MULTIFUNCTIONAL WAX DISPERSANT FOR SUBTERRANEAN CHEMICAL APPLICATIONS

TECHNICAL FIELD OF THE INVENTION

The invention relates to a composition for use as a multifunctional wax dispersant to treat subterranean formations for the recovery of oil and gas from oil and gas wells, as well as to the process for preparation thereof. The invention also relates to a method for treating a crude oil with a wax dispersant composition according to the present invention to reduce interfacial tension between the crude oil and the treatment fluids in the recovery of oil and gas from crude oil and gas wells.

BACKGROUND OF THE INVENTION

The present invention relates to chemical compositions for treating subterranean formations for the recovery of oil and gas from oil and gas wells. In recent years, there has been a growing interest in the use of chemicals in oilfield chemical applications to drill and extract oil and gas more efficiently. For example, during well stimulation such as hydraulic fracturing (frac), a conventional non-emulsifying surfactant is typically used to eliminate strong emulsions that do not break easily, being formed during multiphase oil, gas and water flow, from reservoir to wellhead. These tight emulsions could create unwanted blockage along the pathways of oil and gas flow, potentially limiting oil and gas recovery.

Generally speaking, the addition of surfactant can reduce the interfacial tension between oil and water, inhibit emulsification by reducing the solubility of oil and water. It also reduces oil adsorption on the rock and decrease the viscosity of crude oil by dispersing waxy compounds in the crude oil into the aqueous phase. Additionally, surfactants can help increase oil mobility through the reservoir, thus allowing better displacement of the oil by injected water or gas.

Linear and branched alkyl benzene sulfonates are one of the most commonly used surfactants in EOR (Enhanced Oil Recovery) applications. This family of chemicals is classified as anionic surfactants. However, conventionally formulated non-emulsifying surfactants based on sulfonates do not reduce or mitigate potential wax deposition inside newly created fractures during stimulation. Indeed, conventional non-emulsifying surfactants do not usually disperse and reduce efficiently wax deposit in the interior of the reservoir, because of lack of wax active compounds in its chemical compositions. Therefore, oil and gas recovery producers usually choose to incorporate multifunctional wax dispersant to increase the non-emulsifying effect during oil and gas recovery.

For example, US20170298710 relates to a method for treating subterranean formations with a treatment fluid comprising an aqueous base fluid and one multifunctional surfactant complex comprising at least one sulfonate-based surfactant and at least one polymeric additive, wherein the surfactant and the polymeric additive carry opposite charges; and introducing the treatment fluid into a well bore at a well site penetrating at least a portion of a subterranean formation. It is disclosed that the polymeric additive should carries a charge opposite to the surfactant, thus be cationic.

CN104650824A relates to an oil-gas bed well drilling anti-water blocking composition, which is an aqueous solution containing a surface-active ingredient, wherein the surface-active ingredient is jointly composed of a fluorocarbon surfactant and a biological surfactant. It is described that the biosurfactant is at least one of a lipopeptide, soybean lecithin, sophorolipid, and rhamnolipid.

US20200071600 discloses compositions and methods of microbial enhanced oil recovery using biochemical-producing microbes. In particular, low molecular weight glycolipids such as sophorolipids are discussed.

US8372786 discloses mixing a nanoparticle of polyanions and polycations with typical oilfield chemicals. In a follow-up publication (Yan Gao, Le T. Duc, Affira Ali, Beverly Liang, Jenn-Tai Liang, and Prajnaparamita Dhar Langmuir 2013 29 (11), 3654-3661 DOI: 10.1021/la400062b), it is described that sodium lauryl sulfate and polyethyleneimine were combined to form a nanoparticle for use in oil recovery additives.

The additives for oilfield applications reported in the above-indicated literatures respectively use different surface-active ingredients, but the compositions from polycations are generally complicated, inconvenient to use, and cost prohibitive. Therefore, it would be beneficial to develop a multifunctional wax dispersant composition which would be cost efficient but would also boost oil recovery by lowering interfacial tension, increasing oil mobility, thus allowing better displacement of the oil by injected treatment fluids.

BRIEF SUMMARY OF THE INVENTION

After thorough investigation, the inventors of the present invention have found that the wax dispersant composition as defined in claim 1 solves the above technical problem. Advantageously, as shown in the experimental part of the present invention, the wax dispersant composition according to the present invention can lower oil and water interfacial tension, increase oil mobility, thus allowing better displacement of the oil by injected water. Indeed, improving oil and water interfacial tension allows oil to pass more effectively through porous rocks.

Therefore, in a first aspect, the present invention relates to a wax dispersant composition as defined in claim 1, and its dependent claims.

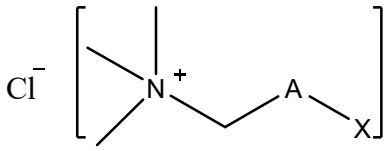
A second aspect of the invention is a method for preparing such compositions.

A third aspect of the invention is a method for increasing the recovery of oil and gas from oil and gas wells by using the wax dispersant composition according to the present invention.

DETAILED DESCRIPTION OF THE INVENTION

Wax dispersant composition according to the invention

The present invention relates to a wax dispersant composition for use in subterranean applications comprising a carrier medium, a compound A) and a compound B),
wherein the compound A) is a glycolipid biosurfactant selected from rhamnolipids, sophorolipids, glucolipids, cellulose lipids, mannosylerythritol lipids, trehalose lipids or a mixture thereof,
wherein the compound B) is a bifunctional quaternary ammonium chloride salt of Formula (IV)



Formula (IV)

wherein A is a branched or unbranched C_1 to C_4 alkyl residue,
wherein X is OY or NHY, wherein Y is H, C_1-C_3 alkyl residue, $COC(CH_3)=CH_2$, $COCH=CH_2$, $COC(CH_3)CH_3$, or $COCHCH_3$,
and wherein the weight ratio of compound A) to compound B) is from 5:1 to 0.2:1, and
wherein the total amount of compounds A) and B) is at least 20% by weight, based on the total weight of all compounds of the wax dispersant composition, not including the carrier medium.

It has been surprisingly observed that the salts B) of Formula (IV) drastically enhance the performance of the biosurfactant A) to boost oil recovery. By combining, according to a certain weight ratio as defined in claim 1, the biosurfactant compound A) with the bifunctional quaternary ammonium chloride salt of Formula (IV), the inventors have observed a synergistic effect between A) and B), in which they believe that the bifunctional quaternary ammonium chloride salt B) of Formula (IV) forms a complex with the biosurfactant A). This complex then behaves like a chemical cargo carrier, releasing its “cargo” chemical at a later time when encountering hydrocarbon compounds in downhole conditions during the oil recovery extraction process, as can be seen in the experimental part with longer emulsion times for the inventive wax dispersant compositions of the invention.

Preferably, the weight ratio of compound A) to compound B) in the wax dispersant composition is from 4.5:1 to 0.3:1.

The term "wax dispersant composition” in the context of the present invention refers to a mixture of surfactant based chemical agents that disperse and suspend visually or light microscopically identifiable wax aggregates that are not precipitating, but instead remain dispersed or suspended in bulk fluids. Indeed, to keep oil flowing and not depositing in downhole or flowlines, it is essential to avoid solid or gel sediments which are unsuitable for further processing on a large industrial scale, because crude oils with wax aggregates are difficult to pump without large pumping pressure drops.

The present invention discloses an additive composition (to be added to the treatment fluid as indicated in the section below “Use of the wax dispersant composition according to the invention“) that comprises water-soluble wax active surfactants A) and bifunctional ammonium quaternary salt compounds B) of Formula (IV). The wax dispersant composition according to the invention is multifunctional because it imparts at least the following properties:

- Disperse waxy crude oil in the aqueous phase
- Reduce surfactant adsorption on the reservoir rock
- Reduce surfactant precipitation in high salinity brine
- Reduce clay swelling
- Reduce or inhibit oil and water emulsion.

Preferably, the total amount of compounds A) and B) is from 20 to 100% by weight, preferably from 25 to 100% by weight, even more preferably from 30 to 100% by weight, based on the total weight of all compounds of the wax dispersant composition not including the carrier medium.

Preferably, the total amount of the carrier medium, the compound A) and the compound B) in the wax dispersant composition sum up to at least 50% by weight, more preferably to at least 60% by weight, even more preferably sum up from 70 to 100% by weight, most preferably sum up from 80 to 100% by weight, based on the total weight of the wax dispersant composition.

Carrier medium

Within the context of the present invention, the term “carrier medium” refers to the liquid in the wax dispersant composition of the invention and is preferably selected from the group consisting of water, acid, liquified hydrocarbon, or a mixture thereof, more preferably water.

Preferably, the total content of carrier medium in the wax dispersant composition is from 10 to 90% by weight, preferably 20 to 90% by weight, even more preferably from 30 to 90% by weight, most preferably from 50 to 90% by weight, based on the total weight of the wax dispersant composition.

Compounds A)

Within the context of the present invention, “biosurfactants” are understood as meaning all glycolipids produced by fermentation. The term “biosurfactant” also covers glycolipids that are chemically or enzymatically modified after fermentation, as long as structurally a glycolipid remains. Raw materials for producing the biosurfactants that can be used are carbohydrates, in particular sugars such as e.g. glucose and/or lipophilic carbon sources such as fats, oils, partial glycerides, fatty acids, fatty alcohols, long-chain saturated or unsaturated hydrocarbons.

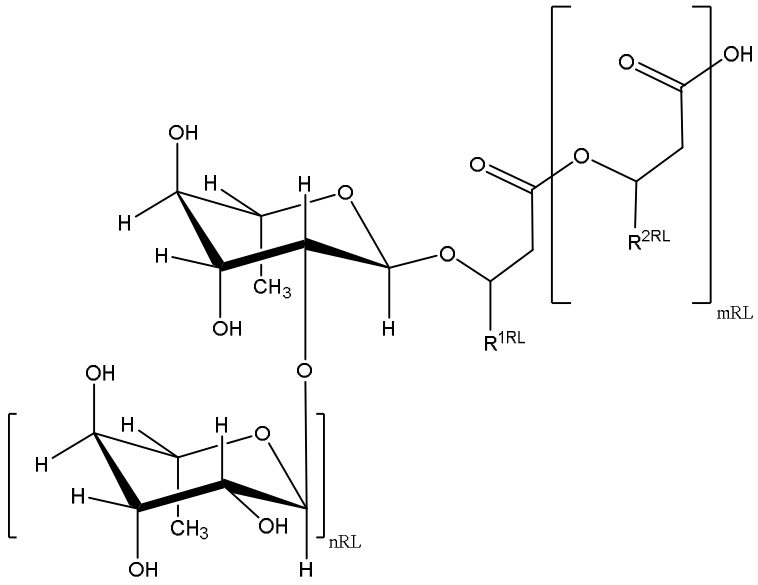
In the context of the present invention, the term “surfactant” is understood to mean organic substances having interface-active properties that has the ability to reduce the surface tension of water. Surface tension is typically determined by tensiometers such as the DuNoüy ring method.

The composition according to the present invention comprises, as compound A), at least one biosurfactant selected from rhamnolipids, sophorolipids, glucolipids, cellulose lipids, mannosylerythritol lipids and trehalose lipids, preferably rhamnolipids, sophorolipids and glucolipids, most preferably sophorolipids.

The biosurfactants can be produced e.g. as in EP 0 499 434, US 7,985,722, WO 03/006146, JP 60 183032, DE 19648439, DE 19600743, JP 01 304034, CN 1337439, JP 2006 274233, KR 2004033376, JP 2006 083238, JP 2006 070231, WO 03/002700, FR 2740779, DE 2939519, US 7,556,654, FR 2855752, EP 1445302, JP 2008 062179 and JP 2007 181789 or the documents cited therein. Suitable biosurfactants can be acquired e.g. from Soliance, France.

Preferably, the composition according to the present invention comprises, as compound A), at least one biosurfactant selected from rhamnolipids, preferably mono-, di- or polyrhamnolipids, glucolipids, preferably mono-, di- or polyglucolipids, and sophorolipids, preferably mono-, di- or polysophorolipids. Most preferred biosurfactants A) are sophorolipids.

The term "**rhamnolipids**" in the context of the present invention preferably is understood to mean particularly compounds of the general Formula (I), and salts thereof:



Formula (I)

wherein

mRL = 2, 1 or 0,

nRL = 1 or 0,

R^{1RL} and R^{2RL} = mutually independently, identical or different, organic residues having 2 to 24, preferably 5 to 13 carbon atoms, in particular optionally branched, optionally substituted, particularly hydroxy-substituted, optionally unsaturated, in particular optionally mono-, bi- or tri-unsaturated alkyl residues, preferably those selected from the group consisting of pentenyl, heptenyl, nonenyl, undecenyl and tridecenyl and $(CH_2)_o$-CH_3 wherein o = 1 to 23, preferably 4 to 12.

If nRL = 1, the glycosidic bond between the two rhamnose units is preferably in the α-configuration. The optically active carbon atoms of the fatty acids are preferably present as R-enantiomers (e.g. (R)-3-{(R)-3-[2-O-(α-L-rhamnopyranosyl)-α-L-rhamnopyranosyl]oxydecanoyl}oxydecanoate).

The term "mono-rhamnolipid" in the context of the present invention is understood to mean compounds of the general formula (I) or salts thereof, where nRL = 0. The term "di-rhamnolipid" in the context of the present invention is understood to mean compounds of the general formula (I) or salts thereof, where nRL = 1.

Distinct rhamnolipids are abbreviated according to the following nomenclature:
"diRL-CXCY" are understood to mean di-rhamnolipids of the general formula (I), in which one of the residues R^{1RL} and R^{2RL} = $(CH_2)_o$-CH_3 where o = X-4 and the remaining residue R^1 or R^2 = $(CH_2)_o$-CH_3 where o = Y-4.
"monoRL-CXCY" are understood to mean mono-rhamnolipids of the general formula (I), in which one of the residues R^{1RL} and R^{2RL} = $(CH_2)_o$-CH_3 where o = X-4 and the remaining residue R^{1RL} or R^{2RL} = $(CH_2)_o$-CH_3 where o = Y-4.
The nomenclature used therefore does not distinguish between "CXCY" and "CYCX".

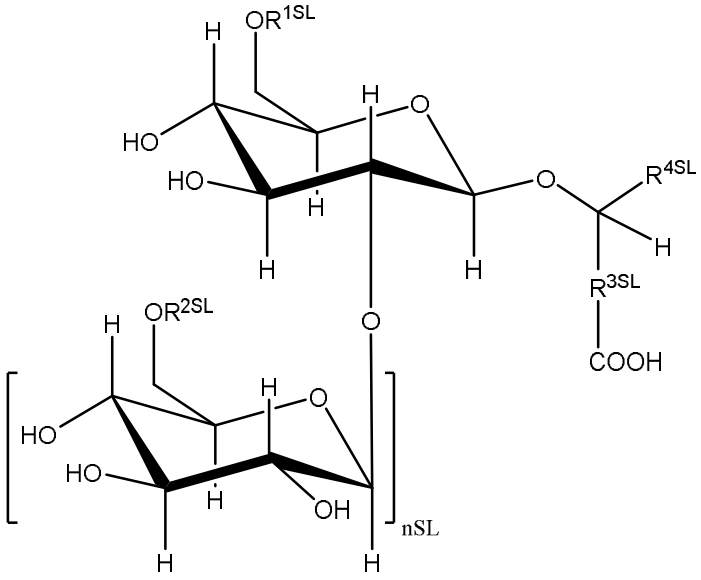
For rhamnolipids where mRL=0, monoRL-CX or diRL-CX is used accordingly.

If one of the abovementioned indices X and/or Y is provided with ":Z", this signifies that the respective residue R^{1RL} and/or R^{2RL} is equal to an unbranched, unsubstituted hydrocarbon residue having X-3 or Y-3 carbon atoms having Z double bonds.

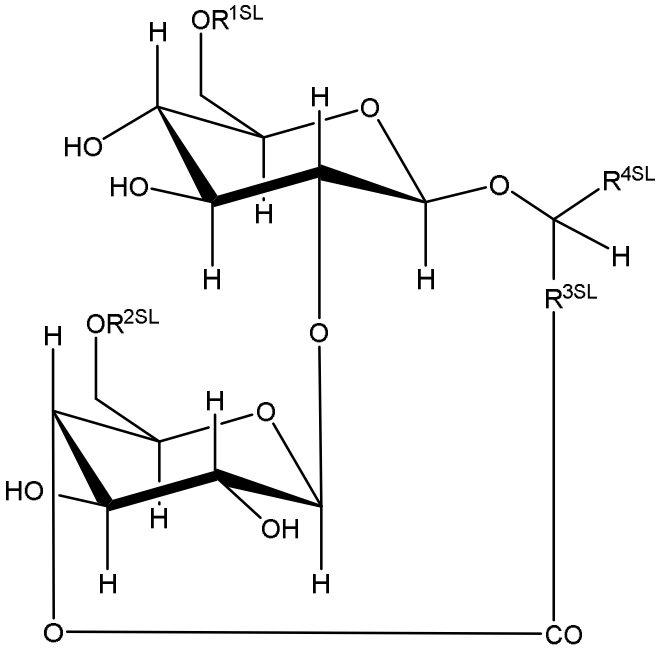
Methods for preparing the relevant rhamnolipids are disclosed, for example, in EP2786743 and EP2787065.

Rhamnolipids applicable in the context of the present invention can also be produced by fermentation of Pseudomonas, especially *Pseudomonas aeruginosa*, which are preferably non genetically modified cells, a technology already disclosed in the eighties, as documented e.g. in EP0282942 and DE4127908. Rhamnolipids produced in *Pseudomonas aeruginosa* cells which have been improved for higher rhamnolipid titres by genetical modification can also be used in the context of the instant invention; such cells have for example been disclosed by Lei *et al.* in Biotechnol Lett. 2020 Jun;42(6):997-1002.

In the context of the present invention, the term “**sophorolipids**” preferably is understood as meaning compounds of the general Formulae (IIa) and (IIb), and salts thereof:



Formula (IIa)



Formula (IIb)

wherein

R^{1SL} = H or CO-CH_3,

R^{2SL} = H or CO-CH_3,

R^{3SL} = a divalent organic moiety which comprises 6 to 32 carbon atoms and which is unsubstituted or substituted by hydroxyl functions, is unbranched and optionally comprises one to three double or triple bonds,

R^{4SL} = H, CH_3 or a monovalent organic radical which comprises 2 to 10 carbon atoms and which is unsubstituted or substituted by hydroxyl functions, which is unbranched and which optionally comprises one to three double or triple bonds, and

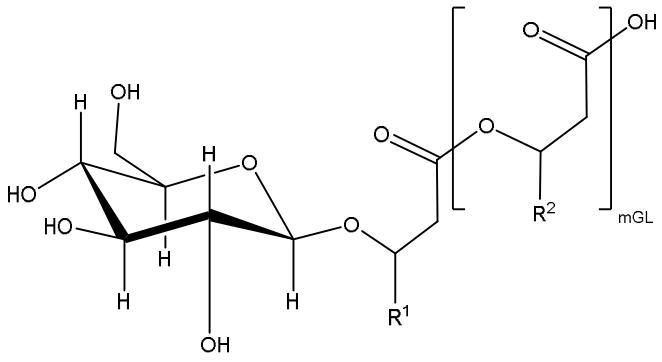
nSL = 1 or 0.

Sophorolipids may be used in accordance with the invention in their acid form or their lactone form.

Preferred compositions according to the present invention comprise a sophorolipid, in which the ratio by weight of lactone form to acid form is in the range of 20:80 to 80:20, especially preferably in the ranges of 30:70 to 40:60.

To determine the content of sophorolipids in the acid or lactone form in a formulation, refer to EP1411111B1, page 8, paragraph [0053].

In connection with the present invention, the term "**glucolipids"** preferably is understood as meaning compounds of the general formula (III) and salts thereof,



Formula (III)

wherein

mGL = 1 or 0,

R^{1GL} and R^{2GL} = independently of one another identical or different organic radical having 2 to 24 carbon atoms, in particular optionally branched, optionally substituted, in particular hydroxy-substituted, optionally unsaturated, in particular optionally mono-, di- or triunsaturated, alkyl radical, preferably one selected from the group consisting of pentenyl, heptenyl, nonenyl, undecenyl and tridecenyl and $(CH_2)_o$-CH_3 where o = 1 to 23, preferably 4 to 12.

Distinct glucolipids are abbreviated according to the following nomenclature:
"GL-CXCY" is understood as meaning glucolipids of the general formula (III) in which one of the radicals R^{1GL} and R^{2GL} = $(CH_2)_o$-CH_3 where o = X-4 and the remaining radical R^{1GL} or R^{2GL} = $(CH_2)_o$-CH_3 where o = Y-4.
The nomenclature used thus does not differentiate between "CXCY" and "CYCX".

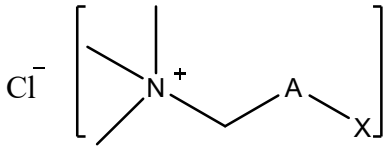
If one of the aforementioned indices X and/or Y is provided with ":Z", then this means that the respective radical R^{1GL} and/or R^{2GL} = an unbranched, unsubstituted hydrocarbon radical with X-3 or Y-3 carbon atoms having Z double bonds.

Methods for production of glucolipids can be carried out as described in WO2019154970.

According to the present invention, the most preferred compounds A) are sophorolipids.

Compounds B)

The compound B) according to the present invention is a bifunctional quaternary ammonium chloride salt of Formula (IV)



Formula (IV)

wherein A is a branched or unbranched C_1 to C_4 alkyl residue,
wherein X is OY or NHY, wherein Y is H, C_1-C_3 alkyl residue, $COC(CH_3)=CH_2$, $COCH=CH_2$, $COC(CH_3)CH_3$, or $COCHCH_3$.

Preferably, in Formula (IV) above, A is an unbranched C_1 to C_4 alkyl residue, more preferably an unbranched C_1 to C_2 alkyl residue.

Preferably, in Formula (IV) above, X is OY with Y=H or $COC(CH_3)=CH_2$, or X is NHY with $COC(CH_3)=CH_2$.

Preferably, the bifunctional quaternary ammonium chloride salt B) of Formula (IV) is selected from the group consisting of 3-trimethylammoniumpropyl methacrylamide chloride (MAPTAC), trimethylaminoethyl methacrylate chloride (TMAEMC), or a mixture thereof. Most preferred compound B) is 3-trimethylammoniumpropyl methacrylamide chloride.

Additional compounds

The wax dispersant composition according to the present invention may comprise further additives used in wax dispersant compositions to treat subterranean formations for the recovery of oil and gas from oil and gas wells used, such as compounds C) or D) described below.

Compounds C)

Preferably, the wax dispersant composition further comprises a compound C), which is a nonionic alcohol ethoxylate surfactant. These alcohol ethoxylates can be branched or linear and contain an ethylene oxide chain attached to a branched or linear alcohol.

Preferably, the alcohol ethoxylate A) is branched or linear and contain an ethylene oxide chain attached to a branched or linear alcohol of Formula $R(OC_2H_4)_nOH$, wherein R is an aliphatic hydrocarbyl radical containing from 6 to 16 carbon atoms, preferably 8 to 14 carbon atoms, and wherein n ranges from 2 to 14, preferably from 2 to 12.

Preferably, the alcohol ethoxylate A) has an average of 1 to 10 ethylene oxide groups with an HLB value of from 5 to 15.

Examples of alcohol ethoxylates are the ethoxylated alcohol product from Evonik, TOMADOL® 91-2.5, containing an average of 2.7 ethylene oxide groups with an HLB value of 8.5 (with the formula $R(OC_2H_4)_nOH$ wherein R is an aliphatic hydrocarbyl radical containing from 9 to 11 carbon atoms and with an average value of n being 2.7), or the ethoxylated alcohol product from Evonik, TOMADOL® 91-6, containing an average of 6 ethylene oxide groups with an HLB value of 12.4 (with the formula $R(OC_2H_4)_nOH$ wherein R is an aliphatic hydrocarbyl radical containing from 9 to 11 carbon atoms and with an average value of n being 6).

Compounds D)

According to another preferred aspect of the invention, the wax dispersant composition may further comprise a compound D), which is an alkylbenzene sulfonate, which belongs to the chemical groups of alkylbenzene sulfonates, which are anionic surfactants, consisting of a hydrophilic sulfonate head-group and a hydrophobic alkylbenzene tail-group. A particularly preferred compound D) is Triethanolamine TEA Dodecylbenzene Sulfonate (TEA-DDBSA).

Preferably, the amounts of the carrier medium, the compound A) and the compound B) in the wax dispersant composition, and optionally compounds C) and D), sum up to at least 90% by weight, more preferably from 90 to 100 % by weight, even more preferably sum up to from 95 to 100% by weight, most preferably sum up to 100% by weight, based on the total weight of the wax dispersant composition.

Process for preparing the wax dispersant composition of the invention

Another aspect of the present invention is a process for preparing a wax dispersant composition according to the invention, which comprises mixing water and the compounds A) and B) to provide the wax dispersant composition as defined above.

In a preferred embodiment, the compounds of the wax dispersant composition are mixed at room temperature (range of 18 to 25°C), preferably for at least 30 minutes to allow efficient mixing of the compounds.

Use of the wax dispersant composition according to the invention

A further aspect of the invention is the use of the wax dispersant composition according to the present invention for treating waxy crude oils and condensates to enhance oil recovery. In the context of the present invention, the wax dispersant composition is an additive composition which is added to the treatment fluid.

In particular, the present invention relates to a method for treating a crude oil with a wax dispersant composition according to the present invention to enhance oil recovery by reducing interfacial tension between the crude oil and the treatment fluid in the recovery of oil and gas from crude oil and gas wells.

In the context of the present invention, the term “crude oil” or “waxy crude oils and condensates” is equally defined as the crude oil that contains high amount of long chain paraffin wax (alkanes) compounds, making the crude possess a high pour point and become viscous at lower temperatures than wax appearance temperatures. The term “treatment fluid” refers to the carrier medium in field applications. Preferably, the treat rate of wax dispersant composition (additive composition) in the treatment fluid is from 0.01% to 1% by weight, based on the total weight of the treatment fluid injected for the recovery of oil and gas from crude oil and gas wells.

EXPERIMENTAL PART

The invention is further illustrated in detail hereinafter with reference to examples and comparative examples, without any intention to limit the scope of the present invention.

Abbreviations

Crude oil (i)	see Table 1 for the crude oil composition
EA	ethoxylated alcohol or amine
REWOFERM SL One(446)	sophorolipid with a lactone:acid ratio of 40:60, 50% active in water
REWOFERM SL P	sophorolipid with a lactone:acid ratio of 60:40, 50% active in water
SPL	sophorolipid
TEA-DDBSA	triethanolamine salt of dodecylbenzene sulfonic acid
POLYCARE133	Poly(Methacrylamidopropyltrimethylammonium) Chloride, 34% in water from Solvay
MAPTAC	3-trimethylammoniumpropyl methacrylamide chloride

Ethoxylated Alcohol 1 is an ethoxylated alcohol product from Evonik, TOMADOL® 91-6, containing an average of 6 ethylene oxide groups with an HLB value of 12.4.

MAPTAC is 3-trimethylammoniumpropyl methacrylamide chloride. VISIOMER® MAPTAC from Evonik was used in the examples and is provided 50% in water.

Sophorolipid-based biosurfactant 1 is REWOFERM SL One produced by Evonik, 50% in water, and Sophorolipid-based biosurfactant 2 is REWOFERM SL P produced by Evonik, 50% in water.

TEA-DDBSA is triethanolamine salt of linear alkylbenzene sulfonic acid. The product BIO-SOFT® N-300 from Stepan Company was used in the examples and corresponds to a is a 60% active aqueous solution of triethanolamine Dodecylbenzene Sulfonate (TEA-DDBSA).

Methods

Emulsion break test according to the invention

The emulsion break test was carried out by adding 10mL of crude oil to a 25mL graduated tube at ambient temperature. 10mL of tap water and the chemical treatment was added to the same graduated cylinder. The graduated tube was vortexed for one minute. After mixing, the mL of oil and

water layers were recorded every minute for the first 10 minutes, then once at 15, 20, 25, and 30 minutes. The “min to break” value represents the time at which the layers were separated and no further change in layer volume was recorded. This simple procedure permits easy testing of products to determine their effectiveness in breaking oil/water emulsions usually occurring with the contact of brine and crude oil under intense flow. Thus, the shorter the “min to break” value, the better the performance of the corresponding wax dispersant composition in crude oil recovery.

Pour point of the dispersions was measured according to ASTM D5853.

Wax Appearance Temperature (WAT), Wax Disappearance Temperature (WDT), and wax content of the crude oils were determined by differential scanning calorimetry.

The percentages by weight of saturates, aromatics, resins, and asphaltenes (SARA analysis) in the crude oils were determined using Iatroscan TLC-FID using the IP-469 standard method.

Crude oil properties

Table 1: Characteristics of the crude oil (i) used in the performance test of the wax dispersants

		Crude oil (i)
Wax content	[wt%]	2.8
Pour Point	[°C]	-33
Wax Appearance Temperature	[°C]	22.4
Wax Disappearance Temperature	[°C]	33
Saturates	[wt%]	54
Aromatics	[wt%]	30
Resins	[wt%]	15.4
Asphaltenes	[wt%]	0.8

Preparation of Comparative Example 1

Comparative Example CE 1 was prepared by adding 22g of REWOFERM SL P and 78g of water into a 200mL beaker. The compounds were blended using an overhead stirrer for 30min at room temperature. Crude oil (i) was treated with 1000ppm of CE1 by adding 0.1g of CE1 to 99.9g of crude oil (i) and blending at room temperature for 60 minutes.

All inventive examples and comparative examples were prepared following the same preparation process as for Comparative Example CE1, according to weight ratios as reflected in Table 2 below. Their corresponding performance with the waxy crude oil (i) is also given in Table 2.

Table 2: Performance of wax dispersant composition in crude oil (i)

			Comparative Examples								Inventive Examples										
Compound		Crude Oil (i)	CE1	CE2	CE3	CE4	CE5	CE6	CE7	CE8	Ex 1	Ex 2	Ex 3	Ex 4	Ex 5	Ex 6	Ex 7	Ex 8	Ex 9	Ex 10	Ex 11
REWOFERM SL One(446), 50wt% in water (compound A)	[wt%]*			11		1	1.35		9.5			2.5	4	5.5		7.5	7.5	4.9	2.45	8.5	9
REWOFERM SL P, 50% in water (compound A)	[wt%]*		11							7.5	7.5				7.5						
MAPTAC, 50wt% in water (compound B)	[wt%]*				11	10	0.65		1.75		3.5	8.5	7	5.5	3.75	3.5		1.65	0.8	2.5	2
POLYCARE 133, 34wt% in water	[wt%]									2.4											
Tomadol 91-6 (compound C)	[wt%]						18	22									2	9	16		
Water	[wt%]		89	89	89	89	80	78	88.75	90.1	89	89	89	89	88.75	89	88	84.45	80.75	89	89
Ratio A) to B) (xx :1)	[xx:1]		-	-	0	0.1	2.1	-	5.4	-	2.1	0.3	0.6	1.0	2.0	2.1	3.0	3.0	3.1	3.4	4.5
Total amount of A) and B) of all active compounds	[wt%]		100	100	100	100	10	0	100	100	100	100	100	100	100	100	83	50	30	100	100
Emulsion break @ RT, 1000ppm in Crude Oil i)	[min to break]	>30	>30	20	30	20	10	10	10	15	4	4	7	6	5	5	5	7	7	5	8

(*) wt% of active component only. The percentages do not include water carrier medium that is part of the wax dispersant composition.

(-) no compound B)

Result discussion

The untreated crude oil (i) had an emulsion result of more than 30 min as measured according to the above-indicated emulsion test.

Comparative Examples CE1 and CE2 only contain SPL, whereas inventive Examples 1-6 and 10-11 also contain MAPTAC. In the emulsion break test, CE1 and CE2 did not break until more than 30min and 20min, respectively, thus an emulsion break result comparable to the untreated crude oil i). In contrast, inventive Examples 1-6 and 10-11 show an emulsion break of from 4 to 8 minutes, thus a great improvement in comparison to the untreated crude oil (i) with an emulsion result of more than 30 min.

Comparative examples CE4 and CE7 contain both SPL and MAPTAC but demonstrate the importance of the ratio between compounds A) and B) to achieve good emulsion break performance. CE4 ratio of compounds A) to B) is 0.1:1 and CE7 ratio of compounds A) to B) is 5.3:1, which are lower and higher than the preferred range. The time required for the emulsion break was much higher than the inventive examples.

Comparative example CE8 corresponds to a mixture of a sulfonate-based surfactant and a polymeric additive POLYCARE 133, which is similar to the composition disclosed in US20170298710. Although an improvement in the emulsion break time is observed in comparison to the untreated crude oil, the time required for the emulsion break was still 15 min, which was much higher than for the crude oil treated with the inventive wax dispersant additive according to the invention which emulsion break time all lower than 8min. Thus, this type of surfactant composition is not as efficient in inhibiting the emulsification of the recovered crude oils.

Inventive Examples 7, 8, 9 contain the preferred ratio of compounds A) and B) and contain an additional formulation compound, TOMADOL 91-6. The emulsion break results remain good. Comparative example CE5 also incorporates TOMADOL 91-6, but the total amount of compounds A) and B) (relative to total active compounds) is now only 10wt%. The emulsion break result is 10min, showing that there must be a minimum amount of at least 20% by weight of compounds A) and B) for the product to be effective in emulsion break.

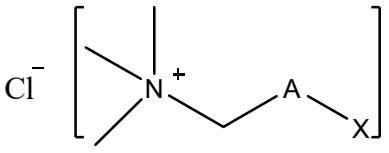
The experimental results show that the wax dispersant compositions of the present invention have improved oil recovery performance due to faster separation of the oil-water emulsions. The wax dispersant compositions of the present invention, combining some compounds at a certain weight ratio, allow to decrease the time before oil and water are separated. Thus, using the wax dispersant compositions in oil drilling boosts oil recovery by significantly lowering the interfacial tension between water and oil, thus increasing oil mobility by allowing better displacement of the oil by injected treatment fluids.

CLAIMS

1. A wax dispersant composition for use in subterranean applications comprising a carrier medium and

A) a biosurfactant selected from rhamnolipids, sophorolipids, glucolipids, cellulose lipids, mannosylerythritol lipids, trehalose lipids or a mixture thereof,

B) a bifunctional quaternary ammonium chloride salt of Formula (IV)



Formula (IV)

wherein A is a branched or unbranched C_1 to C_4 alkyl residue
X is OY or NHY, wherein Y is H, C_1-C_3 alkyl residue, $COC(CH_3)=CH_2$, $COCH=CH_2$, $COC(CH_3)CH_3$, or $COCHCH_3$,
and wherein the weight ratio of compound A) to compound B) is from 5:1 to 0.2:1, and
wherein the total amount of compounds A) and B) is at least 20% by weight, based on the total weight of all compounds of the wax dispersant composition, not including the carrier medium.

2. The composition according to claim 1, wherein the weight ratio of compound A) to compound B) is from 4.5:1 to 0.3:1.

3. The composition according to claim 1 or 2, wherein the total amount of compounds A) and B) is from 20 to 100% by weight, preferably from 25 to 100% by weight, even more preferably from 30 to 100% by weight, based on the total weight of all compounds of the wax dispersant composition not including the carrier medium.

4. The composition according to any one of the previous claims, wherein the compound A) is selected from the group consisting of rhamnolipids, sophorolipids, glucolipids or a mixture thereof.

5. The composition according to claim 4, wherein the compound A) is a sophorolipid, preferably sophorolipid, in which the ratio by weight of lactone form to acid form is in the range of 20:80 to 80:20, preferably in the range of 30:70 to 40:60.

6. The composition according to any one of the previous claims, wherein in Formula (IV) of compound B), A is an unbranched C_1 to C_4 alkyl residue, more preferably an unbranched C_1 to C_2 alkyl residue.

7. The composition according to any one of the previous claims, wherein in Formula (IV) of compound B), X is chosen within the group consisting of OY with Y being hydrogen or $COC(CH_3)=CH_2$, or NHY with Y being $COC(CH_3)=CH_2$.

8. The composition according to any one of the previous claims, wherein the bifunctional quaternary ammonium chloride salt B) of Formula (IV) is 3-trimethylammoniumpropyl methacrylamide chloride, trimethylaminoethyl methacrylate chloride, or a mixture thereof.

9. The wax dispersant composition according to any one of the previous claims, wherein the composition further comprises a compound C), which is a nonionic alcohol ethoxylate, preferably a alcohol ethoxylate with the Formula $R(OC_2H_4)_nOH$, wherein R is a branched or linear aliphatic hydrocarbyl radical containing from 6 to 16 carbon atoms, preferably 8 to 14 carbon atoms, and wherein n ranges from 2 to 14, preferably from 2 to 12.

10. The wax dispersant composition according to any one of the previous claims, wherein the composition further comprises a compound D), which is selected from an alkylbenzene sulfonate preferably triethanolamine salt of dodecylbenzene sulfonic acid.

11. The wax dispersant composition according to any one of the previous claims, wherein the carrier medium is selected from the group consisting of water, acid, liquified hydrocarbon, or a mixture thereof, preferably water.

12. The wax dispersant composition according to any one of the previous claims, wherein the total content of carrier medium in the composition is from 10 to 90% by weight, preferably 20 to 90% by weight, even more preferably from 30 to 90% by weight, based on the total weight of the wax dispersant composition.

13. The wax dispersant composition according to any one of the previous claims, wherein the total amount of carrier medium, compound A) and compound B) in the wax dispersant composition, sums up to 90% by weight, based on the total weight of the wax dispersant composition.

14. Method for preparing a wax dispersant composition as defined in any one of claims 1 to 13, comprising mixing a carrier medium and the compounds as defined in any one of claims 1 to 13 to provide a wax dispersant composition.

15. Method for treating a crude oil with a wax dispersant composition according to any one of claims 1 to 13 to reduce interfacial tension between the crude oil and a treatment fluid in the recovery of oil and gas from crude oil and gas wells.