



(86) Date de dépôt PCT/PCT Filing Date: 2003/11/13  
(87) Date publication PCT/PCT Publication Date: 2004/06/03  
(45) Date de délivrance/Issue Date: 2011/01/11  
(85) Entrée phase nationale/National Entry: 2005/05/05  
(86) N° demande PCT/PCT Application No.: US 2003/036417  
(87) N° publication PCT/PCT Publication No.: 2004/046273  
(30) Priorité/Priority: 2002/11/14 (US10/294,533)

(51) Cl.Int./Int.Cl. *C09K 8/36* (2006.01),  
*C09K 8/34* (2006.01)  
(72) Inventeurs/Inventors:  
SUMMERHILL, JERRY L., US;  
JARRETT, MICHAEL A., US;  
MCKELLAR, ALEXANDER J., US;  
YOUNG, DAVID B., US;  
GROVER, PATRICK E., US;  
GUSLER, WILLIAM J., US  
(73) Propriétaire/Owner:  
BAKER HUGHES INCORPORATED, US  
(74) Agent: SIM & MCBURNEY

(54) Titre : COMPOSES ORGANO-FONCTIONNELS POUR STABILISATION DES SCHISTES DE LA PHASE  
DISPERSEE AQUEUSE D'UNE EMULSION INVERSE A BASE NON AQUEUSE  
(54) Title: ORGANOFUNCTIONAL COMPOUNDS FOR SHALE STABILIZATION OF THE AQUEOUS DISPERSED  
PHASE OF NON-AQUEOUS BASED INVERT EMULSION DRILLING SYSTEM FLUIDS

(57) **Abrégé/Abstract:**

Invert emulsion drilling system fluids comprising an oleaginous continuous phase and a non-oleaginous dispersed phase, the dispersed phase comprising organofunctional compounds(s) effective to provide shale inhibition. The organofunctional compound(s) may be used either as a supplement to or as a substitute for metallic salts.

## (12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property  
Organization  
International Bureau



(43) International Publication Date  
3 June 2004 (03.06.2004)

PCT

(10) International Publication Number  
**WO 2004/046273 A3**

(51) International Patent Classification<sup>7</sup>: **C09K 7/06**

(74) Agent: **DONOUGHUE, Timothy, M.**; Baker Hughes Incorporated, 3900 Essex Lane, Suite 1200, Houston, TX 77027 (US).

(21) International Application Number:  
PCT/US2003/036417

(81) Designated States (*national*): AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NI, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW.

(22) International Filing Date:  
13 November 2003 (13.11.2003)

(25) Filing Language: English

(26) Publication Language: English

(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

(30) Priority Data:  
10/294,533 14 November 2002 (14.11.2002) US

(71) Applicant: **BAKER HUGHES INCORPORATED** [US/US]; 3900 Essex Lane, Suite 1200, Houston, TX 77027 (US).

**Published:**

- with international search report
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

(72) Inventors: **SUMMERHILL, Jerry, L.**; 19318 Wildoats Drive, Katy, TX 77449 (US). **JARRETT, Michael, A.**; 8427 Bluegate Court, Houston, TX 77025 (US). **MCKEL-LAR, Alexander, J.**; 601 Cypress Station Drive #910, Houston, TX 77090 (US). **YOUNG, David, B.**; 47 Wind River Drive, Conroe, TX 77384 (US). **GROVER, Patrick, E.**; 4910 Maple Terrace, Kingwood, TX 77345 (US). **GUSLER, William, J.**; 6523 Pinehurst, Houston, TX 77023 (US).

(88) Date of publication of the international search report:  
30 September 2004

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: ORGANOFUNCTIONAL COMPOUNDS FOR SHALE STABILIZATION OF THE AQUEOUS DISPERSED PHASE OF NON-AQUEOUS BASED INVERT EMULSION DRILLING SYSTEM FLUIDS

(57) Abstract: Invert emulsion drilling system fluids comprising an oleaginous continuous phase and a non-oleaginous dispersed phase, the dispersed phase comprising organofunctional compound(s) effective to provide shale inhibition. The organofunctional compound(s) may be used either as a supplement to or as a substitute for metallic salts.



WO 2004/046273 A3

5                   **ORGANOFUNCTIONAL COMPOUNDS FOR SHALE STABILIZATION OF  
                      THE AQUEOUS DISPERSED PHASE OF NON-AQUEOUS  
                      BASED INVERT EMULSION DRILLING SYSTEM FLUIDS**

**Field of the Invention**

                  [0001] The invention relates to invert emulsion drilling system fluids. More  
10               particularly, the invention relates to invert emulsion drilling system fluids comprising  
                  an oleaginous continuous phase and a non-oleaginous dispersed phase, the dispersed  
                  phase comprising organofunctional compound(s) effective to provide shale inhibition.  
                  The organofunctional compound(s) may be used either as a supplement to or as a  
                  substitute for metallic salts.

15               **Background of the Invention**

                  [0002] Drilling system fluids comprising water as the continuous phase often are  
                  ecologically favored over fluids in which oil is the continuous phase. Unfortunately,  
                  the walls of a wellbore frequently are composed, at least in part, of shale. When  
                  exposed to water, many shales swell, slough, or spall to the extent that they prevent  
20               further operation of the wellbore. Shale also may slough during gravel transport in  
                  open-hole completion, mix with the gravel, and/or reduce the productivity of the well  
                  by choking off the permeability of the gravel pack. Shale sloughing also may cause  
                  screen blinding.

                  [0003] The use of invert emulsion drilling system fluids may help to minimize shale  
25               hydration. An invert emulsion fluid comprises "oil" as the continuous phase and an  
                  emulsified aqueous dispersed phase. In order to minimize hydration of shale, the

aqueous dispersed phase typically comprises a brine comprising metallic salts at a salinity greater than the salinity of the interstitial water in the shale.

[0004] Unfortunately, contamination by highly reactive drilled solids may cause rheological and/or filtration control problems and also may decrease emulsion stability in invert emulsion drilling system fluids. Alternative invert emulsion drilling system fluids are needed.

#### **Summary**

[0005] An invert emulsion drilling system fluid with effective rheology and fluid loss control properties, said drilling system fluid comprising an oleaginous continuous phase and a non-oleaginous dispersed phase, said dispersed phase comprising an amount of at least one organofunctional compound effective to provide shale inhibition.

In accordance with an aspect of the present invention, there is provided an invert emulsion drilling system fluid with effective rheology and fluid loss control properties, said drilling system fluid comprising an oleaginous continuous phase and a non-oleaginous dispersed phase, said dispersed phase comprising an amount of organofunctional compound effective to provide shale inhibition, said organofunctional compound comprising an active ingredient selected from the group consisting of triethanolamine, alkylenediamine, alkylenediamine salts, and combinations thereof, said invert emulsion drilling fluid further comprising a quantity of a polyolefin amide alkene amine.

In accordance with another aspect of the present invention, there is provided an invert emulsion drilling system fluid with effective rheology and fluid loss control properties, said drilling system fluid comprising an oleaginous continuous phase and a non-oleaginous dispersed phase, said dispersed phase comprising an amount of organofunctional compound effective to provide shale inhibition, said organofunctional compound comprising an active ingredient selected from the group consisting of diaminocyclohexane, salts of diaminocyclohexane, and combinations thereof.

In accordance with another aspect of the present invention, there is provided an invert emulsion drilling system fluid with effective rheology and fluid

loss control properties, said drilling system fluid comprising an oleaginous continuous phase and a non-oleaginous dispersed phase, said dispersed phase comprising an amount of hexamethylenediamine effective to provide shale inhibition, wherein said oleaginous continuous phase comprises olefins selected  
5 from the group consisting of isomerized olefins, linear alpha olefins, and combinations thereof, a majority of said olefins having 16 carbon atoms or more.

In accordance with another aspect of the present invention, there is provided an invert emulsion drilling system fluid with effective rheology and fluid loss control properties, said drilling system fluid comprising an oleaginous  
10 continuous phase and a non-oleaginous dispersed phase, said dispersed phase comprising an amount of hexamethylenediamine effective to provide shale inhibition and, said invert emulsion drilling system fluid further comprising a quantity of a polyolefin amide alkene amine.

In accordance with another aspect of the present invention, there is  
15 provided an invert emulsion drilling system fluid with effective rheology and fluid loss control properties, said drilling system fluid comprising an oleaginous continuous phase and a non-oleaginous dispersed phase, said oleaginous continuous phase comprising olefins selected from the group consisting of isomerized olefins, linear alpha olefins, and combinations thereof, a majority of  
20 said olefins having 16 carbon atoms or more, said dispersed phase comprising an amount of organofunctional compound effective to provide shale inhibition, said organofunctional compound comprising an active ingredient selected from the group consisting of urea, salts of urea, and combinations thereof.

In accordance with another aspect of the present invention, there is  
25 provided an invert emulsion drilling system fluid with effective rheology and fluid loss control properties, said drilling system fluid comprising an oleaginous continuous phase and a non-oleaginous dispersed phase, said dispersed phase comprising an amount of organofunctional compound comprising a quantity and type of exchangeable groups effective to provide shale inhibition, said invert  
30 emulsion drilling fluid further comprising a quantity of polyolefins amide alkene amine.

In accordance with another aspect of the present invention, there is provided an invert emulsion drilling system fluid with effective rheology and fluid loss control properties, said drilling system fluid comprising an oleaginous continuous phase and a non-oleaginous dispersed phase, said dispersed phase comprising an amount of at least one organofunctional compound comprising at least two primary functional groups comprising a quantity and type of exchangeable groups effective to provide shale inhibition, said invert emulsion drilling system fluid further comprising a quantity of polyolefins amide alkene amine.

In accordance with another aspect of the present invention, there is provided a method for reducing the concentration of inorganic salts required to provide shale inhibition during drilling operations using invert emulsion drilling system fluids comprising an oleaginous continuous phase and a non-oleaginous dispersed phase, said method comprising: providing said non-oleaginous dispersed phase of said fluid with an amount of organofunctional compound effective to provide shale inhibition; and, providing said invert emulsion drilling system fluid with a quantity of polyolefins amide alkene amine.

In accordance with another aspect of the present invention, there is provided a method for reducing the concentration of inorganic salts required to provide shale inhibition during drilling operations using invert emulsion drilling system fluids, said method comprising: providing said invert emulsion drilling system fluid selected from the group consisting of a drilling fluid and a drill-in fluid, said invert emulsion drilling system fluid comprising an oleaginous continuous phase and a non-oleaginous dispersed phase; and, providing said non-oleaginous dispersed phase with an amount of organofunctional compound comprising an active ingredient selected from the group consisting of diaminocyclohexane, salts of diaminocyclohexane, and combinations thereof; and performing drilling operations using said invert emulsion drilling system fluid, said organofunctional compound providing effective shale inhibition.

In accordance with another aspect of the present invention, there is provided a method for reducing the concentration of inorganic salts required to provide shale inhibition during drilling operations using invert emulsion drilling system fluids, the method comprising: providing said invert emulsion drilling system fluid selected from the group consisting of a drilling fluid and a drill-in fluid, said invert emulsion drilling system fluid comprising an oleaginous continuous phase and a non-oleaginous dispersed phase; and, providing said non-oleaginous dispersed phase with an amount of hexamethylene diamine effective to provide shale inhibition; and performing drilling operations using said invert emulsion drilling system fluid, said hexamethylene diamine providing effective shale inhibition.

In accordance with another aspect of the present invention, there is provided a method for reducing the concentration of inorganic salts required to provide shale inhibition during drilling operations using invert emulsion drilling system fluids, the method comprising: providing said invert emulsion drilling system fluid comprising an oleaginous continuous phase and a non-oleaginous dispersed phase; providing said non-oleaginous dispersed phase with an amount of organofunctional compound effective to provide shale inhibition, said organofunctional compound comprising exchangeable cations derived from primary functional groups selected from the group consisting of nitrogen containing groups, oxygen containing groups, sulfur containing groups, and phosphorus containing groups; and, performing drilling operations selected from the group consisting of rotary drilling operations and drill-in operations using said invert emulsion drilling system fluid, said effective shale inhibition being provided using a reduced concentration of metallic salt(s) compared to the amount of metallic salt(s) required to provide the same effective shale inhibition using said invert emulsion drilling system fluid in the absence of said organofunctional compound.

In accordance with another aspect of the present invention, there is provided a method for reducing the concentration of inorganic salts required to provide shale inhibition during drilling operations using invert emulsion drilling system fluids, the method comprising: providing said invert emulsion drilling  
5 system fluid comprising an oleaginous continuous phase and a non-oleaginous dispersed phase; providing said non-oleaginous dispersed phase with an amount of organofunctional compound comprising exchangeable cations effective to provide shale inhibition; and; performing drilling operations using said invert emulsion drilling system fluid without adding inorganic salt to said invert  
10 emulsion drilling system fluid.

In accordance with another aspect of the present invention, there is provided a method for reducing the concentration of inorganic salts required to provide shale inhibition during drilling operations using invert emulsion drilling system fluids, said method comprising: providing said invert emulsion drilling  
15 system fluid comprising an oleaginous continuous phase and a non-oleaginous dispersed phase; providing said non-oleaginous dispersed phase with an amount of organofunctional compound effective to provide shale inhibition; providing said invert emulsion drilling system fluid with a quantity of a polyolefin amide alkene amine; and, performing drilling operations using said invert emulsion  
20 drilling system fluid.

#### **Detailed Description**

[0007] The present application provides invert emulsion drilling system fluids which are effective to minimize shale hydration by the dispersed phase while maintaining effective rheology, filtration control, and emulsion stability in the  
25 presence of contamination by reactive drilled solids. The invert emulsion drilling system fluids avoid the need to use high concentrations of metallic salts in order to achieve shale stabilization.

[0008] The invert emulsion drilling system fluids comprise a continuous phase comprising an "oleaginous" liquid and a dispersed phase comprising a "non-

oleaginous" liquid. As used herein, the term "oleaginous liquid" means an oil which is immiscible with water and exists as a liquid at 25 °C. The oleaginous liquid preferably is non-toxic. As used herein, the term "non-toxic" is defined to mean that a material meets the applicable EPA requirements for discharge into U.S. waters.

5 Currently, a drilling fluid must have an LC<sub>50</sub> (lethal concentration where 50% of the organisms are killed) of 30,000 parts per million (ppm) suspended particulate phase (SPP) or higher to meet the EPA standards.

[0009] Suitable oleaginous liquids include, but are not necessarily limited to olefins, paraffins, water insoluble polyglycols, water insoluble esters, water insoluble Fischer-  
10 Tropsch reaction products, and other non-toxic organic materials, and combinations thereof. Suitable paraffins are described in U.S. Patent No. 5,837,655.

Suitable polyglycols have a molecular weight sufficiently high to render them water insoluble.

[0010] Preferred oleaginous liquids are relatively non-toxic branched and/or linear  
15 olefins. Examples of suitable olefins include, but are not necessarily limited to polyalphaolefins, linear alpha olefins, and internal olefins, preferably skeletally isomerized olefins, and mixtures thereof. Preferred olefins are described in U.S.

Patent Nos. 5,605,879 and 5,851,958. In a preferred  
embodiment, the oleaginous phase comprises olefins having at least 14 carbon atoms,  
20 more preferably at least 15 carbon atoms, and most preferably at least 16 carbon atoms. In a most preferred embodiment, the oleaginous phase is C16, C18 isomerized olefins, which are available from Chevron Phillips Chemical Company.

[0011] The amount of oleaginous liquid, preferably olefins, in the invert emulsion fluid varies depending upon the particular oleaginous liquid used, the non-oleaginous

liquid used, and the particular application in which the invert emulsion fluid is to be employed. The amount of oleaginous liquid generally is sufficient to form the continuous phase and for the non-oleaginous liquid to form a stable emulsion in the oleaginous liquid. The quantity of oleaginous liquid will increase with the density of  
5 a given fluid. Typically, the amount of oleaginous liquid is at least about 50 vol.% of the total invert emulsion fluid.

[0012] As used herein, the term “non-oleaginous liquid” means a material which is a liquid at 25 °C. and which is not an oleaginous liquid, as defined above. Non-oleaginous liquids are immiscible with the oleaginous liquid, and form an emulsion in  
10 the oleaginous liquid which preferably is stabilized by a suitable emulsifier. Suitable non-oleaginous liquids include aqueous substances such as water, seawater, and/or brine comprising inorganic or organic dissolved salts, as well as water-miscible organic compounds. A most preferred non-oleaginous liquid is seawater.

[0013] The drilling system fluids are useful in rotary drilling processes for drilling  
15 subterranean formations containing oil, gas, or other minerals, and in geothermal drilling, water drilling, and geoscientific drilling. Invert emulsion drilling system fluids provide stability to the drilled hole (typically called the wellbore), form a thin filter cake, lubricate the wellbore, and often penetrate salt beds without undue sloughing or enlargement of the drilled hole. As used herein, the term “invert  
20 emulsion drilling system fluid” also encompasses spotting fluids, lubricating additives, and other additives used during drilling operations, and invert emulsions comprising such additives.

[0014] Preferred invert emulsion drilling system fluids for use herein are “drilling fluids” and “drill-in” fluids. A “drilling fluid” is used to drill a borehole through the

earth to reach the payzone. A “drill-in” fluid is pumped through the drill pipe while drilling through the “payzone,” or the zone believed to hold recoverable oil or gas.

[0015] In order to prevent bit balling and sloughing off of shale which comes into contact with the dispersed phase, it is necessary to provide shale stabilization. It is possible to provide shale stabilization by using a high concentration of inorganic salt in the dispersed phase. Clay chemistry has shown that cationic base exchange with the negatively charged clay minerals commonly found in shale formations, limits their ability to hydrate, soften, and swell, thereby rendering them more stable in the presence of water based fluids and reducing or preventing screen blinding. Unfortunately, concentrated solutions of inorganic salts are toxic.

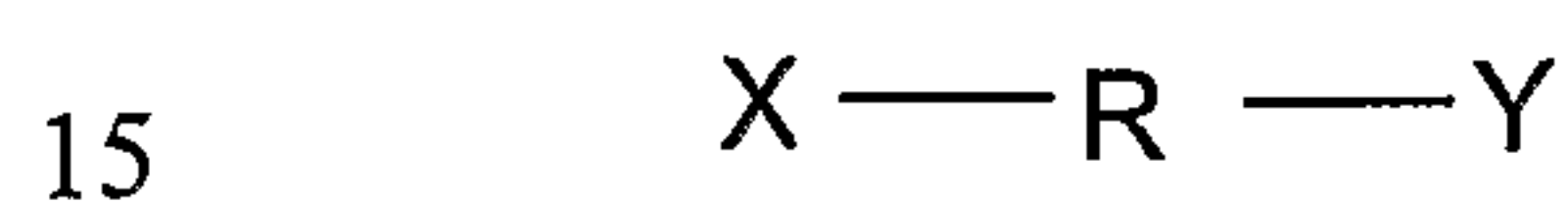
[0016] The present application provides shale stabilization by providing the non-oleaginous phase with a quantity of at least one organofunctional compound comprising “exchangeable groups,” defined as moieties which dissociate from the compound and exchange with water reactive sites present in surrounding clay or shale and reduce or preferably prevent screen blinding. Suitable exchangeable groups are electrophilic groups, most preferably cations. Without limiting the invention to particular theory or mechanism of action, it is believed that the exchangeable groups block water reactive sites in the clay, which prevents those sites from absorbing water, and thereby prevents swelling and/or sloughing of the clay or shale.

[0017] The exchangeable groups preferably are derived from primary functional groups. Most preferably, the organofunctional compound comprises at least two primary functional groups. By “primary functional groups” is meant a functional group which is bound to a single alkyl moiety. For example, an alkyl amine is a primary functional group. A dialkyl amine is not a primary functional group.

[0018] Examples of primary functional groups comprising suitable exchangeable groups include, but are not necessarily limited to nitrogen containing groups, oxygen containing groups, sulfur containing groups, and phosphorus containing groups.

Preferred primary functional groups are selected from the group consisting of amine groups, hydroxyl groups, and salts thereof. More preferred primary functional groups are selected from the group consisting of amine groups and salts thereof, preferably amine groups and protonated amine groups. Even more preferably, the organofunctional compound is selected from the group consisting of a diamine and salts thereof, most preferably an alkylenediamine wherein the alkyl moiety comprises from about 1 to about 7 to carbon atoms, preferably from about 2 to about 7 carbon atoms, and more preferably from about 2 to about 6 carbon atoms, wherein the carbon atoms may be joined to form a cycloalkyl.

[0019] Suitable organofunctional compounds for use in the dispersed phase have the following general structure:



wherein X and Y independently are primary functional groups comprising

exchangeable groups. Preferably, X and Y independently are selected from the group consisting of nitrogen containing groups, oxygen containing groups, sulfur containing groups, and phosphorus containing groups. More preferably X and Y independently are selected from the group consisting of amine groups, hydroxyl groups, and salts thereof; most preferably both X and Y independently are selected from the group consisting of amine groups and salts thereof;

- R is selected from the group consisting of linear alkylene groups having from about 1 to about 7 carbon atoms, preferably from about 2 to about 7 carbon atoms, most preferably from about 2 to about 6 carbon atoms, and cyclic alkylene groups having from about 3 to about 6 carbon atoms, wherein R is either unsubstituted or bears substituents effective to maintain or increase the dissociability of the exchangeable groups. For example, where the exchangeable group is cationic in nature, acceptable substituents either would not affect the charge distribution of the molecule or would be electrophilic or cationic in nature.
- 10 [0020] In a preferred embodiment, the organofunctional salt is selected from the group consisting of urea, alkanolamines, diaminocycloalkanes, substituted or unsubstituted alkylene diamines; and, combinations thereof. In a more preferred embodiment, the organic material is selected from the group consisting of substituted or unsubstituted trialkanolamines; diaminocycloalkanes; alkylene diamines; and, combinations thereof. In a most preferred embodiment, the organofunctional compounds are selected from the group consisting of substituted or unsubstituted triethanolamines, diaminocyclohexanes, hexamethylenediamines, salts thereof, and combinations thereof. A preferred commercially available mixture is CLAYTROL™, which is commercially available from Baker Hughes INTEQ.
- 15
- 20 [0021] A given organofunctional compound is “effective to provide shale inhibition” when the organofunctional compound produces an invert emulsion fluid that exhibits electrical stability of 350-450 volts and HTHP (high temperature high pressure differential filtration) of 6 or less.

[0022] The amount of non-oleaginous liquid in the invert emulsion fluid varies depending upon the particular non-oleaginous liquid used and the particular application in which the invert emulsion fluid is to be employed. The amount of non-oleaginous liquid is effective to produce a stable emulsion and decreases with the density of the fluid. Typically, the amount of non-oleaginous liquid is at least about 1 vol.%, preferably from about 1 vol.% to about 50 vol.% or less of the total invert emulsion fluid.

[0023] The invert emulsions generally may comprise other components known in the art. Composition and Properties of Drilling and Completion Fluids, 5th Edition, H. C. H. Darley, George R. Gray, Gulf Publishing Company, 1988, pp. 328-332 .

Conventional additives include, but are not necessarily limited to shale stabilizer(s) other than the organofunctional compound(s), filtration control additive(s), suspending agent(s), dispersant(s), thinner(s), anti-balling additive(s), lubricant(s), weighting agent(s), seepage control additive(s), lost circulation additive(s), drilling enhancer(s), penetration rate enhancer(s), corrosion inhibitor(s), acid(s), base(s), buffer(s), scavenger(s), gelling agent(s), cross-linker(s), catalyst(s), soluble salts, biocides, and combinations thereof. Lime or another alkaline material may be added to an invert emulsion fluid to maintain a reserve alkalinity and to counter acidic gases, which often are encountered during drilling operations.

[0024] In a preferred embodiment, the invert emulsion fluid comprises: emulsifier(s), clay(s), preferably quaternized clay(s), rheological modifier(s), preferably acrylate or methacrylate based modifier(s), weighting agent(s), and, wetting agent(s) effective to prevent fluid loss. A preferred type of wetting agent is a polyolefin amide alkene



166 of the book, Composition and Properties of Drilling and Completion Fluids, 5th Edition, H. C. H. Darley and George Gray, Gulf Publishing Company, 1988.

[0029] In the following Examples, the following commercial products available from Baker Hughes INTEQ were used: CARBOGEL, a quaternized clay; OMNI-MUL, a polyamide emulsifier; CLAYTROL, a water soluble shale hydration and dispersion inhibitor for water based drilling fluids; DFE-434, a quaternized clay; MIL-BAR<sup>TM</sup> a barite additive; MIL-GEL<sup>TM</sup>, a ground montmorillonite used to simulate formation shale contaminant. The following commercial products, available from sources other than Baker Hughes INTEQ were used: CF-2002, an ester/olefin blend available from Chevron Phillips Chemical Co.; C16, C18 isomerized olefins obtained from Chevron Phillips Chemical Co.; LUBRIZOL (R) 3702 and LUBRIZOL (R) 7720C, rheological modifiers available from the Lubrizol Corporation; REV-DUST<sup>TM</sup>, a simulated drilled product which may be obtained from Mil-White Company, Houston, Texas; RHODIA CS-50, a formate salt of 1,6-diamine hexane, and RHODIA CS-60, a chloride salt of 1,6,-diamine hexane. The following organofunctional compounds are available from a variety of commercial sources: aminoethylpiperazine; diaminocyclohexane; hexamethylenetriamine; urea; triethanolamine; aminoethylethanolamine; hexamethylenediamine; 2-amino-2-methyl-1-propanol; and, tetraethylenepentamine.

[0030] The invention will be better understood with reference to the examples which are illustrative only:

#### Example I

[0031] In order to determine the desired composition of a suitable base fluid, a variety of invert emulsion fluids were made using CF-2002 as the continuous phase

and MIL-GEL NT as the contaminant. The invert emulsion fluids were subjected to standard testing to determine rheological and fluid loss properties. The compositions tested and the results are given in the following Table:

| <b>OP-499: 12.0 lb/gal CF-2002,<br/>using Seawater as Brine Phase</b> |          |            |          |            |          |            |          |            |          |            |          |            |  |
|-----------------------------------------------------------------------|----------|------------|----------|------------|----------|------------|----------|------------|----------|------------|----------|------------|--|
| <b>Sample No.</b>                                                     | <b>1</b> | <b>1-S</b> | <b>2</b> | <b>2-S</b> | <b>3</b> | <b>3-S</b> | <b>4</b> | <b>4-S</b> | <b>5</b> | <b>5-S</b> | <b>6</b> | <b>6-S</b> |  |
| CF-2002, bbl                                                          | 0.575    | 0.575      | 0.575    | 0.575      | 0.575    | 0.575      | 0.575    | 0.575      | 0.575    | 0.575      | 0.575    | 0.575      |  |
| CARBOGEL, lb                                                          | 2        | 2          | 2        | 2          |          |            |          |            |          |            |          |            |  |
| OMNI-MUL, lb                                                          | 14       | 14         | 14       | 14         | 14       | 14         | 14       | 14         | 14       | 14         | 14       | 14         |  |
| Seawater, bbl                                                         | 0.2      | 0.2        | 0.171    | 0.171      | 0.2      | 0.2        | 0.171    | 0.171      | 0.171    | 0.171      | 0.171    | 0.171      |  |
| CLAY-TROL, lb                                                         |          |            | 10       | 10         |          |            | 10       | 10         | 10       | 10         | 10       | 10         |  |
| Lubrizol (R) 3702, lb                                                 |          |            |          |            |          |            |          |            | 3        | 3          |          |            |  |
| Lubrizol (R) 7720C, lb                                                |          |            |          |            |          |            |          |            |          |            | 3        | 3          |  |
| CARBO-TEC S, lb                                                       | 1        | 1          | 1        | 1          | 1        | 1          | 1        | 1          | 1        | 1          | 1        | 1          |  |
| MILBAR, lb                                                            | 255      | 255        | 255      | 255        | 255      | 255        | 255      | 255        | 255      | 255        | 255      | 255        |  |
| MIL-GEL NT, lb                                                        |          | 54*        |          | 54*        |          | 27         |          | 27         |          | 27         |          | 27         |  |
|                                                                       |          |            |          |            |          |            |          |            |          |            |          |            |  |
| O/W Ratio                                                             | 80/20    | 80/20      | 80/20    | 80/20      | 80/20    | 80/20      | 80/20    | 80/20      | 80/20    | 80/20      | 80/20    | 80/20      |  |
| Density, lb/gal                                                       | 12       | 12         | 12       | 12         | 12       | 12         | 12       | 12         | 12       | 12         | 12       | 12         |  |
| Samples hot-rolled 16 hours @ 150°F. Stirred 5 minutes.               |          |            |          |            |          |            |          |            |          |            |          |            |  |
| Plastic Viscosity, Cp @ 120°F                                         | 17       | 33         | 20       | 41         | 18       | 34         | 18       | 30         | 19       | 28         | 20       | 30         |  |
| Yield Point, lb/100 sq ft                                             | 13       | 18         | 17       | 28         | 6        | 22         | 8        | 7          | 12       | 19         | 11       | 13         |  |
| 10-sec Gel, lb/100 sq ft                                              | 5        | 8          | 8        | 14         | 3        | 10         | 4        | 6          | 5        | 8          | 5        | 7          |  |
| 10-min Gel, lb/100 sq ft                                              | 6        | 10         | 9        | 16         | 3        | 14         | 4        | 8          | 6        | 9          | 5        | 9          |  |
| Electrical stability, volts                                           | 400      | 260        | 700      | 480        | 170      | 305        | 270      | 400        | 350      | 365        | 330      | 340        |  |
| HTHP, 30 min @ 250°F, ml                                              |          | 11         |          | 16         |          | 18         |          | 16         |          | 20         |          | 20         |  |
| Water in filtrate, ml                                                 |          | 0.5        |          | 0.5        |          | 0.5        |          | 1          |          | 1          |          | 1          |  |
| * Rev-Dust used                                                       |          |            |          |            |          |            |          |            |          |            |          |            |  |

- 5 As seen from the foregoing, fluid loss was observed in the samples to which contaminant was added.

### **Example II**

[0032] Again, variety of invert emulsion fluids were made using either CF-2002 or C-16,18 olefin as the continuous phase and using the compositions given in the

following Table. The fluids were subjected to standard testing to determine rheological and fluid loss properties. The results are given in the following Table:

| <b>OP-499: 12.0 lb/gal CF-2002 or C-16,18, using Seawater as Brine Phase</b> |          |            |          |            |          |            |           |             |           |             |           |             |  |
|------------------------------------------------------------------------------|----------|------------|----------|------------|----------|------------|-----------|-------------|-----------|-------------|-----------|-------------|--|
| <b>Sample No.</b>                                                            | <b>7</b> | <b>7-S</b> | <b>8</b> | <b>8-S</b> | <b>9</b> | <b>9-S</b> | <b>10</b> | <b>10-S</b> | <b>11</b> | <b>11-S</b> | <b>12</b> | <b>12-S</b> |  |
| CF-2002, bbl                                                                 | 0.575    | 0.575      | 0.575    | 0.575      | 0.575    | 0.575      |           |             |           |             |           |             |  |
| C-16, 18, bbl                                                                |          |            |          |            |          |            | 0.575     | 0.575       | 0.575     | 0.575       | 0.575     | 0.575       |  |
| OMNI-MUL, lb                                                                 | 14       | 14         | 14       | 14         | 20       | 20         | 20        | 20          |           |             |           |             |  |
| OMNI-MUL E, lb                                                               |          |            |          |            |          |            |           |             | 20        | 20          | 20        | 20          |  |
| Seawater, bbl                                                                | 0.171    | 0.171      | 0.171    | 0.171      | 0.171    | 0.171      | 0.171     | 0.171       | 0.171     | 0.171       | 0.171     | 0.171       |  |
| CARBOGEL, lb                                                                 | 1        | 1          |          |            | 1        | 1          | 1         | 1           | 1         | 1           | 1         | 1           |  |
| SD-1, lb                                                                     |          |            | 1        | 1          |          |            |           |             |           |             |           |             |  |
| CLAY-TROL, lb                                                                | 10       | 10         | 10       | 10         | 10       | 10         | 10        | 10          | 10        | 10          |           |             |  |
| Rhodia CS-60, lb                                                             |          |            |          |            |          |            |           |             |           |             | 10        | 10          |  |
| Lubrizol (R) 7720C, lb                                                       | 3        | 3          | 3        | 3          | 3        | 3          | 3         | 3           | 3         | 3           | 3         | 3           |  |
| CARBO-TEC S, lb                                                              | 1        | 1          | 1        | 1          | 1        | 1          | 1         | 1           | 1         | 1           | 1         | 1           |  |
| MILBAR, lb                                                                   | 255      | 255        | 255      | 255        | 255      | 255        | 255       | 255         | 255       | 255         | 255       | 255         |  |
| MIL-GEL NT, lb                                                               |          | 27         |          | 27         |          | 27         |           | 27          |           | 27          |           | 27          |  |
| O/W Ratio                                                                    |          |            |          |            |          |            |           |             |           |             |           |             |  |
|                                                                              | 80/20    | 80/20      | 80/20    | 80/20      | 80/20    | 80/20      | 80/20     | 80/20       | 80/20     | 80/20       | 80/20     | 80/20       |  |
| Density, lb/gal                                                              | 12       | 12         | 12       | 12         | 12       | 12         | 12        | 12          | 12        | 12          | 12        | 12          |  |
| Samples hot-rolled 16 hours @ 150°F. Stirred 5 minutes.                      |          |            |          |            |          |            |           |             |           |             |           |             |  |
| Plastic Viscosity, Cp @ 120°F                                                | 19       | 31         | 19       | 29         | 20       | 35         | 17        | 30          | 18        | 30          | 18        | 23          |  |
| Yield Point, lb/100 sq ft                                                    | 8        | 21         | 5        | 9          | 5        | 18         | 10        | 17          | 9         | 20          | 5         | 9           |  |
| 10-sec Gel, lb/100 sq ft                                                     | 5        | 10         | 4        | 7          | 4        | 9          | 5         | 12          | 4         | 11          | 4         | 6           |  |
| 10-min Gel, lb/100 sq ft                                                     | 6        | 13         | 5        | 9          | 5        | 12         | 6         | 14          | 5         | 13          | 5         | 8           |  |
| Electrical stability, volts                                                  | 300      | 475        | 300      | 425        | 400      | 550        | 550       | 680         | 210       | 550         | 230       | 510         |  |
| HTHP, 30 min @ 250°F                                                         |          | 10         |          | 18         |          | 6          |           | 8           |           | 14          |           | 22          |  |
| Water in filtrate, ml                                                        |          | 0.5        |          | 1          |          | 0.5        |           | 0.5         |           | 1           |           | 1           |  |

Again, fluid loss was observed in the samples to which contaminant was added.

5

### Example III

[0033] C-16, 18 invert emulsions were tested with and without contaminant and with and without BIOCOTE, a polyamide wetting agent, available from Baker Hughes

10 INTEQ, in order to determine whether the wetting agent would successfully prevent fluid loss. The following were the results:

|                                                                              |       |       |       |       |       |       |       |       |       |       |       |       |       |
|------------------------------------------------------------------------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| <b>OP-499: 12.0 lb/gal CF-2002 or C-16,18, using Seawater as Brine Phase</b> |       |       |       |       |       |       |       |       |       |       |       |       |       |
|                                                                              |       |       |       |       |       |       |       |       |       |       |       |       |       |
|                                                                              |       |       |       |       |       |       |       |       |       |       |       |       |       |
| Sample No.                                                                   | 13    | 13-S  | 14    | 14-S  | 14-ST | 15-S  | 16-S  | 17    | 17-S  | 18    | 18-S  | 19    | 19-S  |
| CF-2002, bbl                                                                 |       |       |       |       |       |       |       |       |       |       |       |       |       |
| C-16, 18, bbl                                                                | 0.575 | 0.575 | 0.575 | 0.575 | 0.575 | 0.575 | 0.575 | 0.575 | 0.575 | 0.575 | 0.575 | 0.575 | 0.575 |
| OMNI-MUL, lb                                                                 | 10    | 10    | 20    | 20    | 20    | 14    | 14    | 14    | 14    | 14    | 14    | 14    | 14    |
| OMNI-TEC, lb                                                                 | 4     | 4     |       |       |       |       |       |       |       |       |       |       |       |
| Lime, lb                                                                     | 3     | 3     |       |       |       |       |       |       |       |       |       |       |       |
| Seawater, bbl                                                                | 0.171 | 0.171 | 0.171 | 0.171 | 0.171 | 0.171 | 0.171 | 0.2   | 0.2   | 0.2   | 0.2   | 0.186 | 0.186 |
| CARBOGEL, lb                                                                 | 1     | 1     |       |       |       |       |       |       |       |       |       |       |       |
| DFE-434, lb                                                                  |       |       | 1     | 1     | 1     | 1     | 1     | 1     | 1     | 1     | 1     | 1     | 1     |
| CLAY-TROL, lb                                                                | 10    | 10    | 10    | 10    | 10    | 10    | 10    |       |       |       |       | 5     | 5     |
| Lubrizol (R) 7720C, lb                                                       | 3     | 3     | 3     | 3     | 3     | 3     | 3     | 3     | 3     | 3     | 3     | 3     | 3     |
| CARBO-TEC S, lb                                                              | 1     | 1     | 1     | 1     | 1     | 1     | 1     | 1     | 1     | 1     | 1     | 1     | 1     |
| MILBAR, lb                                                                   | 255   | 255   | 255   | 255   | 255   | 255   | 255   | 255   | 255   | 255   | 255   | 255   | 255   |
| MIL-GEL NT, lb                                                               |       | 27    |       | 27    | 27    | 27    | 27    |       | 27    |       | 27    |       | 27    |
| BIO-COTE                                                                     |       |       |       |       | 2     | 1     | 2     | 2     | 2     |       |       | 2     | 2     |
|                                                                              |       |       |       |       |       |       |       |       |       |       |       |       |       |
| O/W Ratio                                                                    | 80/20 | 80/20 | 80/20 | 80/20 | 80/20 | 80/20 | 80/20 | 80/20 | 80/20 | 80/20 | 80/20 | 80/20 | 80/20 |
| Density, lb/gal                                                              | 12    | 12    | 12    | 12    | 12    | 12    | 12    | 12    | 12    | 12    | 12    | 12    | 12    |
|                                                                              |       |       |       |       |       |       |       |       |       |       |       |       |       |
| Samples hot-rolled 16 hours @ 150°F. Stirred 5 minutes.                      |       |       |       |       |       |       |       |       |       |       |       |       |       |
| Plastic Viscosity, Cp @ 120°F                                                | 19    | 21    | 18    | 26    | 27    | 22    | 24    | 18    | 29    | 17    | 29    | 20    | 28    |
| Yield Point, lb/100 sq ft                                                    | 1     | 5     | 18    | 31    | 18    | 16    | 14    | 10    | 26    | 19    | 27    | 10    | 17    |
| 10-sec Gel, lb/100 sq ft                                                     | 2     | 5     | 7     | 15    | 6     | 6     | 5     | 4     | 7     | 7     | 12    | 5     | 7     |
| 10-min Gel, lb/100 sq ft                                                     | 3     | 9     | 8     | 16    | 7     | 7     | 7     | 5     | 9     | 8     | 16    | 5     | 8     |
| Electrical stability, volts                                                  | 280   | 340   | 400   | 650   | 550   | 380   | 400   | 230   | 340   | 300   | 410   | 280   | 420   |
| HTHP, 30 min @ 250°F                                                         |       | >50   |       | 7     | 4     | 15    | 4     |       | 7     |       | 5     |       | 4     |
|                                                                              |       |       |       |       |       |       |       |       |       |       |       |       |       |
| Water in filtrate, ml                                                        |       | 2     |       | 0.5   |       |       |       |       |       |       | 1     |       |       |
| OP-499: 12.0 lb/gal CF-2002 or C-16,18, using Seawater as Brine              |       |       |       |       |       |       |       |       |       |       |       |       |       |

| Phase                                                   |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
|---------------------------------------------------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| Sample No.                                              | 20    | 20-S  |       |       |       |       |       |       |       |       |       |       |       |       |
| CF-2002, bbl                                            |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
| C-16, 18, bbl                                           | 0.575 | 0.575 |       |       |       |       |       |       |       |       |       |       |       |       |
| OMNI-MUL, lb                                            | 14    | 14    |       |       |       |       |       |       |       |       |       |       |       |       |
| OMNI-TEC, lb                                            |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
| Lime, lb                                                |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
| Seawater, bbl                                           | 0.186 | 0.186 |       |       |       |       |       |       |       |       |       |       |       |       |
| CARBOGEL, lb                                            |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
| DFE-434, lb                                             | 1     | 1     |       |       |       |       |       |       |       |       |       |       |       |       |
| CLAY-TROL, lb                                           | 5     | 5     |       |       |       |       |       |       |       |       |       |       |       |       |
| Lubrizol (R) 7720C, lb                                  |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
| CARBO-TEC S, lb                                         | 1     | 1     |       |       |       |       |       |       |       |       |       |       |       |       |
| MILBAR, lb                                              | 255   | 255   |       |       |       |       |       |       |       |       |       |       |       |       |
| MIL-GEL NT, lb                                          |       | 27    |       |       |       |       |       |       |       |       |       |       |       |       |
| BIO-COTE                                                | 2     | 2     |       |       |       |       |       |       |       |       |       |       |       |       |
| O/W Ratio                                               | 80/20 | 80/20 | 80/20 | 80/20 | 80/20 | 80/20 | 80/20 | 80/20 | 80/20 | 80/20 | 80/20 | 80/20 | 80/20 | 80/20 |
| Density, lb/gal                                         | 12    | 12    | 12    | 12    | 12    | 12    | 12    | 12    | 12    | 12    | 12    | 12    | 12    | 12    |
| Samples hot-rolled 16 hours @ 150°F. Stirred 5 minutes. |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
| Plastic Viscosity, Cp @ 120°F                           | 18    | 26    |       |       |       |       |       |       |       |       |       |       |       |       |
| Yield Point, lb/100 sq ft                               | 10    | 13    |       |       |       |       |       |       |       |       |       |       |       |       |
| 10-sec Gel, lb/100 sq ft                                | 4     | 6     |       |       |       |       |       |       |       |       |       |       |       |       |
| 10-min Gel, lb/100 sq ft                                | 4     | 7     |       |       |       |       |       |       |       |       |       |       |       |       |
| Electrical stability, volts                             | 400   | 430   |       |       |       |       |       |       |       |       |       |       |       |       |
| HTHP, 30 min @ 250°F                                    |       | 11    |       |       |       |       |       |       |       |       |       |       |       |       |
| Water in filtrate, ml                                   |       |       |       |       |       |       |       |       |       |       |       |       |       |       |

The use of the wetting agent BIO-COTE™ prevented the contaminated samples from exhibiting fluid loss.

**Example IV**

[0034] Having determined a preferred base fluid, a variety of organofunctional

amines were added to the base fluid and the shale inhibition and rheological

5 properties were compared. A fluid using calcium chloride as the non-oleaginous

phase was also tested for comparison. All of the organoamines were in the form of

acetate salts, except for CS-6 (formate salt) and CS-60 (chloride salt). The following

parameters (after hot rolling) were used to select candidates with effective rheology

and fluid loss control properties:

|    |                                    |           |
|----|------------------------------------|-----------|
| 10 | Plastic Viscosity (PV), Cp @ 120 F | 26-30     |
|    | Yield Point (YP), lb/100 sq ft     | 12-18     |
|    | 10-sec Gel, lb/100 sq ft           | 4-8       |
|    | 10-min Gel, lb/100 sq ft           | 5-10      |
|    | Electrical stability, volts        | 350-450   |
| 15 | HTHP, 30 min @ 250 F               | 6 or less |
|    | Water in filtrate, ml              | none      |

Organofunctional compounds that exhibited electrical stability of 350-450 volts and

HTHP (high temperature high pressure differential filtration) of 6 or less are defined

20 as "effective to provide shale inhibition" in the invert emulsion fluid.

[0035] The results are given in Fig. 1. The candidate containing

tetraethylenepentamine was the only candidate containing BIOCOTE which exhibited

fluid loss with detrimental water phase. Based on the results in Fig. I, the following

candidates were identified as exhibiting effective rheology and fluid loss control

25 properties:

CLAYTROL  
Diaminocyclohexane  
Triethanolamine  
Hexamethylenediamine

30

Although the plastic viscosity and yield point were not ideal, urea also was identified as a preferred candidate because of its wide availability and relative lack of toxicity.

### Example V

[0036] Shale inhibition and rheological properties were compared for base fluids containing seawater vs. 25% calcium chloride as the non-oleaginous phase. The following parameters (after hot rolling) were measured:

| Sample No.                     | 37-S  | 38-S  | 39-S  | 40-S  | 41-S  | 42-S  |
|--------------------------------|-------|-------|-------|-------|-------|-------|
| C-16, 18, bbl                  | 0.576 | 0.583 | 0.540 | 0.544 | 0.575 | 0.575 |
| OMNI-MUL, lb                   | 16    | 16    | 18    | 18    | 14    | 14    |
| Seawater, bbl                  | 0.11  |       | 0.066 |       | 0.186 | 0.186 |
| 25% Calcium chloride, bbl      |       | 0.111 |       | 0.066 |       |       |
| Freshwater, bbl                |       |       |       |       |       |       |
| DFE-434, lb                    | 1     | 1     | 1     | 1     | 1     | 1     |
| CLAY-TROL, lb                  | 5     |       | 5     |       |       |       |
| Special CLAY-TROL No. 1, lb    |       |       |       |       |       |       |
| Special CLAY-TROL No. 2, lb    |       |       |       |       |       |       |
| CS-50 (1,6-diaminehexane), lb  |       |       |       |       |       |       |
| CS-60 (1,6-diaminehexane), lb  |       |       |       |       |       |       |
| 50% Pure triethanolamine, lb   |       |       |       |       | 5     |       |
| 50% Pure monoethanolamine, lb. |       |       |       |       |       | 5     |
| Lubrizol (R) 7720C, lb         | 3     | 3     | 3     | 3     | 3     | 3     |
| CARBO-TEC S, lb                | 1     | 1     | 1     | 1     | 1     | 1     |
| MILBAR, lb                     | 342   | 331   | 452   | 445   | 255   | 255   |
| BIO-COTE, lb                   | 2     | 2     | 2     | 2     | 2     | 2     |
| MIL-GEL NT, lb                 | 27    | 27    | 27    | 27    | 27    | 27    |
| O/W Ratio                      | 85/15 | 85/15 | 90/10 | 90/10 | 80/20 | 80/20 |
| Density, lb/gal                | 14    | 14    | 16    | 16    | 12    | 12    |
| Plastic Viscosity, Cp @ 120°F  | 30    | 32    | 37    | 46    | 30    | 18    |
| Yield Point, lb/100 sq ft      | 5     | 12    | 6     | 14    | 13    | 4     |
| 10-sec Gel, lb/100 sq ft       | 4     | 4     | 4     | 7     | 5     | 2     |
| 10-min Gel, lb/100 sq ft       | 5     | 5     | 6     | 12    | 7     | 2     |
| Electrical stability, volts    | 510   | 650   | 700   | 1300  | 550   | 170   |
| HTHP, 30 min @ 250°F           | 8     | 10    | 7     | 9     | 6     | 26    |
| Water in filtrate, ml          |       |       |       |       |       |       |

The samples formulated with seawater demonstrated improved stability compared to the calcium chloride samples.

[0037] A study was performed to compare CLAYTROL with triethanolamine. The following were the results:

| Sample No.                    | 43-S  | 44-S  | 45-S  | 46-S  |
|-------------------------------|-------|-------|-------|-------|
| C-16, 18, bbl                 | 0.575 | 0.575 | 0.575 | 0.575 |
| OMNI-MUL, lb                  |       |       |       |       |
| OMNI-MUL (Witco 350783), lb   | 14    | 14    | 14    | 14    |
| Seawater, bbl                 | 0.186 | 0.186 | 0.186 | 0.186 |
| DFE-434, lb                   | 1     | 1     | 1     | 1     |
| Lubrizol (R) 7720C, lb        | 3     | 3     | 3     | 3     |
| CLAY-TROL, lb                 | 5     | 5     |       |       |
| Triethanolamine, lb           |       |       | 5     | 5     |
| CARBO-TEC S, lb               | 1     | 1     | 1     | 1     |
| MILBAR, lb                    | 255   | 255   | 255   | 255   |
| BIO-COTE, lb                  |       | 2     |       | 2     |
| MIL-GEL NT, lb                | 27    | 27    | 27    | 27    |
| O/W Ratio                     | 80/20 | 80/20 | 80/20 | 80/20 |
| Density, lb/gal               | 12    | 12    | 12    | 12    |
| Plastic Viscosity, Cp @ 120°F | 25    | 27    | 25    | 31    |
| Yield Point, lb/100 sq ft     | 40    | 20    | 24    | 21    |
| 10-sec Gel, lb/100 sq ft      | 17    | 7     | 13    | 8     |
| 10-min Gel, lb/100 sq ft      | 18    | 8     | 15    | 10    |
| Electrical stability, volts   | 320   | 240   | 420   | 550   |
| HTHP, 30 min @ 250°F          | 32    | 8     | 17    | 6     |
| Water in filtrate, ml         | 8     | 1     | 2     | 1     |

[0038] Persons of ordinary skill in the art will recognize that many modifications may

5 be made to the present invention without departing from the spirit and scope of the present invention. The embodiment described herein is meant to be illustrative only and should not be taken as limiting the invention, which is defined in the following claims.

**We claim:**

1. An invert emulsion drilling system fluid with effective rheology and fluid loss control properties, said drilling system fluid comprising an oleaginous continuous phase and a non-oleaginous dispersed phase, said dispersed phase comprising an amount of organofunctional compound effective to provide shale inhibition, said organofunctional compound comprising an active ingredient selected from the group consisting of triethanolamine, alkylenediamine, alkylenediamine salts, and combinations thereof, said invert emulsion drilling fluid further comprising a quantity of a polyolefin amide alkene amine.
2. The invert emulsion drilling system fluid of claim 1 wherein said organofunctional compound comprises an alkylene group having from 1 to 7 carbon atoms, wherein the carbon atoms comprise an entity selected from the group consisting of a linear entity, a branched entity, and a cycloalkyl entity.
3. The invert emulsion drilling system fluid of claim 1 selected from the group consisting of a drilling fluid and a drill-in fluid.
4. The invert emulsion drilling system fluid of claim 2 selected from the group consisting of a drilling fluid and a drill-in fluid.
5. The invert emulsion drilling system fluid of claim 4 wherein said oleaginous continuous phase comprises olefins selected from the group consisting of isomerized olefins, linear alpha olefins, and combinations thereof, a majority of said olefins having 16 carbon atoms or more.
6. The invert emulsion drilling system fluid of claim 5 wherein a majority of said olefins have from 16 to 18 carbon atoms.

7. An invert emulsion drilling system fluid with effective rheology and fluid loss control properties, said drilling system fluid comprising an oleaginous continuous phase and a non-oleaginous dispersed phase, said dispersed phase comprising an amount of organofunctional compound effective to provide shale inhibition, said organofunctional compound comprising an active ingredient selected from the group consisting of diaminocyclohexane, salts of diaminocyclohexane, and combinations thereof.
8. The invert emulsion drilling system fluid of claim 7 selected from the group consisting of a drilling fluid and a drill-in fluid.
9. The invert emulsion drilling system fluid of claim 7 wherein said oleaginous continuous phase comprises olefins selected from the group consisting of isomerized olefins, linear alpha olefins, and combinations thereof, a majority of said olefins having 16 carbon atoms or more.
10. The invert emulsion drilling system fluid of claim 9 wherein a majority of said olefins have from 16 to 18 carbon atoms.
11. The invert emulsion drilling system fluid of claim 8 wherein said oleaginous continuous phase comprises olefins selected from the group consisting of isomerized olefins, linear alpha olefins, and combinations thereof, a majority of said olefins having 16 carbon atoms or more.
12. The invert emulsion drilling system fluid of claim 11 wherein a majority of said olefins have from 16 to 18 carbon atoms.
13. The invert emulsion drilling system fluid of claim 7 further comprising a quantity of a polyolefin amide alkene amine.

14. An invert emulsion drilling system fluid with effective rheology and fluid loss control properties, said drilling system fluid comprising an oleaginous continuous phase and a non-oleaginous dispersed phase, said dispersed phase comprising an amount of hexamethylenediamine effective to provide shale inhibition, wherein said oleaginous continuous phase comprises olefins selected from the group consisting of isomerized olefins, linear alpha olefins, and combinations thereof, a majority of said olefins having 16 carbon atoms or more.
15. The invert emulsion drilling system fluid of claim 14 wherein a majority of said olefins have from 16 to 18 carbon atoms.
16. An invert emulsion drilling system fluid with effective rheology and fluid loss control properties, said drilling system fluid comprising an oleaginous continuous phase and a non-oleaginous dispersed phase, said dispersed phase comprising an amount of hexamethylenediamine effective to provide shale inhibition and, said invert emulsion drilling system fluid further comprising a quantity of a polyolefin amide alkene amine.
17. The invert emulsion drilling system fluid of claim 16 wherein said oleaginous continuous phase comprises olefins selected from the group consisting of isomerized olefins, linear alpha olefins, and combinations thereof, a majority of said olefins having 16 carbon atoms or more.
18. The invert emulsion drilling system fluid of claim 17 wherein a majority of said olefins have from 16 to 18 carbon atoms.
19. An invert emulsion drilling system fluid with effective rheology and fluid loss control properties, said drilling system fluid comprising an oleaginous continuous phase and a non-oleaginous dispersed phase, said oleaginous continuous phase comprising olefins selected from the group consisting of isomerized olefins, linear alpha olefins, and combinations thereof, a majority of

said olefins having 16 carbon atoms or more, said dispersed phase comprising an amount of organofunctional compound effective to provide shale inhibition, said organofunctional compound comprising an active ingredient selected from the group consisting of urea, salts of urea, and combinations thereof.

5

20. The invert emulsion drilling system fluid of claim 19 selected from the group consisting of a drilling fluid and a drill-in fluid.

21. The invert emulsion drilling system fluid of claim 19 wherein a majority  
10 of said olefins have from 16 to 18 carbon atoms.

22. The invert emulsion drilling system fluid of claim 20 wherein a majority of said olefins have from 16 to 18 carbon atoms.

15 23. The invert emulsion drilling system fluid of claim 19 further comprising a quantity of a polyolefin amide alkene amine.

24. An invert emulsion drilling system fluid with effective rheology and fluid loss control properties, said drilling system fluid comprising an oleaginous  
20 continuous phase and a non-oleaginous dispersed phase, said dispersed phase comprising an amount of organofunctional compound comprising a quantity and type of exchangeable groups effective to provide shale inhibition, said invert emulsion drilling fluid further comprising a quantity of polyolefin amide alkene amine.

25

25. The invert emulsion drilling system fluid of claim 24 wherein said organofunctional compound comprises a quantity of primary functional groups effective to provide said quantity and type of exchangeable groups.

30 26. The invert emulsion drilling system fluid of claim 24 wherein said exchangeable groups are cations.

27. The invert emulsion drilling system fluid of claim 25 wherein said exchangeable groups are cations.
- 5 28. The invert emulsion drilling system fluid of claim 25 wherein said primary functional groups are selected from the group consisting of nitrogen containing groups, oxygen containing groups, sulfur containing groups, and phosphorus containing groups.
- 10 29. The invert emulsion drilling system fluid of claim 27 wherein said primary functional groups are selected from the group consisting of nitrogen containing groups, oxygen containing groups, sulfur containing groups, and phosphorus containing groups.
- 15 30. The invert emulsion drilling system fluid of claim 25 wherein said primary functional groups are selected from the group consisting of amine groups, hydroxyl groups, and salts thereof.
- 20 31. The invert emulsion drilling system fluid of claim 25 wherein said primary functional groups are selected from the group consisting of amine groups and salts thereof.
- 25 32. An invert emulsion drilling system fluid with effective rheology and fluid loss control properties, said drilling system fluid comprising an oleaginous continuous phase and a non-oleaginous dispersed phase, said dispersed phase comprising an amount of at least one organofunctional compound comprising at least two primary functional groups comprising a quantity and type of exchangeable groups effective to provide shale inhibition, said invert emulsion drilling system fluid further comprising a quantity of polyolefins amide alkene
- 30 amine.

33. The invert emulsion drilling system fluid of claim 32 wherein said exchangeable groups are cations.

34. The invert emulsion drilling system fluid of claim 32 wherein said primary  
5 functional groups are selected from the group consisting of nitrogen containing groups, oxygen containing groups, sulfur containing groups, and phosphorus containing groups.

35. The invert emulsion drilling system fluid of claim 33 wherein said primary  
10 functional groups are selected from the group consisting of nitrogen containing groups, oxygen containing groups, sulfur containing groups, and phosphorus containing groups.

36. The invert emulsion drilling system fluid of claim 32 wherein said primary  
15 functional groups are selected from the group consisting of amine groups, hydroxyl groups, and salts thereof.

37. The invert emulsion drilling system fluid of claim 33 wherein said primary  
functional groups are selected from the group consisting of amine groups and salts  
20 thereof.

38. The invert emulsion drilling system fluid of claim 32 selected from the group consisting of a drilling fluid and a drill-in fluid.

25 39. The invert emulsion drilling system fluid of claim 33 selected from the group consisting of a drilling fluid and a drill-in fluid.

40. The invert emulsion drilling system fluid of claim 34 selected from the group consisting of a drilling fluid and a drill-in fluid.

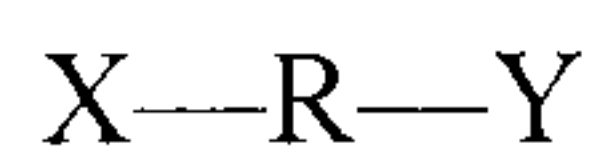
30

41. The invert emulsion drilling system fluid of claim 35 selected from the group consisting of a drilling fluid and a drill-in fluid.
42. The invert emulsion drilling system fluid of claim 36 selected from the group consisting of a drilling fluid and a drill-in fluid.
43. The invert emulsion drilling system fluid of claim 37 selected from the group consisting of a drilling fluid and a drill-in fluid.
44. The invert emulsion drilling system fluid of claim 37 wherein said oleaginous continuous phase comprises olefins selected from the group consisting of isomerized olefins, linear alpha olefins, and combinations thereof, a majority of said olefins having 16 carbon atoms or more.
45. The invert emulsion drilling system fluid of claim 44 wherein a majority of said olefins have from 16 to 18 carbon atoms.
46. A method for reducing the concentration of inorganic salts required to provide shale inhibition during drilling operations using invert emulsion drilling system fluids comprising an oleaginous continuous phase and a non-oleaginous dispersed phase, said method comprising:  
providing said non-oleaginous dispersed phase of said fluid with an amount of organofunctional compound effective to provide shale inhibition; and,  
providing said invert emulsion drilling system fluid with a quantity of polyolefins amide alkene amine.
47. The method of claim 46 further comprising providing said organofunctional compound comprising exchangeable groups derived from primary functional groups selected from the group consisting of nitrogen containing groups, oxygen containing groups, sulfur containing groups, and phosphorus containing groups.

48. The method of claim 46 further comprising providing said organofunctional compound comprising exchangeable groups derived from primary functional groups selected from the group consisting of amine groups, hydroxyl groups, and salts thereof.

49. The method of claim 46 further comprising providing said organofunctional compound comprising at least two primary functional groups comprising exchangeable groups.

50. The method of claim 46 wherein said organofunctional compound has the following general structure:



wherein

X and Y independently are primary functional groups comprising exchangeable groups effective to provide shale inhibition;

R is selected from the group consisting of linear alkylene groups having from 1 to 7 carbon atoms and cyclic alkylene groups having from 3 to 6 carbon atoms, wherein R is either unsubstituted or comprises one or more substituent effective to maintain said exchangeable groups in dissociable form.

51. The method of claim 47 further comprising providing cations as said exchangeable groups.

52. The method of claim 48 further comprising providing cations as said exchangeable groups.

53. The method of claim 49 further comprising providing cations as said exchangeable groups.

54. A method for reducing the concentration of inorganic salts required to provide shale inhibition during drilling operations using invert emulsion drilling system fluids, said method comprising:

5 providing said invert emulsion drilling system fluid selected from the group consisting of a drilling fluid and a drill-in fluid, said invert emulsion drilling system fluid comprising an oleaginous continuous phase and a non-oleaginous dispersed phase; and,

10 providing said non-oleaginous dispersed phase with an amount of organofunctional compound comprising an active ingredient selected from the group consisting of diaminocyclohexane, salts of diaminocyclohexane, and combinations thereof; and

performing drilling operations using said invert emulsion drilling system fluid, said organofunctional compound providing effective shale inhibition.

15 55. The method of claim 54 further comprising providing said effective shale inhibition using a reduced concentration of metallic salt(s) compared to the amount of metallic salt(s) required to provide the same effective shale inhibition using said invert emulsion drilling system fluid in the absence of said organofunctional compound.

20

56. The method of claim 54 further comprising providing said effective shale inhibition without adding inorganic salt to said invert emulsion drilling system fluid.

25 57. A method for reducing the concentration of inorganic salts required to provide shale inhibition during drilling operations using invert emulsion drilling system fluids, the method comprising:

30 providing said invert emulsion drilling system fluid selected from the group consisting of a drilling fluid and a drill-in fluid, said invert emulsion drilling system fluid comprising an oleaginous continuous phase and a non-oleaginous dispersed phase; and,

providing said non-oleaginous dispersed phase with an amount of hexamethylene diamine effective to provide shale inhibition; and performing drilling operations using said invert emulsion drilling system fluid, said hexamethylene diamine providing effective shale inhibition.

5

58. The method of claim 57 further comprising providing said effective shale inhibition using a reduced concentration of metallic salt(s) compared to the amount of metallic salt(s) required to provide the same effective shale inhibition using said invert emulsion drilling system fluid in the absence of said hexamethylene diamine.

10

59. The method of claim 57 further comprising providing said effective shale inhibition without adding inorganic salt to said invert emulsion drilling system fluid.

15

60. A method for reducing the concentration of inorganic salts required to provide shale inhibition during drilling operations using invert emulsion drilling system fluids, the method comprising:

providing said invert emulsion drilling system fluid comprising an oleaginous continuous phase and a non-oleaginous dispersed phase;

20

providing said non-oleaginous dispersed phase with an amount of organofunctional compound effective to provide shale inhibition, said organofunctional compound comprising exchangeable cations derived from primary functional groups selected from the group consisting of nitrogen containing groups, oxygen containing groups, sulfur containing groups, and phosphorus containing groups; and,

25

performing drilling operations selected from the group consisting of rotary drilling operations and drill-in operations using said invert emulsion drilling system fluid, said effective shale inhibition being provided using a reduced concentration of metallic salt(s) compared to the amount of metallic salt(s)

30

required to provide the same effective shale inhibition using said invert emulsion drilling system fluid in the absence of said organofunctional compound.

61. The method of claim 60 further comprising providing said  
 5 organofunctional compound comprising exchangeable cations derived from primary functional groups selected from the group consisting of amine groups, hydroxyl groups, and salts thereof.

62. The method of claim 60 further comprising providing said  
 10 organofunctional compound comprising at least two primary functional groups comprising exchangeable cations.

63. The method of claim 60 wherein said organofunctional compound has the following general structure:

15 X—R—Y

wherein

X and Y independently are primary functional groups comprising exchangeable cations effective to provide shale inhibition;

R is selected from the group consisting of linear alkylene groups having  
 20 from 1 to 7 carbon atoms and cyclic alkylene groups having from 3 to 6 carbon atoms, wherein R is either unsubstituted or comprises one or more substituent effective to maintain said exchangeable cations in dissociable form.

64. A method for reducing the concentration of inorganic salts required to  
 25 provide shale inhibition during drilling operations using invert emulsion drilling system fluids, the method comprising: providing said invert emulsion drilling system fluid comprising an oleaginous continuous phase and a non-oleaginous dispersed phase; providing said non-oleaginous dispersed phase with an amount of organofunctional compound comprising exchangeable cations effective to  
 30 provide shale inhibition; and; performing drilling operations using said invert

emulsion drilling system fluid without adding inorganic salt to said invert emulsion drilling system fluid.

65. The method of claim 64 wherein said performing drilling operations  
5 comprises performing operations selected from the group consisting of drilling and drill-in operations.

66. The method of claim 65 further comprising providing said  
organofunctional compound comprising exchangeable cations derived from  
10 primary functional groups selected from the group consisting of nitrogen containing groups, oxygen containing groups, sulfur containing groups, and phosphorus containing groups.

67. The method of claim 65 further comprising providing said  
15 organofunctional compound comprising exchangeable cations derived from primary functional groups selected from the group consisting of amine groups, hydroxyl groups, and salts thereof.

68. The method of claim 65 further comprising providing said  
20 organofunctional compound comprising at least two primary functional groups comprising exchangeable cations.

69. The method of claim 65 wherein said organofunctional compound has the following general structure:

25 X—R—Y

wherein

X and Y independently are primary functional groups comprising exchangeable cations effective to provide shale inhibition;

R is selected from the group consisting of linear alkylene groups having  
30 from 1 to 7 carbon atoms and cyclic alkylene groups having from 3 to 6 carbon

atoms, wherein R is either unsubstituted or comprises one or more substituent effective to maintain said exchangeable cations in dissociable form.

70. A method for reducing the concentration of inorganic salts required to  
5 provide shale inhibition during drilling operations using invert emulsion drilling  
system fluids, said method comprising: providing said invert emulsion drilling  
system fluid comprising an oleaginous continuous phase and a non-oleaginous  
dispersed phase; providing said non-oleaginous dispersed phase with an amount  
of organofunctional compound effective to provide shale inhibition; providing  
10 said invert emulsion drilling system fluid with a quantity of a polyolefin amide  
alkene amine; and, performing drilling operations using said invert emulsion  
drilling system fluid.

71. The method of claim 70 comprising performing said drilling operations  
15 selected from the group consisting of drilling and drill-in operations.

72. The method of claim 71 wherein said effective shale inhibition is provided  
using a reduced concentration of metallic salt(s) compared to the amount of  
metallic salt(s) required to provide the same effective shale inhibition using said  
20 invert emulsion drilling system fluid in the absence of said organofunctional  
compound.

73. The method of claim 72 wherein said effective shale inhibition is provided  
without adding inorganic salt to said invert emulsion drilling system fluid.  
25

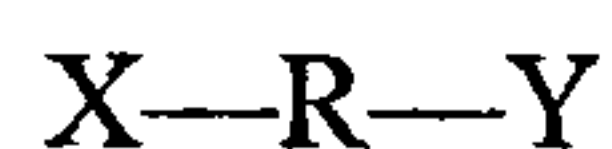
74. The method of claim 72 further comprising providing said  
organofunctional compound comprising exchangeable groups derived from  
primary functional groups selected from the group consisting of nitrogen  
containing groups, oxygen containing groups, sulfur containing groups, and  
30 phosphorus containing groups.

75. The method of claim 72 further comprising providing said organofunctional compound comprising exchangeable groups derived from primary functional groups selected from the group consisting of amine groups, hydroxyl groups, and salts thereof.

5

76. The method of claim 72 further comprising providing said organofunctional compound comprising at least two primary functional groups comprising exchangeable groups.

10 77. The method of claim 72 wherein said organofunctional compound has the following general structure:



wherein

15 X and Y independently are primary functional groups comprising exchangeable groups effective to provide shale inhibition;

R is selected from the group consisting of linear alkylene groups having from 1 to 7 carbon atoms and cyclic alkylene groups having from 3 to 6 carbon atoms, wherein R is either unsubstituted or comprises one or more substituent effective to maintain said exchangeable groups in dissociable form.

20

78. The method of claim 74 further comprising providing cations as said exchangeable groups.