



(51) International Patent Classification:

C09K 8/32 (2006.01) C09K 8/82 (2006.01)

(21) International Application Number:

PCT/US2017/062848

(22) International Filing Date:

21 November 2017 (21.11.2017)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

62/425,357 22 November 2016 (22.11.2016) US

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

(72) Inventors: **CHEN, Yiyan**; 5950 North Course Drive, Houston, TX 77072 (US). **KHRAMOV, Dimitri, M.**; 5950 North Course Drive, Houston, TX 77072 (US). **ADDICKS, Glynda, A.**; 5950 North Course Drive, Houston, TX 77072 (US).

(74) Agent: **HINKLEY, Sara, K.m.** et al.; Schlumberger, IP Center of Excellence, 10001 Richmond Ave., Room 4720-M, Houston, TX 77042 (US).

(81) Designated States (*unless otherwise indicated, for every kind of national protection available*): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP,

KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

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

Published:

— with international search report (Art. 21(3))

(54) Title: INVERT EMULSIFIERS FROM DCPD COPOLYMERS AND THEIR DERIVATIVES FOR DRILLING APPLICATIONS

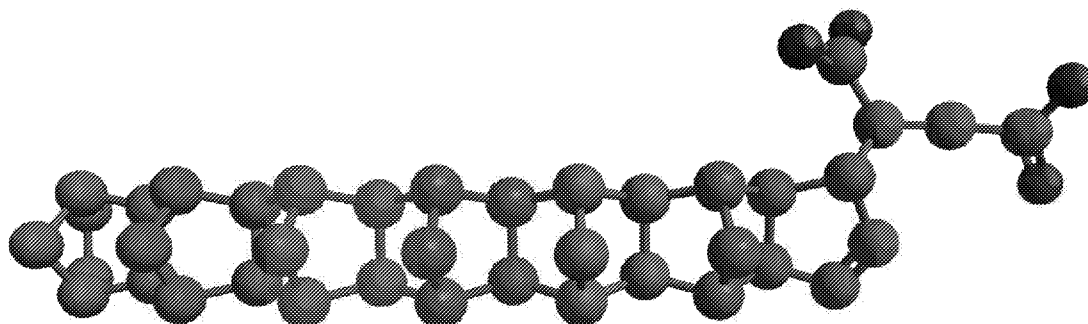


FIG. 1

(57) Abstract: A wellbore fluid, comprising an oleaginous continuous phase, a non-oleaginous discontinuous phase and a polymer having a polycyclic backbone. A method of drilling comprising pumping the said wellbore fluid into a wellbore through an earthen formation is also described.



INVERT EMULSIFIERS FROM DCPD COPOLYMERS AND THEIR DERIVATIVES FOR DRILLING APPLICATIONS

BACKGROUND

[0001] During the drilling of a wellbore, various fluids are used in the well for a variety of functions. The fluids may be circulated through a drill pipe and drill bit into the wellbore, and then may subsequently flow upward through wellbore to the surface. During this circulation, a drilling fluid may act to remove drill cuttings from the bottom of the hole to the surface, to suspend cuttings and weighting material when circulation is interrupted, to control subsurface pressures, to maintain the integrity of the wellbore until the well section is cased and cemented, to isolate the fluids from the formation by providing sufficient hydrostatic pressure to prevent the ingress of formation fluids into the wellbore, to cool and lubricate the drill string and bit, and/or to maximize penetration rate. The drilling fluid should also form a thin, low permeability filter cake that seals openings in formations penetrated by the bit and act to reduce the unwanted influx of formation fluids from permeable rocks.

[0002] Drilling fluids are typically classified according to their base material; in oil base fluids, solid particles are suspended in oil, and water or brine may be emulsified with the oil. The oil is typically the continuous phase. In water base fluids, solid particles are suspended in water or brine, and oil may be emulsified in the water. The water is typically the continuous phase. Pneumatic fluids are a third class of drilling fluids in which a high velocity stream of air or natural gas removes drill cuttings.

[0003] Oil-based drilling fluids are generally used in the form of invert emulsion fluids. An invert emulsion mud may include three-phases: an oleaginous phase, a non-oleaginous phase and a finely divided particle phase. Optionally included are emulsifiers and emulsifier systems, weighting agents, fluid loss additives, alkalinity regulators and the like, for stabilizing the system as a whole and for establishing the desired performance properties.

[0004] Emulsifiers are routinely employed in the drilling business to lower the interfacial tension between oil and water which allows the formation of stable invert emulsion fluids/mud (IEF) with small drops to be formed. There have been many

emulsifiers used in the drilling applications including but not limited to alkyl amine, alkyl amidoamine, and derivatives.

SUMMARY

- [0005] This summary is provided to introduce a selection of concepts that are further described below in the detailed description. This summary is not intended to identify key or essential features of the claimed subject matter, nor is it intended to be used as an aid in limiting the scope of the claimed subject matter.
- [0006] In one aspect, embodiments disclosed herein relate to a wellbore fluid that includes an oleaginous continuous phase, a non-oleaginous discontinuous phase and a polymer having a polycyclic backbone.
- [0007] In another aspect, embodiments of the present disclosure relate to a method of drilling that includes pumping a wellbore fluid into a wellbore through an earthen formation, the wellbore fluid including an oleaginous continuous phase, a non-oleaginous discontinuous phase and a polymer having a polycyclic backbone.
- [0008] Other aspects and advantages of the claimed subject matter will be apparent from the following description and the appended claims.

BRIEF DESCRIPTION OF DRAWINGS

- [0009] FIG. 1 shows the 3D structure of a polymer according to embodiments of the present disclosure.
- [0010] FIGS. 2 and 3 show emulsion droplets distributions according to embodiments of the present disclosure.

DETAILED DESCRIPTION

- [0011] Generally, embodiments disclosed herein are directed to emulsifiers that are used to stabilize emulsified wellbore fluids. More specifically, embodiments disclosed herein relate to wellbore fluids for downhole applications formed of an oleaginous continuous phase, a non-oleaginous discontinuous phase and a polymer having a polycyclic backbone. The inventors of the present disclosure have found

that polymers having a polycyclic backbone may be incorporated as emulsifiers into a wellbore fluid to stabilize the non-oleaginous discontinuous phase within the oleaginous continuous phase, particularly at high temperatures.

[0012] While most of the terms used herein will be recognizable to those of skill in the art, the following definitions are nevertheless put forth to aid in the understanding of the present disclosure. It should be understood, however, that when not explicitly defined, terms should be interpreted as adopting a meaning presently accepted by those of skill in the art.

[0013] As noted above, the wellbore fluids of the present disclosure may be oil-based wellbore fluids, such as emulsions of oleaginous and non-oleaginous fluids. In particular, various embodiments of the present disclosure may provide for an invert emulsion wellbore fluid. Invert emulsion, as used herein, is an emulsion in which a non-oleaginous fluid is the discontinuous phase and an oleaginous fluid is the continuous phase. The non-oleaginous fluid (such as water) is dispersed in spherical form by violent agitation of a mixture of a non-oleaginous and an oleaginous fluid (such as an oil and water mixture) in the presence of an emulsifier.

[0014] Oleaginous liquid, as used herein, means an oil which is a liquid at 25°C and is immiscible with water. Oleaginous liquids may include substances such as hydrocarbons used in the formulation of drilling fluids such as diesel oil, mineral oil, synthetic oil (including linear alpha olefins and internal olefins), ester oils, glycerides of fatty acids, aliphatic esters, aliphatic ethers, aliphatic acetals, or other such hydrocarbons and combinations of these fluids.

[0015] Non-oleaginous liquid as used herein, means any substance that is a liquid at 25°C and that is not an oleaginous liquid as defined above. Non-oleaginous liquids are immiscible with oleaginous liquids but capable of forming emulsions therewith. Non-oleaginous liquids may include aqueous substances such as fresh water, sea water, brine containing inorganic or organic dissolved salts, aqueous solutions containing water-miscible organic compounds and mixtures of these.

[0016] An emulsifier is a kind of surfactant. Surfactants are surface active compounds, that is, they show higher activity (*i.e.*, concentration) at the surface or interface than the bulk solution phase. Due to this property, they lower the surface

tension of a liquid, the interfacial tension between two liquids, or that between a liquid and a solid. Surfactants may act as detergents, wetting agents, emulsifiers, foaming agents, and dispersants. Surfactants are organic compounds that are amphiphilic, meaning they contain both hydrophobic groups (“tails”) and hydrophilic groups (“heads”). Therefore, a surfactant contains both an oil soluble component and a water soluble component.

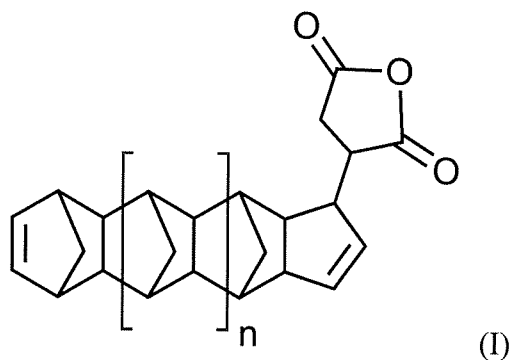
[0017] As defined herein, an emulsifier is a type of surfactant that aids in forming of an emulsion (*i.e.*, a mixture of two or more liquids that are normally immiscible) by decreasing the interfacial tension between immiscible liquids (e.g., oil and water), or a compound that stabilizes an already existing emulsion by decreasing the separation tendency of the liquids, or both.

[0018] As used herein, the term micelle includes any structure or aggregate that minimizes the contact between the hydrophobic (“solvent-repelling”) portion of a surfactant molecule and the solvent, for example, by aggregating the surfactant molecules into structures such as spheres, cylinders, or sheets, wherein the hydrophobic portions are on the interior of the aggregate structure and the hydrophilic (“solvent-attracting”) portions are on the exterior of the structure. For example, in a water phase, surfactants form micelles where the hydrophobic tails form the core of the micelle and the hydrophilic heads are in contact with the surrounding liquid. Such micelles are called normal-phase micelles (or oil-in-water micelles). In the case of inverse micelles (water-in-oil micelles), the head groups are located at the center, while the tails extend out, as it will be described later in greater detail.

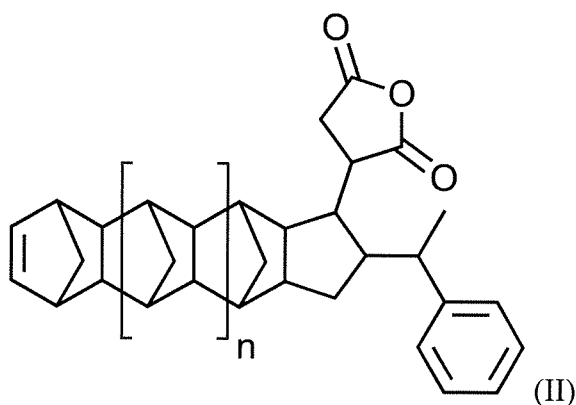
[0019] According to the present embodiments, the wellbore fluids of the present disclosure, such as invert emulsions, may contain polymers which may increase the stability of the emulsion. Specifically, the wellbore fluids of the present disclosure may incorporate a polymer having a polycyclic backbone. Whereas the conventional polymer backbone has a single hydrocarbon chain forming the backbone, the polycyclic backbone of the present disclosure may be more complex, having the cyclic groups forming the “backbone”. Such difference may be considered by equating the polycyclic backbone to a ladder and a conventional polymer backbone to a rope. Pendant groups may extend from the ladder. For example, the polycyclic

backbone of the polymer is a copolymer of dicyclopentadiene (DCPD), where DCPD is a polymer composed of polymerized dicyclopentadiene. In such embodiments, the polycyclic backbone of the polymer has at least a dicyclopentadiene repeating unit.

[0020] In one or more embodiments, the polycyclic backbone of the polymer may be formed by the copolymerization reaction of DCPD and maleic anhydride at the terminal end of the polymer, with the formation of a copolymer DCPD/maleic anhydride as shown below by structure I. It is also envisioned that other derivatives of maleic anhydride may be used. The number of the DCPD repeating units, n , on the polycyclic backbone is selected in such a manner that the average molecular weight of the polymer ranges from about 200 to about 2000.

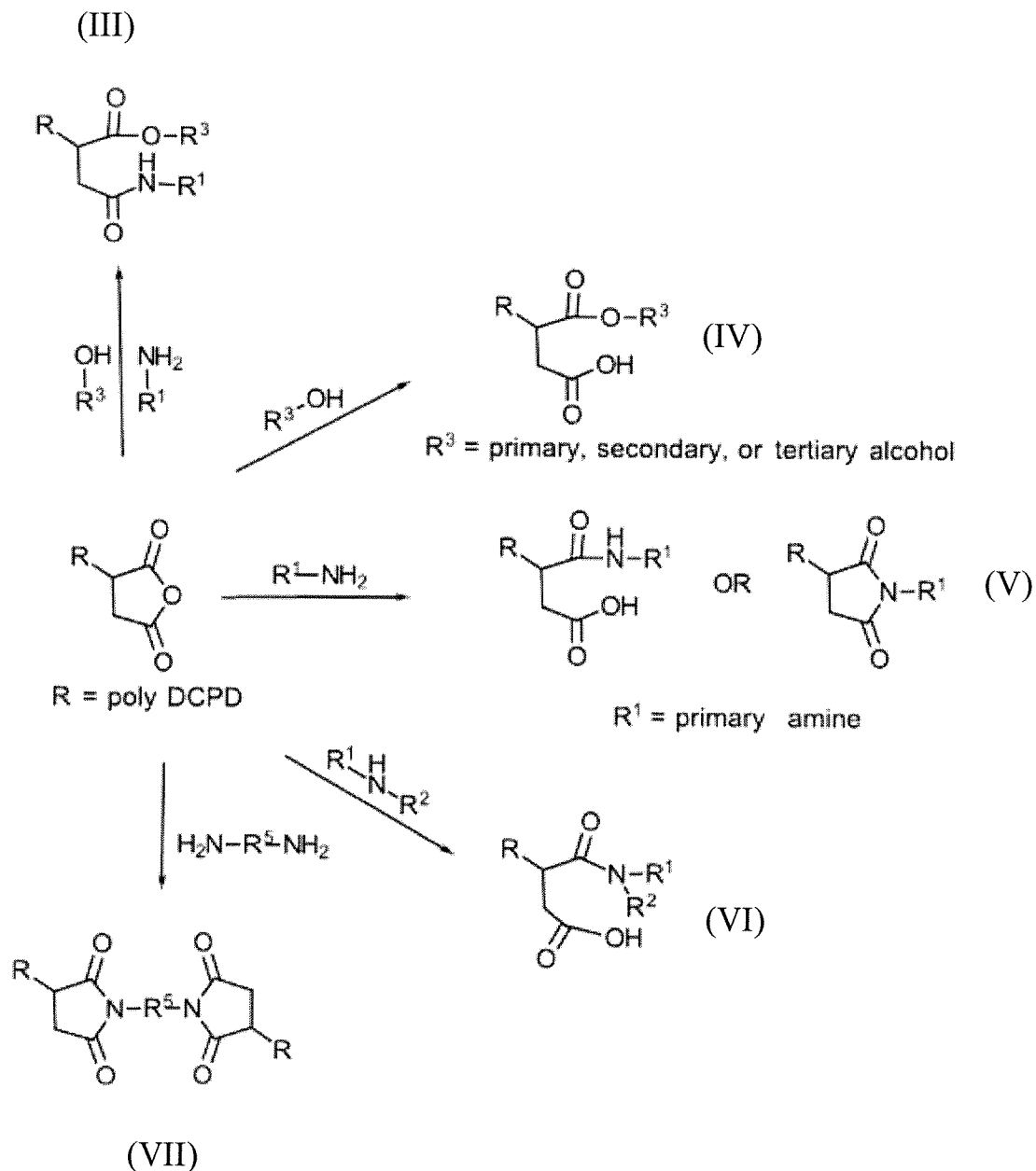


[0021] It is also envisioned that the polymers of the present disclosure are copolymers formed by the copolymerization reaction of at least two monomers, such as dicyclopentadiene and styrene. This is exemplified in structure II below. In such embodiments, the dicyclopentadiene is further derivatized with maleic anhydride, with the formation of a copolymer of dicyclopentadiene, styrene and maleic anhydride, where the DCPD is the repeating unit. As noted above, the number of the DCPD repeating units, n , is selected in such a manner that the molecular weight of the polymer ranges from about 200 to about 2000. However, other combinations are possible, depending on the desired degree of rigidity of the polycyclic backbone of the polymer. For example, the DCPD repeating units may alternate with styrene monomer units (not shown). It is also envisioned that the DCPD repeating units may alternate with other repeating units (not shown). In such embodiments, the molecular weight may be higher than 2000.



As seen above for structures I and II, the maleic anhydride is not functionalized. It is also envisioned that the maleic anhydride may be functionalized using various organic compounds. For example, the maleic anhydride may be functionalized in such a manner that the anhydride group has at least a hydrophilic group. As described later, the presence of the hydrophilic group may be desired for the stability of the invert micelles formed by the polymers of the present disclosure. The functionalization of the anhydride group as shown in structure II, above, may be performed with little effort because of the high reactivity of the intermediate anhydride. A few examples are shown below, in reactions III-VII. As noted below, R is the polymer having the polycyclic backbone, namely the poly DCPD, R^1-NH_2 is a primary amine, R^1-NH-R^2 is a secondary amine, R^3-OH is a primary, secondary or tertiary alcohol and $R^5(NH_2)_2$ is a polyfunctional amine, such as diethylenetriamine (DETA), TETA, DTPA, hexamethylene diamine and similar.

[0022] As the anhydride group acts as the head group of the surfactant polymer, as described later in greater detail, such modifications on the surfactant head group allow tailoring the structure of the polymer to give certain behaviors for any desired invert emulsion fluid, IEF.



[0023] Without being bound by theory, it is believed that the polymers of the present disclosure may act as co-surfactants that may promote intermolecular interactions that enhance the invert emulsion fluid (IEF) mud stability. In such embodiments, the polymers of the present disclosure may be mixed with other surfactants that are capable of generating invert emulsions, such as amidoamines, fatty acids and ethoxylates. It is also envisioned that other surfactants may act as co-surfactants in the presence of the polymers of the present disclosure. According to various embodiments, a polymeric inverse micelle solution may be prepared by adding the

polymers of the present disclosure to a mixture of the oleaginous continuous phase and the non-oleaginous discontinuous phase (such as for example brine and oil mixture), blending the polymers into the mixture, followed by shearing to enhance emulsion formation, where polymeric micelles are formed to provide a micelle solution. Depending on the functionality of the head group of the polymer, it is also envisioned that the polymers may be added into a non-oleaginous discontinuous phase, or may be added into an oleaginous continuous phase, prior to the formation of the emulsion. In one or more embodiments, the polymer as described herein may be used in excess. However, the amount of the emulsion used may be equal to or less than 25 ppb.

[0024] According to the present embodiments, the micelles formed by the emulsifiers of the present disclosure are inverse micelle-type assemblies or water-in-oil micelle (not shown), where the head hydrophilic groups are sequestered in the micelle core (such as an aqueous core) (not shown) and the hydrophobic tail groups (not shown) extend away from the center. Thus, the non-oleaginous phase, such as an aqueous phase (not shown), is an internal phase that is stably emulsified within the external oleaginous phase (not shown). According to various embodiments, the internal aqueous phase may range, for example, up to 60% of the volume of the emulsion, but may have a higher volume in high internal phase ratio invert emulsions.

[0025] As shown above in structures I and II, the hydrophobic tail can be bulky for space filling to better stabilize the invert micelle structure since the outer hydrophobic regime is bigger than the inner head (not shown). Compared to regular fatty acid tails in a conventional surfactant, the fused ring structure of DCPD polymer or other polycyclic polymer will occupy a bigger space to help stabilize the invert micelles.

[0026] Another feature of these fused ring polymer tails is their resistance to thermal breaking down. Generally, conventional unsaturated fatty acid derived surfactants have a few double bond carbon chain tails which are susceptible to oxidative breakings. However, breaking a chain in the DCPD or other polycyclic polymer implies breaking of multiple bonds, providing therefore more thermal stability. The link between the hydrophilic head and the hydrophobic tail is also accomplished through carbon-carbon bonds which are stronger than many polar bonding.

[0027] Another characteristic of the polymers having polycyclic backbone as described herein is their 3D structure. For example, FIG. 1 shows the 3D structure of polymer II presented above, where DPCD is derivatized with maleic anhydride. This material appears to be highly amorphous, meaning that polymers having polycyclic backbone based on a DCPD copolymer are unlikely to crystallize in oil based muds (OBM) and cause unreasonably high low temperature rheology. Furthermore, the lack of crystallization is an indication that the DCPD polycyclic backbone may exhibit increased solubility in a base oil at low temperatures compared to polymers having simple backbones, for example, polyethylene or polypropylene backbones. Additionally, the rigid ladder structure of the polymer as described herein may provide improved steric stabilization for emulsion droplets compared to a more flexible backbone of an emulsifier (an example of a typical emulsifier is represented by fatty acid soaps).

[0028] The synthesis of the polymers of the present disclosure is versatile as the chain length of the polycyclic backbone of the polymer may be controlled through polymerization. In addition, the maleic anhydride content may be modified to give different HLB ratios. As described herein, the term “HLB” (Hydrophilic Lipophilic Balance) refers to the ratio of the hydrophilicity of the polar groups of the surface-active molecules to the hydrophobicity of the lipophilic part of the same molecules. One skilled in the art would appreciate that an HLB value may be calculated by considering the molecular weight contributions of the respective hydrophilic and lipophilic portions and taking the ratio thereof (divided by 5). Generally, the Bancroft rule applies to the behavior of emulsions: emulsifiers and emulsifying particles tend to promote dispersion of the phase in which they do not dissolve very well; for example, a compound that dissolves better in water than in oil tends to form oil-in-water emulsions (that is, they promote the dispersion of oil droplets throughout a continuous phase of water). Emulsifiers are typically amphiphilic. That is, they possess, as noted above, both a hydrophilic portion and a hydrophobic portion. The chemistry and strength of the hydrophilic polar group compared with those of the lipophilic nonpolar group determine whether the emulsion forms as an oil-in-water or water-in-oil emulsion. In particular, emulsifiers may be evaluated based on their HLB value. Generally, to form a water-in-oil emulsion, an emulsifier (or a mixture of emulsifiers)

having a low HLB, such as between 3 and 8, may be desirable. In a particular embodiment, the HLB value of the emulsifier may range from 4 to 6.

[0029] It is also envisioned that tailoring the structure of the polymers of the present disclosure may allow for other applications, depending on the rigidity, as well as functionality of the polycyclic backbone. Polymers as described herein may be added to a continuous phase regardless of composition. However, the presence of a hydrophobic group does not guarantee compatibility or solubility with the continuous phase. Furthermore, the conductivity of the polymer may be modified from non-conductive to conductive or vice versa, depending on the structure of the polymer.

[0030] The base fluids described herein may be oil-based wellbore fluids, such as an invert emulsion where a non-oleaginous phase is emulsified within an oleaginous continuous phase. In one or more embodiments, the oleaginous continuous phase is selected from the group including diesel oil, mineral oil, a synthetic oil, such as hydrogenated and unhydrogenated olefins including polyalpha olefins, linear and branch olefins and the like, polydiorganosiloxanes, siloxanes, or organosiloxanes, esters of fatty acids, specifically straight chain, branched and cyclical alkyl ethers of fatty acids. Generally, the amount of the oleaginous phase may be sufficient to form a stable emulsion when utilized as the continuous phase. The amount of oleaginous phase in the invert emulsion fluid may vary depending upon the particular oleaginous phase used, the particular non-oleaginous phase used, and the particular application in which the invert emulsion fluid is to be employed. The amount of non-oleaginous phase in the invert emulsion fluid may vary depending upon the particular non-oleaginous phase used, the emulsifier selected to stabilize the non-oleaginous phase, and the particular application in which the invert emulsion fluid is to be employed. In one or more embodiments, the oil based fluid may contain up to 40, 50 or 60 vol. % water or other non-oleaginous phase, and at least 40, 50, or 60 vol. % of oleaginous phase.

[0031] As mentioned above, the wellbore fluid may be an invert emulsion having a continuous oleaginous phase and a discontinuous non-oleaginous liquid phase, among other substances and additives. Non-oleaginous liquids may, in some embodiments, include at least one of fresh water, sea water, brine, mixtures of water and water-

soluble organic compounds, and mixtures thereof. In various embodiments, the non-oleaginous phase may be a brine, which may include seawater, aqueous solutions wherein the salt concentration is less than that of sea water, or aqueous solutions wherein the salt concentration is greater than that of sea water. As described later in greater detail, the seawater contains more than one dissolved salt. Therefore, the salinity is expressed as the total dissolved solids (TDS). It is also envisioned that synthetic brines may be used in the wellbore fluids disclosed herein, the synthetic brines tending to be much simpler in constitution than the natural ones.

[0032] Salts that may be found in seawater include, but are not limited to, sodium, calcium, aluminum, magnesium, potassium, strontium, and lithium salts of chlorides, bromides, carbonates, iodides, chlorates, bromates, formates, nitrates, oxides, sulfates, silicates, phosphates and fluorides. Salts that may be incorporated in a brine include any one or more of those present in natural seawater or any other organic or inorganic dissolved salts. Additionally, brines that may be used in the drilling fluids disclosed herein may be natural or synthetic, with synthetic brines tending to be much simpler in constitution.

[0033] The amount of the non-oleaginous fluid is typically less than the theoretical limit needed for forming an invert emulsion. Thus, in one embodiment, the amount of non-oleaginous fluid is at least 40% by volume, or from about 40% to about 60% by volume of the invert emulsion fluid.

[0034] Upon mixing, the fluids of the present embodiments may be used in wellbore operations, such as drilling operations. Such operations are known to persons skilled in the art and involve pumping a drilling fluid into a wellbore through an earthen formation. The wellbore fluids of the present embodiments may have particular applications for drilling operations at high temperatures as they exhibit improved emulsion stability. In addition, such IEF muds are stable, while maintaining a favorable environmental rating.

[0035] One embodiment of the present disclosure includes a method that involves a method of drilling. In such an illustrative embodiment, the method involves pumping a wellbore fluid into a wellbore through an earthen formation, the wellbore fluid including an oleaginous continuous phase, a non-oleaginous discontinuous phase and

the polymer having a polycyclic backbone as described above. In such embodiment, the amount of polymer used as emulsifier ranges from about 3 pounds per barrel to about 25 pounds per barrel, where the lower limit can be any of 3 pounds per barrel, 4 pounds per barrel or 5 pounds per barrel and the upper limit can be any of 10 pounds per barrel, 15 pounds per barrel or 25 pounds per barrel, where any lower limit can be used with any upper limit.

[0036] **EXAMPLES**

[0037] The following examples are presented to further illustrate the emulsifying ability of the polymeric surfactants as described herein.

[0038] Emulsion and temperature stability

[0039] To investigate the stability of the brine-in-oil emulsions created by the polymers (or resins) as described herein, a simple brine/oil mixture was prepared. The brine used was a 25% by weight solution of calcium chloride in water. 28 vol% of this calcium chloride brine was stirred into a synthetic base oil (a C15-C18 olefin blend) using an overhead lab mixer at approximately 3000 rpm. A small amount of calcium hydroxide (lime) was added to generate the carboxylate from acid or anhydride-the actual emulsifier from the test resin. The test solid resin, was crushed into a fine grained powder before adding to the mixture; an amount of 4 grams for every 350 ml liquid mixture was used. After blending the resin into the brine/oil mixture, the mixture was sheared on a Silverson mixer at 6000 rpm for 5 minutes to micronize the brine droplets and enhance emulsion formation. The stability of these emulsions was determined visually. Afterwards, the mixture was divided evenly into three portions and placed into aging cells. The mixtures were aged with rolling for 6 to 16 hours at 250°F (121°C), 350°F (177°C), or 400°F (204°C). After cooling to ambient temperature, the mixtures were removed from the aging cells and the emulsions inspected.

[0040] As observed experimentally, many of these combinations remained in emulsified form (not shown), even after aging at elevated temperatures, and settled slowly after standing quiescent over several hours, with no appearance of an aqueous layer at the bottom (brine is heavier). One of the settled phases had a smooth to fine-

grained appearance. The lack of a visible aqueous phase is an indication of the strong emulsifying ability of these resins.

[0041] Table 1 below summarizes the visual characterization of emulsions prepared using 10 different DCPD based polymers, namely Resin 1-Resin 10. As can be seen from Table 1, many of these emulsions remain stable after 350°F (177°C) hot roll, one of the emulsions is even stable after 400°F (204°C) hot roll. These results indicate that the DCPD copolymer has excellent emulsifier ability at high temperatures.

Table 1. Visual characterization of various emulsions

	Resin 1	Resin 2	Resin 3	Resin 4	Resin 5	Resin 6	Resin 7	Resin 8	Resin 9	Resin 10
Mn	353	364	390	613	588	587	900	914	943	489
Acid number (mg KOH/g)	5.1	13.9	22.5	23.1	14.6	5.3	5.5	14.8	23.7	44
Observations after hot rolled at 250°F	granular solids, quickly settled, no water	fine solids, slowly settled, no water	fine solids, slowly settled, no water	slightly grainy solids, moderate settling, no water	slightly grainy solids, moderate settling, no water	hard rapid settling, large chunks, no water	slightly grainy, moderate settling, no water	fine solids, moderate settling, no water	fine solids, slow settling, no water	fine solids, rapid settling, no water
Observations after hot rolled at 350°F	grainy solids, rapid settling, no water	slightly grainy, moderate settling, no water	slightly grainy, moderate settling, no water	slightly grainy, rapid settling, no water	slightly grainy, moderate settling, no water	chunks and granules, rapid settling, no water	fine solids, rapid settling, no water	grainy, rapid settling, no water	fine solids, moderate settling, no water	dark color, emulsion broke, water layer
Observations after hot rolled at 400°F	emulsion broke, water layer	grainy, rapid settling, no water	slightly grainy, moderate settling, no water	large chunks, rapid settling, no water	chunky, rapid settling, no water	emulsion broke, water layer	emulsion broke, water layer	grainy, rapid settling, no water	big chunks, waxy, rapid settling, no water	skipped because unstable at 350°F

[0042] To further demonstrate the emulsion stability, several emulsion samples were selected to study the particle size distribution (PSD). Examples are shown in FIGS. 2 and 3. Referring now to FIG. 2, 200 represents Resin 9 not hot rolled, 210 represents Resin 9 hot rolled at 250°F (121°C), 220 represents Resin 9 hot rolled at 350°F (177°C) and 230 represents Resin 9 hot rolled at 400°F (204°C). Referring now to FIG. 3, 300 represents Resin 3 not hot rolled, 310 represents Resin 3 hot rolled at 250°F (121°C), 320 represents Resin 3 hot rolled at 350°F (177°C) and 330 represents Resin 3 hot rolled at 400°F (204°C). These results corroborate with the visual observation that Resin 3 emulsion is stable even after 400°F (204°C) hot roll.

[0043] Mud formulation and performances

[0044] Two examples of mud formulations are shown below in Table 2 with different emulsifier loadings. The emulsifier that was used in the system was Resin 3, a polycyclic DCPD resin having maleic grafts and a MW of 773. Though additional functionalization hasn't been tried, it is envisioned that functionalization with amines or esters, similar to reactions III-VII, as described above, may be possible. Typical properties exhibited by various polycyclic DCPD resins are shown below in Table 3. VERSAGEL HT[®] (pure hectorite clay) is a viscosifier, SUREWET[®] is an additive that may function as a secondary emulsifier, ECOTROL HT[®] is a filtration-control synthetic co-polymer and M-I WATE[®] is a high-quality, drilling-grade barite (barium sulfate) used to increase the density of drilling fluids, all available from M-I SWACO, Houston, Texas.

Table 2. 15 ppg Oil Based Mud 80-20 oil-brine ratio, hot rolled at 250°F

Formulation		
Synthetic B	152	152
VERSAGEL HT [®] , g	2	2
Lime, g	5	5
Emulsifier, g	20	12.5
SUREWET [®] , g	1	1
ECOTROL HT [®] , g	3	3
25% CaCl ₂ brine, g	65	65
M-I WATE [®] , g	410	410

Table 3. Typical properties of polycyclic resins that can be used as OBM emulsifiers.

	Resin 1	Resin 2	Resin 3	Resin 6	Resin 5	Resin 4	Resin 7	Resin 8	Resin 9
Mn	353	364	390	587	588	613	900	914	943
Mw	626	682	773	1316	1320	1406	2173	2204	2343
Polydispersity	1.77	1.87	1.98	2.24	2.25	2.29	2.41	2.41	2.48
Acid number (mg KOH/g)	5.1	13.9	22.5	5.3	14.6	23.1	5.5	14.8	23.7
Softening Point, R&B (°C)*	95	100	111	145	148	156	98	103	111
Gardner Color (50% in solvent)	8	8.2	8.8	11.7	11.5	11.6	10.4	10.1	11.3
Typical Specific Gravity @ 25 °C	1.1	1.1	1.1	1.08	1.08	1.08	1.06	1.06	1.06
Viscosity (cps)									
140°C	1700	3320	11500	-	-	-	9400	15900	36100
160°C	383	650	1660	-	-	-	2110	3150	3150
180°C	55	195	407	13700	18500	48000	347	622	622
200°C	-	-	-	2450	3040	6250	-	-	-
220°C	-	-	-	657	745	1320	-	-	-

[0045] The properties of the mud formulated as shown in Table 2 were evaluated using a conventional approach for mud properties analysis. The properties of the mud after heat stress were evaluated by studying the rheology of the mud using a FANN 35 viscometer. The measurements were performed after mud preparation and after mud aging at 250°F (121°C) in a roller oven. The results are shown in Table 4.

Table 4. Rheology and HPHT properties of mud using the formulation as shown in Table 2.

	20 ppb resin			12.5 ppb resin		
	150°F (65°C) before hot roll	100°F (38°C) after hot roll	150°F (65°C) after hot roll	150°F (65°C) before hot roll	100°F (38°C) after hot roll	150°F (65°C) after hot roll
600 rpm	90	238	112	75	188	83
300 rpm	54	153	74	44	120	49
200 rpm	41	121	59	34	94	37
100 rpm	27	85	44	22	65	24
6 rpm	9	46	30	6	30	11
3 rpm	8	46	30	6	28	11
PV	36	85	38	31	68	34
YP	18	68	36	13	52	15
10" Gels	12	45	31	7	28	9
10' Gels	37	79	50	35	50	28
ES	1542		1394	894		804
HTHP fluid loss at 250°F (121°C)			3.6			3.6
Water			0			0
HTHP fluid loss at 350°F (176°C)			4.8			
Water			0			

[0046] As seen in Table 4, above, ES refers to the electrical stability of the emulsion. As noted above, the wellbore fluids of the present disclosure possess an aqueous phase that is stably emulsified within the external oleaginous phase. Upon application of an electric field to an invert emulsion fluid, the emulsified non-oleaginous phase, which possesses charge, will migrate to one of the electrodes used to generate the

electric field. The incorporation of emulsifiers as described herein in the invert emulsion fluid stabilizes the emulsion and results in a slowing of the migration rate and/or increased voltage for breakage of the emulsion. Thus, an electrical stability (ES) test, specified by the American Petroleum Institute at API Recommended Practice 13B-2, Third Edition (February 1998), is often used to determine the stability of the emulsion. ES is determined by applying a voltage-ramped, sinusoidal electrical signal across a probe (consisting of a pair of parallel flat-plate electrodes) immersed in the mud. The resulting current remains low until a threshold voltage is reached, whereupon the current rises very rapidly. This threshold voltage is referred to as the ES ("the API ES") of the mud and is defined as the voltage in peak volts-measured when the current reaches 61 μ A. The test is performed by inserting the ES probe into a cup of 120°F (48.9°C) mud applying an increasing voltage (from 0 to 2000 volts) across an electrode gap in the probe. The higher the ES voltage measured for the fluid, the stronger or harder to break would be the emulsion created with the fluid, and the more stable the emulsion is.

[0047] In addition to 250°F HPHT fluid loss, performed at same temperature as aging, a higher temperature HPHT was performed to demonstrate that Resin 3 is capable of stabilizing emulsion efficiently. The result for HPHT at 350°F (177°C) indicates that no water is present in the filtrate, which is an indication of a strong emulsion. Additionally, the FANN 35 readings shown in Table 4 indicate that the rheology may be controlled by changing the amount of Resin 3 loaded into the formulation.

[0048] Formulations presented below in Table 5 are examples of OBM that were prepared and then heat aged at 350°F (177°C). These examples include two formulations at different resin loadings. In this example, fluid was aged at 350°F (177°C) after preparation. The experiment performed at 350°F (177°C) is an example of severe conditions that can be found in certain drilling operations. The objective of this experiment is to demonstrate that fluid based on Resin 3 is capable of functioning under such demanding conditions.

Table 5. 15 ppg mud at 80-20 oil-brine ratio hot rolled at 350°F

	12.5 ppb resin	8 ppb resin
Synthetic B	152	152
VERSAGEL HT [®] , g	2	2
Lime, g	5	5
Emulsifier, g	12.5	8
SUREWET [®] , g	1	1
Fluid loss additive (FLA), g	3	3
25% CaCl ₂ brine	65	65
M-I WATE	410	410

Table 6. Rheology and HPHT data for 15 ppg mud at 80-20 oil-brine ratio hot rolled at 350°F (176°C)

	12.5 ppb resin			8 ppb resin		
	150°F (65°C) before hot roll	100°F (38°C) after hot roll	150°F (65°C) after hot roll	150°F (65°C) before hot roll	100°F (38°C) after hot roll	150°F (65°C) after hot roll
600 rpm	75	300	271	86	257	158
300 rpm	44	240	211	56	183	118
200 rpm	34	219	179	44	152	103
100 rpm	22	187	131	31	116	74
6 rpm	6	131	55	17	61	26
3 rpm	6	81	43	16	48	20
PV	31	60	60	30	74	40
YP	13	180	151	26	109	78
10" Gels	7	89	48	16	50	22
10' Gels	35	>300	57	36	45	33
ES	894		1023	890		864
HTHP fluid loss at 350°F (176°C)			7.8			13
Water			<0.1			0.1

[0049] Data presented in Table 6 illustrates that fluid prepared with Resin 3 may withstand a temperature of 350°F (176°C) while still maintaining adequate properties, including emulsion strength as shown by the ES and HPHT values. As seen from Table 6, the rheology of the mud with the 12.5 ppb resin loading is too high. However, the rheology of the mud may be adjusted by reducing the resin loading.

[0050] To further expand the scope and application of polycyclic DCPD resins, a 13 ppg fluid was prepared using a 75-25 oil-brine ratio. To establish a structure-activity relationship between different products, two different polycyclic resins were used, namely Resin 3 and Resin 9. Formulations are shown below in Table 7. The fluids were aged at 250°F (121°C) and the rheological properties were measured. Results are shown below in Table 8.

Table 7. 13 ppg 75-25 oil-brine ratio using two different resins

Product	Resin 9	Resin 3
	ECOTROL HT [®]	ECOTROL HT [®]
Synthetic B	157	157
VERSAGEL HT [®] , g	2	2
Lime, g	5	5
Emulsifier, g	8	8
SUREWET [®] , g	1	1
FLA, g	3	3
25% CaCl ₂ brine, g	89	89
M-I WATE [®] , g	294	294

Table 8. Rheology and HPHT results for 13 ppg 75-25 oil-brine ratio using two different resins.

	Resin 9			Resin 3		
	150°F (65°C) before hot roll	100°F (38°C) after hot roll	150°F (65°C) after hot roll	150°F (65°C) before hot roll	100°F (38°C) after hot roll	150°F (65°C) after hot roll
600 rpm	46	75	48	63	90	55
300 rpm	23	41	22	34	48	29
200 rpm	17	30	15	26	34	20
100 rpm	9	18	8	17	19	12
6 rpm	2	3	1	6	2	3
3 rpm	2	2	1	6	2	3
PV	23	34	26	29	42	26
YP	0	7	-4	5	6	3
10" Gels	2	2	1	6	2	3
10' Gels	6	5	2	25	9	11
ES	324		203	292		309
HTHP fluid loss at 250°F (121°C)			1.3			3
Water			0			trace

[0051] With regard to Table 8, it is particularly worth noting the difference in gel strengths. Without being bound by theory, the inventors of the present disclosure believe that the difference in the gel strengths may be attributed to different molecular weights and HLB ratios of the two polycyclic DCPD resins. Specifically, both resins have comparable acid numbers, but large difference in MW (2343 vs. 773). The data presented in Table 8 illustrates the effect of molecular weight of the resin on the rheological properties.

[0052] Furthermore, increased sag of solids was observed during rheology measurements performed for the fluid containing Resin 9 versus the fluid containing Resin 3. Solids sag is an undesirable property and should be minimized. It was observed that selection of proper polycyclic DCPD resin may help minimizing solids sag.

[0053] An additional example illustrating the utility of polycyclic resins as emulsifiers in an OBM is demonstrated using the formulation shown below in Table 9. In this example, a fluid having 40% internal phase was prepared. The main advantage of such a fluid is a decreased cost compared to a fluid that uses less internal phase.

Table 9. 13 ppg 60-40 oil-brine ratio OBM using Resin 3.

Synthetic B	125
VERSAGEL HT [®] , g	2
Lime, g	5
Emulsifier, g	8
SUREWET [®] , g	1
FLA, g	3
25% CaCl ₂ brine, g	142
M-I WATE [®] , g	265

[0054] Table 10, below, illustrates the data obtained after the fluid was aged at 250°F (121°C). These results show that Resin 3 is capable of stabilizing an OBM even at high internal phase ratio.

Table 10. Rheology and HPHT results for 13 ppg 60-40 oil-brine ratio OBM using Resin 3

	Resin 3		
	150°F (65°C)	100°F (38°C)	150°F (65°C)
600 rpm	160	224	120
300 rpm	102	136	70
200 rpm	80	102	51
100 rpm	57	63	31
6 rpm	35	12	9
3 rpm	33	10	9
PV	58	88	50
YP	44	48	20
10" Gels	38	10	8
10' Gels	48	29	29
ES	154		232
HTHP at 250°F (121°C)			1.8
Water			0.05

[0055] Advantageously, embodiments of the present disclosure may provide wellbore fluids and methods of using such fluids that include an oleaginous continuous phase, a non-oleaginous discontinuous phase and a polymer having a polycyclic backbone. The use of a polycyclic backbone based on a DCPD copolymer and its derivatives in the wellbore fluids of the present disclosure advantageously promotes intermolecular interactions that may enhance IEF mud stability at high temperature. As described above, the DCPD copolymer may provide a portfolio of new emulsifiers with beneficial features. In addition, modifications on the surfactant head group of the polymer may allow for tailoring the molecule in such a manner to give specific behaviors for any desired IEF.

[0056] Although only a few example embodiments have been described in detail above, those skilled in the art will readily appreciate that many modifications are possible in the example embodiments without materially departing from this invention. Accordingly, all such modifications are intended to be included within the scope of this disclosure as defined in the following claims. In the claims, means-plus-function clauses are intended to cover the structures described herein as performing the recited function and not only structural equivalents, but also equivalent structures. Thus, although a nail and a screw may not be structural equivalents in that a nail employs a cylindrical surface to secure wooden parts together, whereas a screw employs a helical surface, in the environment of fastening wooden parts, a nail and a screw may be equivalent structures. It is the express intention of the applicant not to invoke 35 U.S.C. § 112, paragraph 6 for any limitations of any of the claims herein, except for those in which the claim expressly uses the words ‘means for’ together with an associated function.

CLAIMS

What is claimed:

1. A wellbore fluid, comprising:
 - an oleaginous continuous phase;
 - a non-oleaginous discontinuous phase; and
 - a polymer having a polycyclic backbone.
2. The wellbore fluid of claim 1, wherein the polycyclic backbone of the polymer has at least a dicyclopentadiene repeating unit.
3. The wellbore fluid of claim 2, wherein the polymer having a polycyclic backbone further contains at least a styrene monomer unit.
4. The wellbore fluid of claim 2, wherein the dicyclopentadiene is derivatized with maleic anhydride.
5. The wellbore fluid of claim 4, wherein the maleic anhydride is not functionalized.
6. The wellbore fluid of claim 4, wherein the maleic anhydride is functionalized at an anhydride group.
7. The wellbore fluid of claim 6, wherein the functionalized anhydride group of the maleic anhydride has at least a hydrophilic group.
8. The wellbore fluid of claim 7, wherein the anhydride group is functionalized with an alcohol, an amine, or combinations thereof.
9. The wellbore fluid of claim 8, wherein the alcohol is selected from the group of primary, secondary and tertiary alcohols.
10. The wellbore fluid of claim 8, wherein the amine is selected from the group of primary, secondary and polyfunctional amines.
11. The wellbore fluid of claim 1, wherein the polymer has a molecular weight ranging from about 200 to about 2000.

12. A method of drilling, comprising:
 - pumping a wellbore fluid into a wellbore through an earthen formation, the wellbore fluid comprising:
 - an oleaginous continuous phase;
 - a non-oleaginous discontinuous phase; and
 - a polymer having a polycyclic backbone.
13. The method of drilling of claim 12, wherein the polycyclic backbone of the polymer has at least a dicyclopentadiene repeating unit.
14. The method of drilling of claim 13, wherein the polymer having a polycyclic backbone further contains at least a styrene monomer unit.
15. The method of drilling of claim 13, wherein the dicyclopentadiene is derivatized with maleic anhydride.
16. The method of drilling of claim 15, wherein the maleic anhydride is not functionalized.
17. The method of drilling of claim 15, wherein the maleic anhydride is functionalized at an anhydride group.
18. The method of drilling of claim 17, wherein the functionalized anhydride group of the maleic anhydride has at least a hydrophilic group.
19. The method of drilling of claim 18, wherein the anhydride group is functionalized with an alcohol, an amine, or combinations thereof.
20. The method of drilling of claim 19, wherein the alcohol is selected from the group of primary, secondary and tertiary alcohols.
21. The method of drilling of claim 19, wherein the amine is selected from the group of primary, secondary and polyfunctional amines.
22. The method of drilling of claim 12, wherein the polymer has a molecular weight ranging from about 200 to about 2000.

23. The method of drilling of claim 12, wherein the polymer is used in an amount ranging from 3 to 25 pounds per barrel.

1/3

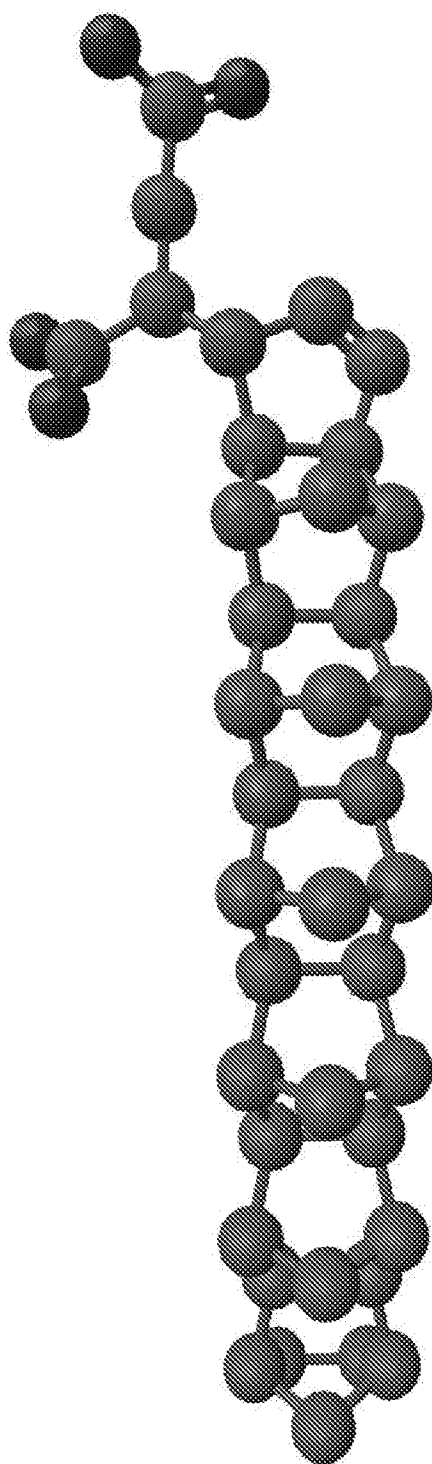


FIG. 1

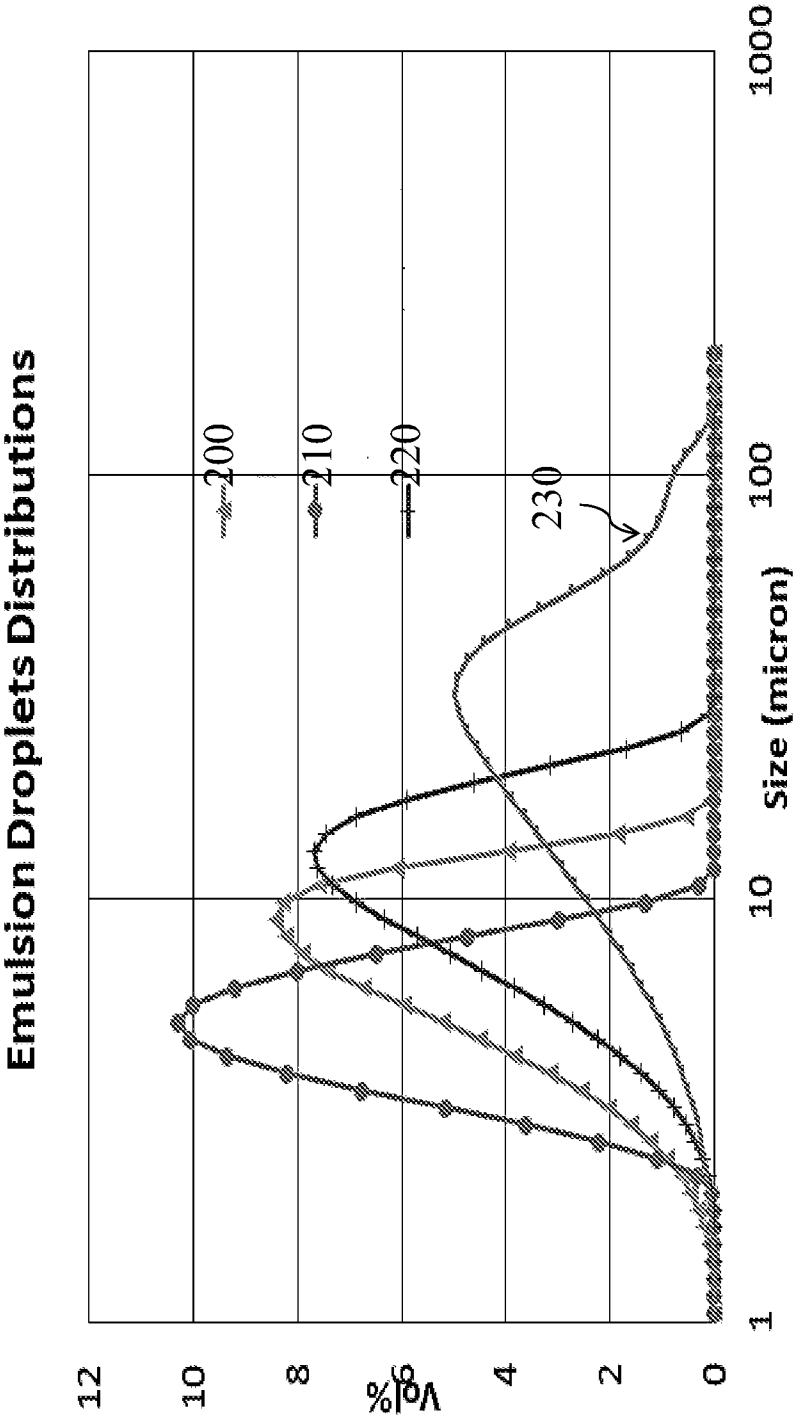


FIG. 2

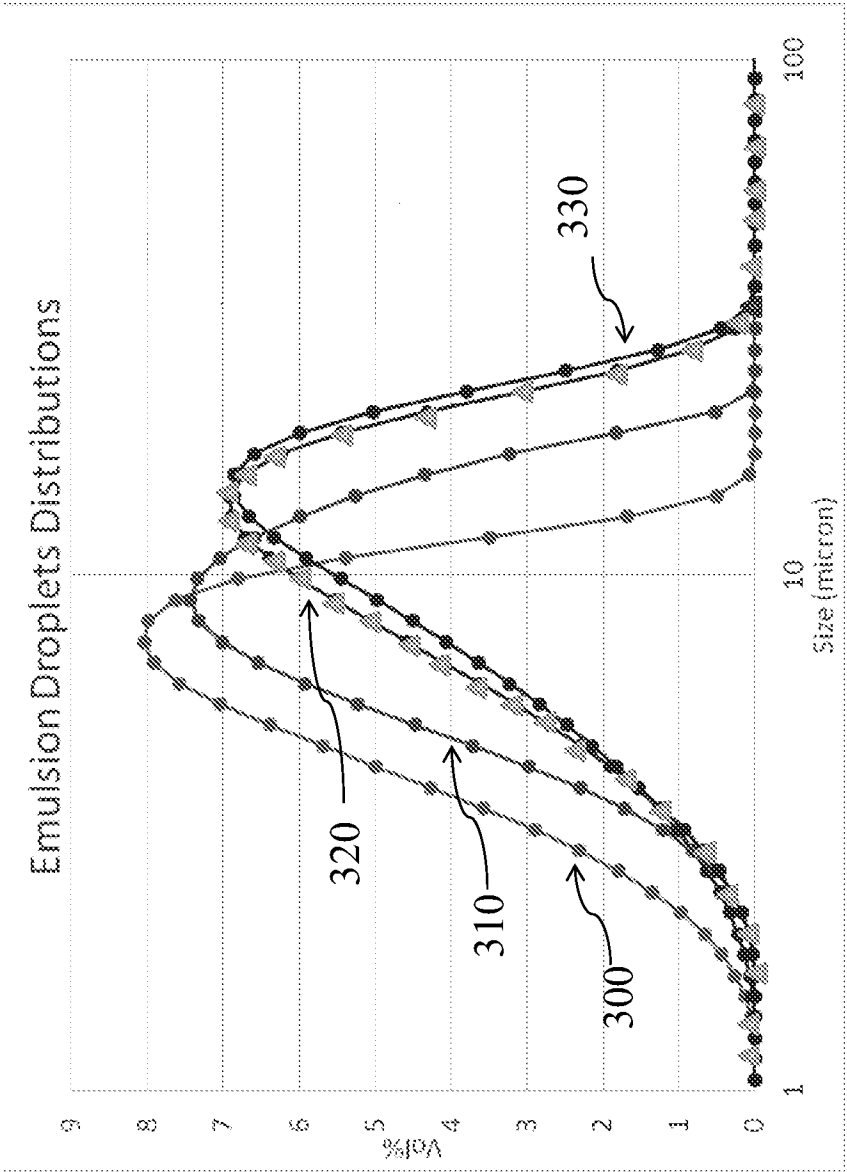


FIG. 3

A. CLASSIFICATION OF SUBJECT MATTER**C09K 8/32(2006.01)i, C09K 8/82(2006.01)i**

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C09K 8/32; E21B 43/00; C09K 8/035; E21B 21/06; E21B 43/26; E21B 33/13; C08L 5/01; C09K 8/82

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

Korean utility models and applications for utility models

Japanese utility models and applications for utility models

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

eKOMPASS(KIPO internal) & Keywords: dicyclopentadiene, styrene, maleic anhydride, invert emulsion, wellbore

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6169134 B1 (JONES, CRUISE K. et al.) 02 January 2001 See column 2, lines 41-42; column 3, lines 24-29; and claims 1, 5, 9-10, 17, 20.	1-23
X	US 2015-0136402 A1 (GEORGIA-PACIFIC CHEMICALS LLC) 21 May 2015 See paragraphs [0005], [0082], [0095], [0157]-[0159].	1-23
X	WO 2009-009343 A2 (M-I LLC et al.) 15 January 2009 See claims 1-30.	1-23
X	WO 2008-123888 A1 (M-I LLC et al.) 16 October 2008 See claims 1-21.	1, 12
A	US 5437331 A (GUPTA, D. V. SATYANARAYANA et al.) 01 August 1995 See the whole document.	1-23



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:

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

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

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

22 February 2018 (22.02.2018)

Date of mailing of the international search report

22 February 2018 (22.02.2018)

Name and mailing address of the ISA/KR

International Application Division

Korean Intellectual Property Office

189 Cheongsa-ro, Seo-gu, Daejeon, 35208, Republic of Korea

Facsimile No. +82-42-481-8578

Authorized officer

NAM, EUI HO

Telephone No. +82-42-481-5580



INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2017/062848

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 6169134 B1	02/01/2001	CA 2254282 A1 CA 2254282 C DE 69838415 T2 DK 0922743 T3 EP 0922743 A1 EP 0922743 B1 NO 985789 A	12/06/1999 15/01/2008 03/01/2008 08/10/2007 16/06/1999 12/09/2007 14/06/1999
US 2015-0136402 A1	21/05/2015	AU 2014-353215 A1 CA 2931283 A1 CN 105874153 A EA 201691038 A1 EP 3071782 A1 EP 3071782 A4 MX 2016006592 A WO 2015-077215 A1	09/06/2016 28/05/2015 17/08/2016 31/10/2016 28/09/2016 03/05/2017 08/12/2016 28/05/2015
WO 2009-009343 A2	15/01/2009	AU 2008-275384 A1 AU 2008-275384 B2 CA 2692794 A1 CA 2692794 C CA 2790667 A1 CA 2790667 C EP 2179129 A2 EP 2179129 A4 US 2010-0210486 A1 US 8067343 B2 WO 2009-009343 A3	15/01/2009 06/09/2012 15/01/2009 14/05/2013 15/01/2009 31/12/2013 28/04/2010 30/03/2011 19/08/2010 29/11/2011 07/05/2009
WO 2008-123888 A1	16/10/2008	AU 2007-350922 A1 AU 2007-350922 B2 CA 2654591 A1 CA 2654591 C EP 2027227 A1 EP 2027227 A4 MX 2008015575 A US 2007-0287640 A1 US 7786052 B2	16/10/2008 03/02/2011 16/10/2008 06/12/2011 25/02/2009 14/07/2010 06/03/2009 13/12/2007 31/08/2010
US 5437331 A	01/08/1995	None	