

C08L 25/08 (2018.01)
 C08L 35/06 (2018.01)
 C08L 87/00 (2018.01)
 C09K 8/52 (2018.01)
 C09K 8/524 (2018.01)
 C09K 8/58 (2018.01)
 C09K 8/588 (2018.01)
 F17D 1/16 (2018.01)

FASCICULE DE BREVET D'INVENTION

21 Numéro de dépôt : 1202000196
PCT/US2018/064157

22 Date de dépôt : 06/12/2018

30 Priorité(s) :
US n° 62/595,960 du 07/12/2017

24 Délivré le : 14/12/2021

45 Publié le : 30/12/2021

73 Titulaire(s) :

M-I L.L.C.,
 5950 North Course Drive,
 HOUSTON,
 Texas 77072 (US)

72 Inventeur(s) :

DESHPANDE, Pradyumna Avinash (US)
 KHANDEKAR, Chandrashekhar Yeshwant (US)
 COLE, Rachael Anne (NO)
 NORDVIK, Tore (NO)

74 Mandataire : SPOOR & FISHER Inc. NGWAFOR &
 PARTNERS Sarl, The House of Gideon,
 Golf/Bastos Quarters, Opposite The American
 Embassy, Entrance-Saint John Paul II Boulevard,
 P.O. Box 8211, YAOUNDE (CM).

54 Titre : Composition of a flow improver and method of using the same in hydrocarbon fluids.

57 Abrégé :

A flow improver composition may include a branched dendritic core having a first quaternary carbon center bonded to four second carbon atoms, where in at least three of the four second carbon atoms are individually bonded to one or more chain extender ligands to produce the branched dendritic core, wherein the branched dendritic core has greater than or equal to about 16 terminal hydroxyl groups, wherein at least one terminal hydroxyl group is esterified with at least one carboxylic acid moiety comprising of 6 to 30 carbon atoms or a combination, and wherein the dendritic core has no nitrogen atom; a polymeric inhibitor having an alkyl side chain of 2 to 40 carbon atoms; and an aromatic solvent.

COMPOSITION OF A FLOW IMPROVER AND METHOD OF USING THE SAME IN HYDROCARBON FLUIDS

BACKGROUND

This application claims the benefit of U.S. Provisional Application having Serial No. 62/595960 filed on 7 December 2017, the entire contents of which are incorporated herein by reference in their entirety.

5 Hydrocarbon fluids, during the production and transportation from reservoir to the surface and onward to refinery undergo pressure and temperature changes. These changes along with changes in operating conditions can lead to destabilization and precipitation of various components in the fluids (e.g., paraffins, asphaltenes, scales,). Under favorable conditions, these precipitated components can cause significant flow assurance challenges including, but not limited to, an
10 increase in fluid viscosity and deposition of solids on pipeline surfaces. These, in turn, can then cause numerous operational challenges such as flow restriction in a pipeline, increased solids during pigging operations leading to decreased cleaning efficiency, or higher pipeline back pressure leading to lower throughput. Various thermal, mechanical and chemical methods are used to prevent and mitigate the precipitation and deposition of these components and to subsequently avoid costly
15 delays due to their interference in the production and transportation process. These remedial methods include pigging or scraping, insulating equipment and flow lines to prevent loss of heat, applying heat by means of a heated liquid (e.g., hot oil or hot water), using a heat generated reaction, or the application of inhibitors, dispersants or solvents.

 Paraffin precipitation, deposition, and its effect of fluid flow in a pipeline remains one of the
20 biggest challenge in the oilfield industry. Precipitation of paraffin (C_nH_{2n+2}) from hydrocarbons is a function of primarily temperature, however there are other parameters, such as pressure, that affect the solubility of paraffin in hydrocarbon fluids and can cause its precipitation. These precipitated paraffin's, under favorable conditions tend to form deposits inside pipelines, vessels and other oilfield equipment causing several problems such as reduction in the flow, higher back pressures,
25 increased fluid viscosity, higher solids in the fluid leading to stable emulsions and oil water separation problems. To overcome these challenges, various thermal, mechanical and chemical methods are used in the oilfield industry including pigging, scraping, hot oiling and using paraffin inhibitors, pour point depressants, paraffin dispersants, paraffin solvents and combinations thereof.

Paraffin inhibitors, typically crystalline/amorphous polymers, also known as wax crystal modifiers, are used in oil field industry to delay the onset of wax precipitation in hydrocarbon fluids and to mitigate the extent of wax deposition on the metal surfaces. These polymers, usually formulated in aliphatic or aromatic solvents, are injected above the wax appearance temperature (“WAT”). A part of the wax inhibitor, which co-crystallizes with the paraffin’s has a structure that is similar to the waxes and is nonpolar in nature. There is typically a polar component present in the structure which limits the degree of co-crystallization. The paraffin inhibitors /wax crystal modifiers interfere with the wax crystallization by modifying the wax crystal morphology. The ill formed crystal (also called a malcrystal) cannot form networks thereby preventing deposition of wax on the pipeline surface.

SUMMARY

Embodiments disclosed herein relate to a flow improver composition that includes a branched dendritic core having a first quaternary carbon center bonded to four second carbon atoms, where in at least three of the four second carbon atoms are individually bonded to one or more chain extender ligands to produce the branched dendritic core, wherein the branched dendritic core has greater than or equal to about 16 terminal hydroxyl groups, wherein at least one terminal hydroxyl group is esterified with at least one carboxylic acid moiety comprising of 6 to 30 carbon atoms or a combination, and wherein the dendritic core has no nitrogen atom; a polymeric inhibitor having an alkyl side chain of 2 to 40 carbon atoms; and an aromatic solvent.

In another aspect, embodiments disclosed herein relate to a method that includes adding a flow improver composition that includes a branched dendritic core having a first quaternary carbon center bonded to four second carbon atoms, where in at least three of the four second carbon atoms are individually bonded to one or more chain extender ligands to produce the branched dendritic core, wherein the branched dendritic core has greater than or equal to about 16 terminal hydroxyl groups, wherein at least one terminal hydroxyl group is esterified with at least one carboxylic acid moiety comprising of 6 to 30 carbon atoms or a combination, and wherein the dendritic core has no nitrogen atom; a polymeric inhibitor having an alkyl side chain of 2 to 40 carbon atoms; and an aromatic solvent to a first hydrocarbon fluid to produce a second hydrocarbon fluid.

In yet another aspect, embodiments disclosed herein relate to a method that includes extracting a hydrocarbon fluid from a well; and adding a flow improver composition that includes a branched dendritic core having a first quaternary carbon center bonded to four second carbon atoms,

where in at least three of the four second carbon atoms are individually bonded to one or more chain extender ligands to produce the branched dendritic core, wherein the branched dendritic core has greater than or equal to about 16 terminal hydroxyl groups, wherein at least one terminal hydroxyl group is esterified with at least one carboxylic acid moiety comprising of 6 to 30 carbon atoms or a combination, and wherein the dendritic core has no nitrogen atom; a polymeric inhibitor having an alkyl side chain of 2 to 40 carbon atoms; and an aromatic solvent to the hydrocarbon fluid.

Other embodiments disclosed herein relate to a method for inhibiting the deposition of paraffin from a hydrocarbon fluid that includes adding an improver to the hydrocarbon fluid, and to a method for adding to subterranean well.

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.

DETAILED DESCRIPTION

The following detailed description is of the best currently contemplated modes of carrying out the various aspects of this disclosure. The description is not to be taken in a limiting sense, but is made merely for the purpose of illustrating the general principles of the disclosure, since the scope of the disclosure is best defined by the appended claims.

In the following description, numerous specific details are set forth to provide a thorough understanding of the present disclosure. However, details unnecessary to obtain a complete understanding of the present disclosure may have been omitted in as much as such details are within the skills of persons of ordinary skill in the relevant art.

Broadly, the present disclosure provides compositions of a flow improver for treating a fluid, and more specifically, a hydrocarbon fluid. For purposes herein, a hydrocarbon fluid refers to any fluid which comprises a hydrocarbon. Hydrocarbon fluids of the present disclosure may include crude oil, crude oil condensate, and the various streams which are produced during extraction of hydrocarbons from wells. Also included are refined streams including various fuel oils, diesel fuel, kerosene, gasoline, and the like.

Broadly, the present disclosure generally provides compositions of a flow improver for treating a hydrocarbon fluid, wherein the flow improver composition comprises combination of a

branched dendritic core with an polymeric inhibitor. The inventors of the present application have found that the combination of the dendrimer with the polymeric inhibitor may result in a synergistic improvement in flow of a hydrocarbon fluid to which the flow improver composition is added. In an embodiment, a combination of flow improvers according to the instant disclosure may be selected to tailor the flow improver to the properties of a particular hydrocarbon fluid and/or a particular set of conditions, such as by varying the relative amount of esterified hydroxyl groups present on the branched dendritic core, the carboxylic acid moieties, the branched dendritic core, the length of the alkyl side chain of the polymeric inhibitor, the presence or type of comonomer, etc. to produce different flow improvers according to the instant disclosure.

In an embodiment, a method comprises adding a flow improver according to any one or combination of embodiments disclosed herein to a first hydrocarbon fluid to produce a second hydrocarbon fluid. In an embodiment, the first hydrocarbon fluid is a hydrocarbon fluid produced during extraction of hydrocarbons from a well, crude oil, a crude oil condensate, a middle distillate, a fuel oil, diesel, or a combination thereof.

In an embodiment, a method comprises extracting a hydrocarbon fluid from a well and adding a flow improver according to any one or combination of embodiments disclosed herein to the hydrocarbon fluid. In an embodiment, flow improver is added to the hydrocarbon fluid prior to the hydrocarbon fluid being extracted from the well, the flow improver is added to the hydrocarbon fluid after the hydrocarbon fluid has been extracted from the well, or a combination thereof. In an embodiment, the well is located underwater. In an embodiment, the well is a deep water well located at least 1000 meters below the surface of the water.

In an embodiment, the flow improver is added to a subterranean well. In an embodiment, the flow improver may be added to a hydrocarbon fluid in the well (i.e. a first hydrocarbon fluid). In an embodiment, a hydrocarbon fluid containing the flow improver (i.e. a second hydrocarbon fluid) may be produced from the well. In another embodiment, the flow improver may be added to a hydrocarbon fluid produced from a well at the well head or at the surface. In still another embodiment, the flow improver is added to a hydrocarbon fluid prior to transporting the hydrocarbon fluid in a pipeline or a tank.

Branched Dendritic Core

As mentioned above, the flow improver composition of the present disclosure may include a branched dendritic core compound. For example, in an embodiment, the branched dendritic core

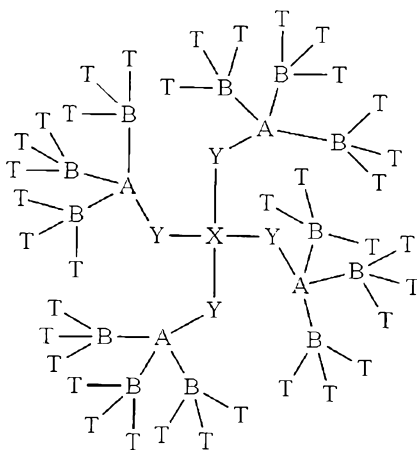
may have a first quaternary carbon center bonded to four second carbon atoms, where in at least three of the four second carbon atoms are individually bonded to one or more chain extender ligands to produce the branched dendritic core, wherein the branched dendritic core has greater than or equal to about 16 terminal hydroxyl groups, wherein at least one terminal hydroxyl group is esterified with at least one carboxylic acid moiety comprising of 6 to 30 carbon atoms or a combination, and wherein the dendritic core has no nitrogen atom.

As described by Tomalia et al, *Angew. Chem. Int. Ed. Engl.*, 29 (1990), 138, dendrimers are three-dimensional highly-ordered oligomers or polymers. They are obtainable by reiterative reaction sequences starting from an initiator core having one or more reactive sites. To each reactive site is attached one functional group only of a polyfunctional reactant. The reactant is then caused to react through its remaining functional group or groups with additional molecules either the same as the original core if it is polyfunctional or a different, polyfunctional, molecule or molecules, and so on, in each case under reaction conditions such that unwanted side reactions, for example, crosslinking, are avoided. In this way, a dendritic body is built up around the central core, each reiterative reaction sequence adding further reactants (or 'units') to the ends of the dendrites. Tomalia describes the manufacture of polyamidoamine (PAMAM) dendrimers; these may be made based on ammonia as a core, which is caused to react by Michael addition with methyl acrylate (Step A). The carboxyl group of the acrylate molecule is caused to react with one amino group only of ethylene diamine (Step B). The resulting triamine core cell is referred to by Tomalia as Generation 0; a further repetition of steps A and B provides a hexamine, referred to as Generation 1. Further repetitions of steps A and B produce higher generations which after Generation 4 result in concentric spheres of cells, the outermost sphere carrying external reactive groups. Other dendrimers described by Tomalia include polyethylenimine, hydrocarbon, polyether, polythioether, polyamide, polyamido-alcohol and polyarylamine dendrimers.

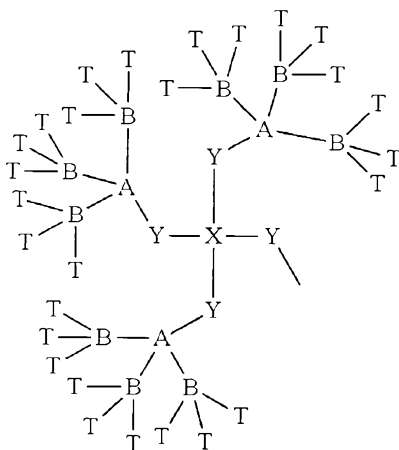
In an embodiment, branched, hyperbranched, and/or dendritic macromolecules (i.e., dendrimers) suitable for use herein may generally be described as three dimensional highly branched (i.e., hyperbranched) molecules having a tree-like structure. Suitable branched dendrimers may be highly symmetric, while similar macromolecules designated as branched, may, to a certain degree, hold an asymmetry, yet maintaining a highly branched tree-like structure. Dendrimers can be said to be monodispersed variations of branched macromolecules.

In an embodiment, branched dendrimers suitable for use herein comprise an initiator or nucleus having one or more reactive sites and a number of surrounding branching layers and optionally a layer of chain terminating molecules. As is known in the art, the layers are usually called generations, a designation hereinafter used. Branched dendritic or near dendritic macromolecules, also referred to herein as a branched dendritic core, may have three or more generations. Embodiments of the branched dendritic core may be illustrated by Formulae (I) and (II),

(I)



(II)



wherein X is a first quaternary carbon center bonded to four second carbon atoms Y, wherein each of the four second carbon atoms Y is each bonded through one or more chain extender ligands, which may be linear or branched, to produce the branched dendritic core.

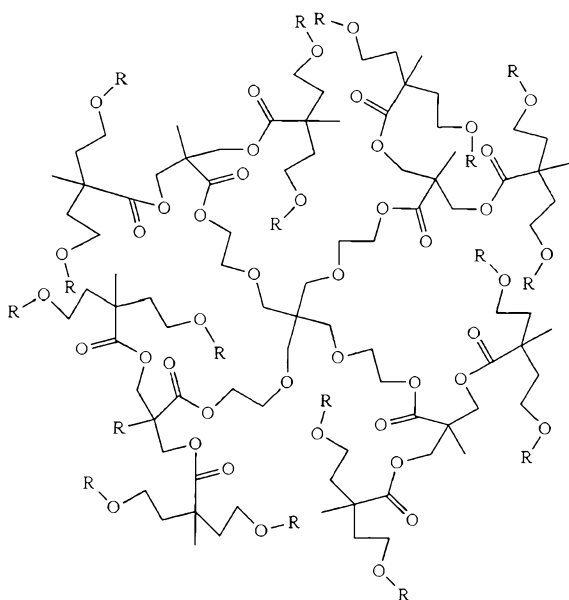
In an embodiment, A and B are chain extender ligands having two or four reactive sites each. Suitable examples include polyfunctional ligands comprising hydroxyl groups, epoxides, carboxylic acids, and the like.

In an embodiment, each of the chain extender forms one generation in the branched dendritic core. As shown above, A and/or B may include a plurality of chain extenders, linked together, each providing a branching point which is eventually terminated by a T functional group. Each of the A and B chain extenders may be the same or different.

In an embodiment, the branched dendrimer core, including the branches and terminating chains, do not include nitrogen atoms. In an embodiment, the branched dendrimer core, including the branches and terminating chains, consists essentially of carbon, hydrogen and oxygen. In an embodiment, A and B may consist essentially of carbon, hydrogen and/or oxygen. As disclosed above, T is a terminating chain stopper forming the last generation. T may either be monofunctional or give a suitable terminal functionality. In an embodiment, T may be selected from at least one of a hydroxyl, carboxyl or epoxide group. Each T may be a terminal hydroxyl group or a terminal hydroxyl group esterified with at least one carboxylic acid moiety comprising from 6 to 30 carbon atoms. The branched dendritic core may have greater than or equal to about 16 terminal hydroxyl groups, wherein at least one of the terminal hydroxyl groups is esterified with at least one carboxylic acid moiety comprising from 6 to 30 carbon atoms.

In an embodiment, the branched dendritic core may be represented by Formula III below.

(III)



In an embodiment, the Formula III branched dendritic core do not comprise nitrogen functionality, and more specifically does not comprise amine or amide functionality. Each R may be a hydrogen (i.e., a hydroxyl terminal group) or an esterified hydroxyl group which has been esterified with at least one carboxylic acid moiety selected from the group consisting of: greater than
 5 or equal to about 6 carbon atoms, greater than or equal to about 10 carbon atoms, and from 6 to 40 carbon atoms, with from 6 to 30 carbon atoms. Embodiments of R may include $\text{—COO—(CH}_2\text{)}_x\text{—(CH)}_y\text{—CH}_z$, wherein $x+y=8-28$, wherein y is from 0 to 5, and wherein z is 1, 2, or 3. Accordingly, the ester linkage may include both saturated and unsaturated carboxylic acids, as well as branched and/or linear carboxylic acids.

10 In an embodiment, prior to being esterified with the carboxylic acid, the branched dendritic core has a hydroxyl number of greater than or equal to about 490 mg KOH/g, wherein the hydroxyl number represents the hydroxyl content of a dendritic core, and is derived by acetylating the hydroxyl and titrating the resultant acid against KOH, as is known in the art. The hydroxyl number is thus the weight of KOH in milligrams that will neutralize the acid from 1 gram of the dendritic
 15 core prior to being esterified with a carboxylic acid.

In an embodiment, the branched dendritic core may comprise at least one carboxylic acid and/or substituted carboxylic acid moiety having from 6 to 30 carbon atoms, or from 8 to 24 carbon atoms, where essentially all of the terminal hydroxyl groups of the branched dendritic core are each esterified with at least one carboxylic acid moiety having from 12 to 22 carbon atoms. In an
 20 embodiment, the terminal hydroxyl groups on the branched dendritic core are each individually esterified with a corresponding number of the same carboxylic acid moiety. The carboxylic moiety may be individually selected from a carboxylic acid moiety and/or a substituted carboxylic acid moiety having from 6 to 30 carbon atoms, or having from 12 to 22 carbon atoms. In an embodiment, the carboxylic acid moieties may be derived from carboxylic acids selected from the
 25 group consisting of substituted or unsubstituted capric acid, undecylic acid, lauric acid, tridecylic acid, myristic acid, pentadecylic acid, palmitic acid, margaric acid, stearic acid, nonadecylic acid, arachidic acid, heneicosylic acid, behenic acid, tricosylic acid, lignoceric acid, pentacosylic acid, cerotic acid, heptacosylic acid, montanic acid, nonacosylic acid, melissic acid, myristoleic acid, palmitoleic acid, sapienic acid, oleic acid, elaidic acid, vaccenic acid, linoleic acid, linoelaidic acid,
 30 α -linolenic acid, arachidonic acid, eicosapentaenoic acid, erucic acid, docosahexaenoic acid, resinolic acid, and combinations thereof.

In an embodiment, the branched dendritic core comprises terminal carboxylic acid moieties selected from the group consisting of carboxylic acids and substituted carboxylic acids having from 8 to 24 carbon atoms, or having 12, 14, 16, 18, 20 and 22 carbon atoms, and combinations thereof. In an embodiment, the at least one carboxylic acid moiety or substituted carboxylic acid moiety is selected from the group consisting of lauric acid, myristic acid, palmitic acid, stearic acid, 12-hydroxy steric acid, and combinations thereof. Accordingly, the term “branched dendritic core” as used herein refers to a branched dendritic core wherein at least one of the terminal hydroxyl groups is esterified with at least one carboxylic acid and/or substituted carboxylic acid moiety comprising from 6 to 30 carbon atoms.

In an embodiment, the carboxylic acid moiety is a substituted carboxylic acid moiety which is substituted with at least one functional group comprising elements from one or more of Groups 13-17 of the periodic table of the elements. In an embodiment, the carboxylic acid moiety is a substituted carboxylic acid moiety which is substituted with at least one functional group comprising elements from one or more of Group 13, 14, 16, or 17 of the periodic table of the elements. In an embodiment, the at least one function group consists essentially of carbon, hydrogen, oxygen, sulfur and/or a halogen. In an embodiment, the substituted carboxylic acid moiety comprises a hydroxyl functional group, a halogen functional group, or a combination thereof. In an embodiment, the substituted carboxylic acid moiety is a hydroxy substituted carboxylic acid. In an embodiment, the substituted carboxylic acid moiety is 12 hydroxy stearic acid.

In an embodiment, the branched dendritic core is present in the flow improver composition in an amount ranging from 0.1 wt.% to 10 wt.%. In another embodiment, the branched dendritic core in the composition is in an amount from 5 wt.% to 10 wt.%.

Polymer Inhibitor

As described above, the flow improver composition may also include an polymer in combination with the dendrimer to provide a synergistic improvement in flow.. In one or more embodiments, the polymeric inhibitor may contain alkyl side chains or other hydrophobic domains that that associate with weakly soluble species and prevent aggregate or crystal formation. The alkyl side chains may, for example, result from an ester-containing monomer (either formed from an esterification or transesterification post-polymerization or by polymerization of an unsaturated alkyl ester, such as an alkyl acrylate), an alpha-olefin, or an alkylated monomer. The length of the alkyl side chain may be based, for example, on the paraffins in the hydrocarbon fluid. In some

embodiments, the alkyl side chain may range from C2 to C40, or from C6 to C30 in more particular embodiments. It is understood that such alkyl side chain (including in all of the polymeric inhibitors described herein) may be linear or branched, saturated or unsaturated.

In more specific embodiments, an ester (or alkyl ester side chain) may result from a monomer such as an alkyl (meth)acrylate (or other similar unsaturated alkyl esters), an unsaturated carboxylic acid (such as (meth)acrylic acid) that may be esterified post-polymerization, or maleic anhydride or other anhydride monomers that may be esterified post-polymerization. In such embodiments, the alkyl side chain in the resulting polymer that is used in the present compositions may have an alkyl side chain such as a C6 to C30 alkyl group as described above. Vinyl acetate is also an ester-containing monomer that may be used in some embodiments.

In some embodiments, inhibitors may include an alpha-olefin or a polyalpha-olefin. Alpha-olefins (or α -olefins) are a family of organic compounds which are alkenes with a chemical formula C_xH_{2x} , distinguished by having a double bond at the primary or alpha (α) position ($CH_2=C_{x-1}H_{2(x-1)}$). There are at least two types of alpha-olefins (or polymers thereof), branched and linear (or normal). The chemical properties of branched alpha-olefins with a branch at either the second or the third carbon are significantly different from the properties of linear alpha-olefins and those with branches on the fourth carbon number and further from the start of the chain. In particular embodiments of the present disclosure, the alpha-olefin of at least one copolymer is a linear alpha-olefin. Alpha-olefins suitable for reaction with the cyclic amide may include any C2-C40 hydrocarbon having an α - β double bond. In one or more embodiments, the inhibitor may include a polyalphaolefin having hyperbranching therein (with at least 10% branching).

Alternatively, the long-chain alkyl groups may be formed by use of an α - β unsaturated monomer that may be subsequently modified through reaction with an alkylated nucleophile. For example, such unsaturated monomers may include vinyl acrylates, maleic anhydride, and 1,2-ethylenedicarboximide, etc. Upon reaction of an unsaturated monomer with a suitable comonomer, the resulting polymer may be transesterfied, in the case that the unsaturated monomer is an acrylic acid for example, with a long chain aliphatic alcohol. Further, one skilled in the art would appreciate that similar types of reactions may occur with maleic anhydride or maleimide to achieve the long chain alkyl functionality.

In addition to the monomers described above, copolymeric inhibitors of the present disclosure may include a styrene monomer or a monomer that form linear polymers such as ethylene

and monomers having alkyl chains of varying length in some embodiments. For example, inhibitors may be copolymers of at least a monomer such as ethylene, propylene, or butene. In other embodiments, the inhibitor may be a copolymer such as ethylene alpha-olefin copolymers. Examples of olefin co-monomers may include propylene, n-butene, isobutene, n-octene-1, isooctene-1, n-decene-1, and n-dodecene-1.

Inhibitors in accordance with embodiments of the present disclosure may also include copolymers having cyclic amides as well as long-chain alkyl groups. The cyclic amide functionality may be achieved from a cyclic amide monomer, which may be reacted with at least one other monomer to form the copolymer. Exemplary cyclic amides, also referred to as lactams, that may be used as monomers in forming the copolymer may include vinylpyrrolidone ($\text{CH}_2=\text{CH}-\text{C}_4\text{H}_6\text{NO}$), a five-membered lactam ring, vinylcaprolactam ($\text{CH}_2=\text{CH}-\text{C}_6\text{H}_{10}\text{NO}$), a seven membered lactam ring, etc.

In some embodiments, additive compositions of the present disclosure may be suitable for improving flow in a wax-containing hydrocarbon fluids containing high molecular weight linear paraffins, i.e., paraffins having at least 12 carbon atoms. Further, additive compositions may be used for treating fluids containing high molecular weight linear paraffins such as those containing 25 carbon atoms or more. For example, the compositions of the present disclosure may alter the wax appearance temperature of a paraffin containing hydrocarbon fluid.

In some embodiments, inhibitors may contain polymers that have been transesterified poly(methyl acrylate) such that the resulting polymer is a methyl acrylate-alkyl acrylate or methyl methacrylate-alkyl methacrylate. Further, it is within the scope of the present disclosure that any of the ester groups may be linear or branched. For example, the alkyl groups of the alkyl-acrylate polymers may include at least 12 carbon atoms. The alkyl groups may include 12 to 40 carbon atoms in some embodiments of the present disclosure, and 20 to 60 carbon atoms in other embodiments.

In some embodiments of the present disclosure, inhibitors may be ethylene-vinyl acetate (EVA) copolymers, vinyl acetate-olefin copolymers, polyalkyl(meth)acrylates, alkyl esters of styrene-maleic anhydride copolymers, olefin-maleic anhydride copolymers, alpha olefin-maleic anhydrides, esters of alpha olefin-maleic anhydrides, alkyl esters of unsaturated carboxylic acid-olefin copolymers, alkyl acrylate-alkyl maleate copolymers, alkyl fumarate-vinyl acetate

copolymers, alkyl phenols, alpha-olefin copolymers, ethylene-vinyl fatty acid ester copolymers, or long-chain fatty acid amides.

For example, in one or more particular embodiments, the inhibitor may be a copolymer having an of an alpha-olefin and an anhydride (such as, but not limited to maleic anhydride) esterified with an alkyl group of 6 to 30 carbon atoms, a copolymer or polymer of an alkyl acrylate monomer, where alkyl is from C6-C30 carbon atoms or a copolymer of styrene and maleic anhydride that is subsequently esterified with a C6 to C30 alkyl group, or ethylene vinyl acetate copolymer (optionally transesterified with a longer alkyl group, such as C6 to C30). In even more particular embodiments, the polymeric inhibitor included in the flow improver composition may be a styrene maleic anhydride copolymer that is esterified with a C6 to C30 alkyl group. The esterification may occur, for example, at a greater than 1:1 ratio with the maleic anhydride monomer content, or a greater than 1.5 ratio, or at a 2:1 ratio with the maleic anhydride content. Thus, in such embodiments, a diester for the maleic anhydride functional units may be formed.

In an embodiment, the polymeric inhibitor (including those described above) is present in the composition in an amount ranging from 0.1 wt.% to 20 wt.%. For example, a lower limit may include any one of 0.1, 1, 5, 10, or 15 weight percent, and an upper limit may include any one of 5, 10, 15, or 20 weight percent, where any lower limit can be used in combination with any upper limit.

Surfactant

Optionally, a surfactant may be included in the flow improver composition. The inclusion of the surfactant may be to assist in the dispersion of any precipitated molecules (if precipitation does occur), rather than the inhibition of deposition. Among the types of surfactants that may be used, non-ionic, anionic, and cationic surfactants may all be used. Examples of non-ionic surfactants include, for example, alcohol ethoxylate, fatty acid esters, polyol esters, alkanolamides, and alkoxylated alkyl phenols, amine and amide derivatives, alkylpolyglucosides, ethyleneoxide / propyleneoxide copolymers, polyalcohols, and ethoxylated polyalcohols. Examples of anionic surfactants include, for example, alkyl benzene sulfonic acid (or sulfonate salts thereof), naphthalene sulfonic acid (or sulfonate salts thereof), alkyl sulfate, alkyl ether sulfate, alkyl aryl ether sulfate, sulfated alkanolamides, glyceride sulfates, alpha olefin sulphonates, lignosulphonates, and phosphate esters. Examples of cationic surfactants include, for example, quaternary ammonium

salts, polyoxyethylene alkyl and cyclic amines, oxy and ethoxylated amines, linear diamines, amide, ester and ether-amines, alkanol amides, amino acids, and hydroxyalkyl imidazolines.

When included, the surfactant may be present in the composition in an amount ranging up to 20 wt.%. For example, the lower limit may be any of 0.1, 1, 5, or 10 weight percent, and the upper
5 limit may be any of 5, 10, 15, or 20 weight percent, where any lower limit may be used with any upper limit.

Aromatic Solvent

The branched dendrimer and the polymeric inhibitor may be added to an aromatic solvent in the formulation of the flow improver composition of the present disclosure. Such aromatic solvents
10 may be xylene, toluene, or aromatic naphtha. In some embodiments, the solvent in the composition is in an amount from 20 wt.% to 80 wt.%. For example, the lower limit may be any of 20, 30, 40, 50, or 60 weight percent, and the upper limit may be any of 50, 60, 70, or 80 weight percent, where any lower limit can be used in combination with any upper limit.

Inhibition of Paraffin Deposition

15 In an embodiment, the composition of hydrocarbon fluid inhibitors described herein functions to inhibit paraffin deposition from a hydrocarbon fluid having a wax appearance temperature. For purposes herein, a hydrocarbon fluid has a wax appearance temperature, when a precipitate (e.g., paraffin, wax, or other solid material) forms upon cooling of the fluid. The wax appearance temperature is the temperature at which the paraffin precipitates. This phenomenon may
20 occur when the fluid contacts a surface having a temperature below the wax appearance temperature. The wax dissolution temperature of the fluid is the temperature at all wax that has come out of solution re-dissolves into the fluid, and the fluid becomes single phase. The wax appearance temperature is determined using a microscope having polarization and phase contrast employing an objective lens of 10× and higher, and an optical lens of 10× and higher. Samples of
25 the fluid are first heated to 140 °F (60 °C), homogenized, and centrifuged to get rid of any free water. Next, a tiny drop of homogenized preheated fluid is placed on a sample slide equilibrated with the stage at 140 °F, and covered by a coverslip such that the sample is positioned within the optical path of microscope. Then, the sample slide is brought into focus. The temperature of the stage is then ramped down via computer control and an optical reading is taken via computer control
30 in 30 second intervals according to methods known in the art. The temperature at which the first wax crystal appeared is detected is recorded as the wax appearance temperature. The temperature is

then ramped upward and the temperature at which the phase contrast disappears is recorded as the wax dissolution temperature. Programmed rate of heating and cooling cycles is shown in Table 1 below.

Table 1. Programmed rate of heating and cooling cycle

Rate °C/min	Temp	Hold time , min	Delay time, sec
10	60	10	30
1	10	10	30
1	60	10	30

In an embodiment, wax inhibition may also be determined by using a cold finger procedure, which determines the ability of the flow improver to inhibit paraffin formation for waxy crude oils. The cold finger test is conducted by using a temperature controlled chamber that keeps the sample at a prescribed temperature, typically above the sample's wax appearance temperature, and a metal tube, referred to as the cold finger, which is maintained at the desired test temperature, typically below that of the surrounding oil. The temperature of the cold finger is typically at the temperature of interest for a particular end use, which is generally very low between 35F and 50F.

In an embodiment, the test may be conducted by contacting a sample of the hydrocarbon fluid being maintained at a temperature above the wax appearance temperature with the cold finger, which is maintained at the temperature of interest, which is below the wax appearance temperature of the hydrocarbon fluid. A heat flux across the finger's metal surface and the bulk hydrocarbon fluid induces precipitation of the paraffin (i.e., wax deposition). The wax deposit that is formed for an untreated hydrocarbon fluid (i.e., in the absence of the flow improver) is determined gravimetrically, and compared the deposit that is formed for a treated hydrocarbon fluid, (i.e., with the flow improver present in the hydrocarbon fluid). A percent inhibition number is then calculated from the ratio of the two values.

In an embodiment, the cold finger test may be conducted by the following procedures, or an equivalent thereof. A hydrocarbon fluid is heated at 130 °F. An 80 ml of the heated hydrocarbon fluid is transferred to a glass jar, followed by injection of a wax inhibitor at 1000 ppm. Upon addition of the wax inhibitor, the glass jar is sealed and shaken. Next, the glass jar is placed back to the water bath at 130 °F for 30 minutes. Then, the glass jar is attached to a cold finger unit and immersed into the water bath which is preheated to 130 °F with constant stirring. After 30 minutes,

the water bath temperature is set to 80 °F and the cold finger temperature is set at 50 °F. After the glass jar is under the conditions for 20 hours, it is removed from the water bath and from the cold finger unit subsequently. The wax deposit is collected and weighed. Wax inhibition percentage is calculated by the following equation.

5

$$\% \text{ Wax inhibition} = \frac{\text{Untreated fluid wax, g} - \text{Treated fluid wax, g}}{\text{Untreated fluid wax, g}} \times 100$$

In an embodiment, a method comprises extracting a hydrocarbon fluid from a well and adding a flow improver according to any one or combination of embodiments disclosed herein to the hydrocarbon fluid. In an embodiment, flow improver is added to the hydrocarbon fluid prior to the hydrocarbon fluid being extracted from the well, the flow improver is added to the hydrocarbon fluid after the hydrocarbon fluid has been extracted from the well, or a combination thereof. In an embodiment, the well is located underwater. In an embodiment, the well is a deep water well located at least 1000 meters below the surface of the water.

In an embodiment, the flow improver is added to a subterranean well. In an embodiment, the flow improver may be added to a hydrocarbon fluid in the well (i.e. a first hydrocarbon fluid. In an embodiment, a hydrocarbon fluid containing the flow improver (i.e. a second hydrocarbon fluid) may be produced from the well. In another embodiment, the flow improver may be added to a hydrocarbon fluid produced from a well at the well head or at the surface. In still another embodiment, the flow improver is added to a hydrocarbon fluid prior to transporting the hydrocarbon fluid in a pipeline or a tank.

Methods in accordance with the present disclosure may include admixing an flow improver composition of the present disclosure with a hydrocarbon fluid in an effective amount, i.e., an amount sufficient to produce some reduction in the appearance of waxes or poorly soluble aggregates at decreased temperatures as compared to an untreated fluid. For example, flow improver compositions may be added at a concentration that may range from a lower limit selected from any of 0.0001 percent by weight (wt %), 0.001 wt %, 0.1 wt %, 1 wt %, and 2 wt % to an upper limit selected from any of 1 wt %, 2 wt %, 5 wt %, 10 wt %, and 15 wt %, where the concentration of the flow improver composition may range from any lower limit to any upper limit. In yet other

embodiments, the concentration of the flow improver composition in the hydrocarbon fluid may range from about 0.001 wt % to about 10 wt %. However, one skilled in the art would appreciate that the desired concentration of flow improver composition may depend on the type of fluid being treated, and that the desirable amount is an amount sufficient to achieve the highest variance in wax appearance temperature and viscosity at the lowest reasonable dosage.

EXAMPLES

Examples of compositions of flow improvers were produced according to the instant disclosure. Isopropyl amine dodecylbenzene sulfonate was used as the surfactant; xylene was used as the solvent; a composition of dendritic hydroxyl groups with C22 carboxylic acid (1:20), under the trade name of EPT 2456, obtained from Schlumberger, was used as the dendrimer, and styrene maleic anhydride ester copolymer, under the trade name of RS-10617 obtained from Schlumberger.

Example 1: The composition of example 1 comprises 15 wt.% of surfactant and 85 wt.% of xylene.

Example 2: The composition of example 2 comprises 20 wt.% of EPT 2456 and 80 wt.% of xylene.

Example 3: The composition of example 3 comprises 20 wt.% of SMA copolymer and 80 wt.% of xylene.

Example 4: The composition of example 4 comprises 5 wt.% of EPT 2456, 15 wt.% of SMA, 15 wt.% of surfactant, and 65 wt.% of xylene.

Method of Preparation

EPT 2456 was heated to 60 °C until the product became completely liquid. Sixty-five grams of xylene was charged into a 500 ml two-neck flask fitted with constant stirring in a water bath at 50 °C. Five grams of preheated EPT 2456 was added to the xylene and mixed for 20 minutes. Fifteen grams of surfactant was added slowly into the mixture. Exotherm was checked, and then 15 gram of SMA was added slowly and stirred for 20 minutes until the final product became a complete clear pale yellow solution.

Comparative Example

A conventional wax inhibitor comprising 12 wt.% of a composition of standard alpha olefin maleic anhydride ester copolymer, 12 wt.% of styrene Maleic anhydride ester copolymer, 29 wt.% of xylene, and 47 wt.% of hexane was compared to Examples 1-4

Wax Appearance Temperature

Table 2. WAT (Wax appearance temperature) of Eagle Ford oils

Oil Name	WAT °F
Fluid 1	Impurities interfering with wax
Fluid 2	102
Fluid 3	99
Fluid 4	103
Fluid 5	Impurities interfering with wax
Fluid 6	Impurities interfering with wax
Fluid 7	102
Fluid 8	102
Fluid 9	104
Fluid 10	105
Fluid 11	100
Fluid 12	102

Wax inhibition percentage

Table 3: wax inhibition of examples 1, 2, 3, and 4 on fluids 1-3 of south Texas Eagle Ford fluids.

Wax inhibitor	Wax inhibition		
	Fluid 1	Fluid 2	Fluid 3
Conventional	57%	6%	34%
Example 1	20%	12%	22%
Example 2	67%	86%	52%
Example 3	41%	8%	32%
Example 4	78%	91%	66%

As illustrated in Table 3, Example 4 has a better wax inhibition effect as compared to Examples 1-3. When comparing Example 4 with Example 2, the difference might seem not as significant as comparing Example 4 with Examples 1 and 3, and Conventional; however, considering that in Example 2, EPT 2456 is used in an amount of 20 wt.%, while in Example 4, only

5 wt.% of EPT 2456 is used, Example 4 demonstrates a more economical and efficient way to inhibit wax formation as compared to Example 2.

Based on the above fluids synergistic effect of Example 4, similar synergy is observed on the rest of Fluids 4-12 when compared with standard wax inhibitor sample (Conventional) as shown in the Table 4 below:

Table 4: wax inhibition of example 4 on fluids 4-12 of south Texas Eagle Ford fluids.

Samples	Fluid 4	Fluid 5	Fluid 6	Fluid 7	Fluid 8	Fluid 9	Fluid 10	Fluid 11	Fluid 12
Conventional	89%	63%	79%	40%	Wax fell off	58%	31%	35%	79%
Example 4	91%	80%	89%	76%	72%	90%	90%	91%	91%

From the results from Table 4 and Figure 2, it can be seen that Example 4 shows more economical and efficient as compared to the conventional wax inhibitor.

While the disclosure includes a limited number of embodiments, those skilled in the art, having benefit of this disclosure, will appreciate that other embodiments may be devised which do not depart from the scope of the present disclosure. Accordingly, the scope should be limited only by the attached claims.

CLAIMS

What is claimed:

1. A flow improver composition, comprising:

5 a branched dendritic core having a first quaternary carbon center bonded to four second carbon atoms, where in at least three of the four second carbon atoms are individually bonded to one or more chain extender ligands to produce the branched dendritic core, wherein the branched dendritic core has greater than or equal to about 16 terminal hydroxyl groups, wherein at least one terminal hydroxyl group is esterified with at least one carboxylic acid moiety comprising of 6 to 30 carbon atoms or a combination, and wherein the dendritic
10 core has no nitrogen atom;

a polymeric inhibitor having an alkyl side chain of 2 to 40 carbon atoms; and
an aromatic solvent.

2. The flow improver composition of claim 1, wherein the polymeric inhibitor comprises a copolymer of styrene and the maleic anhydride monomer esterified with a C6 to C30 alkyl
15 group.

3. The flow improver composition of claim 2, wherein the C6 to C30 alkyl group is present in an amount greater than a ratio of 1.5:1 relative to the maleic anhydride monomer.

4. The flow improver composition of claim 1, wherein the polymeric inhibitor comprises a polymer or copolymer comprising an alkyl acrylate monomer having a C6 to C30 alkyl
20 group.

5. The flow improver composition of claim 1, wherein the polymeric inhibitor comprises an ethylene vinyl acetate copolymer.

6. The flow improver composition of claim 1, wherein the alkyl side chain ranging from 6 to 30 carbon atoms.

25 7. A method comprising:

adding the flow improver composition of claim 1 to a first hydrocarbon fluid to produce a second hydrocarbon fluid, wherein the first hydrocarbon fluid is a hydrocarbon fluid produced during extraction of hydrocarbons from a well, crude oil, a crude oil condensate, a middle distillate, a fuel oil, diesel, or a combination thereof.

5 8. A method comprising:

extracting a hydrocarbon fluid from a well;

adding the flow improver composition of any of claims 1 to 6 to the hydrocarbon fluid.

9. The method of claim 8, wherein the flow improver composition is added to the hydrocarbon fluid prior to the hydrocarbon fluid being extracted from the well.

10 10. The method of claim 8, wherein the flow improver composition is added to the hydrocarbon fluid after the hydrocarbon fluid has been extracted from the well.

11. The method of claim 8, wherein the flow improver composition is added to the hydrocarbon fluid while the hydrocarbon fluid is extracted from the well.

ABSTRACT

A flow improver composition may include a branched dendritic core having a first quaternary carbon center bonded to four second carbon atoms, where in at least three of the four second carbon atoms are individually bonded to one or more chain extender ligands to produce the branched dendritic core, wherein the branched dendritic core has greater than or equal to about 16 terminal hydroxyl groups, wherein at least one terminal hydroxyl group is esterified with at least one carboxylic acid moiety comprising of 6 to 30 carbon atoms or a combination, and wherein the dendritic core has no nitrogen atom; a polymeric inhibitor having an alkyl side chain of 2 to 40 carbon atoms; and an aromatic solvent.