</b>	<b>Concentration (lb/bbl)</b>		
LVT 200	73.8	73.2	72.6
VERSAGEL HT	0.5	0.5	0.5
PTS 200	0	3	5
ECF-1867	12	12	12
PRIMO-MUL	4	4	4
14.2 lb/gal CaBr <sub>2</sub>	260.5	260.2	259.9
Water	89.2	88.1	87
<b>Fluid Properties</b>			
<b>Initial ES, V</b>	178	47	85
<b>1 day at 225°F</b>	Broken emulsion	Stable invert emulsion	Stable invert emulsion
<b>ES, V</b>	< 10	142	151
<b>5 days at 225°F</b>	Broken emulsion	Broken emulsion	Stable invert emulsion
<b>ES, V</b>	< 10	10	76
<b>12 days at 225°F</b>	Broken emulsion	Broken emulsion	Stable invert emulsion
<b>ES, volts</b>	< 10	9	32

[0049] Although only a few example embodiments have been described in detail above, those skilled in the art will readily appreciate that many modifications are possible in the example embodiments without materially departing from this invention. Accordingly, all such modifications are intended to be included within the scope of this disclosure as defined in the following claims. In the claims, means-plus-function clauses are intended to cover the structures described herein as performing the recited function and not only structural equivalents, but also equivalent structures. Thus, although a nail and a screw may not be structural equivalents in that a nail employs a cylindrical surface to secure wooden parts together, whereas a screw employs a helical surface, in the environment of fastening wooden parts, a nail and a screw may be equivalent structures. It is the express intention of the applicant not to invoke 35 U.S.C. § 112, paragraph 6 for any limitations of any of the claims herein, except for those in which the claim expressly uses the words ‘means for’ together with an associated function.

## CLAIMS

What is claimed:

1. A wellbore fluid comprising:  
a non-oleaginous internal phase;  
an oleaginous external phase;  
a reversible emulsifier that stabilizes the invert emulsion by pH; and  
one or more alkanolamines.
2. The wellbore fluid of claim 1, wherein an alkanolamine is a primary alkanolamine.
3. The wellbore fluid of claim 2, wherein the primary alkanolamine is ethanolamine.
4. The wellbore fluid of claim 3, wherein the concentration of ethanolamine is about 1 to 10 lbm/bbl.
5. The wellbore fluid of claim 1, wherein the wellbore fluid has a density of about 9 to 21 pounds per gallon.
6. The wellbore fluid of claim 1, wherein the amount of oleaginous external phase is from about 30% to about 50% by volume of the fluid.
7. The wellbore fluid of claim 1, wherein the amount of non-oleaginous internal phase is from about 50% to about 70% by volume of the wellbore fluid.
8. The wellbore fluid of claim 1, wherein the reversible emulsifier has a concentration of about 8 to 12 lbm/bbl.
9. The wellbore fluid of claim 1, wherein the reversible emulsifier is an amine having a molecular weight of at least 700 daltons.
10. The wellbore fluid of claim 1, further comprising:  
one or more additional emulsifiers.

11. The wellbore fluid of claim 10, wherein an additional emulsifier has a concentration of about 2 to 8 lbm/bbl.
12. The wellbore fluid of claim 1, further comprising:  
an organophilic clay.
13. The wellbore fluid of claim 12, wherein the organophilic clay has a concentration of about 0 to 1 lbm/bbl.
14. The wellbore fluid of claim 1, wherein the wellbore fluid has a concentration of solids less than 1 lbm/bbl.
15. The wellbore fluid of claim 1, wherein the wellbore fluid has an electrical stability of at least 10 V for at least 15 h.
16. The wellbore fluid of claim 15, wherein the electrical stability begins to decrease after at least 15 h.
17. The wellbore fluid of claim 16, wherein the electrical stability begins to decrease after at most 7 days.
18. A method of completing a wellbore operation, comprising:  
injecting a wellbore fluid into a wellbore, the wellbore fluid comprising:  
a non-oleaginous internal phase;  
an oleaginous external phase;  
a reversible emulsifier that stabilizes the invert emulsion by pH; and  
an alkanolamine.
19. The method of claim 18, further comprising:  
emplacing a screen in the wellbore when the wellbore fluid is in the wellbore.
20. The method of claim 18, wherein the alkanolamine of the wellbore fluid is a primary alkanolamine.

21. The method of claim 20, wherein the primary alkanolamine of the wellbore fluid is ethanolamine.
22. The method of claim 21, wherein the wellbore fluid has an ethanolamine concentration of about 1 to 10 lbm/bbl.
23. The method of claim 18, wherein the reversible emulsifier of the wellbore fluid is an amine having a molecular weight of at least 700 daltons.
24. The method of claim 18, wherein the reversible emulsifier of the wellbore fluid has a concentration of about 8 to 12 lbm/bbl.
25. The method of claim 18, wherein the wellbore fluid has a concentration of solids less than 1 lbm/lb.

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 2019/037415

A. CLASSIFICATION OF SUBJECT MATTER		
<i>C09K 8/86 (2006.01)</i> <i>E21B 43/22 (2006.01)</i>		
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)		
B01F 17/00, C09K 8/00-8/94, E21B 43/00-43/32		
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)		
PatSearch (RUPTO Internal), USPTO, PAJ, Espacenet, Information Retrieval System of FIPS		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2013/040427 A2 (M-I L.L.C. et al.) 21.03.2013, claims 19, 25, paragraphs [0037], [0038], [0045], [0049], [0055], [0057], [0060], [0069], [0071], [0073]	1-25
A	WO 2009/087199 A1 (AKZO NOBEL N.V. et al.) 16.07.2009	1-25
A	WO 2009/124920 A2 (BASF SE et al.) 15.10.2009	1-25
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> 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	“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
“E”	earlier document but published on or after the international filing date	“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
“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)	“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
“O”	document referring to an oral disclosure, use, exhibition or other means	“&” document member of the same patent family
“P”	document published prior to the international filing date but later than the priority date claimed	
Date of the actual completion of the international search		Date of mailing of the international search report
16 September 2019 (16.09.2019)		26 September 2019 (26.09.2019)
Name and mailing address of the ISA/RU: Federal Institute of Industrial Property, Berezhkovskaya nab., 30-1, Moscow, G-59, GSP-3, Russia, 125993 Facsimile No: (8-495) 531-63-18, (8-499) 243-33-37		Authorized officer  T. Melnikova  Telephone No. 8(495) 531-64-81