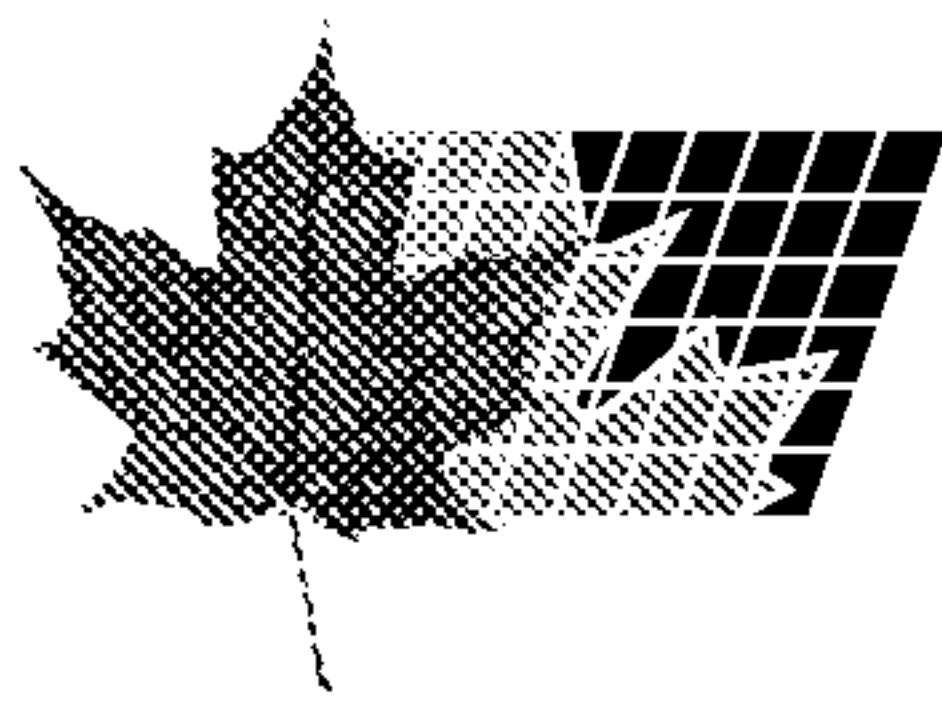




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(72) Bland, Ronald G., US

(72) Clapper, Dennis K., US

(73) BAKER HUGHES INC., US

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(54) **EMULSIONS INVERSES (SAUMURE-GLYCOL) POUR
OPERATIONS DE FORAGE DE PUITS**

(54) **NON-HYDROCARBON INVERT EMULSIONS FOR USE IN
WELL DRILLING OPERATIONS**

(57) Brine-in-glycol emulsions are shown for use as well working fluids. The fluids have a glycol external phase and a brine internal phase. The separate phases are emulsified to create an emulsion and weighted with traditional weighting agents. The external phase is soluble or dispersible in sea water when diluted upon discharge.

ABSTRACT OF THE DISCLOSURE

Brine-in-glycol emulsions are shown for use as well working fluids. The fluids have a glycol external phase and a brine internal phase. The separate phases are emulsified to create an emulsion and weighted with traditional weighting agents. The external phase is soluble or dispersible in sea water when diluted upon discharge.

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BACKGROUND OF THE INVENTION

1. Field of the Invention:

5 This invention relates to well working fluids
useful in drilling, completing or workover of oil and
gas wells, and, specifically, to an invert emulsion type
fluid having a non-hydrocarbon, non-mineral oil
external phase and an aqueous internal phase which
10 provides many of the advantages of an oil-based mud
without the attendant adverse environmental effects.

2. Description of the Prior Art:

15 During the drilling of oil and gas wells, drilling
fluid is circulated through the interior of the drill
string and then back up to the surface through the
annulus between the drill string and the wall of the
borehole. The drilling fluid serves various purposes
20 including lubricating the drill bit and pipe, carrying
cuttings from the bottom of the well borehole to the
surface of the ground, and imposing a hydrostatic head
on the formation being drilled to prevent the escape of
oil, gas or water into the well borehole during the
25 drilling operations.

 Occasionally during drilling, the drill string
becomes stuck and cannot be raised, lowered or rotated.
There are numerous causes for this problem, one of the
30 most common being differential sticking. Differential
sticking usually occurs when drilling permeable
formations and borehole pressures are greater than
formation pressures and when the drill pipe remains at

35

1 rest against the wall of the borehole for enough time
2 to allow mud filter cake to build up around the pipe.
3 The pressure exerted by drilling fluid then holds the
4 pipe against the cake wall.

5
6 For a number of years, oil-based fluids have been
7 popular both as drilling fluids and as stuck pipe
8 fluids. These fluids typically are comprised of a
9 hydrocarbon oil or oils as the major component of the
10 liquid phase to which various materials are added to
11 impart the desired drilling fluid properties. These
12 fluids are well adapted for use in underground
13 formations containing water sensitive clays or shales
14 which swell and disintegrate when contacted by water-
15 based drilling fluids. Such fluids are substantially
16 free of water, lose mostly oil as the filtrate and
17 cause no swelling or disintegration of water sensitive
18 clays and shales. One widely used oil-base fluid is
19 described in U.S. Patent No. 3,099,624, issued July 30,
20 1963, to Doyne L. Wilson. Water-in-oil emulsions are
21 also used as drilling fluids. These fluids contain a
22 high percentage of oil and a lesser percentage of water
23 dispersed in the continuous or external phase of oil.

24
25 In order to free stuck pipe, prior art treatments
26 involve the placement in and movement through the
27 circulating mud system of a volume of a release agent,
28 known as a spotting fluid, which is sufficient to fully
29 contact the region of the borehole where the pipe is
30 stuck. Thus, a suitably weighted oil-based fluid is
31 circulated in the borehole to a position opposite the
32 stuck interval. Over a period of time, the integrity
33 of the mud filter cake between the drill pipe and

borehole is reduced, allowing pressure equalization on all sides of the pipe. The invasion of oil into the filter cake is also thought to reduce the adhesive forces and lubricate the area between the pipe and borehole, resulting in less friction and quicker release.

Oil-based formulations used in the past as spotting fluids are described, for instance, in U.S. Patent Nos. 4,436,638 and 4,464,269. Water-based formulations are also known for use in releasing differentially stuck pipe. They are described, for instance, in U.S. Patent Nos. 3,233,622; 4,230,587; 4,466,486; and 4,614,235. To our knowledge, invert emulsions having a non-hydrocarbon, non-mineral oil external phase and an aqueous internal phase have not been utilized.

Environmental regulations have recently either prohibited or severely limited the use of oil-based and invert emulsion oil muds as either drilling fluids or as spotting fluids. In many offshore areas, such as the Gulf of Mexico, the use of oil muds is strictly regulated. Restrictive regulations have thus created a need for a novel fluid which will fill the niche formerly occupied by oil muds, i.e., drilling fluids for active argillaceous formations, and spotting fluids used to release drill pipe held by differential pressure.

The present invention has as its object to provide such a replacement fluid for an oil-base mud which has

1 significant advantages over water-based fluids when
2 used in the before mentioned well bore operations.

3

4 Another object of the invention is to provide a
5 novel fluid for well bore operations which provides
6 improved hole stability, bit lubrication, and which
7 minimizes hydration and dispersion of shale within the
8 circulating fluid system.

9

10 Another object of the invention is to provide such
11 a fluid which will perform the function of an oil-based
12 spotting fluid but which does not leave a sheen upon
13 receiving waters and which meets current environmental
14 toxicity standards, thereby eliminating environmental
15 problems caused by oil-based fluids.

SUMMARY OF THE INVENTION

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In the method of the invention, an invert emulsion well bore fluid is formed which comprises a non-hydrocarbon, non-mineral oil external phase and an aqueous internal phase. Preferably, the invert emulsion is a water-in-glycol emulsion having a glycol external phase and a salt solution or water internal phase. The water-in-glycol emulsion is formed by addition of water or a salt solution to a glycol that is not soluble in the aqueous phase. An emulsifier and a viscosifier are added to form a stable emulsion and a weighting agent is added to form a weighted well bore fluid. The weighted well bore fluid is then circulated in the well.

The water-in-glycol emulsion can be utilized as a spotting fluid for a stuck drill string by incorporating the brine-in-glycol emulsion into a conventional drilling fluid and contacting the borehole zone contiguous to the stuck drill string with the spotting fluid. This is accomplished by circulating the spotting fluid to the borehole zone contiguous to the stuck drill string.

Additional objects, features and advantages will be apparent in the written description which follows.

DETAILED DESCRIPTION OF THE INVENTION

1
2
3 The novel well bore fluids of the invention are
4 invert emulsions which have a non-hydrocarbon, non-
5 mineral oil external or "continuous" phase and an
6 aqueous internal phase. The term "emulsion" is
7 commonly used to describe systems in which water is the
8 external or continuous phase and, e.g., oil is
9 dispersed within the external phase. By the term
10 "invert" is meant that the non-hydrocarbon, non-mineral
11 oil substance is the continuous or external phase and
12 that the aqueous fluid is the internal phase.

THE EXTERNAL PHASE

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15
16 The non-hydrocarbon, non-mineral oil external
17 phase can be any material which forms a stable emulsion
18 with the internal phase, which is less toxic than
19 invert hydrocarbon oil emulsions, which does not leave
20 a sheen upon receiving waters, i.e., is water soluble
21 or dispersible upon discharge at surface temperature
22 and pressure conditions, as will be presently
23 explained.

24
25 The material selected for the external phase can
26 be any glycol which is otherwise compatible with the
27 purposes of the invention, as will be explained. The
28 preferred materials for the external phase are selected
29 from the group consisting of polypropylene glycols,
30 polypropylene glycol ethers, and propylene oxide
31 polymeric adducts of alcohols or mixtures of alcohols.
32 The preferred materials have molecular weights ranging
33 from about 60 to 1000, most preferably about 250 to

1 1000. The molecular weight of the selected material
2 should be such that the material is soluble or
3 dispersible in sea water at a salinity of about 3% and
4 lower but which is substantially insoluble in a brine
5 such as 20 to 23% (saturated) sodium chloride solution,
6 whereby a stable emulsion can be formed without the
7 selected material forming a homogeneous solution with
8 the aqueous phase.

9
10 In selecting a candidate material for the external
11 phase, the characteristic "cloud point" of the material
12 provides an indication of its molecular weight and thus
13 of its ability to form a stable emulsion. The cloud
14 point of the candidate material is preferably in the
15 range from about 15 to 83°C (59-181°F) for a test
16 solution comprising at least 1% by weight of the
17 candidate material. The "cloud point" for the
18 candidate material can be determined by preparing a
19 fluid comprising at least 1% by volume of the candidate
20 material in deionized water or salt solution and
21 heating the fluid until it first becomes cloudy. The
22 cloud point is that temperature at which the material
23 begins to come out of solution, thereby becoming
24 immiscible in water and behaving in the nature of a
25 free oil.

26
27 Particularly preferred materials for the external
28 phase include polypropylene glycol having a cloud point
29 of 122°F, supplied commercially as *ARNOX D-400 by Baker
30 Performance Chemicals and propoxylated tripropylene
31 glycol bottoms having a cloud point in the range from
32 77-160°F. The most preferred molecular weight range
33 for these materials is about 250-600 for the

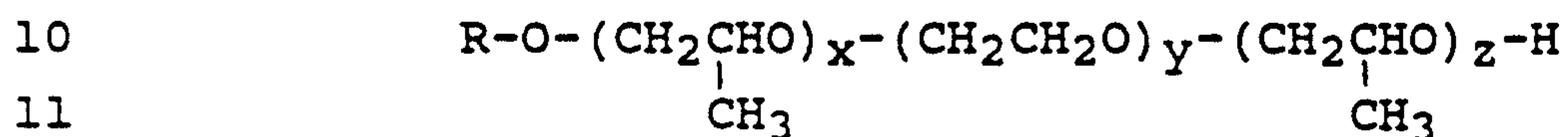
* Trademark

1 polypropylene glycol and 600-1000 for the propoxylated
2 tripropylene glycol bottoms.

3

4 The preferred propylene oxide polymeric adducts
5 are condensates of propylene oxide and optionally
6 ethylene oxide with alcohols and include ethylene
7 oxide-propylene oxide block copolymers of alcohol
8 mixtures represented by the structural formula:

9



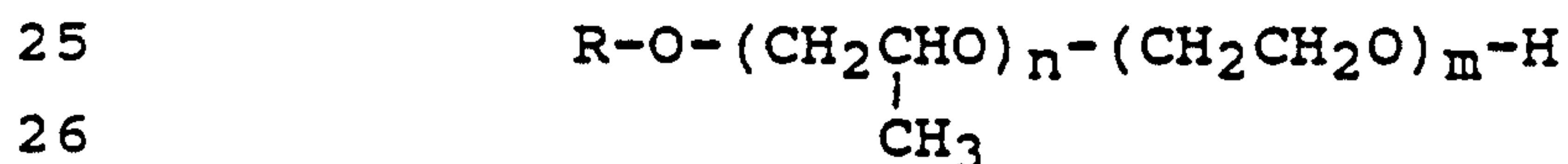
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13 wherein R represents an alkyl group of from about
14 4-12 carbon atoms and x is an integer from about 0 to
15 10, y is an integer from about 5 to 20, and z is an
16 integer from about 5 to 25. This preferred class of
17 material can be obtained from Olin Chemicals under the
18 trade name * "POLY-TERGENT" The preferred material has a
19 total molecular weight in the range of about 500-3000.

20

21 The propylene oxide adducts also include ethylene
22 oxide-propylene oxide random copolymers of alcohols or
23 alcohol mixtures having a structural formula:

24



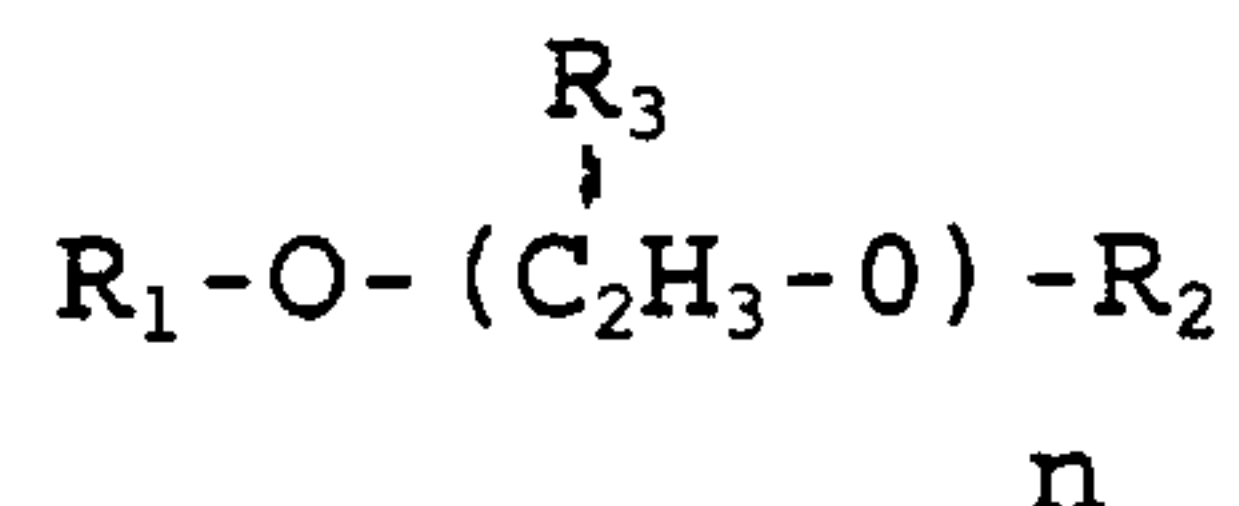
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28 wherein R represents an alkyl group of from about
29 1-10 carbon atoms, n is an integer in the range from
30 about 3-10 and m is an integer in the range from about
31 0-10. This preferred class of materials can be
32 obtained from BASF Wyandotte Corporation under the

* Trademark

trade name * "PLURACOL W" and have a total molecular weight in the range from about 200-2000.

The polypropylene glycol ethers fall within a class of the general formula:



wherein R_1 represents hydrogen or a lower alkyl group of from 1 to 8 carbons, R_2 represents a lower alkyl group of from 1 to 8 carbons, R_3 represents hydrogen, methyl and ethyl and n represents an integer of 1 to 16, preferably 1 to 5. Included in this class are the methyl monoether of propylene glycol, ethyl monoether of propylene glycol, propyl monoether of propylene glycol, methyl monoether of dipropylene glycol and the ethyl monoether of dipropylene glycol.

Recent environmental regulations for offshore drilling fluids require that: (1) no "sheen" be left upon the receiving waters by the drilling fluid; and (2) that the drilling fluid meet stringent toxicity limits as measured by bioassays of *Mysidopsis bahia* shrimp. The Generic muds to be used with the *Mysidopsis* bioassay are described in T.W. Duke et al., "Acute Toxicity of Eight Laboratory Prepared Generic Drilling Fluids to Mysids", 1984, EPA 600, 3-84-067. The Mysid shrimp bioassay measure of toxicity, or LC50, is the lethal concentration to kill 50% of the Mysid shrimp population. Preferably, the lethal concentration of a 10% by volume candidate weighted

* Trade-mark

1 external phase material in a generic mud, as measured
2 by Mysidopsis bahia bioassay LC50 analysis, should be
3 greater than about 30,000 parts per million for a
4 suitable candidate material.

5
6 It is also necessary that the external phase not
7 "leave a sheen on receiving waters" upon discharge.
8 That is, the brine-in-glycol invert emulsion, when
9 diluted with sea water upon discharge is water soluble
10 or dispersible and leaves no oil-like sheen. Thus, the
11 candidate material must be immiscible in brine at a
12 salinity of about 3% or greater but is soluble or
13 dispersible in sea water when salinity drops below
14 about 3%.

15 16 THE INTERNAL PHASE

17
18 The brine used in forming the internal phase can
19 be defined as an aqueous solution containing from about
20 100 to 350,000 parts per million metal ions such as
21 lithium, sodium, potassium, magnesium, or calcium ions.
22 The preferred brines used to form the internal phase of
23 the emulsions of the invention contain from about 10 to
24 about 23% (saturated) by weight sodium chloride and may
25 contain various amounts of other dissolved salts such
26 as sodium bicarbonate, sodium sulfate, sodium acetate,
27 sodium borate, potassium chloride, or calcium chloride.

28
29 The ratio of brine to glycol in the emulsions of
30 the invention should generally provide as high a brine
31 content as possible while still maintaining a stable
32 emulsion since a high water content drilling fluid is
33 less expensive and less objectionable to work with than

a drilling fluid containing a low water content. Glycol/brine ratios in the range from about 82:18 to 55:45 have been found to work satisfactorily, depending upon the particular glycol chosen. Thus the water content of a typical drilling fluid prepared according to the teachings of the invention will have an aqueous (water) content of about 5 to 50 volume percent, with the most preferred range being about 20 to 40 volume percent, most preferably about 30 volume percent of the drilling fluid.

THE EMULSIFIER

In order to form a stable emulsion, a surfactant or emulsifier is added to the external, the internal or both phases. The emulsifier can be any of a number of organic acids which are familiar to those skilled in the art, including the monocarboxyl alkanoic, alkenoic, or alkynoic fatty acids containing from 2 to 22 carbon atoms, and mixtures thereof. Examples of this group of acids include acetic, stearic, oleic, caproic, capric, butyric, behenic, palmitic, arachidic, myristoleic, palmitoleic, elaidic, linoleic, linolenic, elaceostearic, and tarinic. Adipic acid, a member of the aliphatic dicarboxylic acids can also be used. The preferred surfactants or emulsifiers are fatty acid calcium salts, lecithin and lime. Lecithin is a mixture of the diglycerides of stearic, palmitic and oleic acids, linked to the choline ester of phosphoric acid. It is commercially available and is obtained from egg-yolk and soya beans.

VISCOSIFIERS

Viscosifiers can also be added to improve the solids suspending ability of the well bore fluid.

5 Suitable viscosifiers include the commercially available organophilic clays, bentonites, attapulgite clays, sepiolite, guar, carboxymethyl guar, hydroxypropyl
guars, fumed silicas, fumed alumina, and the like. Preferred viscosifiers include sepiolite, organophilic
10 clay and treated fumed silica.

WEIGHTING AGENTS

Weighting materials can also be used to weight the
15 well bore fluids of the invention to a density in the range from about 8.33 pounds per gallon to 15 pounds per gallon and greater. Weighting materials which are known in the art include barite, ilmenite, calcium carbonate, iron oxide and lead sulfide. The preferred weighting
20 material is commercially available barite.

Three exemplary formulations follow which have produced weightable, stable emulsions. These
formulations are based on three different suspending
25 agents - sepiolite, organophillic clay, and treated fumed silica. The method of forming these three types of glycol emulsions can be briefly described as follows:

(1) Sepiolite Formulation

30 Salt water (20% aqueous sodium chloride) is viscosified by mixing sepiolite with the salt water

1 in a blender. The brine/sepiolite slurry is added to a
2 blend of polypropylene glycol, crude tall oil fatty
3 acid, lecithin*(CLEARATE B-60 from W.A. CLEARY CORP.)
4 and lime. The combined mixture is blended vigorously
5 to produce an invert emulsion. Preferably, the
6 emulsion is prepared using a high glycol-to-brine ratio
7 such as 82:18. The glycol/brine ratio may be reduced
8 to 55:45 by the addition of 20% (aq) sodium chloride.

9

10 (2) Organophilic Clay Formulation

11

12 A mixture of polypropylene glycol, crude
13 tall oil fatty acid, lecithin (CLEARATE B-60 from W.A.
14 CLEARY CORP.) and lime is mixed for several minutes in
15 a blender. Organophilic clay is added and the mixture
16 is blended at high shear for ten minutes. Salt water
17 is then added during high shear to produce the
18 emulsion. Barite must be added immediately to maintain
19 the emulsion.

20

21 (3) Treated Fumed Silica Formulation

22

23 Propoxylated tripropylene glycol
24 bottoms, molecular weight around 600, is viscosified
25 with a treated fumed silica*(CAB-O-SIL TS - 610 from
26 CABOT CORP.). This glycol has a relatively low cloud
27 point of 78°F (50% solution in deionized water). A
28 typical formulation includes crude tall oil fatty acid,
29 lime, and 20% (aq) sodium chloride. Glycol/brine
30 ratios range from 60/40 to 80/20. Preparation requires
31 moderate shear, and emulsions are stable without
32 barite.

33 * Trademark

Rheological properties of the brine-in-glycol emulsions were measured with a Fann 35 Viscometer following API RP 13B. Most samples were aged statically and sometimes dynamically at 150°F.

5

The following examples are intended to be illustrative of the invention without being limiting:

10

EXAMPLE I

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A brine-in-glycol emulsion with a glycol/brine ratio of 82:18 (Table 1) was made by first preparing a sepiolite/brine suspension by mixing a sepiolite/20% (aq) sodium chloride slurry for several minutes in a bar mixer or blender. The sepiolite suspension was then added to a mixture of polypropylene glycol 400 (cloud point 122°F for 50% in deionized water), crude tall oil fatty acid, CLEARATE B-60 (W.A. CLEARY CORP.) and lime, and shearing the mixture for several minutes to emulsify the brine. Higher brine content emulsions were prepared by adding while mixing 20% (aq) sodium chloride to produce 70:30 and 55:45 brine-in-glycol emulsions. The densities of the 55:45, 70:30, and 82:18 emulsions were increased by the addition of barite. Rheological properties of these emulsions are listed in Tables 2 and 3.

1 Table 1
2 FORMULATION FOR 82:18 BRINE-IN-GLYCOL EMULSION
3 Example 1A
4

5	<u>Material</u>	<u>Wt %</u>
6	PPG 400	77.29
7	Tall Oil	0.83
8	CLEARATE B-60	0.83
9	Lime	0.21
10	20% (aq) NaCl	19.46
11	Sepiolite	1.38
12	Total	100

13
14 Table 2
15 FORMULATION AND 120°F RHEOLOGY OF
16 12 PPG BRINE-IN-GLYCOL EMULSION
17

18	Example	IB	IC
19	PPG/Brine Ratio, v/v	55/45	82/18
20	Formulation		
21	Emulsion, g	334	334
22	Barite, g	169	179

23
24 Rheology at 120°F
25

26	AV, cP	113	56.5
27	PV, cP	85	56
28	YP, lb/100 ft ²	56	1
29	10 Sec Gel, lb/100 ft ²	12	2
30	10 Min Gel, lb/100 ft ²	16	3

31

Table 3

FORMULATION AND 120°F RHEOLOGY
OF WEIGHTED 70:30 BRINE-IN-GLYCOL EMULSIONS

5	Example	ID	IE	IF
	Density, lb/gal	12	14	15
	Formulation			
	70:30 Emulsion, g	326	298	284
10	Barite, g	177	289	345

Rheology at 120°F

	AV, cP	86.5	116	143.5
15	PV, cP	79	99	120
	YP, lb/100 ft ²	15	34	47
	10 Sec Gel, lb/100 ft ²	4	8	14
	10 Min Gel, lb/100 ft ²	5	12	22

20 EXAMPLE II

25 In order to evaluate the emulsions of the invention as drilling fluids, approximately 29 gallons or 56:44 brine-in-glycol emulsion containing 4% (v/v) REV-DUST to simulate the effects of drill cuttings, and having a density of 9.50 lb/gal were prepared for microbit drilling tests. An 82:18 (glycol/brine) emulsion was made by the addition of a previously prepared sepiolite-in-brine suspension to a mixture of polypropylene glycol 400, crude tall oil fatty acid, CLEARATE B-60, and lime.

30 The fluid was stirred vigorously with two Dispersators for approximately 30 minutes. The 82:18 emulsion was cut to a 56:44 glycol/brine emulsion by adding more 20% (aq) sodium

1 chloride. The fluid was completed by the addition of
2 36 lb/bbl (4% by volume) REV-DUST. Ingredients used to
3 make the glycol emulsion are listed in Table 4.
4 Properties of the glycol emulsion are contained in
5 Table 5.

6

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Table 4

8

FORMULATIONS OF MICRO-BIT TEST FLUIDS

9

Example IIA Invert Glycol Emulsion

10

11	<u>Ingredient</u>	<u>Concentration</u>
12		
13	PPG 400	23.5 gal/bbl
14	Tall Oil	2.1 lb/bbl
15	CLEARATE B-60	2.1 lb/bbl
16	Lime	0.5 lb/bbl
17	Sepiolite	3.5 lb/bbl
18	20% (aq) NaCl	18.3 gal/bbl
19	REV-DUST	36 lb/bbl

20

21

Example IIB Lignosulfonate Fluid

22

23	Deionized Water	40.3 gal/bbl
24	Bentonite	25 lb/bbl
25	Chrome Lignosulfonate	0.2 lb/bbl
26	REV-DUST	36 lb/bbl
27	NaOH	0.1 lb/bbl
28	Barite	28 lb/bbl

29

Table 5
PROPERTIES OF MICRO-BITS TEST FLUIDS

		Example IIA	Example IIB
5	Density, lb/gal	9.5	9.5
	PV, cP	13	75
	YP, lb/100 ft ²	5	53
10	10 Sec Gel, lb/100 ft ²	2	7
	10 Min Gel, lb/100 ft ²	9	9

15 The invert glycol emulsion was used in a microbit drilling testor to measure the ability of glycol emulsions to reduce bit balling on a polycrystalline diamond (PDC) bit when drilling a Pierre shale core. Tests were run on a lignosulfonate fluid for comparison to the performance of the invert glycol emulsion. A formulation and properties of the lignosulfonate mud

20 are listed in Tables 4 and 5 respectively. Tests were conducted using a 2-cutter PDC microbit (1.125" O.D.) equipped with two 0.094" O.D. nozzles. Rotary speed was kept constant at 103 rev/min, and rate of penetration was kept at 25 to 30 ft/hour. Maximum flow

25 rate was 15 gal/minute. During the evaluation of each fluid, flow rate was reduced until bit balling was observed. Under the same experimental conditions, a fluid that prevents bit balling at a lower flow is considered to be more effective than a fluid that requires a higher flow rate to keep the bit clean. The

30 test results in Table 6 indicate that when the glycol emulsion fluid was used, extensive balling occurred when the flow rate was reduced to 3.2 gal/minute. In contrast to the relatively low flow rate required for

bit cleaning while drilling with the glycol emulsion, extensive bit balling was observed with the lignosulfonate mud using a flow rate as high as 13 gallon/minute.

5

Table
MICRO-BIT-TEST RESULTS

	<u>Flow Rate</u> (gal/min)	<u>Observed Balling</u>	
		Example IIA (Invert Glycol Emulsion)	Example IIB (Lignosulfonate Mud)
10	15	---	moderate
	13	---	extensive
	11	none	extensive
	9	slight	extensive
15	4	none	---
	3.5	none	---
	3.2	extensive	---

EXAMPLE III

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Brine-in-glycol emulsions can be prepared by adding 20% (aq) sodium chloride to a mixture of PPG 300 (cloud point of 159°F for 50% solution in deionized water) or PPG 400, tall oil, lecithin (CLEARATE B-60), and lime. First, an organophilic clay such as Bentone SD-1, SD-2, SD-3, or EW (NL Chemicals) is added to a mixture of polypropylene glycol, tall oil, lecithin, and lime. The mixture is sheared for approximately ten minutes with a blender on high speed. Next, aqueous sodium chloride is added with vigorous mixing for several minutes. Finally, barite is added and the emulsion is mixed for several minutes to insure adequate suspension of the barite. These brine-in-

glycol emulsions are not stable until solids such as barite are added.

5 Formulations for these emulsions are listed in Tables 7 and 9 while rheological properties of these emulsions are listed in Tables 8 and 10.

Table 7

10 FORMULATIONS FOR 12 PPG, 70:30 PPF-400 EMULSIONS

<u>Example</u>	<u>IIIA</u>	<u>IIB</u>	<u>IIIC</u>	<u>IIID</u>
PPG 400, g	237	237	237	237
Tall Oil, g	5	5	5	5
15 CLEARATE B-60, g	5	5	5	5
Lime, g	4	4	4	4
Organophilic	8	8	8	8
Clay, g	SD-1	SD-2	SD-3	EW
20% (ag) NaCl, cc	100	100	100	100
20 Barite, g	198	198	198	198

Table 8

120°F RHEOLOGY OF 12 PPG, 70:30 PPG 400 EMULSIONS AFTER
16 HR STATIC AGING AT 60°F

<u>Example</u>	<u>IIIA</u>	<u>IIIB</u>	<u>IIIC</u>	<u>IIID</u>
AV, cP	76.5	84	89.5	75.5
PV, cP	63	69	70	52
YP, lb/100 ft ²	27	30	39	47
30 10 Sec Gel, lb/100 ft ²	5	5	6	4
10 Min Gel, lb/100 ft ²	7	8	9	6

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Table 9

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FORMULATIONS FOR 12 PPG, 70:30 PPG 300 EMULSIONS

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<u>Example</u>	<u>IIIE</u>	<u>IIIF</u>	<u>IIIG</u>	<u>IIIH</u>
PPG 300, g	237	237	237	237
Tall Oil, g	5	5	5	5
CLEARATE B-60, g	5	5	5	5
Lime, g	4	4	4	4
Organophilic Clay, g	8 SD-1	8 SD-2	8 SD-3	8 EW
20% (aq) NaCl, cc	100	100	100	100
Barite, g	198	198	198	198

Table 10
120°F RHEOLOGY OF 12 PPG, 70:30 PPG 300

	<u>Example</u>	<u>IIIE</u>		<u>IIIF</u>		<u>IIIG</u>		<u>IIIH</u>	
		Initial	After* Static Aging	Initial	After Static Aging	Initial	After Static Aging	Initial	After Static Aging
9	AV, cP	81.5	73.5	64.5	69.5	74.5	78	62.5	76.5
10	PV, cP	61	63	60	56	59	64	57	59
11	YP, lb/100 ft ²	41	21	9	27	31	28	11	35
12	10 Sec Gel, lb/100 ft ²	8	4	2	4	6	4	2	3
13	10 Min Gel, lb/100 ft ²	11	5	4	7	10	6	3	5
14									
15									
16									
17									
18	* 16 Hours at 150°F								

EXAMPLE IV

5

10

15

Brine-in-glycol emulsions can be prepared using organophilic silicas such as CAB-O-SIL TS-610 from Cabot Corporation. These emulsions are made by preparing a blend of CAB-O-SIL TS-610 or another organophilic silica, a propaxylated tripropylene glycol bottoms, tall oil, and lime. After the organophilic silica is dispersed in the fluid by mixing, 20% (aq) sodium chloride is added, and the mixture is sheared in a blender or bar mixer to produce a stable emulsion. Formulations and properties both before and after heat aging, of unweighted examples are listed in tables 11 and 12.

20

The densities of these brine-in-glycol emulsions may be increased by the addition of barite, as illustrated in Table 13. These emulsions were found to be stable during either static or dynamic aging.

25

These emulsions were prepared with a propaxylated tripropylene glycol bottoms having an approximate molecular weight of 600 and a cloud point of 78°F for a 50% solution in deionized water.

30

35

Table 11

FORMULATIONS FOR BRINE-IN-PPG 600 EMULSIONS

<u>Example</u>	<u>IVA</u>	<u>IVB</u>	<u>IVC</u>	<u>IVD</u>	<u>IVE</u>	<u>IVF</u>	<u>IVG</u>
Glycol/Brine Ratio, v/v	55/45	55/45	70/30	70/30	70/30	80/20	80/20
PPG 600, g	181	181	236	236	236	404	404
CAB-O-SIL TS-610, g	1.0	3.0	3.0	4.0	6.0	1.5	3.0
Tall Oil, g	15	15	10	10	10	15	15
Lime, g	5	5	4	4	4	6	6
20% (aq) NaCl cc	148	148	100	100	100	104	104

Table 12
120°F RHEOLOGY OF BRINE-IN-PPG 600 EMULSIONS

Example	<u>IVA</u>		<u>IVB</u>		<u>IVC</u>		<u>IVD</u>	
	Initial	After*	Initial	After	Initial	After	Initial	After
10	AV, cP		Static		Static		Static	
	93	92	113	122	83.5	94.5	82	104.5
	PV, cP		Aging		Aging		Aging	
	76	77	88	96	74	84	72	93
15	YP, lb/100 ft ²		Static		Static		Static	
	34	30	50	52	19	21	20	23
	10 Sec Gel,		Aging		Aging		Aging	
	4	5	6	12	4	6	6	4
lb/100ft ²								
15	10 Min Gel,		Static		Static		Static	
	8	9	13	27	9	10	12	7
lb/100 ft ²								

* 16 Hours at 150°F

TABLE 12 (Continued)

	<u>Example</u>	<u>IVE</u>		<u>IVF</u>		<u>IVG</u>	
		Initial	After* Static Aging	Initial	After Static Aging	Initial	After Static Aging
9	AV, CP	91	92	52.5	60	56.5	59.5
10	PV, CP	77	79	50	57	54	57
11	YP, 1b/100 ft ²	29	27	5	6	5	5
12	10 Sec Gel,	6	11	1	1	1	2
13	1b/100 ft ²						
14	10 Min Gel,	11	18	2	2	2	3
15	1b/100 ft ²						
16							
17	* 16 Hours at 150°F						

1	Table 13		
2	FORMULATIONS FOR 12 PPG, PPG 600 EMULSIONS		
3			
4	Example	IVH	IVI
5	Glycol/Brine Ratio, v/v	60:40	70:30
6	Formulation		
7	PPG 600, g	180	211
8	CAB-O-SIL TS-610, g	0.88	1.76
9	Tall Oil, g	8.8	8.8
10	Lime, g	3.5	3.5
11	20% (aq) NaCl, cc	119	88
12	Barite, g	173	177

Table 14
120°F RHEOLOGY OF 12 PPG, PPG 600 EMULSIONS

4 5 6 7 8 9 10 11 12 13 14 15 16	Example	IVH			IVI		
		Initial	After* Static Aging	After + Dynamic Aging	Initial	After Static Aging	After Dynamic Aging
	AV, CP	146.5	128	137	122	124	115
	PV, CP	121	107	118	100	105	99
	YP, 1b/100 ft ²	51	42	38	44	38	32
	10 Sec Gel, 1b/100 ft ²	25	16	13	14	11	8
	10 Min Gel, 1b/100 ft ²	39	27	22	26	21	15

* 16 Hours at 150°F

EXAMPLE V

In order to test the effectiveness of the additive compositions of the invention to release differentially stuck drill pipe, a filter cake was formed in an API filter press at 100 psi using a 13.3 lb/gal gypsum mud. The formulation and typical properties of the gypsum mud are listed in Table 15. After 8 ml of filtrate was collected, the filter cell was opened and a 316SS cone 1 inch high, 1 5/8 inches in diameter at the base and 1 inch in diameter at the top, and having a convex base was placed so that the convex base of the cone rested on top of the filter cake. The filtration cell was reassembled and filtration was continued until a total of 20ml of filtrate was collected. After pressure filtration was completed, excess mud was poured from the cell and the filter cake and attached cone were carefully removed. The cake/cone assembly was then placed in the bed of a Buchner funnel and seated under a vacuum of 29.8 inches of Hg. After the cake was seated, excess fluid which had been removed from the filter press was poured on top of the filter cake. Vacuum filtration was performed for fifteen minutes, after which excess mud was removed from the Buchner funnel. The additive composition of the invention (Table 16) was then placed in the Buchner funnel, and a 2 kg counterweight was suspended from the cone by means of a pulley. The time required for the additive composition to effect release of the cone was measured.

The results of the release times tests (Table 17) illustrate the ineffectiveness of the base mud and

1 deionized water versus the effectiveness of the
2 compositions of the invention.

3

4

Table 15

5

FORMULATION AND PROPERTIES OF 13.3 PPG

6

STUCK PIPE SIMULATION TEST MUD

7

8

Formulation

9

10	4900 cc	Deionized Water
11	350 g	Bentonite
12	56 g	Gypsum
13	17.5 g	Chrome Lignosulfonate
14	4200 g	Barite

15

16

Properties

17

(Fann 35 Rheology At 120°F)

18

19	PV, cP	12
20	YP, lb/100 ft ²	0
21	10 Sec Gel, lb/100 ft ²	2
22	10 Min Gel, lb/100 ft ²	15
23		
24	API Filtrate, cc	52
25		

Table 16
BRINE-IN-GLYCOL EMULSION FORMULATIONS
FOR STUCK PIPE SIMULATION TEST

EXAMPLE VA

<u>Material</u>	<u>Concentration</u>
PPG 400	33.54 gal/bbl
Tall Oil	3.0 lb/bbl
CLEARATE B-60	3.0 lb/bbl
Lime	0.75 lb/bbl
Sepiolite	5.0 lb/bbl
20% (aq) NaCl	7.38 gal/bbl

EXAMPLE VB

<u>Material</u>	<u>Concentration</u>
50:50 PPG 300/600 Blend	32.9 gal/bbl
CAB-O-SIL TS-610	1.1 lb/bbl
Tall Oil	0.4 lb/bbl
Lime	4.0 lb/bbl
20% (aq) NaCl	8.5 gal/bbl

Table 17
RELEASE TIMES FOR STUCK PIPE SIMULATION TEST

<u>Sample</u>	<u>Release Time (min)</u>
Deionized Water	90 (No Release)
13.3 PPG Test Mud	90 (No Release)
Example VA	8.3
Example VB	7.6

1

2 The stable invert emulsion drilling fluid of the
3 invention may be used in a process for drilling or
4 completing a well where the emulsion drilling fluid is
5 circulated down through the interior of the drill pipe
6 and then back up to the surface through the annulus
7 between the drill pipe and the wall of the borehole.

8

9 Alternatively, the invert emulsions of the
10 invention may be used as spotting fluids. By this
11 technique, a weighting material is mixed with the
12 emulsion to produce a weighted spotting fluid. The
13 weighted spotting fluid is then circulated downhole so
14 as to position it to contact the drill string in the
15 area adjacent the stuck zone. Such a fluid is
16 effective as a spotting fluid which can be positioned
17 in the borehole by techniques well known in the art.

18

19 An invention has been provided with significant
20 advantages. When used as a drilling fluid, brine-in-
21 glycol emulsions will have significant advantages over
22 water-based drilling fluids. The novel emulsions will
23 provide improved hole stability, and bit lubrication,
24 and will minimize hydration and dispersion of shale
25 within the mud system. As spotting fluids the glycol
26 emulsions will perform the same function as that
27 provided by oil-based spotting fluids, but without the
28 environmental problems of oil-based fluids.

29

30 While the invention has been shown in only three
31 of its forms, it is not thus limited but is susceptible
32 to various changes and modifications without departing
33 from the spirit thereof.

CLAIMS

2044099

1 1. In a method of drilling a well, the improvement which comprises:
2 forming a replacement fluid for an oil-base mud, the replacement being
3 a brine-in-glycol invert emulsion having a glycol external phase and a brine
4 internal phase by first combining a glycol which is soluble in a brine solution
5 of about 3% salinity or less with a brine solution having a salinity greater than
6 about 3%, thereby rendering the external phase and internal phase immiscible,
7 the emulsion being characterized by the absence of hydrocarbon, mineral,
8 vegetable and animals oils;
9 adding an emulsifier to form an emulsion;
10 adding a weighting agent to the emulsion to form a weighted well bore
11 fluid;
12 circulating said weighted well bore fluid in said well.

1 2. The improvement according to claim 1, wherein the
2 glycol is a polypropylene glycol.

1 3. The improvement according to claim 1, wherein the
2 glycol is propoxylated tripropylene glycol bottoms.

1 4. The improvement according to claim 1, wherein the
2 glycol has a molecular weight between about 250 and 1000.

1 5. A well bore fluid of the type used in drilling a borehole of an
2 underground formation and which serves as a replacement fluid for an oil-base
3 mud, the well bore fluid comprising:
4 an external phase consisting essentially of a glycol, and a brine internal
5 phase, the external phase and the internal phase being combined to form an
6 invert emulsion, the glycol external phase being characterized as having a
7 molecular weight in the range from about 250 to 1000 having a cloud point in
8 the range from about 15° to 83°C. and being soluble or dispersible in sea
9 water at a salinity of about 3% and lower;
10 an emulsifier; and
11 a weighting agent.

C

1 6. The well bore fluid of claim 5, wherein the glycol is selected from
2 the group consisting of polypropylene glycol and propoxylated tripropylene
3 glycol bottoms.

1 7. The well bore fluid of claim 5, wherein the emulsifier is selected
2 from the group consisting of lime, lecithin, fatty acids and fatty acid mixtures.

1 8. The well bore fluid of claim 5, wherein the weighting agent is
2 barite.

1 9. The well bore fluid of claim 5, further comprising:
2 a viscosifier selected from the group consisting of sepiolite, attapulgite,
3 organophilic clay and treated fumed silica.