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(54) Title: DRILLING AND WELL TREATMENT FLUIDS

(57) Abstract: Water in oil drilling and well treatment fluids comprising blown castor oil having Brookfield viscosity RVT at 25°C, 20 rpm higher than 1,000 mPa*s as emulsifier show improved stability and environmental compatibility.

Description

DRILLING AND WELL TREATMENT FLUIDS

FIELD OF THE INVENTION

The present invention relates to water in oil drilling and well treatment fluids (drilling fluids) with improved stability and environmental compatibility, and to their use in subterranean applications; more particularly, the drilling and well treatment fluids comprise blown castor oil as the emulsion stabilizer.

Drilling fluids are meant to include drilling and completion fluids; well treatment fluids include all water based systems used in well operations such as work-over, milling stimulation, fracturing, spotting fluids, cementing, etc

STATE OF THE ART

Emulsions usually comprise two immiscible phases: a continuous (or external) phase and a discontinuous (or internal) phase, the discontinuous phase usually being a liquid dispersed in droplets in the continuous phase.

Oil-in-water emulsions usually include a fluid at least partially immiscible in oil (an aqueous-based fluid) as the continuous phase and an oil phase as the discontinuous phase.

Water-in-oil emulsions are the opposite, having the oil phase as the continuous phase and a fluid at least partially immiscible in the oil phase (usually an aqueous-based fluid) as the discontinuous phase.

Water-in-oil emulsions may also be referred to as invert emulsions. Both kinds of emulsions have been used widely in oil and gas applications, for instance, for drilling and other subterranean treatment applications.

Invert emulsions are preferred as drilling fluids when the formation is remarkably sensitive to contact with water and they usually guarantee better lubrication of the drill strings and downhole tools, thinner filter cake formation, and better thermal resistance and hole stability.

Emulsions are generally stabilized by addition of one or more emulsion stabilizing agents, also referred to as emulsifiers, preventing the droplets coalescence, phase separation and compromising of their performance.

When used in subterranean applications, emulsions undergo exceptional mechanical and thermal stress, and therefore stability is an especially critical aspect of their formulation.

The emulsifiers that are traditionally used in drilling and well treatment fluids have surfactant-character, comprising a hydrophobic portion and a hydrophilic portion.

However, most use of surfactant-like emulsifiers is problematic, as they suffer from problems that include possible toxicity, poor biodegradability, thermal destabilization and intolerance to various salts and other chemical agents.

It is known that the products that are obtained from the amidation of mixtures of fatty acid oligomers with, for example, diethanolamine, have advantageous emulsifying and dispersing properties that are useful in various applications where water-in-oil or oil-in-water emulsions are formed.

The use of certain oxidized natural oils in drilling fluids is also known.

US 2,861,042 is directed to the use of oxidized tall oil as emulsifier for invert drilling fluids, while DE 1071624 cites the use of oxidized soybean oil for a similar purpose.

It is further known from US 2,058,569 that blown castor oil can effectively be used in oil recovery for the purpose of separating oil from crude petroleum emulsions, i.e. as disemulsifier, when used in very small amounts (0.01 to 0.2% by weight).

SUMMARY OF THE INVENTION

The scope of this invention is to describe new drilling and well treatment fluids with better resistance to separation and to contamination from drilling residues even at high temperature, that can be obtained more economically and with a lower environmental impact, with the same performances.

It has now surprisingly been found that blown castor oil possesses excellent properties as emulsifier when it is used in water in oil drilling and well treatment fluids, being able to guarantee optimal stability of the fluids even in the presence of solid contaminants.

In one embodiment, the present invention provides a water in oil drilling fluid or well treatment fluid that comprises an oil phase, an aqueous phase and blown castor oil as the emulsion stabilizing agent.

In another embodiment, the present invention provides a method for drilling a well bore in a subterranean formation using a water in oil drilling fluid comprising an oil phase, an aqueous phase and blown castor oil as the emulsion stabilizing agent.

In yet another embodiment, the present invention provides a method of treating oil wells that comprises: providing a water in oil well treatment fluid containing an oil phase, an aqueous phase and blown castor oil as the emulsion stabilizing agent; and treating the well.

In a further embodiment, the present invention provides a method of fracturing a subterranean formation that comprises: providing a water in oil fluid containing an oil phase, an aqueous phase, blown castor oil as the emulsion stabilizing agent and proppant particulates; placing the water in oil fluid into the subterranean formation at a pressure sufficient to create or enhance at least one fracture therein; and removing the water in oil fluid from the subterranean formation while leaving at least a portion of the proppant particulates in the fracture.

The features and advantages of the present invention will be readily apparent to those skilled in the art upon reading of the description of the preferred embodiments which follows.

DETAILED DESCRIPTION OF THE INVENTION

Blown oils are produced at elevated temperatures by blowing air through unsaturated oils; the oils polymerize by crosslinking and incorporation of O-O bridges.

Blown oils are also known as oxidized, thickened or oxidatively polymerized oils and are generally manufactured to viscosity specifications.

For the realization of the present invention only blown castor oil having Brookfield viscosity RVT at 25°C, 20 rpm higher than 1,000 mPa*s can be used, preferably from 5,000 to 40,000 mPa*s, more preferably from 10,000 to 30,000 mPa*s.

Preferably, the acidity number of the blown castor oil should not exceed 60 mg KOH/g.

The water in oil drilling and well treatment fluids according to the invention contain from 0.5 to 4.0% by weight, based on the total weight of the fluid, of blown castor oil.

In a preferred embodiment, blown castor oil is used in quantity of 1.0 to 3.0% by weight, in order to optimally develop its effect as emulsifier.

The use of blown castor oil as emulsifier of water in oil drilling and well treatment fluids leads to a remarkably improved rheological profile of the fluids when a comparison is made with other oxidized oils; this is especially apparent with drilling fluids contaminated with drill cuttings and comprising concentrated brines, where a more stable rheology, i.e. a rheology profile with less variation before and after heat aging of the fluid, is obtained.

The peculiarity of blown castor oil is possibly due to its characeristic chemical composition, in which ricinoleic chains bearing hydroxyl groups prevail.

The addition of blown castor oil as emulsifier also provides good high pressure and temperature (HPHT) filtrate properties to the corresponding fluids.

According to an advantageous aspect of the present invention, the water in oil fluids do not comprise any additional emulsifier, except blown castor oil.

The water in oil fluids of the present invention comprise an oil phase, an aqueous phase (a water based fluid that is at least partially immiscible with the oil phase), and blown castor oil and may be suitable for use in a variety of oil field applications wherein water-in-oil emulsions are used; these include subterranean applications comprising drilling, completion and stimulation operations (such as fracturing), sand control treatments such as installing a gravel pack, cementing, maintenance and reactivation.

The oil phase used in the invert emulsions of the present invention may comprise any oil-based fluid suitable for use in emulsions.

The oil phase may derive from a natural or synthetic source.

Examples of suitable oil phase include, without limitation, diesel oils, paraffin oils, mineral oils, low toxicity mineral oils, olefins, esters, amides, amines, synthetic oils such as polyolefins, ethers, acetals, dialkylcarbonates, hydrocarbons and combinations thereof.

The preferred oil phases are paraffin oils, low toxicity mineral oils, diesel oils, mineral oils, polyolefins, olefins and mixtures thereof.

Factors determining which oil phase will be used in a particular application, include but are not limited to, its cost and performance characteristics, environmental compatibility, toxicological profile and availability.

The invert emulsions of the present invention also comprise an aqueous phase that is at least partially immiscible in the oil phase.

Suitable examples of aqueous phase include fresh water, sea water, salt water, and brines (e.g., saturated salt waters), glycerine, glycols, polyglycol amines, polyols and derivatives thereof, that are partially immiscible in the oleaginous fluid, and combinations thereof.

Suitable brines may include heavy brines.

Heavy brines, for the purposes of this application, include brines with various salts at variable concentrations, that may be used to weight up a fluid; generally of the use of weighting agents is required to provide the desired density of the fluid.

Brines generally comprise water soluble salts.

Suitable water soluble salts are sodium chloride, calcium chloride, calcium bromide, zinc bromide, sodium formate, potassium formate, sodium acetate, potassium acetate, calcium acetate, ammonium acetate, ammonium chloride, ammonium bromide, sodium nitrate, potassium nitrate, ammonium nitrate, calcium nitrate, sodium carbonate, potassium carbonate, and mixtures thereof.

The aqueous phase is chosen taking into account several factors including cost, environmental and health safety profile, density, availability, and which oil phase has been chosen. Another factor that may be considered is the application of the emulsion.

For example, if the application needs an emulsion with a heavy weight, a zinc bromide brine (for example) may be chosen.

The water in oil drilling and well treatment fluids of the invention may further comprise conventional additives including weighting agents, wetting agents, fluid loss agents, thickeners, thinning agents, lubricants, anti-oxidants, corrosion inhibitors, scale inhibitors, defoamers, biocides, pH modifiers, and the like.

Such fluids, in particular, also contain at least one filtrate reducer preferably chosen among gilsonite, organophilic lignite, organophilic tannins, synthetic polymers, polycarboxylic fatty acids.

When used in certain applications, the fluids may include particulates such as proppant or gravel.

To better illustrate the invention, the following examples are reported to show the effect of the addition of different blown castor oils and of prior art blown soya oil in exemplary water in oil drilling fluids.

EXAMPLE 1

A water in oil fluid (based on mineral paraffinic oil and containing a clay simulating the solid drilling cuttings) was prepared by mixing the here below ingredients with an Hamilton Beach mixer, as described in A.P.I. Specification 13A, in the reported order and with the following stirring times:

Ingredients	**g in the fluid**	**Stirring time**
EDC 99-DW (*)	176.48	
Emulsifier	10	10 min
Bentone 38	5.6	10 min
$Ca(OH)_2$	7	10 min
Brine $CaCl_2$ 35%	84,45	10 min
Barite	182.88	20 min
A.P.I. Standard Evaluation Base Clay (**)	35	5 min

(*) mineral paraffinic oil available from TOTAL UK.
(**) clay from IMERYS France.

The following emulsifiers were tested:

- BSO = blown soybean oil with Brookfield® viscosity about 11,000 mPa∗s at 20 rpm and 25°C.
- BCO lv = low viscosity blown castor oil, with Brookfield® viscosity about 4,500 mPa∗s at 20 rpm and 25°C.
- BCO hv = high viscosity blown castor oil, with Brookfield® viscosity about 22,500 mPa∗s at 20 rpm and 25°C.

The characteristics of the fluids are shown in the table here below:

	Units	
Oil / water	v/v	80/20
Specific gravity	g/ml	1.33
Mud weight	ppg(*)	11.1

(*) pounds per gallon

The rheological properties of the invert emulsion drilling fluids were measured at 50°C before and after hot rolling (BHR and AHR) with a viscosimeter, as reported in ISO standard 10414-2.

Electrical stability has been measured at a temperature of 50°C by means of an electrical stability meter as reported in ISO standard 10414-2.

HTHP fluid loss has been measured at a temperature of 150°C by means of a high temperature/high pressure filter press as reported in ISO 10414-2.

The following operating conditions were used:

Operating conditions	**Units**	
Aging period	hours	16
Aging temperature	°C	150
Dynamic/Static aging	D/S	D
Filtration temperature	°C	150
Filtration delta pressure	psi	500

The results are reported in Table 1, 2 and 3. Table 3 reports the results of the comparative fluid.

Table 1.

	Units	BCO lv BHR	BCO lv AHR
Rheology			
600 rpm		65	69
300 rpm		39	44
200 rpm		30	35
100 rpm		22	25
6 rpm		11	15
3 rpm		11	14
gels 10''	$lbs/100ft^2$	15	30
gels 10'	$lbs/100ft^2$	17	26
AV	mPa*s	32.5	34.5
PV	mPa*s	26	25
YP	$lbs/100ft^2$	13	19
HTHP fluid loss			
Total	ml		4.4
Water in filtrate	ml		/
Emulsion in filtrate	ml		0.2
Electrical stability @ 50°C			
	volts	287	401

Table 2.

	Units	BCO hv BHR	BCO hv AHR
Rheology			
600 rpm		62	77
300 rpm		39	48
200 rpm		30	38
100 rpm		21	28
6 rpm		12	16
3 rpm		11	16
gels 10''	$lbs/100ft^2$	23	28
gels 10'	$lbs/100ft^2$	27	29
AV	mPa*s	31	38.5

PV	mPa∗s	23	29
YP	lbs/100ft^2	16	19
HTHP fluid loss			
Total	ml		5.8
Water in filtrate	ml		/
Emulsion in filtrate	ml		0.6
Electrical stability @ 50°C			
	volts	513	715

Table 3 (comparative).

	Units	**BSO BHR**	**BSO AHR**
Rheology			
600 rpm		68	243
300 rpm		40	175
200 rpm		30	142
100 rpm		22	104
6 rpm		12	86
3 rpm		12	100
gels 10''	lbs/100ft^2	19	89
gels 10'	lbs/100ft^2	30	160
AV	mPa∗s	34	121.5
PV	mPa∗s	28	68
YP	lbs/100ft^2	12	107
HTHP fluid loss			
Total	ml		5.8
Water in filtrate	ml		/
Emulsion in filtrate	ml		0.6
Electrical stability @ 50°C			
	volts	513	715

The fluids where blown soybean oil is used as the emulsifier do not resist the drill solids contamination simulated by A.P.I. Standard Evaluation Base Clay, whereas blown castor oils provide fluids resisting very well to contamination (as can be seen from the rheology of the aged fluids which is similar to the rheology of the initial fluid).

EXAMPLE 2

To study the behaviour of the same emulsifiers in a different system, further tests were conducted in an olefinic hydrocarbon based fluid prepared by mixing the here below ingredients with an Hamilton Beach mixer as described in A.P.I. Specification 13A, in the reported order and with the following stirring times:

Ingredients	**g in the fluid**	**Stirring time**
IO C16-18 (*)	176.48	
Emulsifier	10	10 min
Bentone 38	5.6	10 min
$Ca(OH)_2$	7	10 min
Brine $CaCl_2$ 35%	84,45	10 min
Barite	182.88	20 min
A.P.I. Standard Evaluation Base Clay (**)	35	5 min

(*) internal olefins C16-C18, available as Amodrill 1000 from Ineos France

(**) clay is from IMERYS France.

The characteristics of the fluids are shown in the table here below:

	Units	
Oil / water	v/v	80/20
Specific gravity	g/ml	1.43
Mud weight	ppg(*)	11.9

(*) pounds per gallon

The rheological properties of the invert emulsion drilling fluids were measured at 50°C before and after hot rolling (BHR and AHR) with a viscosimeter, as reported in ISO standard 10414-2.

Electrical stability has been measured at a temperature of 50°C by means of an electrical stability meter as reported in ISO standard 10414-2.

HTHP fluid loss has been measured at a temperature of 150°C by means of a high temperature/high pressure filter press as reported in ISO 10414-2.

The following operating conditions were used:

Operating conditions	**Units**	
Aging period	hours	16
Aging temperature	°C	150
Dynamic/Static aging	D/S	D
Filtration temperature	°C	150
Filtration delta pressure	psi	500

The results are reported in Table 4, Table 5 and in Table 6 (comparative fluids).

Table 4.

	Units	**BCO lv BHR**	**BCO lv AHR**
Rheology			
600 rpm		59	69
300 rpm		36	41
200 rpm		28	30.5
100 rpm		19	22
6 rpm		9	10
3 rpm		9	9.5
gels 10''	lbs/100ft^2	13	12
gels 10'	lbs/100ft^2	18	22
AV	mPa*s	29.5	34.5
PV	mPa*s	23	28
YP	lbs/100ft^2	13	13

HTHP fluid loss			
Total	ml		7.8
Water in filtrate	ml		/
Emulsion in filtrate	ml		0.8
Electrical stability @ 50°C			
	volts	417	642

Table 5.

	Units	**BCO hv BHR**	**BCO hv AHR**
Rheology			
600 rpm		61	77
300 rpm		37	45
200 rpm		28	34
100 rpm		20	23
6 rpm		10	12
3 rpm		10	11
gels 10''	lbs/100ft^2	14	17
gels 10'	lbs/100ft^2	21	28
AV	mPa*s	30.5	38.5
PV	mPa*s	24	32
YP	lbs/100ft^2	13	13
HTHP fluid loss			
Total	ml		13.6
Water in filtrate	ml		/
Emulsion in filtrate	ml		0.6
Electrical stability @ 50°C			
	volts	526	661

Table 6 (comparative).

	Units	BSO BHR	BSO AHR
Rheology			
600 rpm		93	132
300 rpm		65	78
200 rpm		47	60
100 rpm		33	38
6 rpm		17	17
3 rpm		17	17
gels 10''	lbs/100ft^2	21	33
gels 10'	lbs/100ft^2	29	65
AV	mPa*s	46.5	66
PV	mPa*s	28	54
YP	lbs/100ft^2	37	24
HTHP fluid loss			
Total	ml		6
Water in filtrate	ml		/
Emulsion in filtrate	ml		0.8
Electrical stability @ 50°C			
	volts	246	976

The tests were conducted in a contaminated system to check the resistance to drill solids contamination of the drilling fluid simulated by A.P.I. Standard Evaluation Base Clay.

Also in an olefinic system, the blown castor oils give better resistance to the contamination than blown soybean oil (the rheology of the aged drilling fluids with blown castor oils is better than the rheology of the aged drilling fluid with blown soybean oil).

Claims

1. Water in oil drilling or well treatment fluid that comprises an aqueous phase, an oil phase and blown castor oil having Brookfield viscosity RVT at 25°C, 20 rpm higher than 1,000 mPa*s.
2. Water in oil drilling or well treatment fluid according to claim 1 containing from 0.5 to 4.0% by weight, based on the total weight of the fluid, of the blown castor oil.
3. Water in oil drilling or well treatment fluid according to claim 2 wherein the blown castor oil has Brookfield viscosity RVT at 25°C, 20 rpm from 5,000 to 40,000 mPa*s.
4. Water in oil drilling or well treatment fluid according to claim 3 wherein the blown castor oil has Brookfield viscosity RVT at 25°C, 20 rpm from 10,000 to 30,000 mPa*s.
5. Water in oil drilling fluid or well treatment fluid according to claim 4. containing from 1.0 to 3.0% by weight of the blown castor oil.
6. Method for drilling a well bore in a subterranean formation using a water in oil drilling fluid containing an aqueous phase, an oil phase and blown castor oil having Brookfield viscosity RVT at 25°C, 20 rpm higher than 1,000 mPa*s.
7. Method for drilling a well bore according to claim 6. in which the water in oil drilling fluid contains from 0.5 to 4.0% by weight of the blown castor oil.
8. Method for drilling a well bore according to claim 7. in which the blown castor oil has Brookfield viscosity RVT at 25°C, 20 rpm from 5,000 to 40,000 mPa*s

9. Method for drilling a well bore according to claim 8. in which the blown castor oil has Brookfield viscosity RVT at 25°C, 20 rpm from 10,000 to 30,000 mPa*s.
10. Method for drilling a well bore according to claim 9. in which the water in oil drilling fluid contains from 1.0 to 3.0% by weight of the blown castor oil.
11. Method of treating a well comprising: providing a water in oil well treatment fluid containing an oil phase, an aqueous phase and blown castor oil having Brookfield viscosity RVT at 25°C, 20 rpm higher than 1,000 mPa*s; and treating the well by injecting the thus prepared fluid.
12. Method of treating a well according to claim 11. in which the well treatment fluid contains from 0.5 to 4.0% by weight of the blown castor oil.
13. Method of treating a well according to claim 12. in which the blown castor oil has Brookfield viscosity RVT at 25°C, 20 rpm from 5,000 to 40,000 mPa*s
14. Method of treating a well according to claim 13. in which the blown castor oil has Brookfield viscosity RVT at 25°C, 20 rpm from 10,000 to 30,000 mPa*s.
15. Method of treating a well according to claim 14. in which the well treatment fluid contains from 1.0 to 3.0% by weight of the blown castor oil.
16. Method of fracturing a subterranean formation comprising providing a water in oil fluid composition comprising an oil phase, an aqueous phase and blown castor oil having Brookfield viscosity RVT at 25°C, 20 rpm higher than 1,000 mPa*s and proppant particulates; placing the

water in oil fluid into the subterranean formation at a pressure sufficient to create or enhance at least one fracture therein; and removing the water in oil fluid from the subterranean formation while leaving at least a portion of the proppant particulates in the fracture.

17. Method of fracturing a subterranean formation according to claim 16. in which the water in oil fluid contains from 0.5 to 4.0% by weight of the blown castor oil.

18. Method of fracturing a subterranean formation according to claim 17. in which the blown castor oil has Brookfield viscosity RVT at 25°C, 20 rpm from 5,000 to 40,000 mPa*s

19. Method of fracturing a subterranean formation according to claim 18. in which the blown castor oil has Brookfield viscosity RVT at 25°C, 20 rpm from 10,000 to 30,000 mPa*s.

20. Method of fracturing a subterranean formation according to claim 19. in which the water in oil fluid contains from 1.0 to 3.0% by weight of the blown castor oil.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2009/054281

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09K8/36

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C09K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2 994 660 A (REDDIE WILLIAM A ET AL) 1 August 1961 (1961-08-01) claims 1,23 column 1, line 9 - line 11 column 4, line 20 - line 36 column 5, line 18 - line 49 column 6, lines 15-18 - lines 31-36 -----	1-15
X	WO 2006/123143 A (HALLIBURTON ENERGY SERV INC [US]; CURTIS PHILIP ANTHONY [GB]; WEAVER J) 23 November 2006 (2006-11-23) claim 11 page 21, paragraph 2 page 22, paragraph 1 -----	16-20
A	GB 2 115 459 A (MILCHEM INC) 7 September 1983 (1983-09-07) the whole document -----	1-15

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

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Date of the actual completion of the international search	Date of mailing of the international search report
11 August 2009	20/08/2009

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2009/054281

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