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(71) Applicant: SAUDI ARABIAN OIL COMPANY
[SA/SA]; Post Office Box 5000, Dhahran, 31311 (SA).

(71) Applicant (for AG only): ARAMCO SERVICES COMPANY [US/US]; 1200 Smith Street, Two Allen Building, Houston, Texas 77002 (US).

(72) Inventors: WAGLE, Vikrant; c/o Saudi Arabian Oil Company, Post Office Box 5000, Dhahran, 31311 (SA). AL-YAMI, Abdullah; c/o Saudi Arabian Oil Company, Post Office Box 5000, Dhahran, 31311 (SA). ALHEHAL, Abdulaziz; c/o Saudi Arabian Oil Company, Post Office Box 5000, Dhahran, 31311 (SA).

(74) Agent: SAYRE, Elias C. et al.; Dinsmore & Shohl LLP, One South Main Street, Fifth Third Center, Suite 1300, Dayton, Ohio 45402 (US).

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(54) Title: DRILLING FLUIDS THAT INCLUDE WATER-SOLUBLE ACID CATALYSTS AND USES FOR SUCH

(57) Abstract: In accordance with one or more embodiments of the present disclosure, a drilling fluid may include a base fluid, one or more formaldehyde-based resins, and one or more water-soluble acid catalysts. The base fluid may include an aqueous or non-aqueous solution. The one or more water-soluble acid catalysts may be present in an amount sufficient to reduce the pH of the drilling fluid to less than or equal to 6. The presently disclosure also describes sealed subterranean petroleum formations that include such drilling fluids and methods for sealing subterranean wellbores by utilizing such drilling fluids.



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DRILLING FLUIDS THAT INCLUDE WATER-SOLUBLE ACID CATALYSTS AND USES FOR SUCH

CROSS REFERENCE TO RELATED APPLICATION

[0001] This application claims priority to U.S. Application Serial No. 16/449,921 filed on June 24, 2019, the entire disclosure of which is hereby incorporated by reference.

BACKGROUND

Field

[0002] The present disclosure relates to wellbore drilling technology and, more specifically, to drilling fluids utilized in wellbore drilling.

Background

[0003] Drilling operations to, for example, drill wellbores for hydrocarbon extraction may include the practice of continuously circulating a drilling fluid (sometimes referred to as a drilling mud) through the formed wellbore during the drilling operation. The drilling fluid may be pumped into the drill pipe and to the bottom of the borehole where the drilling fluid then flows upwardly through an annular space between the wellbore wall and the drill pipe, and finally returns to the surface and flows out of the wellbore where it is recovered for secondary processing. During drilling, the drilling solids, such as portions of the drilled geological formation, may be carried by the drilling fluid from at or near the bottom of the wellbore to the surface. When the drill head encounters an area of reduced formation pressure, such as a fracture, drilling fluid can leak out of the wellbore in what is known as a “lost circulation zone.” The consequences of encountering a lost circulation zone can range from drilling fluid leaks to drill head and drill string damage. Lost circulation zones may even lead to blowouts and loss of life. Remediation of a lost circulation zone generally requires the introduction of a sealing composition into the wellbore. However, this process is resource-intensive and time consuming.

BRIEF SUMMARY

[0004] Faster and more efficient lost circulation zone remediation techniques are desired. It has been discovered that drilling fluids may be fabricated which can be pumped in a liquid state and converted to a gel as desired. The drilling fluid, in gel form, may then be suitable to seal the porous areas, cracks, fractures, or other geological features which cause the lost circulation zone. According to one or more embodiments presently described, a drilling fluid which is gellable may include a base fluid and a formaldehyde-based resin. The introduction of a water-soluble catalyst may initiate the conversion of the drilling fluid from a liquid state to a gelled state. For example, the addition of the water-soluble acid catalyst may polymerize at least a portion of the formaldehyde-based resins present in the drilling fluid, which may cause the drilling fluid to become a gelled state material. Furthermore, it should be understood that while such a drilling fluids may be suitable for use in loss-circulation zones, these drilling fluids may find applicability for other uses such as when controlled gelling of a drilling fluid is desired.

[0005] In accordance with one or more embodiments of the present disclosure, a drilling fluid may include a base fluid, one or more formaldehyde-based resins, and one or more water-soluble acid catalysts. The base fluid may include an aqueous or non-aqueous solution. The weight ratio of the one or more formaldehyde-based resins to the base fluid may be from 1:100 to 50:100. The one or more water-soluble acid catalysts may be present in an amount sufficient to reduce the pH of the drilling fluid to less than or equal to 6. The drilling fluid may optionally include latex. If latex is present in the drilling fluid, the weight ratio of the latex to the total weight of the drilling fluid may be less than or equal to 10:100. The drilling fluid may optionally include polyvinyl alcohol or vinyl alcohol copolymers. If the polyvinyl alcohol or vinyl alcohol copolymers are present in the drilling fluid, the weight ratio of the sum of the polyvinyl alcohol and vinyl alcohol copolymers to the total weight of the drilling fluid may be less than or equal to 1.5:100.

[0006] In accordance with one or more additional embodiments of the present disclosure, a sealed subterranean petroleum formation may include a subterranean wellbore positioned adjacent a subterranean petroleum formation. The sealed subterranean petroleum formation may further include and a drilling fluid positioned in the subterranean wellbore.

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The drilling fluid may include a base fluid, one or more formaldehyde-based resins, and one or more water-soluble acid catalysts. The base fluid may include an aqueous or non-aqueous solution. The weight ratio of the one or more formaldehyde-based resins to the base fluid may be from 1:100 to 50:100. The one or more water-soluble acid catalysts may be present in an amount sufficient to reduce the pH of the drilling fluid to less than or equal to 6. The drilling fluid may optionally include latex. If latex is present in the drilling fluid, the weight ratio of the latex to the total weight of the drilling fluid may be less than or equal to 10:100. The drilling fluid may optionally include polyvinyl alcohol or vinyl alcohol copolymers. If the polyvinyl alcohol or vinyl alcohol copolymers are present in the drilling fluid, the weight ratio of the sum of the polyvinyl alcohol and vinyl alcohol copolymers to the total weight of the drilling fluid may be less than or equal to 1.5:100.

[0007] In accordance with one or more yet additional embodiments of the present disclosure, a method for sealing a subterranean wellbore may include introducing a drilling fluid into a subterranean wellbore and contacting one or more water-soluble acid catalysts with the drilling fluid in an amount operable to transition the drilling fluid from a liquid state to a gelled state. The subterranean wellbore may be positioned adjacent to a subterranean petroleum formation. The drilling fluid may include a base fluid and one or more formaldehyde-based resins. The base fluid may include an aqueous or non-aqueous solution. The weight ratio of the one or more formaldehyde-based resins to the base fluid may be from 1:100 to 50:100. The drilling fluid may optionally include latex. If latex is present in the drilling fluid, the weight ratio of the latex to the total weight of the drilling fluid may be less than or equal to 10:100. The drilling fluid may optionally include polyvinyl alcohol or vinyl alcohol copolymers. If the polyvinyl alcohol or vinyl alcohol copolymers are present in the drilling fluid, the weight ratio of the sum of the polyvinyl alcohol and vinyl alcohol copolymers to the total weight of the drilling fluid may be less than or equal to 1.5:100.

ABBREVIATIONS

[0008] One or more abbreviations are used in the present application, in which:

[0009] ASTM = American Society for Testing and Materials;

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- [0010] API = American Petroleum Institute;
- [0011] C_x = carbon chain of x length;
- [0012] cP = centipoises;
- [0013] °F = degrees Fahrenheit;
- [0014] g = grams;
- [0015] lb/100 ft² = pounds per 100 square feet;
- [0016] min. = minutes;
- [0017] ml = milliliters;
- [0018] Pa = pascals;
- [0019] PCF = pounds per cubic foot;
- [0020] psi = pounds per square inch;
- [0021] rpm = revolutions per minute;
- [0022] sec. = seconds;
- [0023] SOBM = synthetic oil based mud; and
- [0024] wt.% = weight percent.

DETAILED DESCRIPTION

[0025] The present disclosure is directed to drilling fluids which may be suitable for use in sealing natural resource extraction wells. The present disclosure is further directed to the fabrication of such drilling fluids, as well as the uses of such. According to one or more embodiments of the present disclosure, a drilling fluid is provided that may include a base fluid and one or more formaldehyde-based resins. The drilling fluid may further include one or more gel initiator additives such as water-soluble acid catalysts.

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[0026] In one or more embodiments, the base fluid may comprise an aqueous solution. For example, the aqueous solution may include one or more of deionized, tap, distilled, or fresh waters; natural, brackish, or saturated salt waters; natural, salt dome, hydrocarbon formation produced, or synthetic brines; filtered or untreated seawaters; mineral waters; or other potable or non-potable waters containing one or more dissolved salts, minerals, or organic materials. In one or more embodiments, the base fluid may comprise at least 80 wt.%, at least 90 wt.%, at least 95 wt.%, at least 99 wt.%, or even at least 99.9 wt.% of water.

[0027] According to additional embodiments, the base fluid may include a non-aqueous solution. The non-aqueous solution may include one or more crude oils or crude oil derivatives such as gasoline, diesel, kerosene, bunker fuel, jet fuel, naptha, or any fraction of a crude oil. For example, in some embodiments non-aqueous drilling fluids may be referred to as synthetic oil based muds (also referred to in the present disclosure as oil-based muds and SOBMs). Synthetic oil-based muds may include crude oil derivatives that have been chemically treated, altered, or refined to enhance certain chemical or physical properties. In comparison, partially-refined crude oil, which may contain several classes (for example, alkane, aromatic, sulfur-bearing, nitrogen-bearing) of thousands of individual compounds, a SOBM may comprise one class with only tens of individual compounds (for example, ester compounds in a C₈₋₁₄ range). Examples of materials used as base fluids for SOBMs include linear alpha olefins, isomerized olefins, poly alpha olefins, linear alkyl benzenes, and vegetable and hydrocarbon-derived ester compounds. In one or more embodiments, the base fluid may comprise at least 80 wt.%, at least 90 wt.%, at least 95 wt.%, at least 99 wt.%, or even at least 99.9 wt.% of a non-water material such as an oil.

[0028] According to some additional embodiments of the present disclosure, the drilling fluid may be characterized as an emulsion. The emulsion may be a mixture of the aqueous and non-aqueous base fluids or it may be a mixture of the base fluid and a natural fluid such as water ingress into the fluid. The drilling fluid emulsion may include a surfactant. In such embodiments, the base fluid may comprise water and a non-water component such as an oil. In one or more embodiments, the base fluid may comprise at least 80 wt.%, at least 90 wt.%, at least 95 wt.%, at least 99 wt.%, or even at least 99.9 wt.% of the combination of water and a non-water material such as an oil.

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[0029] According to one or more embodiments of the present disclosure, the formaldehyde-based resin may be any resin which includes formaldehyde. For example, the formaldehyde-based resin may be one or more of a melamine-formaldehyde resin, a urea-formaldehyde resin, or a phenol-formaldehyde resin. A urea-formaldehyde resin should be understood to include any products of the reaction of urea and formaldehyde. A phenol-formaldehyde resin should be understood to include any products of the reaction of a phenol or substituted phenol with formaldehyde. A melamine-formaldehyde resin should be understood to include any products of the condensation of formaldehyde and melamine. Suitable commercially available melamine-formaldehyde resins, without limitation, may include MELFORES 101P. Suitable formaldehyde based resins may be distributed as powders, liquids, or dispersions. Suitable formaldehyde-based resins may be formed in-situ in the drilling fluid by the reaction of melamine, phenol, or urea with formaldehyde.

[0030] The weight ratio of the one or more formaldehyde-based resins to the base fluid may be from 1:100 to 50:100. For example, the weight ratio of the one or more formaldehyde resins to the base fluid may be from 0.1:100 to 5:100, from 5:100 to 10:100, from 10:100 to 15:100, from 15:100 to 20:100, from 20:100 to 25:100, or from 25:100 to 30:100, from 30:100 to 35:100, from 35:100 to 40:100, from 40:100 to 45:100, from 45:100 to 50:100, or any combination of these. It should be understood that the sum of the any one or more presently disclosed formaldehyde based resins may be present in a weight ratio with respect to the base fluid in any of the disclosed ranges. For example, a single formaldehyde-based resin may be in one of the disclosed weight ratios with respect to the base fluid, or the sum of a combination of disclosed formaldehyde-based resins may be in one of the disclosed weight ratios with respect to the base fluid.

[0031] The drilling fluid may become gelled when contacted by the gel initiator additive. The one or more gel initiator additives may include one or more water-soluble acid catalysts present in an amount sufficient to reduce the pH of the drilling fluid to less than or equal to 6. For example, the one or more water-soluble acid catalysts may be present in an amount sufficient to reduce the pH of the drilling fluid to less than or equal to 6, less than or equal to 5, less than or equal to 4, less than or equal to 3, less than or equal to 2, or less than or equal to 1. The one or more water-soluble acid catalysts may be present in an amount sufficient to reduce the pH of the drilling fluid to from 1 to 6, from 2 to 6, from 3 to 6, from

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4 to 6, from 1 to 4, or from 2 to 4. As used in this disclosure, a “water-soluble acid catalyst” may refer to any acid that is water-soluble and acts to cause a reaction (for example, catalyze a reaction) which causes gelling of the drilling fluid. Without being limited by theory, the water-soluble acid catalyst is believed to be operable to initiate polymerization of the formaldehyde-based resin. According to some embodiments of the present disclosure, the water-soluble acid catalyst may include one or both of organic acids or mineral acids.

[0032] According to one or more embodiments, it is believed to be advantageous to use a water-soluble acid, as opposed to a material that is not water-soluble, due at least to their ability to rapidly polymerize the formaldehyde-based resin in a controllable manner. For example, water-soluble acids may be operable to immediately catalyze the viscosity-increasing reaction in the drilling fluid, whereas some water-insoluble materials may require prior reaction to become an acid and catalyze the gelation reaction. Water solubility may be advantageous because it may allow for dispersion of the acid throughout at least the aqueous phase portions of the drilling fluid.

[0033] According to some embodiments of the present disclosure, the gel initiator additive may include an organic acid. The organic acid may include one or more of citric acid, lactic acid, formic acid, acetic acid, glycolic acid, benzoic acids, formic acid, glucuronic acid, aminomethanesulfonic acid, anthrallic acid, ascorbic acid, barbituric acid, benzenesulfonic acid, benzoic acid, folic acid, oxalic acid, salicylic acid, or succinic acid. In one or more embodiments, at least 80 wt.%, at least 90 wt.%, at least 95 wt.%, at least 99 wt.%, or even at least 99.9 wt.% of the water-soluble acid catalyst may comprise organic acid.

[0034] According to some embodiments of the present disclosure, the gel initiator additive may include mineral acid. According to some embodiments of the present disclosure, the mineral acid may include one or more of hydrochloric acid, sulfuric acid, nitric acid, phosphoric acid, perchloric acid, hydrobromic acid, hydroiodic acid, or boric acid. In one or more embodiments, at least 80 wt.%, at least 90 wt.%, at least 95 wt.%, at least 99 wt.%, or even at least 99.9 wt.% of the water-soluble acid catalyst may comprise mineral acid.

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[0035] According to some embodiments of the present disclosure, the drilling fluid may include one or more weighting agents. The weighting agent may include, for example, one or more of barite, hematite, calcium carbonate, siderite, or limenite. The weight ratio of the one or more weighting agents to the base fluid may be from 10:100 to 300:100, from 1:100 to 10:100, from 10:100 to 25:100, from 25:100 to 50:100, from 50:100 to 100:100, from 100:100 to 150:100, from 150:100 to 200:100, from 200:100 to 250:100, from 250:100 to 300:100, from 300:100 to 350:100, from 350:100 to 400:100, from 400:100 to 450:100, from 450:100 to 500:100, or any combination of these.

[0036] According to some embodiments of the present disclosure, the drilling fluid may include a rheology modifier. The rheology modifier may include, for example, one or more of bentonite, montmorillonite, sodium carbonate, polymers, carboxymethylcellulose (CMC), starch, or phosphorylates. The polymer may include one or both of guar gum (sometimes called XC-Polymer) or polyanionic cellulose polymer (such as PAC L, commercially from Halliburton). The weight ratio of the rheology modifier to the base fluid may be from 0.001:100 to 10:100. For example, the weight ratio may be from 0.001:100 to 0.005:100, from 0.005:100 to 0.01:100, from 0.01:100 to 0.5:100, from 0.5:100 to 1:100, from 0.5:100 to 1:100, from 1:100 to 2:100, from 2:100 to 3:100, from 3:100 to 4:100, from 4:100 to 5:100, from 5:100 to 6:100, from 6:100 to 7:100, from 8:100 to 9:100, from 9:100 to 10:100, any combination of these. The concentration of the rheology modifier in the drilling fluid may be from 0.1 pounds per barrel (ppb) to 20 ppb. For example, the concentration may be from 0.1 ppb to 0.5 ppb, from 0.5 ppb to 1 ppb, from 1 ppb to 1.5 ppb, from 1.5 ppb to 2 ppb, from 2.5 ppb to 3 ppb, from 3 ppb to 4 ppb, from 4 ppb to 5 ppb, from 5 ppb to 6 ppb, from 6 ppb to 7 ppb, from 7 ppb to 8 ppb, from 8 ppb to 9 ppb, from 9 ppb to 10 ppb, from 10 ppb to 11 ppb, from 11 ppb to 12 ppb, from 12 ppb to 13 ppb, from 13 ppb to 14 ppb, from 14 ppb to 15 ppb, from 15 ppb to 16 ppb, from 16 ppb to 17 ppb, from 17 ppb to 18 ppb, from 18 ppb to 19 ppb, from 19 ppb to 20 ppb, or any combination of these.

[0037] According to some embodiments of the present disclosure, the drilling fluid may include a basic additive. The basic additive may include one or both of sodium hydroxide or potassium hydroxide. Without being limited by theory, it is believed that in some embodiments the formaldehyde-based resin may not cause the drilling fluid to gel at

pH values greater than 6. It may be beneficial to keep the pH of the drilling fluid as basic as possible until it is desired for the drilling fluid to gel.

[0038] In one or more embodiments, a standard drilling fluid may be converted to an embodiment of the drilling fluid of this disclosure as a leak is detected by addition of the formaldehyde-based resin and acid, causing subsequent gelling. The standard drilling fluid may have any characteristics expected of a drilling fluid such as a basic pH.

[0039] The weight ratio of the basic additive to the base fluid may be from 0.001:100 to 5:100. For example, the weight ratio may be from 0.001:100 to 0.005:100, from 0.005:100 to 0.01:100, from 0.01:100 to 0.5:100, from 0.5:100 to 1:100, from 0.5:100 to 1:100, from 1:100 to 2:100, from 2:100 to 3:100, from 3:100 to 4:100, from 4:100 to 5:100, or any combination of these. The concentration of the basic additive in the drilling fluid may be from 0.1 pounds per barrel (ppb) to 10 ppb. For example, the concentration may be from 0.1 ppb to 0.5 ppb, from 0.5 ppb to 1 ppb, from 1 ppb to 1.5 ppb, from 1.5 ppb to 2 ppb, from 2.5 ppb to 3 ppb, from 3 ppb to 4 ppb, from 4 ppb to 5 ppb, from 5 ppb to 6 ppb, from 6 ppb to 7 ppb, from 7 ppb to 8 ppb, from 8 ppb to 9 ppb, from 9 ppb to 10 ppb, or any combination of these.

[0040] According to some embodiments of the present disclosure, the drilling fluid may include cement. Generally, cements may be added to increase strength but may have several disadvantages as compared with drilling fluids which contain little or no cement. Cements may have relatively long cure times and may require the operator to re-drill through the cured cement. The ratio of cement to drilling fluid may be from 0.1:100 to 0.5:100, from 0.5:100 to 1:100, from 1:100 to 2:100, from 2:100 to 4:100, from 4:100 to 8:100, from 8:100 to 12:100, from 12:100 to 15:100, from 15:100 to 25:100, from 25:100 to 50:100, from 50:100 to 75:100, from 75:100 to 100:100, from 100:100 to 150:100, from 150:100 to 200:100, or any combination of these.

[0041] According to some embodiments of the present disclosure, the drilling fluid may not include latex, or latex may be included in only relatively small amounts in the drilling fluid. If latex is present in the drilling fluid, the weight ratio of the latex to the total weight of the drilling fluid may be from 0:100 to 10:100, from 0:100 to 8:100, from 0:100 to 6:100, from 0:100 to 4:100, from 0:100 to 2:100, from 0:100 to 1:100, or even from 0:100 to

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0.1:100. According to some embodiments, latex may not be present in the drilling fluid. As used in this disclosure, "latex" may refer to rubber materials commercially available in aqueous latex form, such as aqueous dispersions or emulsions. These include natural rubbers such as (cis-1,4-polyisoprene), modified types of these, synthetic polymers, or combinations of these. The synthetic polymers may include styrene/butadiene rubber, cis-1,4-polybutadiene, high styrene resin, butyl rubber, ethylene/propylene rubber, neoprene rubber, nitrile rubber, cis-1,4-polyisopren rubber, silicone rubber, chlorosulfonated rubber, polyethylene rubber, epichlorohydrin rubber, fluorocarbon rubber, fluorosilicone rubber, polyurethane rubber, polyacrylic rubber, or polysulfide rubber. It is believed to be advantageous to use a minimal amount of latex at least for cost savings. It should be understood that while some conventional drilling fluids may require latex as an additive, the presently disclosed drilling fluids may not require latex for their desired functionality. The formaldehyde-based resin and gel initiator additive of the presently disclosed drilling fluids may provide suitable gelling characteristics in the absence of latex, or with relatively small amounts of latex included.

[0042] According to some additional embodiments of the present disclosure, the drilling fluid may not include polyvinyl alcohol and vinyl alcohol copolymers, or polyvinyl alcohol and vinyl alcohol copolymers may be included in only relatively small amounts in the drilling fluid. If the polyvinyl alcohol or vinyl alcohol copolymers are present in the drilling fluid, the weight ratio of the polyvinyl alcohol or vinyl alcohol copolymers to the total weight of the drilling fluid may be from 0:100 to 1.5:100, from 0:100 to 1:100, from 0:100 to 0.5:100, or even from 0:100 to 0.1:100. In additional embodiments, the weight ratio of the combination of polyvinyl alcohol and vinyl alcohol copolymers to the total weight of the drilling fluid may be from 0:100 to 1.5:100, from 0:100 to 1:100, from 0:100 to 0.5:100, or even from 0:100 to 0.1:100. It is believed to be advantageous to use a minimal amount of polyvinyl alcohol and vinyl alcohol copolymers at least for cost savings. It should be understood that while some conventional drilling fluids may require polyvinyl alcohol or vinyl alcohol copolymers as an additive, the presently disclosed drilling fluids may not require polyvinyl alcohol or vinyl alcohol copolymers for their desired functionality. The formaldehyde-based resin and gel initiator additive of the presently disclosed drilling fluids may provide suitable gelling characteristics in the absence of polyvinyl alcohol and vinyl

alcohol copolymers, or with relatively small amounts of polyvinyl alcohol and vinyl alcohol copolymers added.

[0043] According to some embodiments or the present disclosure, the drilling fluid may be present in a gelled state, such as after it contains the presently disclosed gel initiator additive. The addition of the gel initiator additive may reduce the pH of the drilling fluid, which may cause gelation. The drilling fluid may be “gelled” or exist in a “gelled state” by meeting the criteria that the apparent viscosity at 300 rpm and 25 °C is greater than 50,000 cP. For example, conventional drilling fluids, or the disclosed drilling fluids prior to the described reducing of pH, may have an apparent viscosity at 300 rpm and 25 °C of less than 500 cP, such as from 10 to 250 cP. Gelled state drilling fluids, as presently described, may have a viscosity of at least 50,000 cP, such as at least 100,000 cP, or even at least 150,000 cP. Apparent viscosity may be measured according to API “RP 13B-1: Recommended Practice for Field Testing Water-based Drilling Fluids.”

[0044] According to some embodiments of the present disclosure, the drilling fluid may have (following introduction of the gel initiator additive) a storage modulus of at least 50 Pa. For example, the drilling fluid may have (following introduction of the gel initiator additive) a storage modulus of at least 100 Pa, at least 150 Pa, at least 200 Pa, at least 250 Pa, at least 300 Pa, at least 400 Pa, at least 500 Pa, from 1 Pa to 10 Pa, from 10 Pa to 25 Pa, from 25 Pa to 50 Pa, from 50 Pa to 75 Pa, from 75 Pa to 100 Pa, from 100 Pa to 150 Pa, from 150 Pa to 200 Pa, from 200 Pa to 300 Pa, from 300 Pa to 400 Pa, from 400 Pa to 500 Pa, from 500 Pa to 600 Pa, from 600 Pa to 800 Pa, from 800 Pa to 1000 Pa, or any combination of these. The storage modulus may be measured according to ASTM “D5026-15, Standard Test Method for Plastics: Dynamic Mechanical Properties: In Tension.”

[0045] According to some embodiments of the present disclosure, the drilling fluid (following introduction of the gel initiator additive) may have a 10 min. gel strength of at least 10 lb/100ft². For example, the gel strength of the drilling fluid may be at least 15 lb/100ft², at least 20 lb/100ft², at least 40 lb/100ft², at least 80 lb/100ft², at least 120 lb/100ft², at least 160 lb/100ft², at least 200 lb/100ft², or any combination of these. The gel strength may be measured by the method API “RP 13B-1: Recommended Practice for Field Testing Water-based Drilling Fluids.”

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[0046] According to one or more embodiments of the present disclosure, the drilling fluid may have a density of from 50 PCF to 160 PCF. For example, the density of the drilling fluid may be from 50 PCF to 80 PCF, from 80 PCF to 120 PCF, from 120 PCF to 160 PCF, or any combination of these. Drilling fluid density may be important to maintain the appropriate hydrostatic pressure in the wellbore. Inappropriate density drilling fluid can cause the flow of formation fluids into the wellbore during drilling operations (such as kicks or blowouts). It should be understood that the density of the drilling fluid is not expected to change as it transitions from a liquid to a gelled state.

[0047] In one or more embodiments, the presently disclosed drilling fluids may be positioned in a wellbore during drilling of the wellbore. According to some embodiments of the present disclosure, a sealed subterranean petroleum formation may include a subterranean wellbore positioned adjacent a subterranean petroleum formation and a drilling fluid positioned in the subterranean wellbore. The sealed subterranean petroleum formation may not be completely sealed but may have its leakage rate decreased relative to what it would be in the absence of the drilling fluids of the present disclosure.

[0048] According to some embodiments of the present disclosure, a method for sealing a well may include introducing a drilling fluid into a subterranean wellbore positioned adjacent to a subterranean petroleum formation and introducing to the drilling fluid one or more gel initiator additives in an amount operable to reduce the pH of at least a portion of the drilling fluid to less than or equal to 6 to transition the drilling fluid from a liquid to a gelled state. For example, the pH may be reduced to a pH range of from 0 to 1, a pH range of from 1 to 2, a pH range of from 2 to 3, a pH range of from 3 to 4, a pH range of from 4 to 5, a pH range of from 5 to 6, or any combination of these. It should be understood that in some embodiments, the drilling fluid may be fabricated by adding the various components in different orders. For example, the acid may be added to the base fluid before the formaldehyde-based resin is added to the base fluid to constitute the drilling fluid.

[0049] According to some embodiments, the pH of the drilling fluid before the addition of the gel initiator additive may be from 8 to 12. For example, the pH of the drilling fluid before the addition of the gel initiator additive may be from 8 to 9, from 9 to 10, from 10 to 11, from 11 to 12, or any combination of these. Without being limited by theory, it is

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believed that a starting pH of greater than 8 will enable normal drilling fluid operation and prevent premature gelling of the drilling fluid.

[0050] In one or more embodiments, the one or more gel initiator additives may be introduced to the drilling fluid inside of the subterranean wellbore. For example, a drilling fluid including the base fluid and formaldehyde-based resin may be inside the subterranean wellbore and the gel initiator additive may be subsequently pumped down into the wellbore. The gel initiator additive may be pumped near a site of a suspected leak, casing fracture, or site otherwise requiring sealing. Alternatively, the gel initiator additive may be pumped generally into the drilling fluid in the wellbore and cause the bulk drilling fluid to gel. In further embodiments, the one or more gel initiator additives may be introduced to the drilling fluid outside of the subterranean wellbore. Introducing the gel initiator additives to the drilling fluid outside the subterranean wellbore may be more convenient. The drilling fluid including the gel initiator additive may then be pumped back down into the subterranean wellbore before it has gelled.

EXAMPLES

[0051] Using the embodiments of the present disclosure, drilling fluid additives were produced which exemplify the catalytic attributes presently described. It should be understood that the ensuing Examples are illustrative of one or more embodiments presently disclosed, and should not be construed as in any way as limiting on the appended claims or other portions of the present application.

Example 1

[0052] A conventional 90 PCF aqueous drilling fluid was produced by combining bentonite and water, and the mixture was allowed to sit for 4 hours. The water and bentonite were then mixed for twenty minutes. Then, in order, XC Polymer, PAC L, starch, NaOH, and barite were each added individually with five minutes of mixing after each addition. The concentrations given in Table 1 are for the final drilling fluid.

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Table 1

Additive	wt. %
Water	58.84
Bentonite	0.59
XC polymer	0.30
PAC L	0.39
Starch	0.79
NaOH	0.01
Barite	38.98

[0053] The resultant conventional drilling fluid was then hot rolled for 16 hours at 200 °F in an aging cell. After hot rolling, the conventional drilling fluid was allowed to cool and was then transferred to a mud cup. The conventional drilling fluid was subsequently subjected to a variety of standard rheological and filtration property tests at 120 °F. The rheological and filtration properties are shown in Table 2.

Table 2

Measurement	Value
600 rpm	80 lb/100ft ²
300 rpm	53 lb/100ft ²
200 rpm	41 lb/100ft ²
100 rpm	28 lb/100ft ²
6 rpm	4 lb/100ft ²
3 rpm	3 lb/100ft ²
Plastic viscosity	27 cP
Yield point	26 lb/100ft ²
10 sec. Gel Strength	3 lb/100ft ²
10 min. Gel Strength	5 lb/100ft ²
pH	10.3
API fluid loss, 30 min	4 ml

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[0054] As can be seen in from the data of Table 2, the conventional drilling fluid does not form a gel.

Example 2

[0055] To form a drilling fluid, 350 ml of the conventional drilling fluid of Example 1 was mixed with 50 g of powdered melamine formaldehyde resin (commercially available as MELFORES 101 P) for 5 minutes. Then, 5 g of citric acid was added and the solution was mixed for another 5 minutes.

[0056] The resultant gellable drilling fluid was then static aged in a curing chamber at 200 °F and 1000 psi for 16 hours. After removal from the curing chamber, it was observed that the gellable drilling fluid had formed a gelled solid. The gelled solid maintained a cylindrical shape with no external support. It had well defined corners and no observable sagging along the vertical walls.

[0057] It is noted that recitations in the present disclosure of a component of the present disclosure being "operable" or "sufficient" in a particular way, to embody a particular property, or to function in a particular manner, are structural recitations, as opposed to recitations of intended use. More specifically, the references in the present disclosure to the manner in which a component is "operable" or "sufficient" denotes an existing physical condition of the component and, as such, is to be taken as a definite recitation of the structural characteristics of the component.

[0058] Having described the subject matter of the present disclosure in detail and by reference to specific embodiments, it is noted that the various details disclosed in the present disclosure should not be taken to imply that these details relate to elements that are essential components of the various embodiments described in the present disclosure. Further, it will be apparent that modifications and variations are possible without departing from the scope of the present disclosure, including, but not limited to, embodiments defined in the appended claims.

[0059] It is noted that one or more of the following claims utilize the term "where" as a transitional phrase. For the purposes of defining the present subject matter, it is noted that this term is introduced in the claims as an open-ended transitional phrase that is used to

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introduce a recitation of a series of characteristics of the structure and should be interpreted in like manner as the more commonly used open-ended preamble term “comprising.”

CLAIMS

1. A drilling fluid comprising:
 - a base fluid comprising an aqueous or non-aqueous solution;
 - one or more formaldehyde-based resins, where the weight ratio of the one or more formaldehyde-based resins to the base fluid is from 1:100 to 50:100;
 - optionally latex, where if latex is present in the drilling fluid, the weight ratio of the latex to the total weight of the drilling fluid is less than or equal to 10:100;
 - optionally polyvinyl alcohol or vinyl alcohol copolymers, where if the polyvinyl alcohol or vinyl alcohol copolymers are present in the drilling fluid, the weight ratio of the sum of the polyvinyl alcohol and vinyl alcohol copolymers to the total weight of the drilling fluid is less than or equal to 1.5:100; and
 - one or more water-soluble acid catalysts in an amount sufficient to reduce the pH of the drilling fluid to less than or equal to 6.
2. The drilling fluid of claim 1, where the one or more formaldehyde-based resins comprise melamine-formaldehyde resin, urea-formaldehyde resin, phenol-formaldehyde resin, or combinations of these.
3. The drilling fluid of claim 1, where the one or more water-soluble acid catalysts comprise one or more organic acids, one or more mineral acids, or combinations of these.
4. The drilling fluid of claim 1, where the base fluid comprises an aqueous solution or a non-aqueous solution.
5. The drilling fluid of claim 1, further comprising one or more weighting agents, where the weight ratio of the one or more weighting agents to the base fluid is from 10:100 to 300:100.
6. The drilling fluid of claim 1, where the drilling fluid has a density of from 50 pounds per cubic foot to 160 pounds per cubic foot.

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7. The drilling fluid as in any preceding claim, where the drilling fluid is in a gelled state such that the apparent viscosity at 300 rpm and 25 °C of the drilling fluid is at least 50,000 centipoises (cP).

8. A sealed subterranean petroleum formation comprising:

a subterranean wellbore positioned adjacent a subterranean petroleum formation;

and

a drilling fluid positioned in the subterranean wellbore, the drilling fluid

comprising:

a base fluid comprising an aqueous or non-aqueous solution;

one or more formaldehyde-based resins, where the weight ratio of the one or more formaldehyde-based resins to the base fluid is from 1:100 to 50:100;

optionally latex, where if latex is present in the drilling fluid, the weight ratio of the latex to the total weight of the drilling fluid is less than or equal to 10:100 and

optionally polyvinyl alcohol or vinyl alcohol copolymers, where if the polyvinyl alcohol or vinyl alcohol copolymers are present in the drilling fluid, the weight ratio of the sum of the polyvinyl alcohol and vinyl alcohol copolymers to the total weight of the drilling fluid is less than or equal to 1.5:100; and

one or more water-soluble acid catalysts in an amount sufficient to reduce the pH of the drilling fluid to less than or equal to 6.

9. The drilling fluid of claim 8, where the one or more formaldehyde-based resins comprise melamine-formaldehyde resin, urea-formaldehyde resin, phenol-formaldehyde resin, or combinations of these.

10. The drilling fluid of claim 8 or claim 9, where the one or more water-soluble acid catalysts comprise one or more organic acids, one or more mineral acids, or combinations of these.

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11. A method for sealing a subterranean wellbore, the method comprising:
introducing a drilling fluid into a subterranean wellbore, the subterranean wellbore positioned adjacent to a subterranean petroleum formation, where the drilling fluid comprises:
a base fluid comprising an aqueous or non-aqueous solution;
one or more formaldehyde-based resins, where the weight ratio of the one or more formaldehyde-based resins to the base fluid is from 1:100 to 50:100;
optionally latex, where if latex is present in the drilling fluid, the weight ratio of the latex to the total weight of the drilling fluid is less than or equal to 10:100; and
optionally polyvinyl alcohol or vinyl alcohol copolymers, where if the polyvinyl alcohol or vinyl alcohol copolymers are present in the drilling fluid, the weight ratio of the sum of the polyvinyl alcohol and vinyl alcohol copolymers to the total weight of the drilling fluid is less than or equal to 1.5:100; and
contacting one or more water-soluble acid catalysts with the drilling fluid in an amount operable to transition the drilling fluid from a liquid state to a gelled state such that the apparent viscosity at 300 rpm and 25 °C of the drilling fluid in the gelled state is at least 50,000 centiPoises.
12. The method of claim 11, where the introducing of the one or more water-soluble acid catalysts reduces the pH of at least a portion of the drilling fluid to less than or equal to 6.
13. The method of claim 11, where the one or more water-soluble acid catalysts are initially contacted with the drilling fluid inside of the subterranean wellbore.
14. The method of claim 11, where the one or more water-soluble acid catalysts are initially contacted with the drilling fluid outside of the subterranean wellbore.
15. The method of claim 11, 12, 13 or 14, where the pH of the drilling fluid prior to the addition of the water-soluble acid catalysts is from 8 to 12.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2020/019580

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09K8/035 C09K8/512 E21B33/138
ADD.

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 E21B

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

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

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6 508 306 B1 (REDDY B RAGHAVA [US] ET AL) 21 January 2003 (2003-01-21) * column 1, line 42 through column 2, line 40, Examples, claims *	1-15
X	----- WO 2005/121500 A1 (SHELL OIL CO [US]; SHELL CANADA LTD [CA]; COWAN KENNETH MICHAEL [US]) 22 December 2005 (2005-12-22) * page 3, line 29 through page 4, line 14, page 4, line 20 through page 5, line 2, page 7, lines 10-24, page 8, lines 13-14, Examples, claims *	1-15
A	----- WO 2005/100739 A1 (HALLIBURTON ENERGY SERV INC [US]; REDDY BAIRREDDY RAGHAVA [US] ET AL.) 27 October 2005 (2005-10-27) the whole document ----- -/-	1-15



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

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"&" document member of the same patent family

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Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer

Nemes, Csaba A.

INTERNATIONAL SEARCH REPORT

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

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