

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
21 December 2007 (21.12.2007)

PCT

(10) International Publication Number
WO 2007/146644 A2

(51) International Patent Classification:
E21B 43/22 (2006.01)

(21) International Application Number:
PCT/US2007/070329

(22) International Filing Date: 4 June 2007 (04.06.2007)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
11/422,922 8 June 2006 (08.06.2006) US

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

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, MT, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

- as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))
- as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))

Published:

- without international search report and to be republished upon receipt of that report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: DOWNHOLE FLOW IMPROVEMENT

(57) Abstract: A system for reducing pressure drop associated with turbulent fluid flow through conduits located in remote locations (e.g., deep under ground and/or deep under sea). Such reduction in pressure drop is accomplished by transporting a drag reducer through a long conduit of small diameter and thereafter injecting the drag reducer into a host fluid at the remote location, to make a treated fluid. The treated fluid is then extracted from the remote location via a production/transportation conduit. The presence of the drag reducer in the treated fluid reduces pressure drop associated with flow through the production/transportation conduit.



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DOWNHOLE FLOW IMPROVEMENT

BACKGROUND OF THE INVENTION

1. Field of the Invention

5 The present invention relates generally to systems for producing fluids from subterranean formations. In another aspect, the invention involves downhole introduction of a drag reducer into a hydrocarbon-containing host fluid (e.g., crude oil) produced from a subterranean formation.

2. Description of the Prior Art

10 A variety of drag reducers have been used in the past to reduce pressure loss associated with turbulent flow of a fluid through a pipeline. Ultra-high molecular weight polymers are known to function well as drag reducers. In general, increasing the molecular weight and concentration of the polymer in the drag reducer increases the effectiveness of the drag reducer, with the limitation that the polymer must be capable of
15 dissolving into the host fluid. However, drag reducers containing large concentrations of high molecular weight polymers generally can not be transported through small lines over large distances because the high viscosity of such drag reducers requires unacceptably high line pressures and/or the polymer particle size of such drag reducers can cause the lines to plug. Thus, drag reducers have not been delivered to remote (e.g.,
20 subsea and/or downhole) locations because economical delivery to such remote locations typically requires passage through long conduits having small diameters.

SUMMARY OF THE INVENTION

25 In one embodiment of the present invention, there is provided a method that includes the step of introducing a drag reducer into a host fluid at an injection point located at least about 500 feet below ground surface.

30 In another embodiment of the present invention, there is provided a method of producing a hydrocarbon-containing fluid from a subterranean formation. The method includes the following steps: (a) transporting a latex drag reducer downwardly to an injection point located at least about 500 feet below ground surface; (b) introducing said latex drag reducer into said hydrocarbon-containing fluid at said injection point to

thereby form a treated fluid comprising said latex drag reducer and said hydrocarbon-containing fluid; and (c) transporting at least a portion of said treated fluid upwardly toward the ground surface.

In yet another embodiment of the present invention, there is provided a production system for extracting a fluid from a subterranean formation. The production system generally comprises a well and an additive injection system. The well includes production tubing extending into the subterranean formation. The additive injection system includes an additive source and an additive passageway. The additive source contains an additive comprising a drag reducer. The additive passageway extends into the subterranean formation and is operable to transport the additive. The additive passageway includes a discharge opening for discharging at least a portion of the additive out of the passageway. The discharge opening is located at least about 500 feet below ground.

BRIEF DESCRIPTION OF THE DRAWING FIGURES

A preferred embodiment of the present invention is described in detail below with reference to the attached drawing figures, wherein:

FIG. 1 is a simplified depiction of a well used to produce a fluid from a subterranean formation, where the well is equipped with a treater string for introducing one or more additives (including a drag reducer) into the produced fluid prior to transporting the fluid to the ground surface;

FIG. 2 is a simplified depiction of a production well equipped with a gas-lift valve that permits additives (including a drag reducer) to flow downwardly in the annulus between the casing and the production tubing of the well;

FIG. 3 is a simplified depiction of an offshore production system including a plurality of subsea wells connected to a common production manifold which is tied back to an offshore platform via a subsea flowline, particularly illustrating an umbilical line running from the offshore platform to the production manifold;

FIG. 4 is a partial cut-away view of an umbilical line, particularly illustrating the various electrical and fluid conduits contained in the umbilical line;

FIG. 5 is a schematic diagram of an Engineering Loop Re-circulation Test apparatus used to measure the effectiveness of drag reducers;

FIG. 6 is a schematic illustration of a test apparatus used to perform dissolution rate tests on various drag reducers;

5 FIG. 7 is an isometric view of the stirrer employed in the dissolution rate tests;

FIG. 8 is a top view of the stirrer employed in the dissolution rate tests;

FIG. 9 is a side view of the stirrer employed in the dissolution rate tests;

10 FIG. 10 is a graph showing the effect that modification of the initial latex has on the hydrocarbon dissolution rate constant of the drag reducer over a range of temperatures;

FIG. 11 is a graph of the dissolution rate constant for various drag reducer formulations over a range of temperatures; and

FIG. 12 is a plot of the drag reduction in the Engineering Loop Re-circulation Test apparatus using various drag reducing materials.

15

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

Referring initially to FIG. 1, there is illustrated a production well 20 that is operable to extract one or more production fluids 24 from a subterranean formation 22. In one embodiment of the present invention, production fluid 24 contains at least one hydrocarbon-containing fluid such as, for example, crude oil and/or natural gas. For example, production fluid 24 can contain at least about 10, at least about 25, or at least 50 weight percent crude oil.

20 Well 20 generally includes an outer casing 26 and an inner production tubing 28 extending downwardly from the ground surface 30 into subterranean formation 22. 25 Casing 26 can have a plurality of perforations 32 located near the deposit of production fluid 24. During operation of production well 20, production fluid 24 flows from subterranean formation 22, through perforations 32, and into casing 28, from which it can be extracted via production tubing 28.

30 In accordance with one embodiment of the present invention, well 20 is equipped with a downhole additive injection system 34 that is operable to introduce an additive 36 into production fluid 24 at a location below ground surface 30. Additive 36 contains a

drag reducer, which will be described in detail below. For example, additive 36 can contain at least about 10, at least about 50, at least about 75, or at least 90 weight percent drag reducer. In one embodiment, additive 36 consists essentially of the drag reducer alone. In another embodiment, additive 36 contains the drag reducer in combination
5 with one or more conventional flow assurance chemicals. Typical flow assurance chemicals include, but are not limited to, hydrate inhibitors, corrosion inhibitors, paraffin inhibitors, scale inhibitors, biocides, demulsifiers, hydrogen sulfide scavengers, oxygen scavengers, water treatments, and asphaltene inhibitors. In one embodiment, additive 36 comprises in the range of from about 5 to about 75 weight percent of solid polymer
10 particles, or in the range of from about 10 to about 60 weight percent of solid polymer particles, or in the range of from 15 to 45 weight percent of solid polymer particles. When additive 36 is introduced into production fluid 24, at least about 50 weight percent, at least about 75 weight percent, or at least 95 weight percent of the solid polymer particles are dissolved by production fluid 24. The amount of drag reducer injected can
15 be expressed in terms of concentration of drag-reducing polymer in the hydrocarbon-containing liquid component of the produced fluid. The concentration of the drag-reducing polymer in the hydrocarbon-containing liquid component can be in the range of from about 0.1 to about 100 ppmw, or in the range of from about 0.5 to about 50 ppmw, or in the range of from about 1 to about 20 ppmw, or in the range of from 1 to 5 ppmw.

20 Additive injection system 34 generally includes at least one additive source 38, an additive pump 40, and an additive injection conduit 42. Injection conduit 42 extends downwardly through a passageway (e.g., an annulus) defined between casing 26 and tubing 28. Injection conduit 42 includes at least one outlet 44 for discharging additive 36 into production fluid 24. In the embodiment illustrated in FIG. 1, additive 36 is
25 introduced into production fluid 24 at an injection location inside casing 26 and outside tubing 28. Alternatively or additionally, additive 36 can be introduced into production fluid 24 outside casing 26 and/or inside tubing 28.

After additive 36 has been discharged into production fluid 24, the resulting combined/treated fluid 46 is transported upwardly through production tubing 28 to or
30 near ground surface 30. When the natural pressure of production fluid 24 in subterranean formation 22 is insufficient to cause treated fluid 46 to flow upwardly

through production tubing 28 to or near ground surface 30, an extraction means 48 is employed to pump treated fluid 46 upwardly through production tubing 28. In practice, extraction means 48 can take on a variety of forms known to those skilled in the art, including a downhole pump or a gas lift.

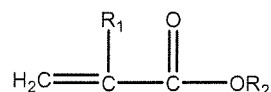
5 After being brought to or near ground surface 30, treated fluid 46 can then be transported via pipeline 50. FIG. 1 depicts pipeline 50 as being an above-ground pipeline. Alternatively, pipeline 50 can be a buried pipeline. Treated fluid 46 can be transported in pipeline 50 for a distance of at least about 1 mile, at least about 10 miles, or at least 100 miles. Since treated fluid 46 contains a drag reducer, the pressure drop
10 associated with the flow of treated fluid 46 through production tubing 28 and pipeline 50 is reduced relative to the pressure drop that would be associated with the flow of the untreated production fluid 24.

In one embodiment of the present invention, at least a portion of additive 36 is introduced into production fluid 24 at an injection location that is a substantial distance
15 below ground surface 30. For example, the injection location can be at least about 500 feet, at least about 1,000 feet, or at least 2,000 feet below ground surface. Thus, injection conduit 42 can have a length of at least about 500 feet, at least about 1,000 feet, or at least 2,000 feet. The average inside diameter of injection conduit 42 can be about 2.5 inches or less, about 1 inch or less, about 0.5 inches or less, or even 0.25 inches or
20 less.

In one embodiment of the present invention, the downhole additive can include a drag reducer that is capable of being transported via a long injection conduit having a small diameter. The drag reducer employed in the present invention can be a latex drag reducer comprising a high molecular weight polymer dispersed in an aqueous continuous
25 phase. The polymer of the latex drag reducer can be prepared via emulsion polymerization of a reaction mixture comprising one or more monomers, a continuous phase, at least one surfactant, and an initiation system. The continuous phase generally comprises at least one component selected from the group consisting of water, polar organic liquids, and mixtures thereof. When water is the selected constituent of the
30 continuous phase, the reaction mixture can also comprise at least one of a solvent and buffer.

The monomer used in formation of the high molecular weight polymer can include, but is not limited to, one or more of the monomers selected from the group consisting of:

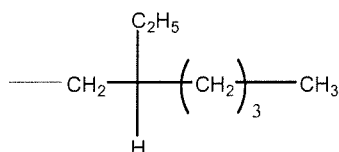
5 (A)



wherein R_1 is H or a C1-C10 alkyl radical, more preferably R_1 is H, CH_3 , or C_2H_5 , and
 10 R_2 is H or a C1-C30 alkyl radical, more preferably R_2 is a C4-C18 alkyl radical, and is most preferably represented by formula (i) as follows

(i)

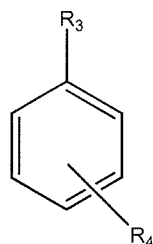
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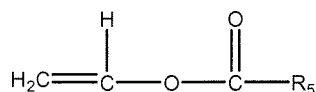
(B)



wherein R_3 is $\text{CH}=\text{CH}_2$ or $\text{CH}_3\text{-C}=\text{CH}_2$ and R_4 is H or a C1-C30 alkyl radical, more
 25 preferably R_4 is H or a C4-C18 alkyl radical, a phenyl ring with 0-5 substituents, a naphthyl ring with 0-7 substituents, or a pyridyl ring with 0-4 substituents;

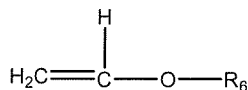
(C)

30



wherein R_5 is H or a C1-C30 alkyl radical, and preferably R_5 is a C4-C18 alkyl radical;

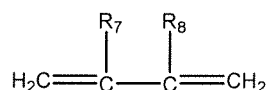
(D)



5

wherein R_6 is H or a C1-C30 alkyl radical, preferably R_6 is a C4-C18 alkyl radical;

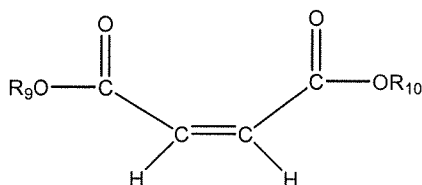
10 (E)



wherein R_7 is H or a C1-C18 alkyl radical, more preferably R_7 is H or a C1-C6 alkyl radical, and R_8 is H or a C1-C18 alkyl radical, more preferably R_8 is H or a C1-C6 alkyl radical, and most preferably R_8 is H or CH_3 , also, the H_2 's on the 1 and 4 carbons depicted above could be replaced by C1-C18 alkyl radicals or C1-C6 alkyl radicals;

(F) maleates such as

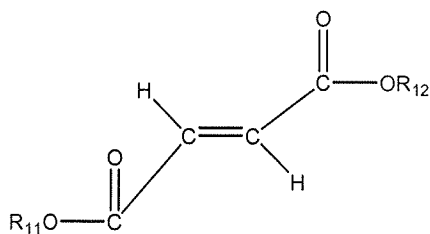
20



25 wherein R_9 and R_{10} are independently H, C1-C30 alkyl, aryl, cycloalkyl, or heterocyclic radicals;

(G) fumarates such as

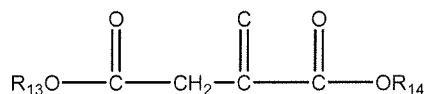
30



wherein R_{11} and R_{12} are independently H, C1-C30 alkyl, aryl, cycloalkyl, or heterocyclic radicals;

5

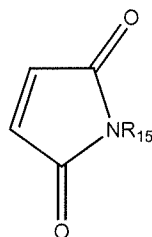
(H) itaconates such as



10

wherein R_{13} and R_{14} are independently H, C1-C30 alkyl, aryl, cycloalkyl, or heterocyclic radicals;

15 (I) maleimides such as



20

wherein R_{15} is H, a C1-C30 alkyl, aryl, cycloalkyl, or heterocyclic radical.

In one embodiment, monomers of formula (A) are preferred, especially methacrylate monomers of formula (A), and most especially 2-ethylhexyl methacrylate monomers of formula (A).

25

The surfactant used in the reaction mixture can include at least one high HLB anionic or nonionic surfactant. The term “HLB number” refers to the hydrophile-lipophile balance of a surfactant in an emulsion. The HLB number is determined by the method described by W.C. Griffin in *J. Soc. Cosmet. Chem.*, 1, 311 (1949) and *J. Soc. Cosmet. Chem.*, 5, 249 (1954), which is incorporated by reference herein. As used

30

herein, “high HLB” shall denote an HLB number of 7 or more. The HLB number of

surfactants for use with forming the reaction mixture can be at least about 8, about 10, or 12.

Exemplary high HLB anionic surfactants include high HLB alkyl sulfates, alkyl ether sulfates, dialkyl sulfosuccinates, alkyl phosphates, alkyl aryl sulfonates, and sarcosinates. Commercial examples of high HLB anionic surfactants include sodium lauryl sulfate (available as RHODAPONTM LSB from Rhodia Incorporated, Cranbury, NJ), dioctyl sodium sulfosuccinate (available as AEROSOLTM OT from Cytec Industries, Inc., West Paterson, NJ), 2-ethylhexyl polyphosphate sodium salt (available from Jarchem Industries Inc., Newark, NJ), sodium dodecylbenzene sulfonate (available as NORFOXTM 40 from Norman, Fox & Co., Vernon, CA), and sodium lauroylsarcosinic (available as HAMPOSYLTM L-30 from Hampshire Chemical Corp., Lexington, MA).

Exemplary high HLB nonionic surfactants include high HLB sorbitan esters, PEG fatty acid esters, ethoxylated glycerine esters, ethoxylated fatty amines, ethoxylated sorbitan esters, block ethylene oxide/propylene oxide surfactants, alcohol/fatty acid esters, ethoxylated alcohols, ethoxylated fatty acids, alkoxyated castor oils, glycerine esters, linear alcohol ethoxylates, and alkyl phenol ethoxylates. Commercial examples of high HLB nonionic surfactants include nonylphenoxy and octylphenoxy poly(ethyleneoxy) ethanols (available as the IGEPALTM CA and CO series, respectively from Rhodia, Cranbury, NJ), C8 to C18 ethoxylated primary alcohols (such as RHODASURFTM LA-9 from Rhodia Inc., Cranbury, NJ), C11 to C15 secondary-alcohol ethoxylates (available as the TERGITOLTM 15-S series, including 15-S-7, 15-S-9, 15-S-12, from Dow Chemical Company, Midland, MI), polyoxyethylene sorbitan fatty acid esters (available as the TWEENTM series of surfactants from Uniquema, Wilmington, DE), polyethylene oxide (25) oleyl ether (available as SIPONICTM Y-500-70 from Americal Alcolac Chemical Co., Baltimore, MD), alkylaryl polyether alcohols (available as the TRITONTM X series, including X-100, X-165, X-305, and X-405, from Dow Chemical Company, Midland, MI).

The initiation system for use in the reaction mixture can be any suitable system for generating free radicals necessary to facilitate emulsion polymerization. Possible initiators include persulfates (e.g., ammonium persulfate, sodium persulfate, potassium

persulfate), peroxy persulfates, and peroxides (e.g., tert-butyl hydroperoxide) used alone or in combination with one or more reducing components and/or accelerators. Possible reducing components include, but are not limited to, bisulfites, metabisulfites, ascorbic acid, erythorbic acid, and sodium formaldehyde sulfoxylate. Possible accelerators
5 include, but are not limited to, any composition containing a transition metal having two oxidation states such as, for example, ferrous sulfate and ferrous ammonium sulfate. Alternatively, known thermal and radiation initiation techniques can be employed to generate the free radicals.

When water is used to form the reaction mixture, the water can be a purified
10 water such as distilled or deionized water. However, the continuous phase of the emulsion can also comprise polar organic liquids or aqueous solutions of polar organic liquids, such as those listed below.

As previously noted, the reaction mixture optionally can include at least one solvent and/or a buffer. The at least one solvent can be an organic solvent such as a
15 hydrocarbon solvent (e.g., pentane, hexane, heptane, benzene, toluene, xylene), a halogenated solvent (e.g., carbon tetrachloride), a glycol (e.g., ethylene glycol, propylene glycol, glycerine), an ether (e.g., diethyl ether, diglyme, polyglycols, glycol ethers). In one embodiment, the solvent is a hydrocarbon solvent, such as toluene. The buffer can comprise any known buffer that is compatible with the initiation system such as, for
20 example, carbonate, phosphate, and/or borate buffers.

In forming the reaction mixture, the monomer, water, the at least one surfactant, and optionally the at least one solvent, can be combined under a substantially oxygen-free atmosphere that is maintained at less than about 1000 ppmw oxygen or less than about 100 ppmw oxygen. The oxygen-free atmosphere can be maintained by
25 continuously purging the reaction vessel with an inert gas such as nitrogen and/or argon. The temperature of the system can kept at a level from the freezing point of the continuous phase up to about 60°C, or from about 0°C to about 45°C, or from 0°C to 30°C. The system pressure can be maintained in the range of from about 5 to about 100 psia, or about 10 to about 25 psia, or about atmospheric. However, higher pressures up
30 to about 300 psia can be necessary to polymerize certain monomers, such as diolefins. Next, a buffer can be added, if required, followed by addition of the initiation system,

either all at once or over time. The polymerization reaction is carried out for a sufficient amount of time to achieve at least 90 percent conversion by weight of the monomers. Typically, this time period is in the range of from between about 1 to about 10 hours, or 3 to 5 hours. During polymerization, the reaction mixture can be continuously agitated.

- 5 The following table sets forth approximate broad and narrow ranges for the amounts of the ingredients present in the reaction mixture.

Ingredient	Broad Range	Narrow Range
Monomer (wt. % of entire reaction mixture)	10 - 60%	40 - 50%
Water (wt. % of entire reaction mixture)	20 - 80%	50 - 60%
Surfactant (wt. % of entire reaction mixture)	0.1 - 10%	0.25 - 6%
Initiation system		
Monomer:Initiator (molar ratio)	$1 \times 10^3:1 - 5 \times 10^6:1$	$1 \times 10^4:1 - 2 \times 10^6:1$
Monomer:Reducing Comp. (molar ratio)	$1 \times 10^3:1 - 5 \times 10^6:1$	$1 \times 10^4:1 - 2 \times 10^6:1$
Accelerator: Initiator (molar ratio)	0.01:1 - 10:1	0.01:1 - 1:1
Solvent	0 to twice the amount of the monomer	
Buffer	0 to amount necessary to reach pH of initiation (initiator dependent, typically between about 6.5-10)	

- 10 The emulsion polymerization reaction yields an initial latex composition comprising a dispersed phase of solid particles and a liquid continuous phase. The initial latex can be a stable colloidal dispersion comprising a dispersed phase of high molecular weight polymer particles and a continuous phase comprising water. The colloidal particles can form in the range of from about 10 to about 60 percent by weight of the
- 15 initial latex, or in the range of from 40 to 50 percent by weight of the initial latex. The continuous phase can comprise water, the at least one high HLB surfactant, the at least one solvent (if present), and buffer as needed. Water comprises in the range of from about 20 to about 80 percent by weight of the initial latex, or about 40 to about 60

percent by weight of the initial latex. The high HLB surfactant comprises in the range of from about 0.1 to about 10 percent by weight of the initial latex, or from 0.25 to 6 percent by weight of the initial latex. As noted in the table above, the buffer is present in an amount necessary to reach the pH required for initiation of the polymerization reaction and is initiator dependent. Typically, the pH required to initiate a reaction is in the range of from 6.5 to 10.

The polymer of the dispersed phase can have a weight average molecular weight (M_w) of at least about 1×10^6 g/mol, or at least about 2×10^6 g/mol, or at least 5×10^6 g/mol. The colloidal particles can have a mean particle size of less than about 10 microns, less than about 1000 nm (1 micron), in the range of from about 10 to about 500 nm, or in the range of from 50 to 250 nm. At least about 95 percent by weight of the colloidal particles can be larger than about 10 nm and smaller than about 500 nm. At least about 95 percent by weight of the particles can be larger than about 25 nm and smaller than about 250 nm. The polymer of the dispersed phase can exhibit little or no branching or crosslinking. The continuous phase can have a pH in the range of from about 4 to about 10, or from about 6 to about 8, and contains few if any multi-valent cations.

In order for the polymer to function as a drag reducer, the polymer should dissolve or be substantially solvated in the produced fluid (e.g., crude oil and/or water). The efficacy of the high molecular weight polymer particles as drag reducers when added directly to the produced fluid is largely dependent upon the temperature of the produced fluid. For example, at lower temperatures, the polymer dissolves at a lower rate in the produced fluid, therefore, less drag reduction can be achieved. However, when the temperature of the produced fluid is above about 30°C, or above 40°C, the polymer is more rapidly solvated and appreciable drag reduction is achieved. As shown in the examples below, it can be possible to achieve greater drag reduction at a greater range of temperatures by modifying the initial latex through the addition of a low HLB surfactant and/or a solvent. The resulting modified latex can be provided as a "one package" system wherein the drag reduction properties of the polymer are available to the produced fluid stream in a much faster time period.

In accordance with one embodiment of the present invention, the initial latex can be modified to increase the dissolution rate of the polymer. Such modification can also provide a stable colloidal dispersion that will not significantly flocculate or agglomerate over time, thereby ensuring that the latex will not become fully broken or inverted. The modified latex can be formed by adding at least one low HLB surfactant and/or at least one solvent to the initial latex. In one embodiment, the initial latex can be modified with both a low HLB surfactant and a solvent. As used herein, "low HLB" shall denote an HLB number less than 7. The low HLB surfactant can have an HLB number of less than about 6, less than about 5, or in the range of from 1 to 4.

Exemplary suitable low HLB surfactants include low HLB sorbitan esters, PEG fatty acid esters, ethoxylated glycerine esters, ethoxylated fatty amines, ethoxylated sorbitan esters, block ethylene oxide/propylene oxide surfactants, alcohol/fatty acid esters, ethoxylated alcohols, ethoxylated fatty acids, alkoxylated castor oils, glycerine esters, polyethylene glycols, linear alcohol ethoxylates, alkyl phenol ethoxylates, and oil soluble polymeric emulsifiers such as polyisobutylene succinic anhydride copolymer diethanol amine salt/amide or salt/amide mixtures, and Hypermer B-206, and mixtures thereof.

Commercial examples of suitable nonanionic low HLB surfactants include sorbitan trioleate (available as SPANTM 85 from Uniqema, Wilmington, DE), sorbitan tristearate (available as SPANTM 65 from Uniqema, Wilmington, DE), sorbitan sesquioleate (available as LUMISORBTM SSO from Lambent Technologies, Skokie, IL), sorbitan monooleate (available as ALKAMULSTM SMO from Rhodia Inc., Cranbury, NJ), sorbitan monostearate (available as SPANTM 60 from Uniqema, Wilmington, DE), ethylene glycol fatty acid ester (available as MONOSTRIOLTM EN-C from Undesa, Barcelona, Spain), polyethylene glycol dioleate (such as ALKAMULSTM 600 DO from Rhodia Inc., Cranbury, NJ) propylene glycol monostearate (available as MONOSTRIOLTM PR-A from Undesa, Barcelona, Spain), glycerol monostearate (available as KEMFLUIDTM 203-4 from Undesa, Barcelona, Spain), polyisobutylene succinic anhydride copolymer diethanol amine salt (available as LUBRIZOLTM 2700, from The Lubrizol Corporation, Wickliffe, OH), and proprietary hydrophobic polymeric surfactants (such as HYPERMERTM B-206 from Uniqema, Wilmington, DE).

The amount of the at least one low HLB surfactant required to modify the initial latex depends on the desired dissolution rate for the polymer as well as the amount of solvent used, in order to provide the flexibility needed to adjust the dissolution rate to pipeline conditions. The finished formulation (i.e., the modified latex drag reducer) can contain in the range of from about 1 to about 95 percent by weight of the low HLB surfactant, or in the range of from about 1 to about 50 percent by weight of the low HLB surfactant, or in the range of from about 1 to about 30 percent by weight of the low HLB surfactant, or in the range of from 1 to 25 percent by weight of the low HLB surfactant.

Suitable solvents for use in forming the modified latex drag reducer include aromatic solvents (such as benzene, toluene, xylene, ethylbenzene, dibenzyl toluene, benzyltoluene, butylxylene, diphenylethane, diisopropylbiphenyl, triisopropylbiphenyl, etc.), partially or fully hydrogenated aromatic solvents (such as tetrahydronaphthalene or decahydronaphthalene), glycols (such as ethylene glycol, propylene glycol, butylenes glycol, hexylene glycol, polyglycols such as diethylene glycol, triethylene glycol, polyethylene glycol, polypropylene glycol and ethylene oxide propylene oxide block copolymers, glycol ethers, polypropylene glycol butyl ether, ethylene glycol butyl ether, propylene glycol methyl ether, propylene glycol butyl ether, propylene glycol phenyl ether, diethylene glycol methyl ether, dipropylene glycol methyl ether, triethylene glycol methyl ether), esters (such as butyl formate, ethyl acetate, lactate esters), nitrogen containing solvents (such as dimethylformamide), aliphatic and aromatic alcohols (such as methanol, ethanol, isopropanol, hexyl alcohol, 2-ethylhexyl alcohol, benzyl alcohol, tetrahydrofurfuryl alcohol), ketones (such as acetone, methyl ethyl ketone, methyl isobutyl ketone, methyl isoamyl ketone, cyclohexanone), sulfur containing solvents (such as dimethyl sulfoxide), tetrahydrofuran, alkyl halides (such as methylene chloride, 1,1,1-trichloroethane, perchloroethylene), and combinations thereof. Most preferred are low molecular weight glycols having a molecular weight of less than about 1000, or having a molecular weight in the range of from about 100 to about 600, or in the range of from 200 to 500. Polyethylene glycol having a molecular weight of about 200 can also be used.

The amount of solvent required depends on the desired dissolution rate for the polymer. The minimum amount of solvent is that which is necessary to provide the

minimum desired dissolution rate in the conduit(s) carrying the treated fluid in order to maximize the amount of active drag reducing polymer. The modified latex drag reducer can contain in the range of from about 1 to about 95 percent by weight of the solvent, or in the range of from about 1 to about 50 percent by weight of the solvent, or in the range of from about 10 to about 30 percent by weight of the solvent, or in the range of from 15 to 25 percent by weight of the solvent.

Modification of the initial latex can be accomplished through a simple mixing operation. Mixing can be accomplished using a simple overhead mixer, or the materials can be metered and proportionately fed into a continuous or static mixer depending on the viscosity of the materials selected for the modification. The order of addition of the modification materials has been observed to have an effect on the ease of preparation in the case of materials that have a high viscosity. In this situation, it is generally easiest to add the solvent first followed by the surfactant and lastly the latex. However, in most cases, the order of addition does not appear to have an impact on the properties of the finished mixture. Mixing can occur at a temperature in the of from about 5 to about 60°C, or in the range of from 15 to 30°C, under about atmospheric pressure. If a high viscosity surfactant is used, a dispersion mixer can be employed such as those used to prepare pigment dispersions. The time of mixing depends largely on the viscosity of the materials being used. Low viscosity mixtures can be prepared within minutes, however, mixtures of high viscosity surfactants can require extended mixing periods.

The molecular weight of the polymer from the initial latex is substantially unaffected by the addition of the at least one modifying low HLB surfactant and the at least one solvent. The particle size of the colloidal particles are generally the same as in the initial latex, however, it is possible that some swelling of the particles can occur depending on the type of solvent used in the modification step. Because of this swelling, the particle size distribution can also be affected. The viscosity of the latex drag reducer can be increased by the addition of the surfactant and solvent. The maximum concentration of surfactant and solvent should be selected so that the modified latex composition remains relatively easy to pump.

The solubility of the modified and initial latexes in a hydrocarbon-containing liquid is described herein in terms of a hydrocarbon dissolution rate constant "k." The

hydrocarbon dissolution rate constant (k) is determined in the manner described in Example 2, below. The modified latex, described above, has a hydrocarbon dissolution rate constant (k_m) that is greater than the hydrocarbon dissolution rate constant of the initial (i.e., unmodified) latex (k_i). The hydrocarbon dissolution rate constant of the modified latex (k_m) in kerosene at 20, 40, and/or 60°C can be at least about 10, 25, 50, 100, or 500 percent greater than the hydrocarbon dissolution rate constant of the initial latex (k_i) in kerosene at the same temperature (i.e., 20, 40, and/or 60°C). The hydrocarbon dissolution rate constant of the modified latex (k_m) in kerosene at 20°C can be at least about 0.004 min⁻¹, at least about 0.008 min⁻¹, or at least 0.012 min⁻¹. The hydrocarbon dissolution rate constant of the modified latex (k_m) in kerosene at 40°C can be at least about 0.01 min⁻¹, at least about 0.02 min⁻¹, or at least 0.04 min⁻¹. The hydrocarbon dissolution rate constant of the modified latex (k_m) in kerosene at 60°C can be at least about 0.05 min⁻¹, at least about 0.2 min⁻¹, or at least 0.4 min⁻¹. The hydrocarbon dissolution rate constant of the initial latex (k_i) in kerosene at 20°C can be less than about 0.004 min⁻¹, less than about 0.002 min⁻¹, or less than 0.001 min⁻¹. The hydrocarbon dissolution rate constant of the initial latex (k_i) in kerosene at 40°C can be less than about 0.01 min⁻¹, less than about 0.008 min⁻¹, or less than 0.006 min⁻¹. The hydrocarbon dissolution rate constant of the initial latex (k_i) in kerosene at 60°C can be less than about 0.005 min⁻¹, than about 0.004 min⁻¹, or less than 0.003 min⁻¹.

The drag reducer employed in the present invention should be relatively stable so that it can be stored for long periods of time and thereafter employed as an effective drag reducer without further modification. As used herein, “shelf stability” shall denote the ability of a colloidal dispersion to be stored for significant periods of time without a significant amount of the dispersed solid phase dissolving in the liquid continuous phase. The modified drag reducer can exhibit a shelf stability such that less than about 25, about 10, or 5 weight percent of the solid particles of high molecular weight polymer dissolves in the continuous phase over a 6-month storage period, where the modified drag reducer is stored without agitation at standard temperature and pressure (STP) during the 6-month storage period.

As used herein, “dissolution rate stability” shall denote the ability of a drag reducer to be stored for significant periods of time without significantly altering the

hydrocarbon dissolution rate constant of the drag reducer. The drag reducer employed in the present invention can exhibit a dissolution rate stability such that the hydrocarbon dissolution rate constant of the drag reducer at the end of a 6-month storage period, defined above, is within about 25, about 10, or 5 percent of the hydrocarbon dissolution rate constant of the modified latex drag reducer at the beginning of the 6-month storage period.

The drag reducers employed in the present invention can provide significant percent drag reduction. For example, the drag reducers can provide at least about a 2 percent drag reduction, at least about 5 percent drag reduction, or at least 8 percent drag reduction. Percent drag reduction and the manner in which it is calculated are more fully described in Example 2, below.

Referring now to FIG. 2, there is illustrated a well 100 similar to well 20 of FIG. 1 and including an outer casing 102 and an inner production tubing 104. Well 100 is equipped with an alternative additive injection system 106 having a different configuration than the additive injection system of FIG. 1. Additive injection system 106 generally includes an additive source 108, an additive pump 110, an additive feeder conduit 112, and a valved sealing device 114. Valved sealing device 114 can be any device that controls fluid flow through the passageway (e.g., annulus) defined between casing 102 and tubing 104. For example, valved sealing device 114 can be a conventional gas-lift valve. Although FIG. 2 illustrates only a single valved sealing device 114, it should be understood that well 100 can be equipped with multiple vertically-spaced valved sealing devices.

In operation, the additive (which includes a drag reducer, as discussed above) is pumped from additive source 108 to additive feeder conduit 112 by additive pump 110. The outlet of additive feeder conduit 112 is in fluid communication with the passageway defined between casing 102 and packing 104. The additive is permitted to fall down the passageway until it reaches valved sealing device 114. The pressure in the passageway can be controlled to selectively open and close the valve of sealing device 114. Passageway pressure can be controlled by additive injection pump 110 or by a separate pressure control system (not shown). After the additive passes through valved sealing means 114, it can fall down into the produced fluid. The resulting treated fluid can

thereafter be extracted and transported in the manner described above with reference to FIG. 1.

Referring now to FIG. 3, a simplified offshore production system is illustrated as including a plurality of subsea wells 200, a common production manifold 202, an offshore platform 204, a subsea flowline 206, and an umbilical line 208. Each well 200 can have a configuration similar to wells 20 and 100, described above with reference to FIGS. 1 and 2. Each well 200 is operable to produce a hydrocarbon-containing fluid from a subterranean formation. The hydrocarbon-containing fluids produced by each well 200 are combined in production manifold 202 and are thereafter transported via flowline 206 to platform 204. A first end of umbilical line 208 is connected to a control facility on platform 204, while a second end of umbilical line 208 is connected to wells 200, manifold 202, and/or flowline 206.

Referring now to FIG. 4, umbilical line 208 generally includes a plurality of electrical conduits 214, a plurality of fluid conduits 216, and a plurality of protective layers 218 surrounding electrical conduits 214 and fluid conduits 216. Referring to FIGS. 3 and 4, electrical conduits 214 carry power from platform 204 to wells 200 and/or manifold 202. Fluid conduits 216, commonly referred to as chemical injection lines, are typically used to inject low-viscosity flow assurance chemicals into the produced hydrocarbon-containing fluids transported back to platform 204 via flowline 206. Typical flow assurance chemicals which are injected through fluid conduits 216 include, but are not limited to, hydrate inhibitors, corrosion inhibitors, paraffin inhibitors, scale inhibitors, biocides, demulsifiers, hydrogen sulfide scavengers, oxygen scavengers, water treatments, and asphaltene inhibitors.

In accordance with one embodiment of the present invention, an additive comprising a drag reducer is transported through chemical injection lines (such as fluid conduits 216) in umbilicals (such as umbilical line 208). The drag reducer can thereafter be employed downhole in the manner described above with respect to wells 20 and 100 of FIGS. 1 and 2. In such a subsea well configuration, the "ground surface" can be the surface of the sea or the sea floor.

The length of umbilical line 208 can be at least about 500 feet, or at least about 1,000 feet, or at least about 1,000 feet, or in the range of from 5,000 feet to 30 miles.

The average inside diameter of each fluid conduit 216 can be about 5 inches or less, or about 2.5 inches or less, or about 1 inch or less, or about 0.5 inches or less, or about 0.25 inches or less.

In one embodiment of the invention, a drag reducer, such as one of those described above, is transported from platform 204 to production manifold 202 via at least one of the fluid conduits 216 making up umbilical line 208. At least one fluid conduit 216 can be kept available for transporting a flow assurance chemical simultaneously with the drag reducer through umbilical line 208.

The inventive drag reducers described in detail above can possess physical properties which allow them to be pumped through fluid conduit 216 of umbilical line 208 at typical operating conditions with a pressure drop of less than about 5 psi (pounds per square inch) per foot, less than about 2.5 psi per foot, or less than 1 psi per foot. Generally, the temperature at which the drag reducer will be transported through fluid conduit 216 is relatively low due to the cool ocean-bottom environment around umbilical line 208. Thus, the temperature of the drag reducer during transportation through fluid conduit 26 is generally less than about 60°F, more typically less than about 40°F for deep sea systems.

EXAMPLES

Example 1

Emulsion Polymerization of 2-Ethylhexyl Methacrylate Using Redox Initiation

In this example, a drag-reducing initial latex was prepared. Generally, 2-ethylhexyl methacrylate was polymerized in an emulsion comprising water, surfactant, initiator, and a buffer.

More specifically, the polymerization was performed in a 300 mL jacketed reaction kettle with a condenser, mechanical stirrer, thermocouple, septum ports, and nitrogen inlets/outlets. The kettle was charged with 0.231 g of disodium hydrogenphosphate, 0.230 g of potassium dihydrogenphosphate, and 4.473 g of sodium dodecyl sulfonate. The kettle was purged with nitrogen overnight. Next, the kettle was charged with 125 g of deoxygenated HPLC-grade water, the kettle contents were stirred

at 300 rpm, and the kettle temperature set to 5 °C using the circulating bath. The 2-ethylhexyl methacrylate monomer (100 mL, 88.5 g) was then purified to remove any polymerization inhibitor present, deoxygenated (by bubbling nitrogen gas through the solution), and transferred to the kettle.

5 In this example, four initiators were prepared for addition to the kettle: an ammonium persulfate (APS) solution by dissolving 0.131 g of APS in 50.0 mL of water; a sodium formaldehyde sulfoxylate (SFS) solution by dissolving 0.175 g of SFS in 100.0 mL of water; a ferrous sulfate solution by dissolving 0.021 g of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in 10.0 mL water; and a tert-butyl hydroperoxide (TBHP) solution by dissolving 0.076 g of 70%
10 TBHP in 50.0 mL of water.

The kettle was then charged with 1.0 mL of ferrous sulfate solution and over a two-hour period, 1.0 mL of APS solution and 1.0 mL of SFS solution were added concurrently. Following APS and SFS addition, 1.0 mL of TBHP solution and 1.0 mL of SFS solution were added concurrently over a two-hour period.

15 The final latex was collected after the temperature cooled back to the starting temperature. The final latex (216.58 g) comprised 38.3% polymer and a small amount of coagulum (0.41 g).

Example 2

20 In this example, the drag reduction capabilities of the 38% poly-2-ethylhexyl methacrylate polymer emulsion prepared in Example 1 were evaluated in a #2 diesel fuel system. The test device used in this example was a two inch Engineering Loop Recirculation Test apparatus as shown in FIG. 5. This test allowed for the evaluation of drag reducer performance when injected in non-predissolved form into a hydrocarbon
25 fluid in the flow loop. The test was used to simulate performance profiles and drag reducer behavior in field pipelines over a three-hour time period in terms of dissolution, peak performance, and degradation of the drag-reducing polymer.

 In the two inch pipe-loop recirculation test, 600 gallons of diesel at 70 °F was recirculated from a mixed reservoir through a 2-inch diameter pipe loop and back to the
30 reservoir. Approximate holdup in the pipe was 100 gallons. The diesel was recirculated at 42.3 gpm using a low-shear progressing cavity pump. Pressure drop was measured

over a 440-ft section of the pipe loop. "Base" case pressure drop was measured during a period of non-injection. "Treated" case pressure drop was measured during and following injection of the drag reducer sample. In the two inch pipe-loop recirculation test, sample material was injected for a 2-minute period into the pipe just downstream of the reservoir and pump, with the volume of material injected being equal to that required to obtain the target ppm for the full 600 gallon reservoir. Monitoring of pressure drop continued for a 3-hour period following injection. In this particular example, sufficient drag reducer polymer emulsion was injected into the test loop to yield a 5 ppm concentration of poly-2-ethylhexylmethacrylate (w/w) based on the #2 diesel fuel. No measurable drop in pressure was recorded in 3 hours of recirculation. This was equal to 0% drag reduction (% DR).

Percent drag reduction is the ratio of the difference between the baseline pressure drop (ΔP_{base}) and the treated pressure drop ($\Delta P_{\text{treated}}$) to the baseline pressure drop (ΔP_{base}) at a constant flow rate:

$$\% \text{ DR} = (\Delta P_{\text{base}} - \Delta P_{\text{treated}}) / \Delta P_{\text{base}}$$

The rate at which the polymer dissolves into the hydrocarbon stream is a very important property. The most effective drag reduction cannot occur until the polymer is dissolved or substantially solvated in the conduit. The rate at which the polymer dissolves can be determined by a vortex inhibition test in kerosene at various temperatures. At a constant stirring speed, the depth of the vortex is proportional to the amount of dissolved polymer in the kerosene. The dissolution rate is a first order function:

$$d/dt (\text{Conc}_{\text{undissolved}}) = (-k) (\text{Conc}_{\text{undissolved}})$$

wherein k is the dissolution rate constant. The time ,T, for a certain fraction of the polymer to be dissolved is a function of k as follows:

$$T_{\% \text{ dissolved}} = [\ln 100/(100-\% \text{ dissolved})]/k$$

FIG. 6 schematically illustrates the dissolution rate test apparatus used to determine the dissolution rate constant. The dissolution rate test apparatus included a rotating stirrer that was placed in a jacketed graduated 250 mL cylinder having an internal diameter of 48 mm. The upper end of the rotating stirrer was connected to a variable-speed motor

(not shown). The specific configuration of the rotating stirrer is illustrate in detail in FIGS. 7-9. The rotating stirrer employed in the dissolution rate tests was a Black & Decker paint stirrer made from a casting of oil resistant plastic. The stirrer head was formed of a 45 mm diameter disk made up of a central disk and an outer ring. The central disk was 20 mm in diameter and 1.5 mm thick and was centered on a hub that was 12 mm in diameter and 12 mm thick. The hub was drilled in the center for attachment of the stirring head to a 4 mm diameter shaft. The shaft was threaded for 27 mm so that two small nuts held the stirring head to the shaft. The outer ring was 45 mm in diameter, 9 mm wide, and 1.5 mm thick. The outer ring was attached to the inner disk by 13 evenly spaced arcs 13 mm long and 1 mm thick. The outer disk resided 6 mm below the level of the inner disk. The arcs that attached the outer ring to the inner disk acted as paddles to stir the fluid in the test cylinder. The shaft that attached the stirring head to the stirring motor (not shown) was 300 mm long. It should be noted that dissolution rate test results can vary somewhat if different stirrer configurations are used.

To conduct the dissolution rate test, the stirrer was positioned inside the cylinder and adjusted so that the bottom of stirrer head was about 5 millimeters from the bottom of the cylinder. The cylinder jacket was then filled with water recirculated from a recirculating water bath with controlled heating and cooling capability. The desired temperature was selected and the bath was allowed to reach that temperature. The jacketed graduated cylinder was filled with kerosene to the 200 mL line with the stirrer in place. The circulation of cooling fluid through the graduated cylinder jacket was initiated. The kerosene inside the graduated cylinder was stirred for sufficient time to allow the temperature to equilibrate at the set temperature, usually 10-15 minutes. The kerosene temperature was checked with a thermometer to insure that the kerosene was at the desired test temperature. The speed of the motor was adjusted to stir rapidly enough to form a vortex in the kerosene that reached to the 125 mL graduation in the cylinder.

An aliquot of pre-dissolved polymer containing the desired concentration of polymer was added to the kerosene while the vortex was formed. The pre-dissolved polymer was prepared by mixing the latex emulsion with a solvent having suitable solubility parameters to achieve full dissolution. The container with the emulsion and solvent was rolled overnight. In the case of an emulsion of poly-2-

ethylhexylmethacrylate, a mixture of 20% isopropanol and 80% kerosene (v/v) allowed full dissolution of the polymer at room temperature within this time period. For example, a 3% solution of poly-2-ethylhexylmethacrylate was prepared by adding 7.83 grams of a 38.3% polymer emulsion into 92.17 grams of 20% isopropanol and 80% kerosene (v/v) and followed by shaking to disperse the emulsion in an 8 ounce jar. The solvent system rapidly became viscous. The jar was then placed onto a roller rotating at a slow speed and allowed to homogenize overnight.

Aliquots of the pre-dissolved polymer were added quickly (i.e., within about 5 seconds) to the stirred kerosene in the graduated cylinder to determine the amount of polymer required to achieve full vortex closure, defined as closure at the 175 ml mark in the graduated cylinder. In the case of the 38.3% poly-2-ethylhexylmethacrylate emulsion prepared in Example 1, it was determined that 200 ppm active polymer was needed to completely close the vortex.

Emulsions which had not been pre-dissolved had their dissolution rates measured using the same polymer concentration required for full vortex closure for the pre-dissolved polymer by the following procedure. An aliquot of the emulsion, either modified or unmodified, was added to the kerosene at the desired concentration and temperature. A timer was used to monitor and record the time that the vortex reached the 130, 135, 140, 145, 150, 155, 160, 165, 170, and 175 mL marks on the cylinder. However, the determination was stopped when the time exceeded 30 minutes.

The dissolution constant, k , was calculated by first determining the relative vortex, R_v , and then plotting the time required to reach the various vortex marks vs. the log of the relative vortex. The relative vortex is the decimal fraction of the full vortex at 125 mL. The full vortex is the difference between 200 mL (the volume in the graduated cylinder) and the vortex at 125 mL (i.e., 75 mL).

$$R_v = (200 - \text{actual vortex}) / \text{full vortex}$$

For example, when the actual vortex is 130 ml, the relative vortex is 0.833. The time required to reach the various vortex marks was plotted versus the log of the relative vortex. A data trendline was then developed and a regression was performed on the

trendline. The slope of the trendline was multiplied by -2.303 to convert the data back to linear values. This was the dissolution rate constant, k , for a given temperature and concentration of active polymer.

The dissolution rate of the 38.3% poly-2-ethylhexylmethacrylate emulsion prepared in Example 1 was measured using the dissolution rate test at 500 ppm active polymer. Results show that the emulsion polymer had virtually no dissolution at 20°C and 30°C and very low dissolution rates at temperatures up to 60°C.

Temperature, °C	Dissolution Rate Constant, k (min^{-1})
20	<0.001
30	<0.001
40	0.005
50	0.009
60	0.022

In Examples 3-5, various solvents and surfactants were incorporated into the latex emulsion prepared in Example 1 in order to determine the effect thereof on the dissolution rate of the emulsion polymer in a hydrocarbon.

Example 3

Toluene (104.15 g) was added to a 600 ml beaker and the beaker placed under an overhead stirrer equipped with a 2 inch diameter 3-blade propeller. The stirrer was adjusted to 250 rpm and 41.675 grams of sorbitan sesquioleate (available as Lumisorb[®] SSO from Lambent Technologies, Skokie, IL) was added and mixed for 10 minutes until it dissolved. A portion of the emulsion prepared in Example 1 (104.175 g) was then added and the system mixed for 20 minutes. The composition had a density of 0.939 g/ml and a Brookfield LVDVII+ viscosity of 3700 mPa·s using a # 4 spindle at 12 rpm. The composition in terms of percent by weight was as follows:

Emulsion from Example 1	41.67%
Toluene	41.66%
Sorbitan sesquioleate	16.67%

- 5 The dissolution rate of this material was measured using the dissolution rate test described above. The results show that the modified emulsion polymer had good dissolution properties which improve with increasing temperature.

Temperature, °C	Dissolution Rate Constant, k (min ⁻¹)
20	0.015
30	0.023
40	0.047
50	0.072
60	0.60

Example 4

- 10 Toluene (104.15 g) was added to a 600 ml beaker and the beaker placed under an overhead stirrer equipped with a 2 inch diameter 3-blade propeller. The stirrer was adjusted to 250 rpm. A quantity of the emulsion prepared in Example 1 (145.85 g) was then added and the system mixed for 20 minutes. The composition had a density of 0.937 g/ml. The Brookfield LVDVII+ viscosity was too high to be measured using this
15 instrument at 12 rpm. The composition in terms of percent by weight was as follows:

Emulsion from Example 1	58.34%
Toluene	41.66%
Sorbitan sesquioleate	0%

20

The dissolution rate this material was measured using the dissolution rate test described above. Results show that the emulsion polymer had no dissolution at 20°C and 30°C and very low dissolution rates at temperatures up to 60°C.

Temperature, °C	Dissolution Rate Constant, k (min ⁻¹)
20	<0.001
30	0.007
40	0.016
50	0.029
60	0.037

5

Example 5

A quantity of the emulsion prepared in Example 1 (208.325 g) was added to a 600 ml beaker and the beaker placed under an overhead stirrer equipped with a 2 inch diameter 3-blade propeller. The stirrer was adjusted to 250 rpm and 41.675 g of sorbitan sesquioleate was then added and the system mixed for 20 minutes. The composition had a density of 0.991 g/ml and the Brookfield LVDVII+ viscosity was too high to be measured using this instrument at 12 rpm. The mixture had a smooth, paste-like consistency. The composition in terms of percent by weight is as follows:

15	Emulsion from Example 1	83.33%
	Toluene	0%
	Sorbitan sesquioleate	16.67%

The dissolution rate this material was measured using the dissolution rate test described above. Results show that the emulsion polymer had no dissolution at 20°C and 30°C and very low dissolution rates at temperatures up to 60°C.

20

Temperature, °C	Dissolution Rate Constant, k (min ⁻¹)
20	<0.001
30	<0.001
40	<0.001
50	0.002
60	0.010

The three examples above (Examples 3, 4 and 5) illustrate the dramatic improvement in dissolution rate realized by using both a surfactant and a solvent to modify the dissolution properties of the subject emulsion polymers in hydrocarbons.

5 Much faster dissolution can be obtained by using both a surfactant and a solvent than can be obtained by the use of either class of additive singly. A plot of the dissolution rate factor, k, vs. the temperature of the hydrocarbon used (kerosene) is presented in FIG. 10.

Example 6

10 In this example, 75 g of acetone was added to a 600 mL beaker and the beaker placed under an overhead stirrer equipped with a 2 inch diameter 3-blade propeller. The stirrer was adjusted to 250 rpm and 50 g of sorbitan sesquioleate was added and mixed for 10 minutes until it dissolved. A quantity of the emulsion prepared in Example 1 (125 g) was then added and the system mixed for 20 minutes. The composition had a density

15 of 0.94 g/mL and a Brookfield LVDVII+ viscosity of 6700 mPa·s using a # 4 spindle at 12 rpm. The composition in terms of percent by weight was as follows:

Emulsion from Example 1	50%
Acetone	30%
20 Sorbitan sesquioleate	20%

The dissolution rate this material was measured using the dissolution rate test described above. Results show that the modified emulsion polymer had good dissolution properties which improve with increasing temperature.

Temperature, °C	Dissolution Rate Constant, k (min ⁻¹)
20	0.117
30	0.078
40	0.101
50	0.094
60	0.309

This example illustrates how an alternate solvent can be used to achieve faster dissolution properties at a lower temperature. This can be important in many pipeline applications where the crude oil or refined products are transported at lower temperatures.

Example 7

A quantity of polyethylene glycol (96.15 g) having a molecular weight of 200 (PEG-200) was added to a 600 mL beaker and the beaker placed under an overhead stirrer equipped with a 2 inch diameter 3-blade propeller. The stirrer was adjusted to 250 rpm and 57.7 g of polyisobutylene succinic anhydride copolymer diethanolamine salt (PIBSA) was added and the system mixed for 30 minutes until the PIBSA dissolved. Next, 96.15 g of the emulsion prepared in Example 1 was added and the system mixed for 20 minutes. The composition had a density of 0.971 g/ml and a Brookfield LVDVII+ viscosity of 32000 mPa·s using a # 4 spindle at 6 rpm. The composition had a thick, paste-like consistency. The composition in terms of percent by weight was as follows:

Emulsion from Example 1

38.46%

PEG-200	38.46%
PIBSA	23.08%

The dissolution rate of this material was measured using the dissolution rate test described above. The results show that the modified emulsion polymer had good dissolution properties which improve with increasing temperature.

Temperature, °C	Dissolution Rate Constant, k (min ⁻¹)
20	0.025
30	0.040
40	0.106
50	0.107
60	0.255

This example illustrates that the use of a non-flammable, less hazardous solvent than toluene or acetone can be used and enhanced dissolution properties over broad temperature ranges can still be achieved.

Example 8

In this example, 50 g of PEG-200 was added to a 600 mL beaker and the beaker placed under an overhead stirrer equipped with a 2 inch diameter 3-blade propeller. The stirrer was adjusted to 250 rpm and 12.5 g of an ethoxylated tallow amine (Rhodameen[®] PN-430) and 37.5 g of polyisobutylene succinnic anhydride copolymer, diethanolamine salt were added and mixed for 20 minutes until dissolved. Next, 150 g of the emulsion prepared in Example 1 was then added and the system mixed for 20 minutes. The composition had a density of 1.0078 g/ml and a Brookfield LVDVII+ viscosity of 1120 mPa·s using a # 4 spindle at 30 rpm. The composition in terms of percent by weight was as follows:

	Emulsion from Example 1	60%
	PEG-200	20%
	Rhodameen PN-430	5%
5	PIBSA	15%

The dissolution rate of this material was measured using the dissolution rate test described above. The results show that the modified emulsion polymer had good dissolution properties which improve with increasing temperature.

10

Temperature, °C	Dissolution Rate Constant, k (min ⁻¹)
20	0.007
30	0.016
40	0.057
50	0.072
60	0.276

This example illustrates the use of more than one low HLB surfactant to achieve an enhanced dissolution rate over the emulsion alone and allows the use of a lower concentration of solvent and low HLB surfactants to achieve a given dissolution rate at certain temperatures.

15

Example 9

In this example, 60 g of PEG-200, 60 g of tripropylene glycol methyl ether and 6 g of 1-hexanol were added to a 1000 mL beaker and the beaker placed under an overhead stirrer equipped with a 3 inch diameter 3-blade propeller. The stirrer was adjusted to 250 rpm. Next, 30 g of an ethoxylated tallow amine (Rhodameen PN-430) and 90 g of polyisobutylene succinic anhydride copolymer, diethanolamine salt were added and

20

mixed for 30 minutes until dissolved. Then, 354 g of the emulsion prepared in Example 1 was added and the system mixed for 20 minutes. The composition had a density of 0.9979 g/ml and a Brookfield LVDVII+ viscosity of 3071 mPa·s using a # 4 spindle at 30 rpm. The composition in terms of percent by weight was as follows:

5

Emulsion from Example 1	59%
PEG-200	10%
Tripropylene glycol methyl ether	10%
1-hexanol	1%
Rhodameen PN-430	5%
PIBSA	15%

10

The dissolution rate of this material was measured using the dissolution rate test described above. Results show that the modified emulsion polymer had good dissolution properties which improve with increasing temperature.

15

Temperature, °C	Dissolution Rate Constant, k (min^{-1})
20	0.011
30	0.028
40	0.046
50	0.084
60	0.290

This example illustrates the use of more than one low HLB surfactant and more than one solvent to achieve an enhanced dissolution rate over the emulsion alone and allows the use of a lower concentration of solvent and low HLB surfactants to achieve a given dissolution rate at certain temperatures.

20

FIG. 11 is a plot of dissolution rate vs temperature for Examples 7, 8 and 9. This comparison of the dissolution rates of the various systems illustrates that the use of more

than one solvent and or low HLB surfactant can be used to achieve similar dissolution properties. In the case of Example 7, much higher additive concentrations were needed using a single surfactant and solvent to achieve only marginal improvements in dissolution rates. By using multiple surfactants and/or solvents to enable the use of a lower concentration of additives one can also achieve a mixture with a lower viscosity.

Example 10

In this example, 104.15 g of toluene was added to a 600 mL beaker and the beaker placed under an overhead stirrer equipped with a 2 inch diameter 3-blade propeller. The stirrer was adjusted to 250 rpm and 41.675 g of sorbitan sesquioleate was added and the system mixed for 10 minutes until dissolved. Next, 104.175 g of the emulsion prepared in Example 1 was added and mixed for 20 minutes. The composition had a density of 0.939 g/ml and a Brookfield LVDVII+ viscosity of 3700 mPa·s using a # 4 spindle at 12 rpm. The composition in terms of percent by weight was as follows:

Emulsion from Example 1	41.67%
Toluene	41.66%
Sorbitan sesquioleate	16.67%

The mixture prepared above was injected into the two inch Engineering Loop Recirculation Test apparatus described in Example 2 in a sufficient amount to yield a concentration of 3 ppm of poly-2-ethylhexylmethacrylate (w/w) based on the weight of the #2 diesel fuel. After injection, the pressure of the test loop quickly began to drop. A pressure drop equal to 10.75% DR was measured after 600 seconds (10 minutes).

Example 11

In this example, 104.15 g of toluene was added to a 600 mL beaker and the beaker placed under an overhead stirrer equipped with a 2 inch diameter 3-blade propeller. The stirrer was adjusted to 250 rpm and 145.85 g of the emulsion prepared in Example 1 was then added and mixed for 20 minutes. The composition had a density of

0.937 g/ml and the Brookfield LVDVII+ viscosity was too high to be measured using this instrument at 12 rpm. The composition in terms of percent by weight is as follows:

5	Emulsion from Example 1	58.34%
	Toluene	41.66%
	Sorbitan sesquioleate	0%

The mixture prepared above was injected into the two inch Engineering Loop Re-circulation Test apparatus as described in Example 2 in a sufficient amount to yield a concentration of 3 ppm of poly-2-ethylhexylmethacrylate (w/w) based on the weight of the #2 diesel fuel. During the 3 hour test no significant drag reduction was measured.

Example 12

In this example, 208.325 g of the emulsion prepared in Example 1 was added to a 600 mL beaker and the beaker placed under an overhead stirrer equipped with a 2 inch diameter 3-blade propeller. The stirrer was adjusted to 250 rpm and 41.675 g of sorbitan sesquioleate was then added and mixed for 20 minutes. The composition had a density of 0.991 g/ml and the Brookfield LVDVII+ viscosity was too high to be measured using this instrument at 12 rpm. The mixture had a smooth, paste-like consistency. The composition in terms of percent by weight was as follows:

25	Emulsion from Example 1	58.34%
	Toluene	0%
	Sorbitan sesquioleate	16.67%

The mixture prepared above was injected into the two inch Engineering Loop Re-circulation Test apparatus as described in Example 2 in a sufficient amount to yield a concentration of 3 ppm of poly-2-ethylhexylmethacrylate (w/w) based on the weight of the #2 diesel fuel. During a 3 hour test, no significant drag reduction was measured.

FIG. 12 is a plot of the drag reduction in the 2-inch Engineering Loop Re-circulation Test for Examples 2, 10, 11 and 12. In this plot of % Drag reduction vs

circulation time, the injection into the recirculating fluid occurred at 100 seconds. During the next 120 seconds the modified emulsions were injected at a higher concentration (21.5 ppm polymer for the modified and 35.8 ppm for the unmodified emulsion) and at a rate proportional to the flow of one pass of the diesel fuel through the
5 loop calculated as:

$$\text{Initial concentration (ppm)} = \text{injection rate} / (\text{injection rate} + \text{loop rate})$$

This equilibrated with the balance of the diesel fuel in the storage tank so that
10 within about 300 seconds total elapsed time the polymer was at the equilibrium concentration described (i.e. 3 ppm polymer for the modified emulsions and 5 ppm for the unmodified emulsion). The equilibrium concentration was calculated as:

$$\text{Equilibrium concentration (ppm)} = \text{mass polymer} / \text{mass diesel}$$

15 This plot illustrates the rapid rate of drag reduction of an emulsion modified with both toluene and sorbitan sesquioleate (Example 10) compared to the emulsion modified with either toluene alone (Example 11) or sorbitan sesquioleate alone (example 12) at an equilibrium polymer concentration of 3 ppm. Additionally the drag reduction performance of an unmodified emulsion at an equilibrium polymer concentration of 5
20 ppm is illustrated. The plot shows that the emulsion modified with both toluene and sorbitan sesquioleate exhibited rapid development of drag reduction properties in this test loop while the unmodified and the materials modified with either toluene or sorbitan sesquioleate singly did not develop any measurable drag reduction.

The preferred forms of the invention described above are to be used as illustration
25 only, and should not be used in a limiting sense to interpret the scope of the present invention. Obvious modifications to the exemplary embodiments, set forth above, could be readily made by those skilled in the art without departing from the spirit of the present invention.

NUMERICAL RANGES

The present description uses numerical ranges to quantify certain parameters relating to the invention. It should be understood that when numerical ranges are provided, such ranges are to be construed as providing literal support for claim limitations that only recite the lower value of the range as well as claims limitation that only recite the upper value of the range. For example, a disclosed numerical range of 10 to 100 provides literal support for a claim reciting “greater than 10” (with no upper bounds) and a claim reciting “less than 100” (with no lower bounds).

The present description uses specific numerical values to quantify certain parameters relating to the invention, where the specific numerical values are not expressly part of a numerical range. It should be understood that each specific numerical value provided is to be construed as providing literal support for a broad, intermediate, and narrow range. The broad range associated with each specific numerical value is the numerical value plus and minus 60 percent of the numerical value, rounded to two significant digits. The intermediate range associated with each specific numerical value is the numerical value plus and minus 30 percent of the numerical value, rounded to two significant digits. The narrow range associated with each specific numerical value is the numerical value plus and minus 15 percent of the numerical value, rounded to two significant digits. For example, if the specification describes a specific temperature of 62°F, such a description provides literal support for a broad numerical range of 25°F to 99°F (62°F +/- 37°F), an intermediate numerical range of 43°F to 81°F (62 +/- 19°F), and a narrow numerical range of 53°F to 71°F (62 +/- 9°F). These broad, intermediate, and narrow numerical ranges should be applied not only to the specific values, but should also be applied to differences between these specific values. Thus, if the specification discloses a first pressure of 110 psia and a second pressure of 48 psia (a difference of 62 psi), the broad, intermediate, and narrow ranges for the pressure difference would be 25 to 99 psi, 43 to 81 psi, and 53 to 71 psi, respectively.

DEFINITIONS

As used herein, the term “drag reducer” denotes a composition that when added to a host fluid is effective to reduce pressure loss associated with turbulent flow of the host fluid through a conduit.

5 As used herein, the term “latex drag reducer” denotes a composition containing a liquid continuous phase and a dispersed phase comprising particles of a drag reducing polymer. When the drag reducing polymer of a latex drag reducer is formed by emulsion polymerization, the continuous phase of the latex drag reducer can be formed at least partly of the liquid employed for emulsion polymerization or the continuous phase can
10 be formed of a liquid entirely different from the liquid employed for emulsion polymerization. However, the continuous phase of the latex drag reducer should be a non-solvent for the dispersed phase.

As used herein the term “average inside diameter” denotes the inside diameter of a conduit averaged along the length of the conduit.

15 As used herein, the terms “comprising,” “comprises,” and “comprise” are open-ended transition terms used to transition from a subject recited before the term to one or elements recited after the term, where the element or elements listed after the transition term are not necessarily the only elements that make up of the subject.

As used herein, the terms “including,” “includes,” and “include” have the same
20 open-ended meaning as “comprising,” “comprises,” and “comprise.”

As used herein, the terms “having,” “has,” and “have” have the same open-ended meaning as “comprising,” “comprises,” and “comprise.”

As used herein, the terms “containing,” “contains,” and “contain” have the same open-ended meaning as “comprising,” “comprises,” and “comprise.”

25 As used herein, the terms “a,” “an,” “the,” and “said” mean one or more.

As used herein, the term “and/or,” when used in a list of two or more items, means that any one of the listed items can be employed by itself or any combination of two or more of the listed items can be employed. For example, if a composition is described as containing components A, B, and/or C, the composition can contain A
30 alone; B alone; C alone; A and B in combination; A and C in combination; B and C in combination; or A, B, and C in combination.

What is claimed is:

1. A method comprising: introducing a drag reducer into a host fluid at an injection point located at least about 500 feet below ground surface.

5

2. The method of claim 1, wherein said introducing includes causing said drag reducer to travel through a passage defined between an outer casing and an inner production tubing of a production well.

10

3. The method of claim 1, wherein said introducing includes transporting said drag reducer through an injection conduit having a length of at least about 500 feet and an average inside diameter of less than about 2.5 inches.

15

4. The method of claim 3, wherein said injection conduit has a length of at least about 1,000 feet and an average inside diameter of less than about 1 inch.

20

5. The method of claim 3, wherein at least a portion of said injection conduit is located in an annulus defined between an outer casing and an inner production tubing of a production well.

25

6. The method of claim 3, wherein at least a portion of said injection conduit forms at least part of a subsea umbilical line and wherein said ground surface is the sea floor.

30

7. The method of claim 6, wherein a first portion of said injection conduit is part of said subsea umbilical line, wherein a second portion of said injection conduit is a treater string, and wherein said first and second portions of said injection conduit each have a length of at least about 500 feet and an average inside diameter of less than about 2.5 inches.

8. The method of claim 1, wherein said host fluid comprises crude oil.

9. The method of claim 1, further comprising transporting the combined host fluid and drag reducer from said injection point to the ground surface via a production conduit.

5

10. The method of claim 1, wherein said drag reducer comprises a high molecular weight polymer having a weight average molecular weight of at least about 1×10^6 g/mol.

10

11. The method of claim 1, wherein said drag reducer comprises a liquid continuous phase and a plurality of particles of polymer dispersed in said continuous phase.

15

12. The method of claim 11, wherein said particles have a mean particle size of less than about 1000 nm.

13. The method of claim 11, wherein at least about 95 percent of said particles have particle sizes in the range of from about 10 to about 500 nm.

20

14. The method of claim 11, wherein said continuous phase comprises water.

15. The method of claim 14, wherein said continuous phase further comprises at least one hydrocarbon solvent.

25

16. The method of claim 11, wherein said continuous phase comprises at least one high HLB surfactant and at least one low HLB surfactant, wherein said at least one high HLB surfactant has an HLB number of at least about 8, and wherein said at least one low HLB surfactant has an HLB number of less than about 6.

30

17. The method of claim 11, wherein said polymer is formed via the emulsion polymerization of 2-ethylhexyl methacrylate.

18. The method of claim 1, wherein said drag reducer has a hydrocarbon dissolution rate constant of at least about 0.004 min^{-1} in kerosene at 20°C .

- 5 19. The method of claim 1, wherein said drag reducer has a hydrocarbon dissolution rate constant of at least about 0.01 min^{-1} in kerosene at 40°C .

20. A method of producing a hydrocarbon-containing fluid from a subterranean formation, said method comprising:

- (a) transporting a latex drag reducer downwardly to an injection point located at least about 500 feet below ground surface;
- 5 (b) introducing said latex drag reducer into said hydrocarbon-containing fluid at said injection point to thereby form a treated fluid comprising said latex drag reducer and said hydrocarbon-containing fluid; and
- (c) transporting at least a portion of said treated fluid upwardly toward the ground surface.

10

21. The method of claim 20, wherein said transporting of step (a) includes transporting said latex drag reducer through a passage defined between an outer casing and an inner production tubing of a production well and wherein said transporting of step (c) includes transporting at least a portion of said treated fluid upwardly through said
15 production tubing.

20

22. The method of claim 20, wherein said transporting of step (a) includes transporting at least a portion of said latex drag reducer through an injection conduit having an average inside diameter less than about 2.5 inches.

23. The method of claim 22, wherein said injection conduit is at least about 1,000 feet long and has an average inside diameter less than about 1 inch.

25

24. The method of claim 22, wherein said injection conduit is at least partly disposed in an annulus defined between an outer casing and an inner production tubing of a production well and wherein said transporting of step (c) includes transporting at least a portion of said treated fluid through said production tubing.

30

25. The method of claim 20, wherein said latex drag reducer comprises polymer particles having a weight average molecular weight of at least about 1×10^6 g/mol and a mean particle size of less than about 1,000 nm.

26. The method of claim 25, wherein at least about 95 percent of said particles have particle sizes in the range of from about 10 to about 500 nm.

5 27. The method of claim 20, wherein said latex drag reducer has a hydrocarbon dissolution rate constant of at least about 0.004 min^{-1} in kerosene at 20°C .

28. The method of claim 20, wherein said latex drag reducer has a hydrocarbon dissolution rate constant of at least about 0.01 min^{-1} in kerosene at 40°C .

10

29. The method of claim 20, wherein said latex drag reducer comprises at least one low HLB surfactant having an HLB number of less than about 6 and at least one high HLB surfactant having an HLB number of at least about 8.

30. A production system for extracting a fluid from a subterranean formation, said production system comprising:

a well comprising production tubing extending into said subterranean formation;
and

5 an additive injection system comprising an additive source and an additive passageway, wherein said additive source contains an additive comprising a drag reducer, wherein said additive passageway extends into said subterranean formation and is operable to transport said additive, wherein said additive passageway includes a discharge opening for discharging at
10 least a portion of said additive out of said passageway, wherein said discharge opening is located at least about 500 feet below ground surface.

31. The production system of claim 30, wherein said additive passageway is defined by an elongated additive conduit.

15

32. The production system of claim 31, wherein said additive conduit has an average inside diameter of less than about 2.5 inches.

33. The production system of claim 31, wherein said additive conduit has a
20 length of at least about 1,000 feet and an average inside diameter of less than about 1 inch.

34. The production system of claim 31, wherein said well further comprises a casing and wherein said additive conduit is disposed between said casing and said
25 production tubing.

35. The production system of claim 30, wherein said well further comprises a casing and wherein said additive passageway is defined between said production tubing and said casing.

30

36. The production system of claim 35, wherein said additive injection system includes a valved sealing device disposed in said additive passageway and wherein said valved sealing device is operable to control fluid flow through said additive passageway.

5 37. The production system of claim 36, wherein said valved sealing device is a gas-lift valve.

38. The production system of claim 30, wherein said fluid comprises crude oil.

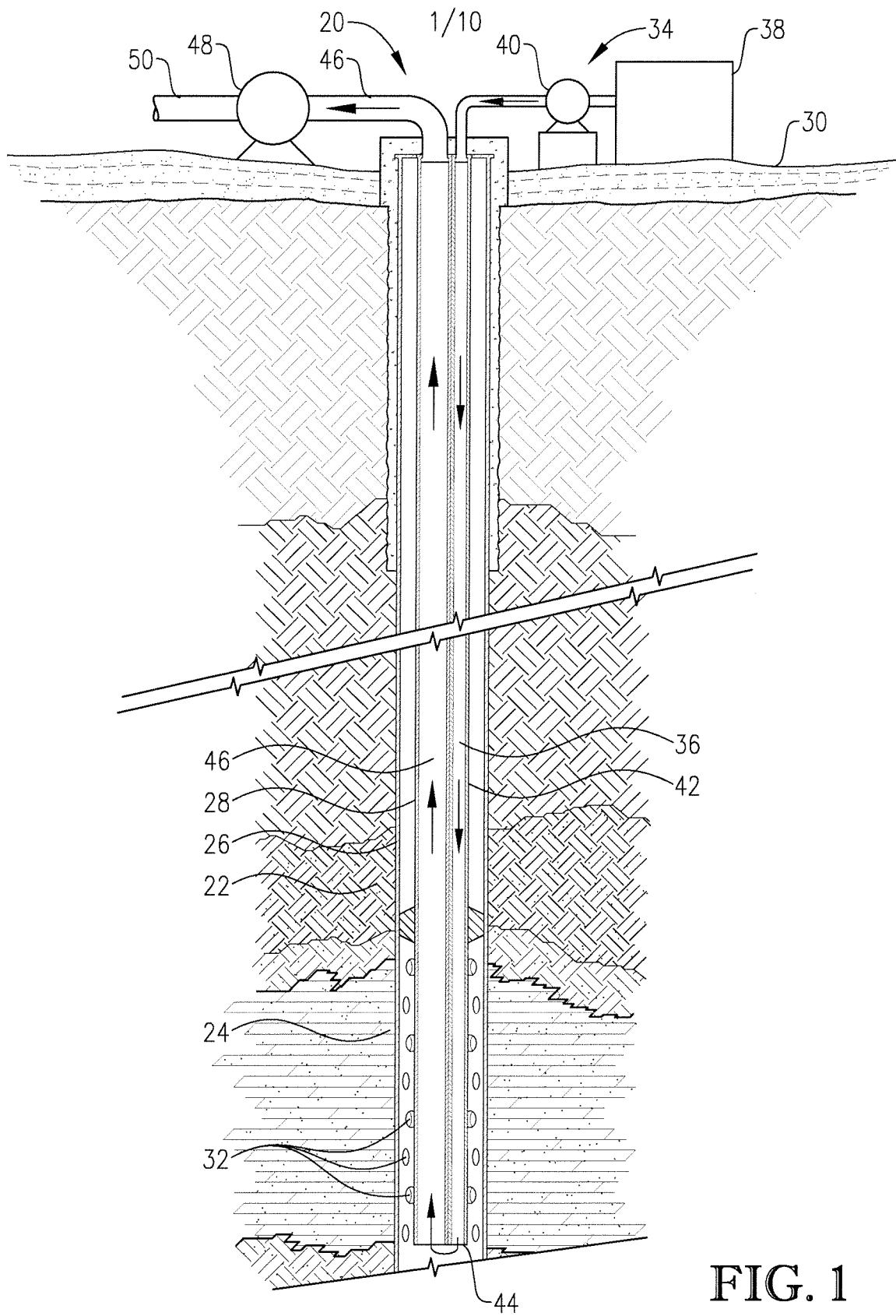


FIG. 1

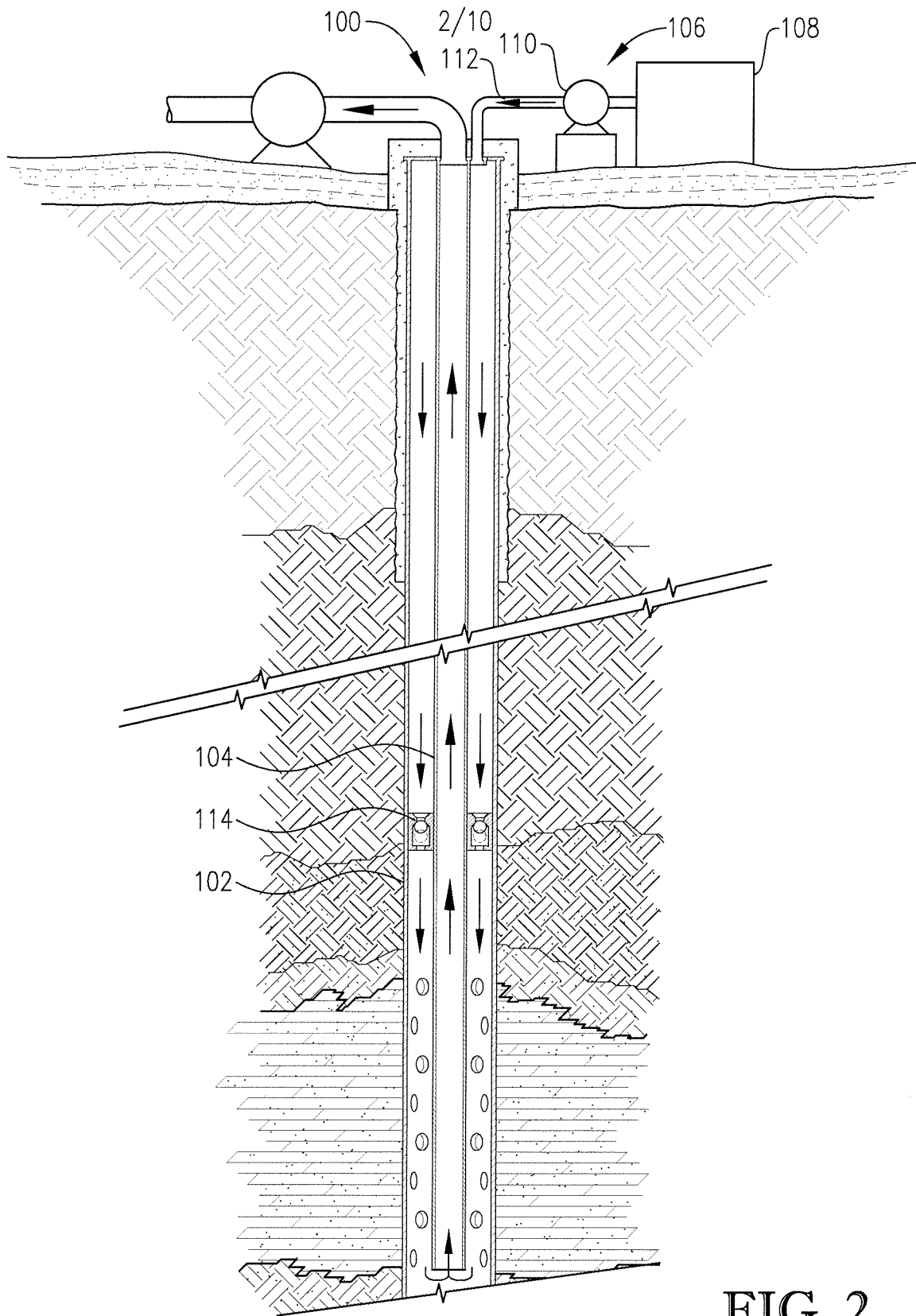


FIG. 2

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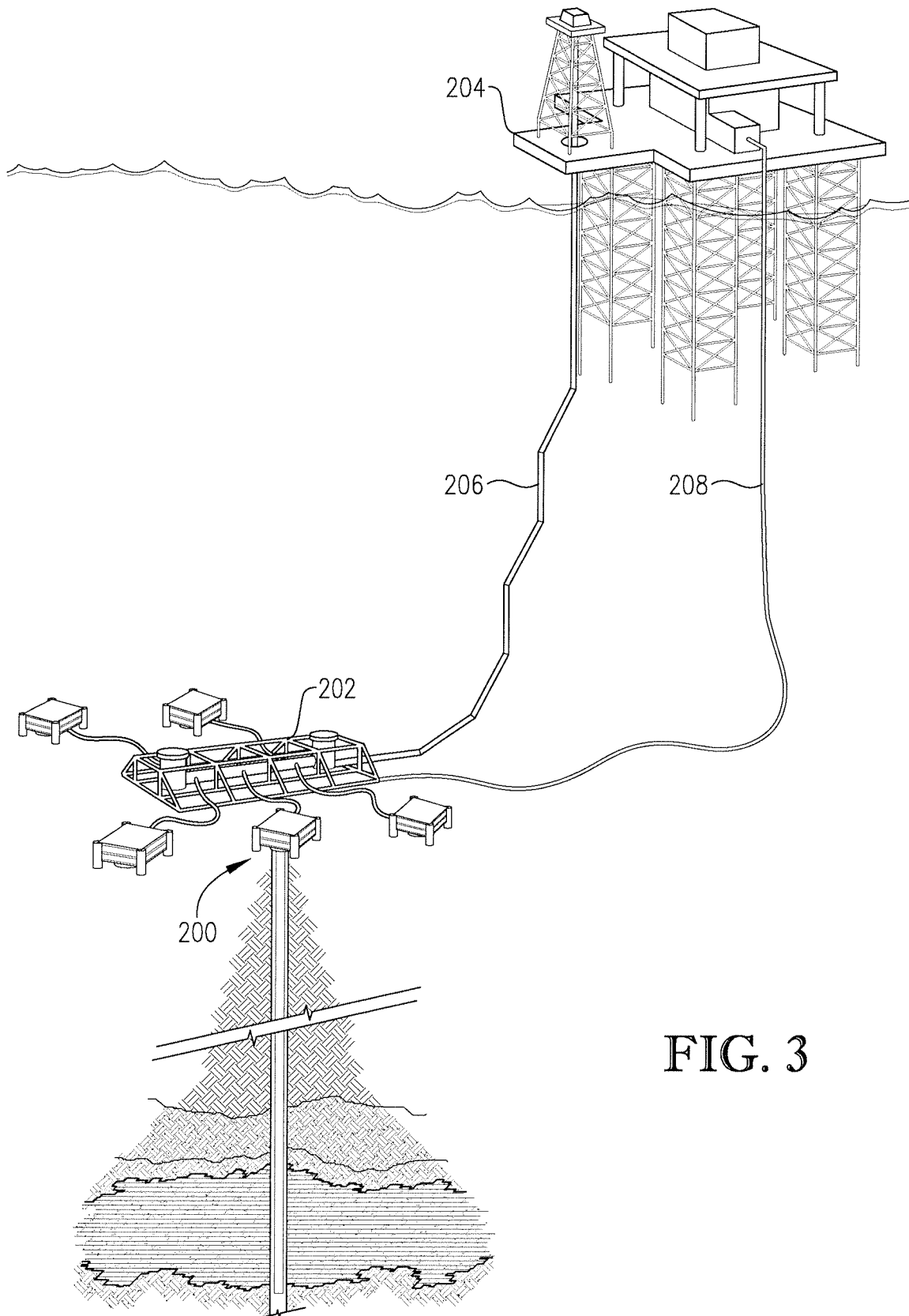


FIG. 3

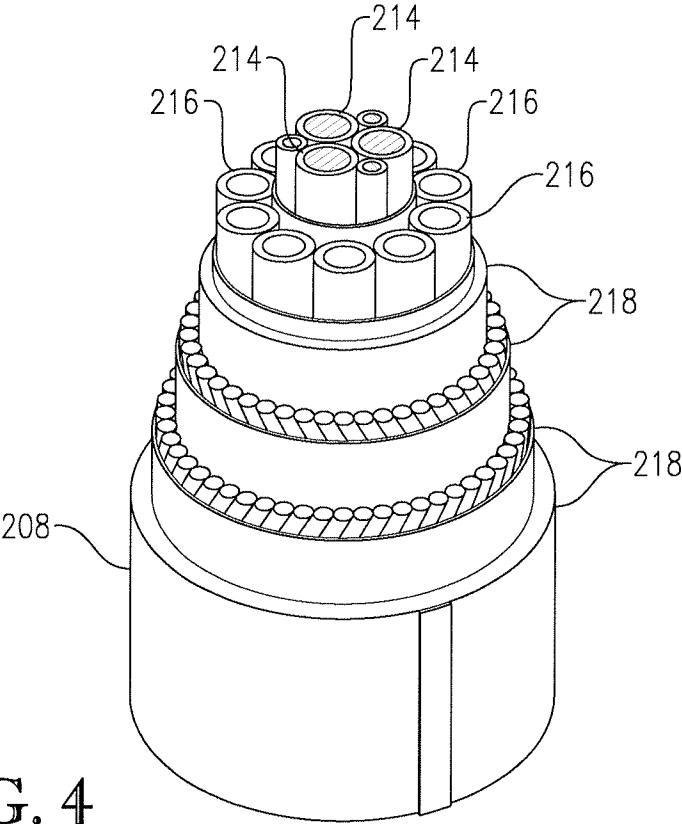


FIG. 4

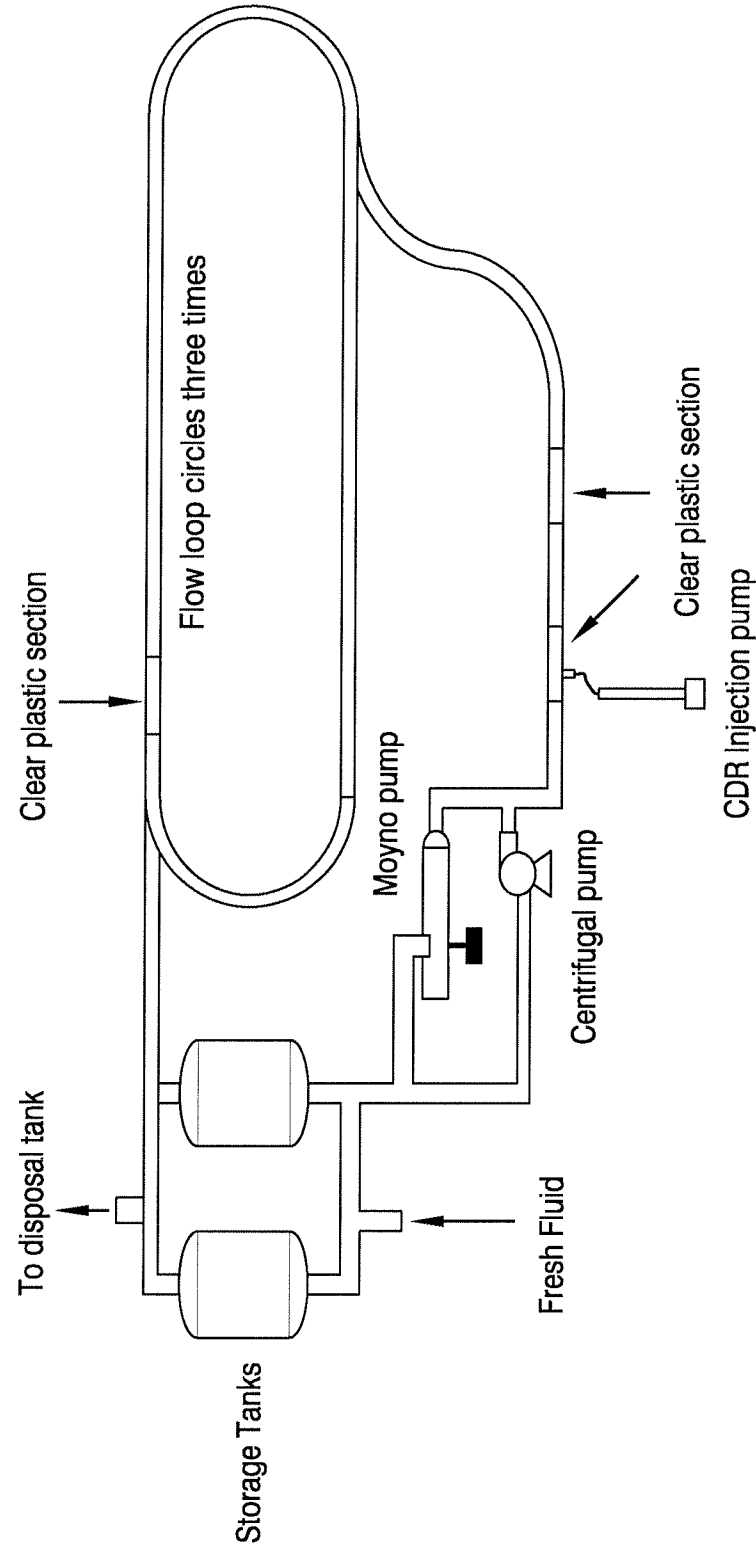


FIG. 5

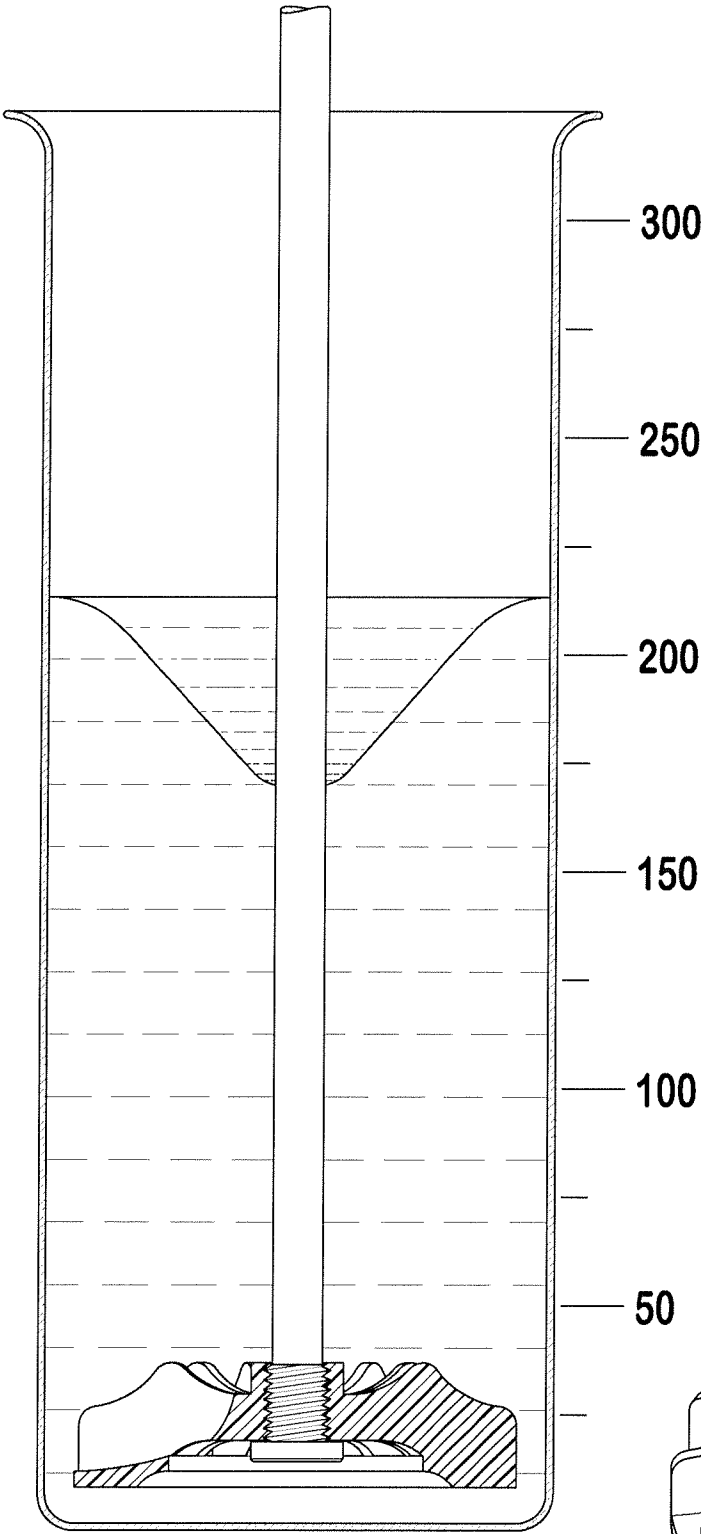


FIG. 6

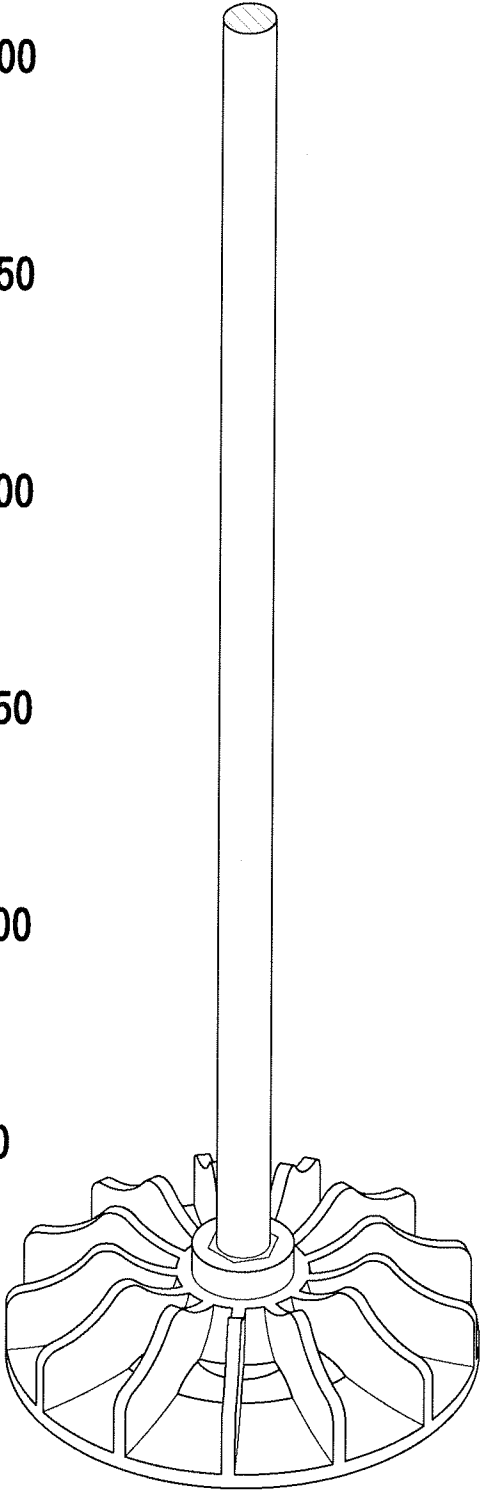


FIG. 7

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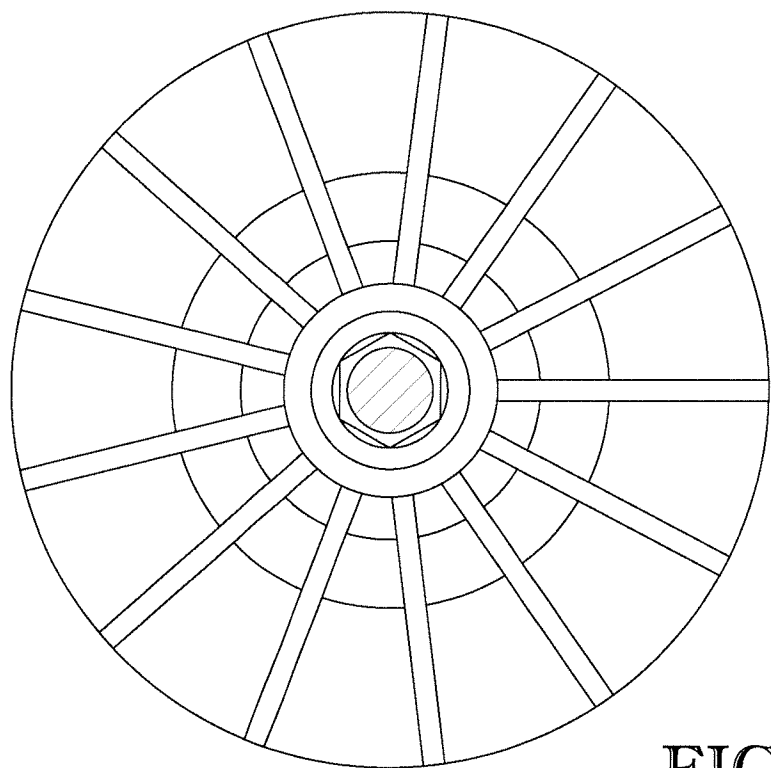


FIG. 8

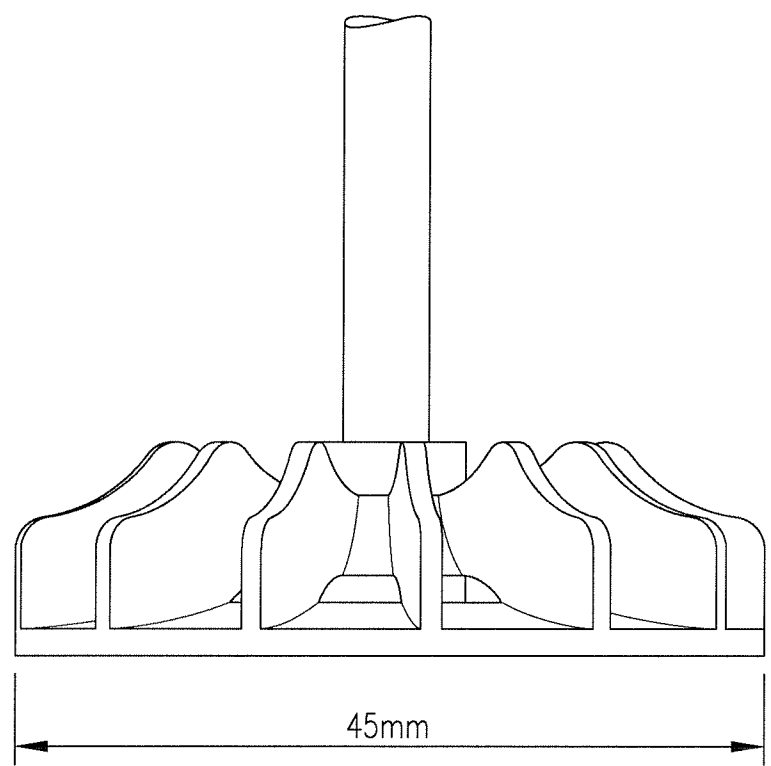
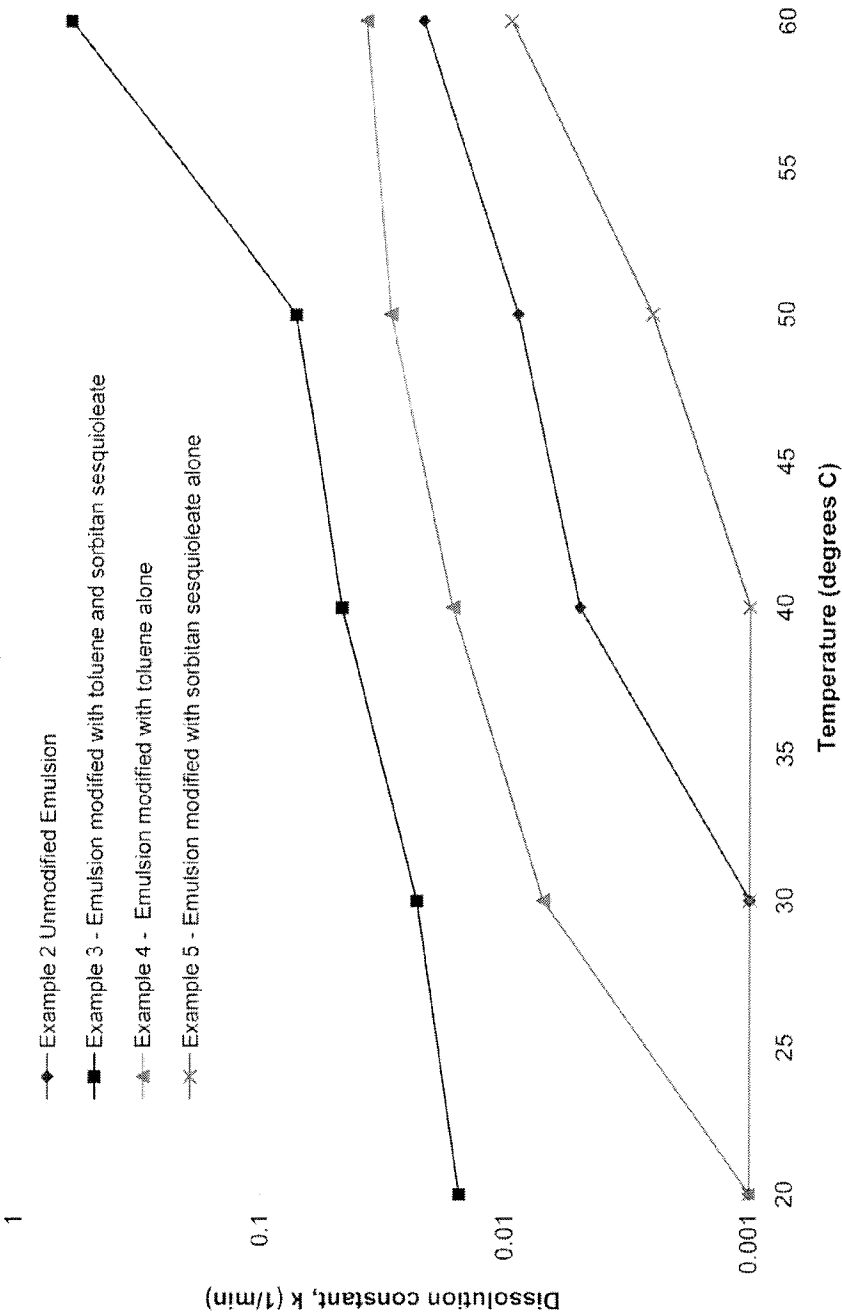


FIG. 9

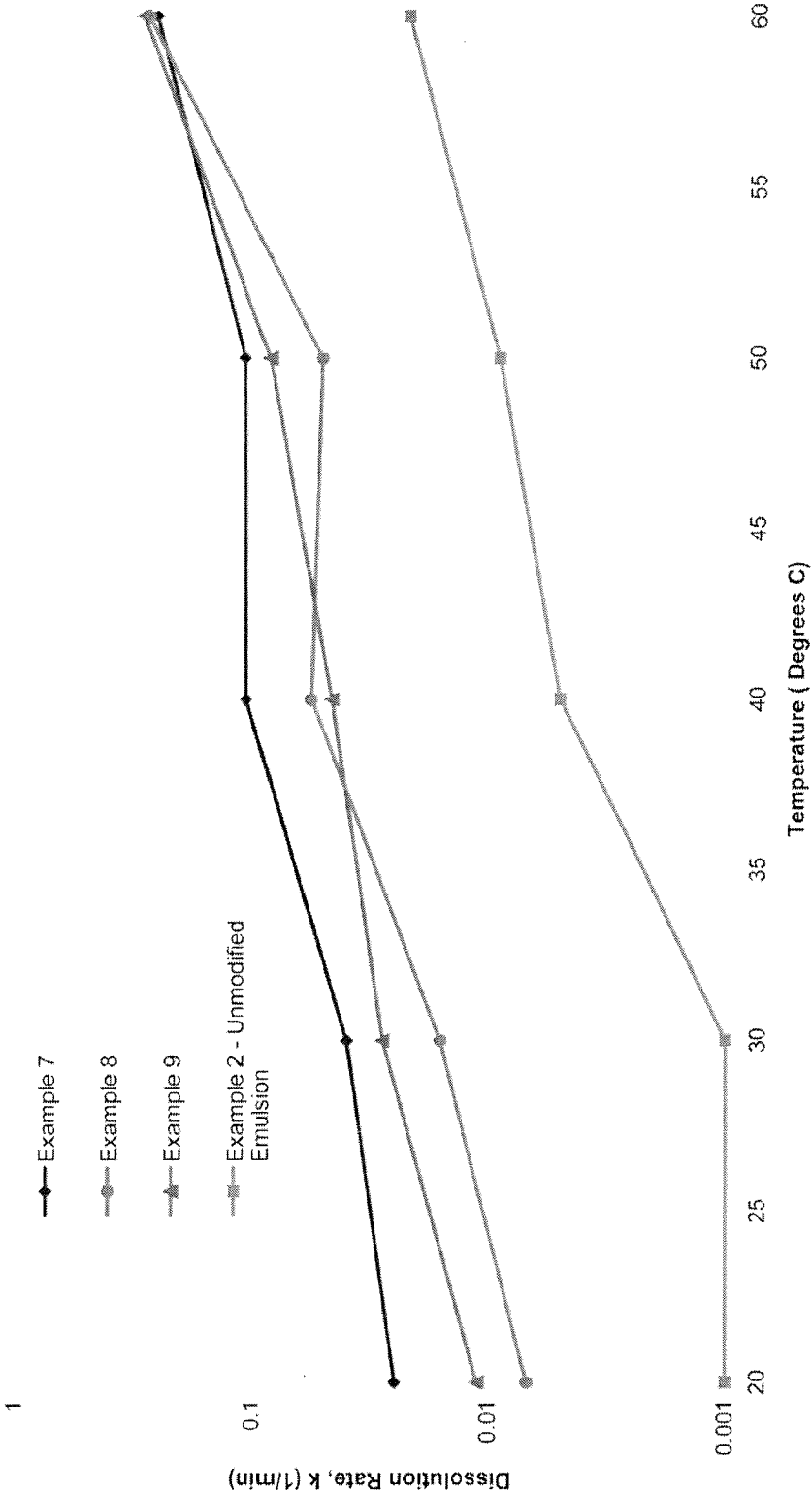
Dissolution Rate of Modified Emulsions
500 ppm polymer concentration



Note: Values less than 0.001 are reflected as 0.001 for ease of illustration.

FIG. 10

Dissolution Rate vs Temperature
500 ppm polymer



Note: Values less than 0.001 are reflected as 0.001 for ease of illustration.

FIG. 11

10/10

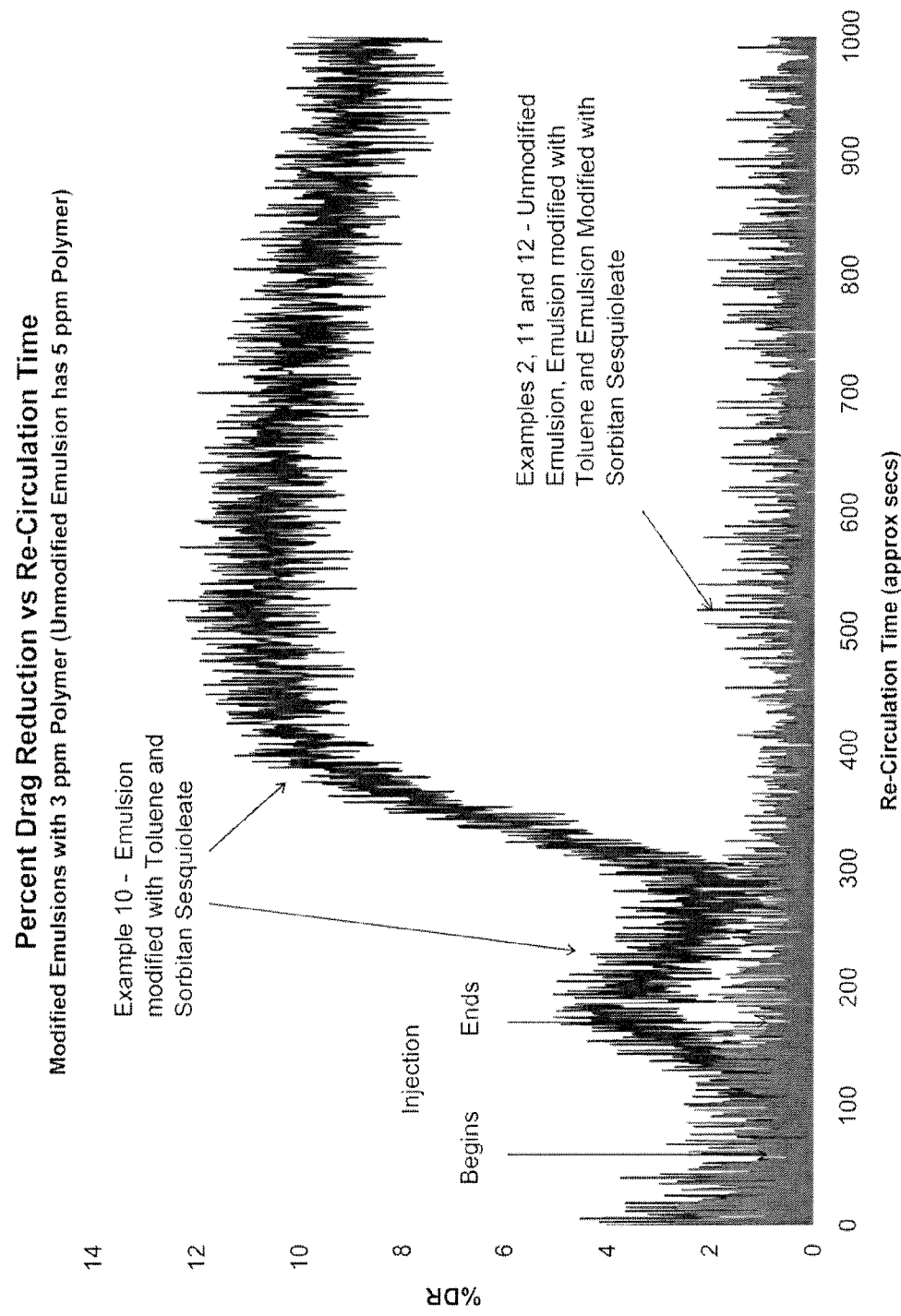


FIG. 12