



(51) International Patent Classification:

C10G 75/04 (2006.01) C09K 8/524 (2006.01)

(21) International Application Number:

PCT/US2018/039821

(22) International Filing Date:

27 June 2018 (27.06.2018)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

62/525,416 27 June 2017 (27.06.2017) US

(71) Applicant: **M-I L.L.C.** [US/US]; 5950 North Course Drive, Houston, TX 77072 (US).

(72) Inventors: **KHANDEKAR, Chandrashekhar, Yeshwant**; 5515 Barleycorn Lane, Katy, TX 77494 (US). **DESHPANDE, Pradyumna, Avinash**; 1415 Eldridge Parkway, Apt. 1137, Houston, TX 77077 (US). **REGNAULT DE LA MOTHE, Loic**; 3711 Shadow Wick Lane,

Houston, TX 77082 (US). **LI, Lingling**; 96 Olcott Way, Ridgefield, CT 06877 (US). **GADBERRY, James, Frederick**; 17 Chambers Road, Danbury, CT 06811 (US). **O'NEAL, Tiara**; 15 Hayestown Heights, Danbury, CT 06811 (US).

(74) Agent: **SMITH, David, J.** et al.; 10001 Richmond Avenue, IP Administration Center Of Excellence, Room 4720, Houston, TX 77042 (US).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(54) Title: WAX INHIBITOR COMPOSITIONS IN WINTERIZED CONDITIONS FOR PETROLEUM FLUIDS

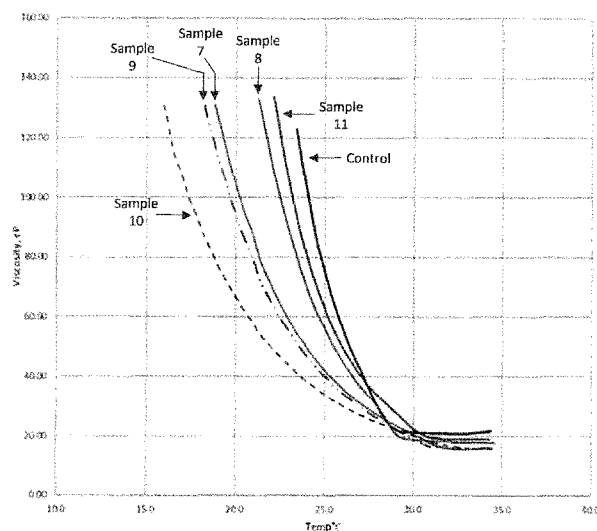


FIG. 1

(57) Abstract: A method of treating petroleum fluids includes adding a wax inhibitor composition to the petroleum fluids, the wax inhibitor composition, including a wax inhibitor; a non-ionic surfactant or a cationic surfactant; and a co-solvent blend. A method of treating a petroleum fluid, includes adding a wax inhibitor composition to the petroleum fluid, the wax inhibitor composition including a wax inhibitor; an anionic surfactant selected from at least one of an isopropylamine dodecylsulfonic acid salt or an isopropylamine linear dodecylbenzene sulfonate; and a co-solvent blend.

(84) Designated States (*unless otherwise indicated, for every kind of regional protection available*): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

- *with international search report (Art. 21(3))*
- *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))*

WAX INHIBITOR COMPOSITIONS IN WINTERIZED CONDITIONS FOR PETROLEUM FLUIDS

BACKGROUND

[0001] This application claims the benefit of and priority to a US Provisional Application having Serial No. 62/525416, filed 27 June 2017, which is incorporated by reference herein.

[0002] Produced petroleum fluids contain paraffins which may precipitate during the production process due to their cooling and/or depressurization upon removal from the earthen formation. For example, at low temperature paraffins may precipitate as large crystals or spherulites of wax in such a way as to form a gel structure which can cause produced petroleum fluids or other oil-based fluids to lose their ability to flow. Paraffin precipitation and deposition is a function of many parameters including but not limited to fluid composition, water cut, fluid velocity, temperature etc. Paraffins have a general chemical formula of C_nH_{2n+2} and petroleum hydrocarbons can contain paraffins from C_1 , where $n=1$, to C_{100+} . Usually C_{18+} paraffins present difficulties due to their precipitation and deposition as a result of cooling and depressurization processes.

[0003] Paraffin precipitation occurs when the process temperature falls below a critical temperature known as wax appearance temperature (WAT) and an increasing quantity of wax precipitates as the temperature of the process is reduced. As the temperature is decreased, some of the waxy components come out of solution as tiny crystals, and the solution begins to appear hazy to the naked eye. The temperature at which this occurs is called the cloud point. As additional wax precipitates, the crystals may grow into plates and, finally, if the temperature is decreased far enough, the plates may grow together to form a three-dimensional network that can totally immobilize the petroleum fluids. This solidification process is sometimes referred to as gelation. The lowest temperature at which the oil is fluid is called the pour point. Thus, wax deposits, once formed, can present significant challenges in production processes, problems such as plugging of flow lines and other equipment such as heat

exchangers, accumulation in storage tanks to form paraffin sludges, reduced production, stabilized emulsion, and accumulation of solids in the pipelines etc.

[0004] Wax deposition may be responsible for a reduction in oil production, and in terms of maintenance and removal of deposits already formed, increasing the cost of producing and transporting oil products. These issues cause a number of handling problems in regions where the service temperatures are, or become seasonally very low. The ability of an oil to flow under low-temperature, low-shear conditions is crucial to the operation of production equipment expected to run in cold climates. Without the proper selection and treat rate of a pour point depressant, an oil may exhibit poor low-temperature properties, leading, in the worst case, to lubrication “starvation” and equipment failure.

SUMMARY

[0005] This summary is provided to introduce a selection of concepts that are further described below in the detailed description. This summary is not intended to identify key or essential features of the claimed subject matter, nor is it intended to be used as an aid in limiting the scope of the claimed subject matter.

[0006] In one aspect, embodiments disclosed herein relate to a method of treating petroleum fluids that includes adding a wax inhibitor composition to the petroleum fluids, the wax inhibitor composition, including a wax inhibitor; a non-ionic surfactant or a cationic surfactant; and a co-solvent blend.

[0007] In another aspect, embodiments disclosed herein relate to a method of treating petroleum fluids that includes adding a wax inhibitor composition to the petroleum fluids, the wax inhibitor composition, including a wax inhibitor; an anionic surfactant selected from at least one of an isopropylamine dodecylsulfonic acid salt or an isopropylamine linear dodecylbenzene sulfonate; and a co-solvent blend.

[0008] Other aspects and advantages of the claimed subject matter will be apparent from the following description and the appended claims.

BRIEF DESCRIPTION OF DRAWINGS

[0009] FIGS. 1 and 2 show plots of the viscosity as a function of temperature for petroleum fluid samples treated according to the description in the examples.

DETAILED DESCRIPTION

[0010] As mentioned above, wax deposits, once formed, can present significant challenges in production processes. Several thermal, mechanical and chemical treatments are used to attempt to delay paraffin precipitation and subsequent deposition. Thermal techniques include pipeline insulation to preserve the heat, which can delay paraffin precipitation and subsequent deposition. While this is an effective technique, it is extremely uneconomical especially in long transportation pipelines and hence not commonly used. Hot oiling and hot watering is commonly used on land wells to melt or otherwise mobilize the paraffin deposits and is a relatively inexpensive technique. However, there are several drawbacks to thermal techniques such as the energy input required, paraffin re-deposition, and long term formation damage.

[0011] Pigging is a very commonly used mechanical treatment to remove paraffin deposits in the flow lines. This technique is very effective and used widely throughout industry, as a remediation technique to mitigate deposition issues. However, this technique merely treats the end-result of paraffin precipitation and does nothing to prevent the precipitation and deposition of paraffins in a system.

[0012] To overcome these challenges, particularly to stop the growth of wax crystals in hydrocarbon fluids, amounts of paraffin/wax inhibitors may be continuously added into the petroleum fluids. The paraffin/wax inhibitors modify and disrupt the normal paraffin crystal formation mechanism and thus decrease the crystal growth of paraffin/wax particles, thereby reducing their precipitation and deposition. These paraffin inhibitors may be polymers that possess long segments of repeating saturated or saturated and unsaturated carbon chains (C_8 - C_{50}) that are contained in or attached to a polymer backbone

[0013] The wax inhibitors, when added above the wax appearance temperature (WAT or the temperature at which waxes or paraffins in a petroleum fluid first crystallize), prevent or reduce paraffin deposition by modification of paraffin crystal size and

shape. However, it is extremely difficult to winterize paraffin/wax inhibitor polymers due to the low solubility they exhibit at low temperatures in the solvents that are used to formulate the inhibitor compositions. Thus, in order to make homogenous conventional inhibitor compositions, the polymers used for paraffin inhibition are highly diluted in solvents to achieve a low temperature stability. As a result of the high dilution factor needed, in practice large applications/dosages of the conventional inhibitor compositions are required to achieve the required inhibitor performance.

[0014] Embodiments disclosed herein relate generally to production chemical compositions, including wax inhibitor compositions, with improved winterization properties and methods of using said compositions. Improved winterization refers to the ability of compositions to remain stable and functional at low temperatures. For example, production chemicals are often stored in aboveground tanks and applied as needed. In regions of the world where temperatures may fall below the freezing/gel point of the production chemical compositions, their storage in aboveground tanks may result in the need for a higher dilution in a solvent to avoid their becoming unstable. Improved winterization of the production chemical compositions may improve their stability in colder environments and negate the need for a high dilution of the active ingredient.

[0015] More specifically, the present disclosure describes embodiments of wax inhibitor compositions that exhibit stability and are flowable at temperatures as low as -30 °C, or as low as -40 °C, or as low as -45 °C, or as low as -50 °C without need for significant dilution. In general, the wax inhibitor compositions of the present disclosure include a wax inhibitor, at least one surfactant, and a solvent system including at least two solvents.

[0016] Wax Inhibitor

[0017] In one or more embodiments, the wax inhibitor may be a copolymer of an alpha olefin monomer and an unsaturated dicarboxylic acid anhydride monomer, converted to an ester or imide. The alpha olefin monomer may have between 10 and 40 carbon atoms per molecule, or between 16 and 30 carbon atoms, or between 20 and 24 carbon atoms, individually or in combinations thereof. The alpha olefin monomer of the copolymer may comprise individual olefins or mixtures of various

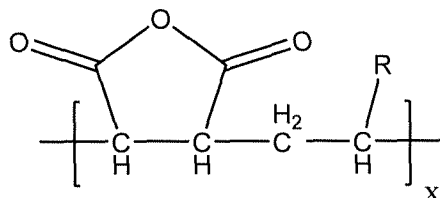
types of olefins. Further, the alpha olefin monomer of the copolymer may be linear or branched. Representative non-limiting examples of such alpha olefins include 1-decene, 1-undecene, 1-dodecene, 1-tridecene, 1-tetradecene, 1-pentadecene, 1-hexadecene, 1-heptadecene, 1-octadecene, 1-nonadecene, 1-eicosene, 1-docosene, 1-tetracosene, 1-hexacosene, 1-octacosene, 1-triacontene, 1-dotriacontene, 1-tetratriacontene, 1-hexatriacontene, 1-octatriacontene, or 1-tetracontene. In some embodiments, the alpha olefin monomer is a mixture of C20 to C24 components. For example, in one or more embodiments, the alpha-olefin monomers may be mixed alkyl olefins wherein the alkyl groups are about 60-90% (or 80-90% in particular embodiments) in the range of C20 to C24, with the rest of the alkyl components including C16, C18, and C26 to C30 alkyl groups.

[0018] In one or more embodiments, the unsaturated dicarboxylic acid anhydride monomer may be itaconic anhydride, citraconic anhydride, aconitic anhydride, acrylic anhydride, maleic anhydride, chloromaleic anhydride, dichloromaleic anhydride, citraconic anhydride, cyclohexyl maleic anhydride, benzyl maleic anhydride, phenyl maleic anhydride, propyl maleic anhydride, and 1,2-diethyl maleic anhydride, and other various alkyl maleic anhydrides. The unsaturated dicarboxylic acid anhydride monomers described above may be used individually or in combinations thereof. In some embodiments, the unsaturated dicarboxylic acid anhydride in the copolymer is maleic anhydride.

[0019] In one or more embodiments, the wax inhibitor may be an olefin maleic anhydride ester. More specifically, the wax inhibitor may be an alpha olefin maleic anhydride copolymer reacted via esterification (with an acid catalyst) with fatty alcohols and/or glycols having between 10 and 40 carbon atoms per molecule, or from between 14 and 28 carbon atoms per molecule. In one or more embodiments, up to 2 moles of the alcohol and/or glycol may be reacted with the copolymer. In one or more embodiments, the alcohol and/or glycol may be linear, cyclic or branched, saturated or unsaturated, or Guerbet alcohols, either individually or in combinations thereof. The olefin maleic anhydride ester may be prepared by reacting a fatty alcohol and/or glycol with a copolymer made from maleic anhydride monomers and alpha-olefin monomers.

[0020] In embodiments where maleic anhydride is used as a comonomer, the copolymer has a general formula according to Formula I below:

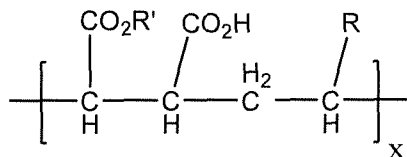
Formula I



wherein the R group is from the alpha olefin monomer and is one of a C16 to C30 alkyl group, as described above, and X= a value between 3 and 150. In embodiments where alkyl maleic anhydride is used as a comonomer, at least one of the hydrogens shown on the anhydride moiety of Formula I is instead a C12-C30 alkyl group, while the other hydrogen may remain a hydrogen or may also be a C12-C30 alkyl group. In one or more embodiments the copolymer produced from the alpha olefin monomer and the unsaturated dicarboxylic acid anhydride monomer may have a number average molecule weight (M_n) of about 1000 to 50000, or about 1500 to 30000 or about 2000 to 10000.

[0021] In some embodiments, the addition product is then esterified. Upon esterification of the copolymer of Formula I with the fatty alcohol and/or glycol, the olefin maleic anhydride ester according to Formula II may be created.

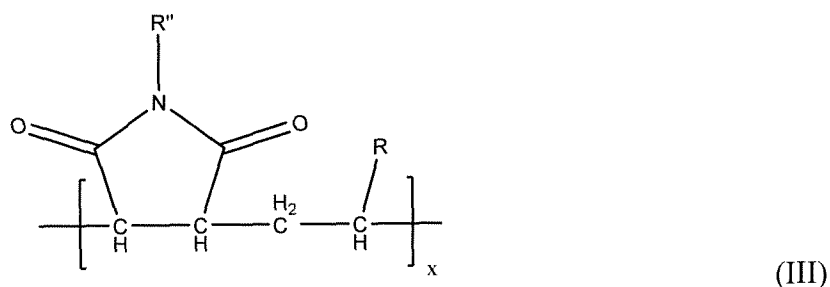
Formula II



wherein R and X are as described above and at least about 95% of the R' groups on the created olefin maleic anhydride ester may be C16 to C20 alkyl groups with the remainder being C14 and C22 alkyl groups. As discussed above, with respect to Formula I, in embodiments where alkyl maleic anhydride is used as a comonomer, at least one of the hydrogens shown on the esterified portion of Formula II is instead a C12-C30 alkyl group, while the other hydrogen may remain a hydrogen or may also

be a C12-C30 alkyl group. Thus, the resultant copolymer product contains both alkyl ester and carboxylic acid functionalities. In one or more embodiments, the copolymer is a C20 to C24 alpha olefin and maleic anhydride copolymer known as Armohib® PC-105, available from Akzo Nobel Surface Chemistry LLC.

[0022] In one or more embodiments, the resultant copolymer (nonesterified) may be further reacted with a suitable amine to form an imide of the copolymer, rather than an ester. Suitable amines may be a primary, secondary or tertiary amine, having the general formula of $R - NH_2$, wherein R is an alkylene group having from 2 to 30 carbon atoms per molecule. Such amines may include monoethylamine, isopropylamine, sec-butylamine, t-butylamine, n-pentylamine, tallow amine, hydrogenated tallow amine, cocoamine, soyamine, oleylamine, octadecylamine, hexadecylamine, dodecylamine, 2-ethylhexylamine, dehydrogenated tallowamine, N-coco-1,3-diaminopropane, N-tallow-1,3-diaminopropane, N-oleyl-1,3-diaminopropane, individually or in combinations thereof. In some embodiments, the amine is tallow amine, or hydrogenated tallow amine. When maleic anhydride is the copolymer, upon conversion with the above mentioned amine, an imide according to Formula (III) may be created:



[0023] wherein R is as described above and R'' is C8-30 or R'' is such that at least about 95% of the R'' groups on the imide functional group are C16 to C20 alkyl groups with the remainder being C14 and C22 alkyl groups, and X = a value between 3 and 150. As discussed above, with respect to Formula I, in embodiments where alkyl maleic anhydride is used as a comonomer, at least one of the hydrogens shown on the esterified portion of Formula III is instead a C12-C30 alkyl group, while the other hydrogen may remain a hydrogen or may also be a C12-C30 alkyl group.

[0024] In one particular embodiment, the imidized copolymer is an imide of a C18 alpha olefin and maleic anhydride copolymer reacted with hydrogenated tallow

amine, known as Armohib® PC-301H, available from Akzo Nobel Surface Chemistry LLC. In another particular embodiment, the imidized copolymer is an imide of a C24 to C28 alpha olefin and maleic anhydride copolymer reacted with tallow amine, known as Armohib® PC-308, available from Akzo Nobel Surface Chemistry LLC. In another particular embodiment, the copolymer is an imide of a C20 to C24 alpha olefin and maleic anhydride copolymer reacted with tallow amine, known as Armohib® PC-304, available from Akzo Nobel Surface Chemistry LLC.

[0025] In some embodiments, the resultant copolymer may be blended with ethylene vinyl acetate copolymer, solvent, and isopropylamine dodecylbenzene sulfonate. Such blend is known as Armohib® PC-150, available from Akzo Nobel Surface Chemistry LLC.

[0026] In one or more embodiments, the wax inhibitor composition may include a wax inhibitor as described above in an amount from a lower limit of any of 0.5, 1, 2, 3, or 5 percent by weight and an upper limit of any of 10, 12.5, 15, 20, 25, or 30 percent by weight, where any lower limit can be used in combination with any upper limit.

[0027] Surfactants

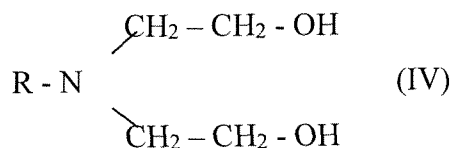
[0028] In one or more embodiments, the composition may include at least one surfactant selected from anionic surfactants, cationic surfactants, or non-ionic surfactants. In general the surfactant may make up 1% to 50% by weight of the wax inhibitor compositions according to the present disclosure. However, this value may vary depending on the exact surfactant type or combination of surfactants chosen for the wax inhibitor composition.

[0029] In one or more embodiments, an anionic surfactant used in the wax inhibitor compositions may be a sulfonic acid salt or sulfonate. More specifically, the anionic surfactant comprises an amine salt of a straight or branched chain alkylbenzene sulfonate salt in which the alkyl group contains from about 9 to about 18 carbon atoms, including nonyl benzene sulfonate (C9), decyl benzene sulfonate (C10), undecyl benzene sulfonate (C11), dodecylbenzene sulfonate (C12), tridecyl benzene sulfonate (C13), tetradecyl benzene sulfonate (C14), pentadecyl benzene sulfonate (C15), hexadecyl benzene sulfonate (C16), heptadecyl benzene sulfonate (C17) and

octadecyl benzene sulfonate (C18). Among these, dodecylbenzene sulfonate and mixtures of salts having carbon number of from 10 to 16 are more preferred.

[0030] The amine may be a primary, secondary or tertiary amine, having the general formula of $R - NH_2$, wherein R is an alkylene group having from 2 to 30 carbon atoms per molecule. Such amines may include monoethylamine, dimethylamine, triethylamine, diethyl methylamine, diethylamine, diglycol amine, ethylpropylamine, dipropylamine, isopropylamine, sec-butylamine, t-butylamine, n-pentylamine, tallowamine, hydrogenated tallowamine, cocoamine, soyamine, oleylamine, octadecylamine, hexadecylamine, dodecylamine, 2-ethylhexylamine, dicocoamine, ditallowamine, dehydrogenated tallowamine, didecylamine, dioctadecylamine, N-coco-1,3-diaminopropane, N-tallow-1,3-diaminopropane, N,N,N-trimethyl-N-tallow-1,3-diaminopropane, N-oleyl-1,3-diaminopropane, N,N,N-trimethyl-N-9-octadecenyl-1,3-diaminopropane, 3-tallowalkyl-1,3-hexahydropyrimidine, individually or in combinations thereof. In one or more embodiments, the anionic surfactant used in the wax inhibitor compositions may be an isopropylamine dodecylsulfonic acid salt or an isopropylamine linear dodecylbenzene sulfonate. An example of isopropylamine dodecylbenzene sulfonate is Witconate® 93S, available from Akzo Nobel Surface Chemistry LLC. When included, anionic surfactants may be included in the wax inhibitor compositions in an amount of a lower limit of any of 1, 2.5, 5, or 10 percent by weight and an upper limit of any of 40, 45, or 50 percent by weight, where any lower limit can be used with any upper limit.

[0031] In one or more embodiments, a cationic surfactant used in the wax inhibitor compositions may be at least one alkoxyated amine. Suitable alkoxyated amines include any ethoxylated amines or ethoxylated diamines capable of forming a water soluble salt. Examples include primary, secondary and tertiary (particularly tertiary) alkoxyated amines and alkoxyated diamines, ethoxylate ether amines, as well as mixtures thereof. In some aspects, the alkoxyated amine is an ethoxylated amine or ethoxylated diamine that is sold under the Ethomeen®, Ethomeen C/12, or Ethoduomeen® name, available from Akzo Nobel Surface Chemistry LLC. In some embodiments, the alkoxyated amine has the formula (IV)



wherein R is coconut oil derivative acids (e.g., $\text{CH}_3(\text{CH}_2)_{11}$)

[0032] In one or more embodiments, the ethoxylated aliphatic amine may be produced by reaction of an alkylamine with two molar equivalents of ethylene oxide. The alkyl group on the alkylamines may be derived from coconut fatty acids and may have a chain length distribution from C-8 to C-18, where about 70% of the alkyl groups are C-12 or C-14. When included, cationic surfactants may be included in the wax inhibitor compositions in an amount of a lower limit of any of 1, 2, 2.5, or 5 percent by weight and an upper limit of any of 35, 40, or 45 percent by weight, where any lower limit can be used with any upper limit.

[0033] In one or more embodiments, the non-ionic surfactant used in the wax inhibitor compositions may be selected from the group consisting of alkanolamides, alkoxyated alcohols, alkyl phenyl polyethoxylates, lecithin, hydroxylated lecithin, fatty acid esters, glycerol esters and their ethoxylates, glycol esters and their ethoxylates, esters of propylene glycol, sorbitan, ethoxylated sorbitan, polyglycosides and the like, and mixtures thereof. In one or more embodiments, the non-ionic surfactant used in the wax inhibitor compositions may be an alkoxyated alcohol, and more specifically may be an alcohol ethoxylate. The alcohol ethoxylate used herein may be an alkoxyated 2-propyl heptanol, which can be illustrated by the formula (V)



wherein A is an alkyleneoxy group having 2-4 carbon atoms and n is 2-16, preferably 3-12. Preferably, 50-100% of all alkyleneoxy groups are ethyleneoxy groups. In those cases where different alkyleneoxy groups are present in the same compound, they may be added randomly or in block. Generally, the alkoxyate is an ethoxylate having 2-7, preferably 3-5 ethyleneoxy groups.

[0034] The alkoxyated alcohols described above can be prepared by adding in a conventional manner in the presence of a conventional alkali catalyst, such as potassium hydroxide or sodium hydroxide, the above-mentioned amounts of alkylene oxide to 2-propyl heptanol.

[0035] In some aspects, the addition of ethylene oxide is performed using a conventional catalyst which gives a narrower distribution of added ethylene oxide than any alkali catalyst, such as NaOH or KOH. Examples of conventional catalysts giving a narrow distribution of added alkylene oxide are $\text{Ca}(\text{OH})_2$, $\text{Ba}(\text{OH})_2$, $\text{Sr}(\text{OH})_2$ and hydrotalcite. The reaction is preferably conducted in the absence of free water to reduce the amount of by-products and usually at a temperature of about 70° to about 180° C.

[0036] In some aspects, the nonionic surfactant is Ethylan® 1003, a nonionic surfactant of 2-propyl heptanol ethoxylate, available from Akzo Nobel Surface Chemistry LLC. When included, non-ionic surfactants may be included in the wax inhibitor compositions in an amount of a lower limit of any of 0.5, 1, 2.5 percent by weight and an upper limit of any of 15, 20, 25, 30, or 40 percent by weight, where any lower limit can be used in combination with any upper limit.

[0037] Solvent System

[0038] In one or more embodiments, the solvent system of the wax inhibitor composition may include two or more solvents. The solvent used in the composition may be chosen from the group including, but not limited, to aliphatic hydrocarbons including cyclic hydrocarbons (e.g., cyclohexane, cyclopentane), organic esters (i.e. ethyl acetate), aromatic hydrocarbons (e.g., benzene, toluene, xylene, light or heavy solvent naphtha, Aromatic 150), and ethers. The solvents are typically mixed with either any or all of the preceding components (anionic surfactants, nonionic surfactants, and/or cationic surfactants, and copolymer of alpha olefin and unsaturated dicarboxylic acid anhydride). Other solvents include lower alcohols such as methanol, ethanol, 1-propanol, 2-propanol and the like, glycols such as ethylene glycol, propylene glycol, diethylene glycol, dipropylene glycol, polyethylene glycol, polypropylene glycol, polyethylene glycol-polyethylene glycol block copolymers, and

the like, and glycol ethers such as 2-methoxyethanol, diethylene glycol monomethylether, 2-butoxyethanol, and the like, and water.

[0039] In some embodiments, the solvent system is present in an amount of about 45 to about 99 weight percent of the total weight of the composition, or more particularly from about 50 to about 95 weight percent of the total weight of the composition.

[0040] In one or more particular embodiments, the solvent system may include a saturated cyclic hydrocarbon solvent and an aromatic hydrocarbon solvent. In one or more embodiments, the solvent system may include cyclohexane in an amount from about 1.5% to 50%, or from 2.5% to 47.5%, or from 5% to 45% by weight of the wax inhibitor composition and also at least one solvent containing aromatics including heavy naphtha, xylene, toluene, and alkyl benzenes in an amount from 20 to 90%, or from 30% to 85%, or from 40% to 80% by weight of the wax inhibitor composition.

[0041] The wax inhibitor composition may also contain various optional ingredients for improving low temperature flowability and/or other properties, including, without limitation, antioxidants, corrosion inhibitors, cold flow improvers (including, without limitation, comb polymers, polar nitrogen compounds, compounds containing a cyclic ring system, hydrocarbon polymer, polyoxyalkylene compounds, mixtures thereof and the like), dehazers, demulsifiers, antifoaming agents, cetane improvers, cosolvents, corrosion inhibitors, scale inhibitors, biocides, and lubricity additives, either used individually or in combinations thereof.

[0042] Upon formulation with the solvents and surfactant, the wax inhibitor composition of the present disclosure may form a single phase system, *i.e.* a clear liquid without a suspension or emulsion. Further, the wax inhibitor composition of the present disclosure may have a reduced pour point when compared to wax inhibitor compositions that do not include a solvent system and surfactant according to what is described above for example by at least 2 degrees Celsius or at least 4 degrees Celsius.

[0043] In use, the wax inhibitor compositions according to one or more embodiments of the present disclosure may be mixed with petroleum fluids, including, but not limited to crude oil to minimize wax deposition. Crude oils, *i.e.* oil obtained directly from drilling and before refining, vary widely in their physical and chemical

properties from one geographical production region to another, and even from field to field. Crude oils are usually classified into three groups according to the nature of the hydrocarbons they contain: paraffinic, naphthenic, asphaltic, and mixtures thereof. The differences are due to the different proportions of the various molecular types and molecular sizes of the molecules making up the crude oil. Paraffinic crude oils often have a relatively high wax content, e.g. a wax content of 0.1 to 20% by weight percent of oil, or in some instances 3 to 5 wt %, measured at 10° C below the wax appearance temperature.

[0044] The mixing of the wax inhibitor compositions according to the present disclosure into a petroleum fluid may occur either downhole or aboveground, after the petroleum fluids have been produced from a reservoir. In one or more embodiments, the composition of the present disclosure may be added to a hydrocarbon fluid produced from a well at the well head or at the surface. For example, in some embodiments, the wax inhibitor composition may be added to a hydrocarbon fluid prior to transporting the hydrocarbon fluid in a pipeline or a tank. In one or more embodiments, the wax inhibitor composition may be mixed with the hydrocarbon fluid batch wise (e.g., in a tank prior to transport) or continually/continuously, such as added to a line containing flowing liquid hydrocarbon. Significantly, the wax inhibitor compositions does not require dilution and maintains liquidity and phase stability at low temperatures, thereby allowing the end user to directly dose the products as-is. .

[0045] The amount of wax inhibitor composition used in treating petroleum fluids will vary according to various factors such as the base fluid type, the paraffin content in the fluid, the n-paraffin carbon number distribution for the fluid, the type of polymers, the degree of WAT corrections desired, the ambient conditions, etc. The optimum dose rate is normally estimated by means of laboratory measurements such as wax appearance temperature, viscosity, gel strength, wax deposition tendency, etc. Therefore, there are no limitations in this regard. Thus, the copolymers may be added in effective amount, i.e., an amount sufficient to produce some reduction in the wax appearance temperature of a wax-containing fluid. Generally, however, the wax inhibitor composition may be added in a concentration of at least 50 ppm in some embodiments, and in a concentration of from 50 and 5000 ppm in other embodiments.

In some other embodiments, the concentration varies from 250 to 2000 ppm. Further, one skilled in the art would appreciate that ranges may depend on the types of oil being treated, and that the desirable amount is an amount sufficient to achieve the highest variance in WAT at the lowest dosage possible. In one or more embodiments, the amount of wax inhibitor composition mixed with the petroleum fluids may be about 1000 ppm.

[0046] At the temperature of the reservoir, hydrocarbons may be primarily liquid or gaseous. As the production stream rises to the surface and leaves the wellhead, the temperature and pressure start to decrease; the stream begins to cool from the elevated temperature and pressure as compared to the temperature and pressure of the wellhead. This chilling may have a number of effects, including gelling, undesirable rheology changes, or deposition of waxes, asphaltenes, etc., which may affect downstream production operations. The wax deposits formed may contain n- paraffins (linear alkanes) and small amounts of branched or isoparaffins and aromatic compounds (cycloparaffins, naphthalenes). The carbon number of paraffinic molecules present in wax deposits is may be C15 or higher and may reach up to C80. Studies have also indicated that the quantity of wax formation that will prevent flow or gel for an oil is quite small.

[0047] It is also understood that the wax inhibitor composition may be used alone or in combination with other additives including dewaxing auxiliaries, corrosion inhibitors, asphaltene inhibitors, scale inhibitors, hydrate inhibitors, antioxidants, lubricity additives, dehazers, conductivity improvers, cetane number improvers, sludge inhibitors, and the like.

[0048] Examples

[0049] Samples of wax inhibitor compositions were prepared and subjected to testing to determine their effectiveness. Table 1 below shows the formulation of the wax inhibitor compositions tested. The non-ionic surfactant was an alcohol ethoxylate prepared by the ethoxylation of 2-propylheptanol with three or five equivalents of ethylene oxide. The anionic surfactant was an isopropylamine linear dodecylbenzene sulfonate. The cationic surfactant was an ethoxylated aliphatic amine.

Table 1

Sample	Wax Inhibitor (%)	Non-Ionic Surfactant(%)	Anionic Surfactant(%)	Cationic Surfactant(%)	Cyclohexane (1 st Co-Solvent) (%)	Aromatics (2 nd Co-Solvent) (%)
1	10	-	30	-	10	50
2	10	-	30	-	40	20
3	10	-	20	-	28	42
4	10	3.5	20	-	36.8	29.8
5	10	-	-	-	10	80
6	10	7.5	-	-	25.6	55.6
7	10	-	-	23.5	36.8	29.8
8	7	-	-	8	26	59
9	7	-	-	12	26	55
10	5	-	-	9.3	25.4	60.3
11	5	-	-	33.3	40.8	20.9

[0050] Test Results

[0051] The above samples were subjected to a variety of tests including a low temperature centrifuge test, a static low temperature test, and a test to determine a sample's pour point. In the low temperature centrifuge test, a volume of the particular sample was centrifuged for 6 hours at -9 °C to see if there is any precipitation at high shear conditions. In the static low temperature test, a volume of the particular sample was held in static conditions at -10 °C for four days to see if there is precipitation or solidification of the sample. The pour point tests were conducted using a MPP 5Gs mini pour point tester, available from PAC LP, the tester using ASTM Ref: D7346-14 and D7689-11 test methods. The results of these tests are shown in Table 2 below.

Table 2

Sample	Centrifuge Test	Static Test	Pour Point (°C)
1	Liquid	Unstable	-34
2	Liquid	Unstable	-37
3	Liquid	Unstable	-30
4	Liquid	Unstable	-30
5	Liquid	Unstable	-27
6	Liquid	Unstable	-27
7	Liquid	Liquid	-21
8	Liquid	Liquid	-30
9	Liquid	Liquid	-27

10	Liquid	Liquid	-18
11	Liquid	Liquid	-30

[0052] Wax Inhibition Test

[0053] Samples 1-11 were dosed into oil samples collected from South Texas oil fields and tested on a cold finger unit and their performance was evaluated against untreated oil samples (blank). During the test an 80 mL volume of each oil sample was heated by water bath to about 140 °F prior to the addition of the wax inhibitors of Samples 1-11. The wax inhibitors were dosed into the heated oil samples at a concentration of 1000 ppm and the sample jars with the oil samples were sealed and shaken before being placed back into the 140 °F water bath for 1 hour. The oil samples were then attached to a cold finger apparatus and the apparatus (including the sample jar) was placed in a water bath preheated to 130 °F with stirring. After 30 minutes at 130 °F, the test is started by setting the bath temperature to 80 °F and cooling the cold finger to 35 °F. After 20 hours under these conditions, the apparatus is removed from the bath, and the deposit is retrieved from the cold finger and weighed.

[0054] The weight of the deposit formed by a fluid containing a wax inhibitor treatment (e.g., Sample 1-11) is compared to the weight of a deposit formed by a fluid not containing a wax inhibitor treatment (e.g., blank) to calculate a percentage inhibition for each treatment tested. More specifically the following formula is used to determine the percentage inhibition:

$$\text{Percent Inhibition} = (W_u - W_t) / W_u * 100$$

where W_u is the weight of the deposit obtained from the untreated sample and W_t is the weight of the deposit obtained from the treated sample. The results of the wax inhibition tests are shown in Table 3 below.

Table 3

Sample	Oil Sample 1		Oil Sample 2	
	Wax Deposit Weight (g)	% Inhibition	Wax Deposit Weight (g)	% Inhibition
Blank	1.240	---	2.790	---

1	0.317	75.502	1.014	63.656
2	0.512	60.433	1.18	57.706
3	0.306	76.352	1.0140	63.656
4	0.626	51.623	0.815	71.038
5	0.614	52.70	0.41	85.430
6	0.276	78.74	1.1	60.910
Sample	Oil Sample 3		Oil Sample 4	
	Wax Deposit Weight (g)	% Inhibition	Wax Deposit Weight (g)	% Inhibition
Blank	2.892	---	1.94	---
7	0.776	73.2	1.03	46.6
8	1.512	47.7	1.439	25.8
9	1.498	48.2	1.425	26.46
10	2.266	21.0	1.522	21.54
11	1.74	39.6	1.145	40.97

[0055] Flow Improver Test

[0056] The treatment of petroleum fluids with the wax inhibitor compositions of samples 6-11 were tested for their ability to improve the flow of the petroleum fluids at low temperature. The wax inhibitor compositions were dosed into two Romanian sourced petroleum fluid samples in an amount that provides 1000 ppm of the wax inhibitor chemical to the petroleum fluids. The viscosity of the petroleum fluids as a function of temperature were then tested using a Brookfield viscometer. FIGS. 1 and 2 show the viscosity of the petroleum fluids as a function of temperature. The sample labeled "Control" in each figure was not dosed with a wax inhibitor composition and thus represents the viscosity of only the petroleum fluid sample.

[0057] Although only a few example embodiments have been described in detail above, those skilled in the art will readily appreciate that many modifications are

possible in the example embodiments without materially departing from this invention. Accordingly, all such modifications are intended to be included within the scope of this disclosure as defined in the following claims.

CLAIMS

What is claimed:

1. A method of treating petroleum fluids, comprising:
adding a wax inhibitor composition to the petroleum fluids, the wax inhibitor composition, comprising:
a wax inhibitor;
a non-ionic surfactant or a cationic surfactant; and
a co-solvent blend.
2. The method of claim 1, wherein the wax inhibitor is an alpha olefin maleic anhydride copolymer.
3. The method of claim 1, wherein the copolymer is converted to an ester or imide.
4. The method of claim 1, wherein the wax inhibitor is about 0.5% to 15% by weight of the composition.
5. The method of claim 1, wherein the surfactant is a non-ionic surfactant.
6. The method of claim 5, wherein the non-ionic surfactant is an alcohol ethoxylate.
7. The method of claim 5, wherein the non-ionic surfactant is about 0.5% to 25% by weight of the composition.
8. The method of claim 1, wherein the surfactant is a cationic surfactant.
9. The method of claim 8, wherein the cationic surfactant is an ethoxylated aliphatic amine.
10. The method of claim 8, wherein the cationic surfactant is about 2.5% to 45% by weight of the composition.
11. The method of claim 1, wherein the co-solvent blend includes saturated cyclic hydrocarbons and aromatic hydrocarbons.

12. The method of claim 11, wherein the saturated cyclic hydrocarbons are about 1.5% to 50% by weight of the composition and the aromatic hydrocarbons are about 20 to 90% by weight of the composition.
13. The method of claim 1, wherein the wax inhibitor composition is added to the petroleum fluids at a concentration of 50 to 5000 ppm.
14. A method of treating a petroleum fluid, comprising:
 - adding a wax inhibitor composition to the petroleum fluid, the wax inhibitor composition, comprising:
 - a wax inhibitor;
 - an anionic surfactant selected from at least one of an isopropylamine dodecylsulfonic acid salt or an isopropylamine linear dodecylbenzene sulfonate; and
 - a co-solvent blend.
15. The method of claim 14, wherein the wax inhibitor is an alpha olefin maleic anhydride copolymer.
16. The method of claim 15, wherein the copolymer is converted to an ester or imide.
17. The method of claim 14, wherein the wax inhibitor is about 0.5% to 15% by weight of the composition.
18. The method of claim 14, wherein the anionic surfactant is about 5% to 50% by weight of the composition.
19. The method of claim 14, wherein the co-solvent blend includes saturated cyclic hydrocarbons and aromatic hydrocarbons.
20. The method of claim 19, wherein the saturated cyclic hydrocarbons are about 1.5% to 50% by weight of the composition and the aromatic hydrocarbons are about 20 to 90% by weight of the composition.
21. The method of claim 14, wherein the wax inhibitor composition is added to the petroleum fluid at a concentration of 50 to 5000 ppm.

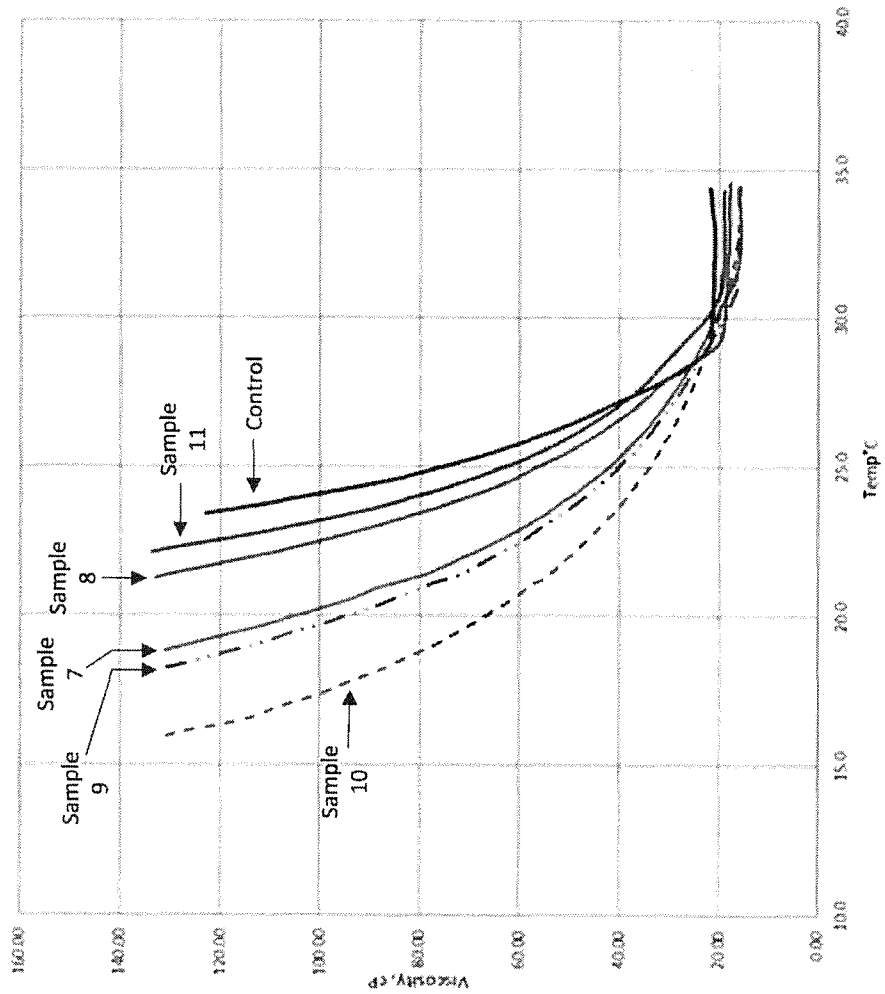


FIG. 1

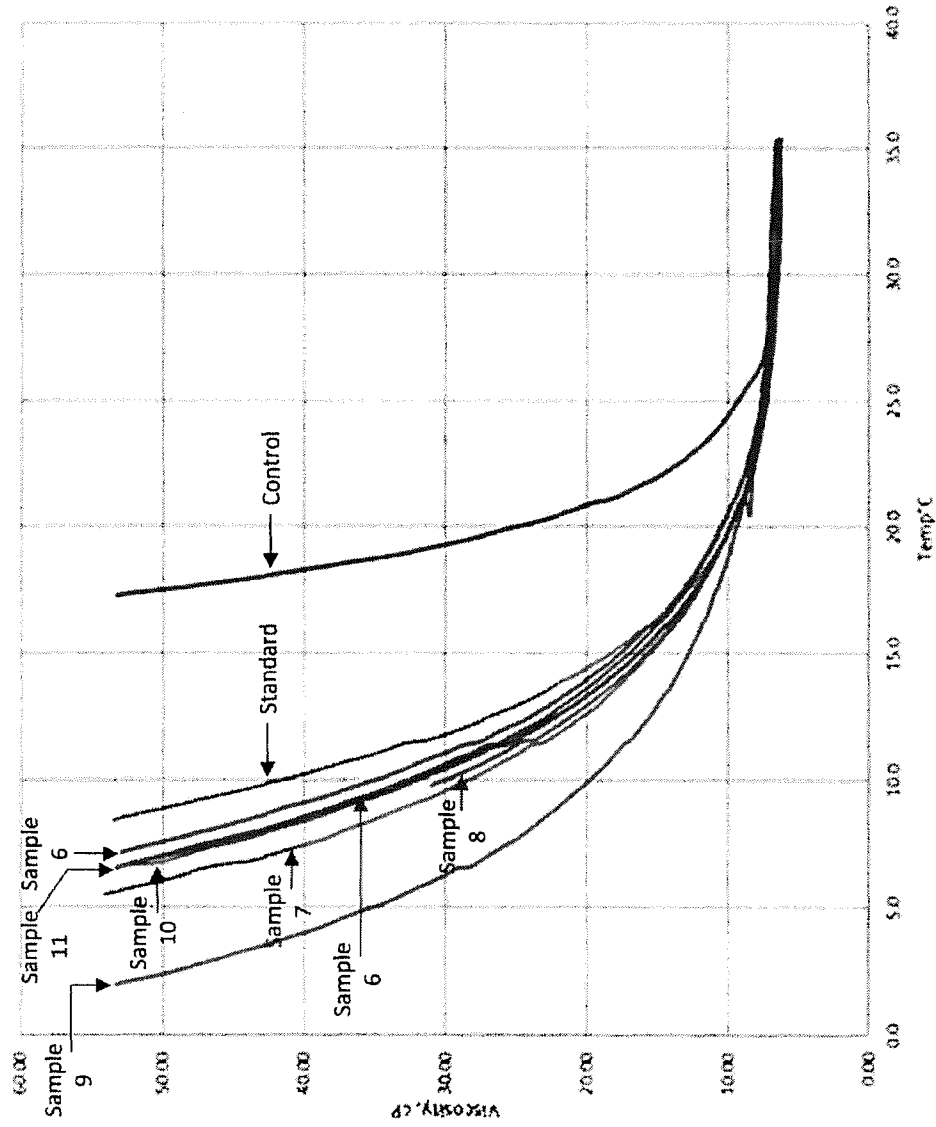


FIG. 2

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 2018/039821

A. CLASSIFICATION OF SUBJECT MATTER														
C10G 75/04 (2006.01) C09K 8/524 (2006.01) 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)														
C10G 75/04, C09K 8/524														
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 practicable, search terms used)														
PatSearch, esp@cenet, USPTO, Google														
C. DOCUMENTS CONSIDERED TO BE RELEVANT														
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.												
X	US 6342553 B1 (BP CHEMICALS LIMITED) 29.01.2002, col. 1 lines 9-51, col. 10 line 53 - col. 11 lines 11, 22-30, col. 13 lines 48-56, col. 14 lines 12-20	1, 4-5, 7-8, 10, 14, 17-18												
Y		2-3, 11-13, 15-16, 19-21												
A		6, 9												
Y	US 2002/0166995 A1 (ISP INVESTMENTS INC.) 14.11.2002, paragraphs [0002], [0022]-[0023]	2, 11-12, 15, 19-20												
☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.														
<table border="0"> <tr> <td>* Special categories of cited documents:</td> <td>“T” later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</td> </tr> <tr> <td>“A” document defining the general state of the art which is not considered to be of particular relevance</td> <td>“X” document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</td> </tr> <tr> <td>“E” earlier document but published on or after the international filing date</td> <td>“Y” document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</td> </tr> <tr> <td>“L” document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</td> <td>“&” document member of the same patent family</td> </tr> <tr> <td>“O” document referring to an oral disclosure, use, exhibition or other means</td> <td></td> </tr> <tr> <td>“P” document published prior to the international filing date but later than the priority date claimed</td> <td></td> </tr> </table>			* Special categories of cited documents:	“T” later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention	“A” document defining the general state of the art which is not considered to be of particular relevance	“X” document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone	“E” earlier document but published on or after the international filing date	“Y” document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art	“L” document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	“&” document member of the same patent family	“O” document referring to an oral disclosure, use, exhibition or other means		“P” document published prior to the international filing date but later than the priority date claimed	
* Special categories of cited documents:	“T” later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention													
“A” document defining the general state of the art which is not considered to be of particular relevance	“X” document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone													
“E” earlier document but published on or after the international filing date	“Y” document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art													
“L” document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	“&” document member of the same patent family													
“O” document referring to an oral disclosure, use, exhibition or other means														
“P” document published prior to the international filing date but later than the priority date claimed														
Date of the actual completion of the international search		Date of mailing of the international search report												
05 October 2018 (05.10.2018)		25 October 2018 (25.10.2018)												
Name and mailing address of the ISA/RU: Federal Institute of Industrial Property, Berezhkovskaya nab., 30-1, Moscow, G-59, GSP-3, Russia, 125993 Facsimile No: (8-495) 531-63-18, (8-499) 243-33-37		Authorized officer T. Gladysenko Telephone No. 8 (495)-531-64-81												

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 2018/039821

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4045360 A (UNION OIL COMPANY OF CALIFORNIA) 30.08.1977, col. 1 lines 14-46, col. 2 lines 37-46, col. 3 lines 37-42, col. 5 line 66 - col. 6 lines 13, 26-38	13, 21
Y	US 2013/0087480 A1 (BAKER HUGHES INCORPORATED) 11.04.2013, paragraph [0017]	3, 16