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INVERT EMULSION WELL SERVICING FLUIDS

The present invention relates to well servicing fluids. More specifically, the present invention relates to water-in-oil (invert) emulsions for use in well servicing operations such as work-overs, fracturing, completing or hole abandonment.

Oil based well servicing fluids find particular application in fracturing and packing operations. For example, oil bearing sands of low permeability are commonly subjected to extremely high fluid pressure so as to crack them open, generally along bedding planes, and the fractures so formed are held open by solid propping agents introduced with the fracturing fluid. Such fracturing fluids are desirably oil based, having a low filtration loss. Oil based fluids are also commonly used as packer fluids to fill the annular space between the casing and the walls of the hole, the oil based fluids serving to minimize corrosion and provide low fluid loss properties so that the packing fluid remains in place over a long period of time.

Invert emulsion well fluids have been developed to overcome certain deficiencies of simple oil-based fluids which have long been utilized in well servicing operations described above. However, such invert emulsions, while overcoming many of the deficiencies of simple oil based fluids, have suffered from certain problems, for example the tendency for the oil phase to separate at least partially from the emulsion. Additionally, in many invert emulsion well servicing systems, there are problems in controlling solids settling.

It is therefore an object of the present invention to provide an improved well servicing fluid of the invert emulsion type.

Another object of the present invention is to provide an invert emulsion well servicing fluid exhibiting minimized oil phase separation.

Yet another object of the present invention is to

provide an invert well servicing fluid which minimizes solids settling.

Still a further object of the present invention is to provide a well servicing fluid having reduced fluid loss.

The present invention provides a well servicing fluid which comprises an invert emulsion having a liquid oleaginous phase and an aqueous phase, in a volume ratio of from 99:1 to 1:1, an invert emulsifying agent, and from 2.75 to 57.5 g/litre of a solid, particluate linear polyethylene having a density of at least 0.94g/cc and near spherical particles with an average particle size of from 15 to 40 microns.

The oleaginous liquid (oil phase) in the well servicing fluids of the present invention is usually petroleum oil (hydrocarbons). Preferably, the oleaginous liquid should contain at least some component boiling above the gasoline boiling range, i.e. above 200°C at atmospheric pressure. Oils with too high a content of highly volatile hydrocarbons in the gasoline boiling range are undesirable because of the danger of fire, and because of their low viscosity. It is preferred that the oleaginous liquid have a flash point above 60°C. Non-limiting examples of suitable oleaginous liquids which can be employed in the well servicing fluids of the present invention include: topped crude oil, gas oils, kerosene, diesel fuel, heavy alkylates, and fractions of heavy alkylates and mixtures thereof. The more preferred oils are predominantly paraffinic in character, since these are less detrimental to rubber components in pumps or lines. It is preferred that the oleaginous liquid have a specific gravity within the range of 0.825 to 0.966. The invert emulsion well servicing fluids of the present invention contain the oleaginous liquid, the continuous phase, as the major portion, and the aqueous phase as the minor portion.

Thus, the volume ratio of the oleaginuous phase to the aqueous phase is from 99/1 to 1/1, preferably from 20/1 to 2/1, most preferably from 10/1 to 2/1. The aqueous phase can be fresh water or a solution in water as a brine-forming, water soluble salt such as sodium chloride or calcium chloride. The amount of the water soluble salt in the aqueous phase will vary, depending on the conditions under which the well servicing fluid is to be used. It is common, however, to use fluids in which the aqueous phase is saturated with respect to the brine-forming water soluble salt.

In accordance with the present invention, it has been found that the addition of certain solid, particulate polyethylenes to invert emulsion well servicing fluids produces minimized oil phase separation, less solids settling and lower fluid loss. Generally speaking, such polyethylenes have molecular weights of greater than 6000 and contain no unsaturated linkages in the polymer chains. The useful polyethylenes have a density of at least 0.94 g/cc. Such polyethylenes are generally referred to as high density polyethylenes and are linear, isostatic polymers of 95% crystallinity.

The polyethylenes used in the well servicing fluids of the present invention are particulate in nature, i.e. they are finally divided solids comprising near-spherical particles, the average particle diameter being from 15 to 40 microns. A particularly preferred linear, high density polyetheylene is Super Dylan, SDP-113 (hereinafter referred to as SDP-113) marketed by Atlantic Richfield Polymers. SDP-113 has the following physical properties:

Density	0.947	g/cc
Melt Index	0.4	g/10 min
Melting Point	126	°C
Particle Dia., Avg.	25	Microns
Bulk Density	0.32	g/cm^3
Yield	417.7	Pascals
Appearance	White free flowing powder	

The polyethylene will be present in the well servicing fluid in an amount within the range of from 2.75 to 57.5 gram per litre (g/l), which is effective to prevent oil separation from the invert emulsion, reduce fluid loss, and aid in controlling solids settling when used with a suitable viscosifier.

The well servicing fluids of the present invention will also contain an invert emulsifying agent such as disclosed in U.S. Patent No. 2,861,042; 2,946,746; 3,259,572; 3,346,489; 3,590,005; or 3,654,177. Typical water-in-oil emulsifiers include the polyamide type formed by the reaction of a polyamine with fatty acids and a dibasic acid, as well as the anionic water-in-oil emulsifiers disclosed aforementioned U.S. Patent No. 2,861,042. Mixtures of various emulsifiers can be used, if desired. The emulsifying agent will generally be present, in the well servicing fluid, in an amount of from 5.5 to 57.5 g/l, and more preferably from 7.5 to 40 g/l.

It is also desirable that the well servicing fluids of the present invention contain a filtration control agent to aid in preventing fluid loss. Although many oil mud filtration control agents, such as those disclosed in U.S. Patents Nos. 3,168,475 and 3,494,865, can be employed, organophilic lignitic colloids prepared by reacting lignite and a quarternary ammonium salt have been found to be quite effective.

Well servicing fluids containing such invert mud filtration control agents and the particulate polyolefin are especially effective in controlling settling of solids. The filtration control agent will generally be present in an amount of from 2.75 to 57.5 g/l of the well servicing fluid.

If desired , the well servicing fluids of the present invention can also contain suitable viscosifying agents, for example, organiphilic clays produced by reacting a smectite type clay, e.g. bentonite, and a quaternary ammonium salt. Such viscosifying agents are disclosed in U.S. Patent 4,105,578. When employed, the viscosifier will be present in the well servicing fluids in amounts of from 1.4 to 11.5 g/l.

The well servicing fluids of the present invention can advantageously also contain lime. The term lime, as used herein, includes calcium oxide as well as any of the various chemical and physical forms of quicklime or hydrated lime. The lime will generally be present in the fluids in an effective amount, up to and including 45 g/l.

The well servicing fluids of the present invention can also contain, with advantage, weighting agents such as barite, the amount of such weighting agents present in the well servicing fluid being dependent upon the environment in which the well servicing fluid is to be employed. It is especially desirable, when a weighting agent is employed, that a viscosifying agent (suspension agent) such as described above be employed in the well servicing fluids.

The well servicing fluids of the present invention can be prepared by methods well known to those skilled in the art.

To illustrate more fully the present invention, the following non-limiting examples are presented. All test results were obtained in accordance with standard API procedures (API RP 13B, 7th Ed., April 1978) and the results obtained were converted, where necessary into metric units. In all cases, the polyethylene employed was Super Dylan SDP-113.

Example 1

Laboratory-prepared, base invert muds were prepared by mixing together the following components in the amounts indicated:

Diesel oil, l	90.62
INVERMUL "L",[1] Kg	4.54
Lime, Kg	3.175
EZ MUL,[2] Kg	0.91
Water, l	22.25
GELTONE,[3] Kg	0-0.91
BAROID,[4] Kg	172.37
$CaCl_2$, Kg	12.25

[1,2] Registered Trademarks for invert emulsifiers marketed by NL Baroid, Houston, Texas.

[3] Registered Trademark for a synthetic organophilic colloid viscosifying agent marketed by NL Baroid, Houston, Texas.

[4] Registered Trademark for a barite weighting agent marketed by NL Baroid, Houston, Texas.

The base muds as prepared above, were used to prepare 1.80 g/cm^3 invert muds incorporating DURATONE (Registered Trademark, an oil mud filtration control agent marketed by NL Baroid, Houston, Texas) or SDP-113. The compositions of the thus prepared muds and the test results as to oil separation, fluid loss, solids settling and rheological projections are given in Table 1 below.

Table 1

Sample Mark	A	B	C	D	E
Diesel oil, litres	90.62	90.62	90.62	90.62	90.62
INVERMUL "L", Kg	4.54	4.54	4.54	4.54	4.54
Lime, Kg	3.175	3.175	3.175	3.175	3.175
DURATONE, Kg	3.63	-	-	-	-
SDP-113, Kg	-	3.63	3.63	3.63	1.81
EZ MUL, Kg	0.91	0.91	0.91	0.91	0.91
Water, litres	22.25	22.25	22.25	22.25	22.25
GELTONE, Kg	0.91	0.91	-	0.45	0.91
BAROID, Kg	172.37	172.37	172.37	172.37	172.37
$CaCl_2$, Kg	12.25	12.25	12.25	12.25	12.25
Stirred, min	15	15	15	15	15
Test temp, °C	36.5	36.5	36.5	35	35
Plastic Viscosity, cp	38	35	26	32	26
Yield Point, Kg/m^2	0.44	0.68	0	0.10	0.34
10-sec gel, Kg/m^2	0.29	0.34	0.05	0.10	0.24
10-min gel, Kg/m^2	0.49	0.49	0.05	0.15	0.34
Stability, volts	1280	920	1000	1600	940
Settling	None	None	Severe	Slight	None
Rolled, hr at 65.5°C	16	16			16
Stirred, min	5	5			5
Test temp, °C	49 35	49 35			54.5 32
Plastic Viscosity, cp	32 37	32 37			22 28
Yield Point, Kg/m^2	0.68 0.73	1.12 1.03			0.73 0.63
10-sec gel, Kg/m^2	0.44 0.44	0.73 0.78			0.44 0.59
10-min gel, Kg/m^2	0.63 0.54	1.03 1.07			0.63 0.78
Stability, volts	1180	1200			1240
Filtrate, ml at 205°C-35 Kg/m^2	7.2	0.8			20.4

As can be seen from the data in Table 1, the particulate polyethylene (SDP-113) is much more effective than conventional oil mud filtration control agents (DURATONE) in reducing fluid loss in invert muds (compare the results on Samples A and B).

Example 2

Several of the invert emulsion muds shown in Table 1 were subjected to static aging under conditions shown in Table 2 below. Table 2 also gives the results of the rheological measurements, fluid loss, oil separation and solids settling.

Table 2

Mud Sample (From Table 1)	A	B	E
Aged, hr, at 205°C and 35 Kg/cm²	168	168	168
Shear, Kg/m²	2.83	9.57	5.32
Settling, mm.	89	0	0
Settling, relative hardness	Firm	None	None
Stability, volts	840	880	1440
Top oil separation, mm	32	0	0
Stirred, min	5	5	5
Test temp, °C	32	32	38
Plastic Viscosity, cp	37	155	65
Yield Point, Kg/m²	0.15	7.32	2.39
10-sec gel, Kg/m²	0.24	2.44	0.98
10-min gel, Kg/m²	0.49	3.42	1.51
Stability, volts	760	640	960
Filtrate, ml at 205°C and 35 Kg/cm²	162 (14 ml emulsion)	7.0 All oil	37.2 All oil
Cake, mm	39.7	7.9	11.1

As can be seen from the results in Table 2, the fluid loss of invert muds containing the polyethylene (SDP-113) and after static aging is much less than that of muds containing no polyethylene Compare, for example, the results for mud sample A against the results for Samples B and E. As can also be seen from Table 2, there is no oil phase separation (top oil separation) in aged samples which contain the polyolefin. Lastly, the data in Table 2 show that the addition of the polyethylene to the invert muds prevents solids settling, even after the muds have been aged under rather severe conditions.

Example 3

To demonstrate the effectiveness of the present invention with a typical field invert mud, a 2.277 g/cm³ invert mud (Shell's Hinojosa No. 1, Zapata County, Texas E-896) was diluted 10% with a 50/50 volume mix of diesel oil and water to produce a 2.18 g/cm³ mud having an 86/14 (vol) oil-water ratio. To obtain comparative results, a sample of the original 2.277 g/cm³ mud (Sample A) was compared with samples of the 2.18 g/cm³ mud one of which

(Sample B) employed a typical viscosifying agent (GELTONE), a second sample of which (Sample C) contained SDP-113. Table 3 below shows the compositions of the muds, the results of the rheological property measurements and the measurements of oil and solids separation.

Table 3

Sample Mark	A	B	C
E-896, l	159	143	143
Diesel oil, l		7.95	7.95
Water, l		7.95	7.95
INVERMUL "L", Kg		0.91	0.91
Lime, Kg		1.36	1.36
GELTONE, Kg		0.91	
SDP-113, Kg			0.45
Stirred, min	15	15	15
Test temp, °C	38	38	38
Plastic Viscosity, cp	104	94	76
Yield Point, Kg/m^2	0.54	1.56	0.39
10-sec gel, Kg/m^2	0.54	1.27	0.39
10-min gel, Kg/m^2	0.98	1.86	0.68
Electrical stability, volts	1120	1120	980
Aged, hr at 202°C-35Kg/cm^2	16	16	16
Shear, Kg/m^2	3.9	6.74	5.86
Settling, mm-hardness	49-hard	9.5-moderate	None
Stability, volts	980	1080	1380
Top oil separation, mm	3	0	0
Stirred, min	5	5	5
Test temp, °C	38	38	38
Plastic Viscosity, cp	124	114	93
Yield Point, Kg/m^2	0.39	0.44	0.93
10-sec gel, Kg/m^2	0.39	0.39	0.49
10-min gel, Kg/m^2	0.49	1.07	1.22
Electrical stability, volts	1120	1040	1080
Density, g/cm^2	2.277	2.18	2.18

As can be seen from the data in Table 3, Sample C which contained the polyethylene showed no solids settling, while Sample B (containing the conventional viscosifying agent normally used to prevent solids separation in oil based muds) showed moderate solids settling. Note that the untreated field mud, without any viscosifying agent or polyethylene (Sample A), showed significant solids settling.

* C L M S *

CLAIMS

1. A well servicing fluid which comprises an invert emulsion having a liquid oleaginous phase and an aqueous phase, in a volume ratio of from 99:1 to 1:1, an invert emulsifying agent, and from 2.75 to 57.5 g/litre of a solid, particulate linear polyethylene having a density of at least 0.94 g/cc and near spherical particles with an average particle size of from 15 to 40 microns.

2. A fluid as claimed in claim 1 which comprises a viscosifying agent.

3. A fluid as claimed in claim 1 or 2 wherein the volume ratio of oleaginous phase to aqeuous phase is from 10:1 to 2:1.

4. A fluid as claimed in any preceding claim which comprises a filtration control agent.

5. A fluid as claimed in any preceding claim wherein the oleaginous phase comprises a hydrocarbon oil, at least a part of which boils above 200°C and which is topped crude oil, gas oil, kerosene, diesel fuel, heavy alkylate, fractions of heavy alkylate, or a mixture thereof.

6. A fluid as claimed in claim 1 and substantially as hereinbefore described with reference to any of the Examples.