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(54) Title: METHOD OF MAKING LIQUID MIXTURES FOR USE IN OIL FIELDS

(57) Abstract: A method of making a drilling fluid for use in an oil field is described. A liquid component to be included in the drilling fluid is coated onto a solid ingredient to be dispersed into the drilling fluid to form a flowable solid mixant. The flowable solid mixant is then dispersed into a base liquid medium. The flowable solid mixant may be made from more than one solid fraction, such as an acid-bearing flowable solid component and a reaction precursor bearing flowable solid component, which are separately prepared and mixed prior to dispersing in the base liquid medium.



**WO 2016/099581 A1**

## METHOD OF MAKING LIQUID MIXTURES FOR USE IN OIL FIELDS

### FIELD

[0001] Embodiments described herein are generally related to oil field operations. More specifically, a novel method of making liquid mixtures for use in oil fields is described.

### BACKGROUND

[0002] Drilling for oil and gas is a technologically challenging business. A drill bit must be introduced into a well bore and powered through rock and soil to reach petroleum deposits. A fluid is typically used to provide hydrostatic pressure against the petroleum deposits entering the well bore, lubricate the well bore, cool the bit, and provide "cuttings control" to remove particles produced by the drilling operation from the well bore and prevent those particles from settling rapidly when operation of the bit stops. The fluid is usually engineered to have a moderate viscosity at high temperatures to retain lubricity at conditions encountered in the well bore. Most wells have to be drilled through shale or other rocks containing high percentage of clay (*i.e.* shale rock). Clays can swell to multiples of their original volume upon absorbing water. If the drilling mud is water based, or a water/oil emulsion type, the clay swelling upon contact with mud may result in wellbore deformation or even wellbore collapse. Water containing drilling muds must be formulated with additives protecting clays from swelling. Typical drilling mud is composed of 60-70% of base fluid, 10-15% weighting agent, 0.5-10% viscosifier and small amounts of lubricants, clay control chemicals, wetting and emulsifying surfactants, and pH control agents or stabilizers.

[0003] Much drilling for oil and gas occurs in cold climates. In some cases, drilling may proceed at temperatures below zero degrees Fahrenheit. At these temperatures, the fluids used for oil drilling may become so viscous as to be

unpourable and unpumpable. There is a need in the industry for ways of handling oil field drilling fluids and components effectively in cold climates.

## **SUMMARY**

[0004] A method of making a drilling fluid for use in an oil field is described. A liquid component to be included in the drilling fluid is coated onto a solid ingredient to form a flowable solid mixant. The flowable solid mixant is then dispersed into a base liquid medium to form the drilling fluid. The flowable solid mixant may be made from more than one solid fraction, such as an acid-bearing flowable solid component and a reaction precursor bearing flowable solid component, which are separately prepared and mixed prior to dispersing in the base liquid medium.

[0005] The reaction precursor may be a diamine such as a polyol diamine or a polyalkylene glycol diamine, which forms a viscous salt with the acid component upon mixing in the base liquid medium.

## **DETAILED DESCRIPTION**

[0006] The inventors have discovered new ways of making a drilling fluid composition in cold climates. In conventional methods, the liquid components of the drilling fluid are mixed together, and then the solid components are blended in to make a suspension, commonly called "mud". The liquid components may be oil, water, acid, and an acid-reactive monomer material, such as a diamine. Other components, such as stabilizers, may also be added.

[0007] Some components to be mixed to make the drilling fluid may have substantial viscosity. For example, if the acid and the acid-reactive material are mixed to perform a reaction prior to including in the drilling fluid, the acid and the acid-reactive material react to form viscous salts useful for clay control in drilling fluids. In cold climates, the salts may become so thick that blending, mixing, and

pouring becomes impossible. In some cases, the salts are solid at low temperatures. Other components of drilling mud may be emulsifiers or wetting surfactants that are also difficult to handle at low temperature. A common method of lowering the viscosity and pour point of such products is by adding a low freezing solvent like methanol or ethylene glycol, which may have a negative effect on some formulated drilling mud.

[0008] The inventors have discovered a way of co-delivering some of the liquid components with the solid components, so that the liquid mixture has not yet developed significant viscosity at the time the solid components are added. A liquid component, which may be a reaction precursor such as a polymerizable liquid component, is blended with a solid component such that the liquid component coats and penetrates the particles of the solid component. The amount of the liquid component added to the solid component is typically selected to maintain the resulting mixture as a flowable solid mixture. In some embodiments, a first liquid component may be blended with a first solid component and a second liquid component may be blended with a second solid component. The first and the second solid component are then blended together to make a mixant to be added to a liquid base to form a drilling fluid mixture. Any number of such mixtures may be made as flowable solid mixtures for blending into a base liquid medium to form a drilling fluid.

[0009] The base liquid medium may be a water-based medium, to form a water-based drilling fluid, or an oil-based medium to form an oil-based drilling fluid. The liquid medium may have a pre-dispersed solid-component. In the case of an oil-based medium, the oil-based medium may be a reverse emulsion, in which an aqueous phase is dispersed into a continuous oil phase. Some typical mixtures have compositions shown in Table 1.

**Table 1**

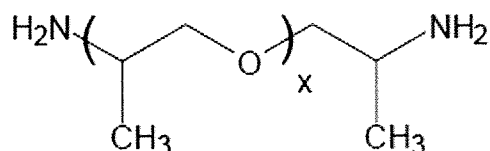
|   | Type                       | Water base                       | Oil base                                 | Inverted Emulsion                |
|---|----------------------------|----------------------------------|------------------------------------------|----------------------------------|
| 1 | Base fluid, 60-70%         | Water                            | Oil                                      | Water and oil                    |
| 2 | Weighting agent, 10-30%    | Barite and/or hematite           | Barite and/or hematite                   | Barite and/or hematite           |
| 3 | Brine salt, 15-20%         | CaCl <sub>2</sub> , NaCl, KCl    |                                          | CaCl <sub>2</sub> , NaCl, KCl    |
| 4 | Viscosifier, 0.5-10%       | Water soluble polymer            | Oil soluble polymer<br>Organophilic clay | Surfactant emulsifier            |
| 5 | Clay activator 0.1-0.5%    |                                  | MeOH, carbonate ester                    |                                  |
| 6 | pH control agent 0.5-0.8   | Base                             |                                          | Base                             |
| 7 | Clay control agent, 0.1-3% | Polymer and polyether amine salt |                                          | Polymer and polyether amine salt |
| 8 | Wetting agent 1-2%         | Nonionic surfactant              | Nonionic surfactant                      | Nonionic surfactant              |

[0010] Viscosifiers and clay control agents can be very viscous. In cold climates, some viscosifiers and clay control agents may be essentially solid, or so thick that they cannot be poured, mixed, or dispersed readily. To overcome the handling difficulties with such agents, it is possible to make them in-situ when mixing up a drilling fluid composition. The reactants that are used to make viscosifiers and clay control agents, typically liquid components, may be

separately added to solid components in a flowable form. The solid components act, in this regard, as carriers for the liquid components, allowing them to mix thoroughly before forming the viscosifier or clay control agent in situ.

[0011] One example of a clay control agent is an amine salt that may be formed from an amine and an acid. The amine salts typically used as clay control agents are viscous polymers, and diluting them to be pourable and mixable in a cold climate would compromise the composition of the drilling fluid by adding too much water. The liquid components used to make the clay control agent (or a viscosifier) may be mixed by mixing the flowable solid mixtures. The liquid components may react to form a clay control agent adsorbed onto solid particles, so that the resulting mixture remains a flowable, pourable, mixable powder. In this way, a clay control agent or viscosifier may be readily handled and mixed into a drilling fluid composition in cold climates.

[0012] The liquid component to be blended with a solid component may include a diamine, such as a polyetherdiamine like polypropylene glycol diamine, for example a JEFFAMINE<sup>®</sup> polyetheramine product like JEFFAMINE D-230<sup>®</sup> polyetheramine, available from Huntsman Corporation of The Woodlands, Texas. The JEFFAMINE<sup>®</sup> series polyetheramines have the general formula



where x is 2 to 8. For the JEFFAMINE D-230<sup>®</sup> polyetheramine product, x is about 2.5. The solid component may include a drilling mud weighting agent such as barite or hematite, or a solid adsorbent such as magnesium silicate (sometimes called Magnesol), precipitated silica, and/or fine sand. Flow improvement agents such as fumed silica may also be included.

**[0013]** A solid ingredient for a drilling fluid may be made, according to some embodiments, by mixing a first solid component with a first liquid component to form a first flowable solid mixant. Separately, a second solid component may be mixed with a second liquid component to form a second flowable solid mixant. The first and the second flowable solid mixant may then be mixed to form the solid ingredient. A drilling fluid may then be made by mixing the solid ingredient with a liquid base material. All the mixing operations described herein may be performed using any convenient mixing means, such as a rolling mixer. The proportion of liquid to solid in the mixants may be up to about 25% by weight. Depending on the liquid and solid components, a proportion of liquid above about 20% may result in some agglomeration of the solid into pellets or pastilles, which may be convenient for some applications. Each liquid component and solid component used for blending here may be a pure substance or a mixture of substances. For example, each of the solid components may be a blend of a weighting material, such as barite, with a flow improvement agent or another additive.

**[0014]** In some embodiments, an acid component such as sulfuric acid or acetic acid may be blended with a first solid component to form a flowable acid-bearing solid portion, and a precursor component, reactive with the acid component, for example a diamine such as the diamines described above, may be blended with a second solid component to form a flowable precursor bearing solid portion, after which the acid-bearing solid portion and the precursor bearing solid portion are blended to form a solid mixant that is flowable or dispersable in a liquid medium. The solid mixant is then mixed or dispersed into a base liquid to form a drilling fluid. The base liquid typically contains hydrocarbon fluids, water, and other fluids having a low viscosity at substantially all temperatures. Upon adding the solid mixant, the acid component and the precursor component come into intimate aqueous contact and react to produce a salt in-situ. The salt may provide clay control for the drilling fluid in some embodiments, and may have

substantial viscosity in neat form. Because the viscosity-promoting ingredients are carried into the mixture as a coating on solid particles, the liquid into which the solid particles are dispersed does not develop high viscosity at low temperatures, and the blending is straightforward.

## EXAMPLES

[0015] In one example, 100 g of powdered barite was mixed with 6.85 g of glacial acetic acid in a rolling mixer. After mixing for 30 minutes, the mixture was a uniform free-flowing powder. In a separate container, 150 g of barite was uniformly mixed with 13.14 g of JEFFAMINE® D-230 polyetheramine (which is a polypropylene glycol diamine) to form a second free-flowing powder. The two free-flowing powders were then added together and mixed for another 30 minutes. The resulting mixture was a free-flowing powder containing about 7.5% by weight of the formerly liquid components. A drilling fluid, such as the compositions described in Table 1, may be made from such a flowable solid mixture by dispersing the mixture into a liquid base material using any convenient method.

[0016] In a second example, 20 g of powdered barite was mixed with 7.2 g of concentrated (98%) sulfuric acid in a rolling mixer to produce an acid flowing slurry. In a separate container, 180 g of powdered barite was mixed with 42.8 g of polypropyleneglycol diamine to produce an amine flowing slurry. The acid flowing slurry was slowly added to the amine flowing slurry while mixing. The resulting mixture was slowly reacted, increasing the temperature by 30°C as the product solidified. The mixture was transferred into a rolling mixer where it was converted to solid granules after one hour of rolling. The granules readily disintegrate upon contact with water. The final concentration of clay control agent in this solid carrier is 20% by weight.

[0017] In a third example, 67.5 g of JEFFAMINE<sup>®</sup> D-230 polyetheramine was added to 100 g of magnesium silicate and rolled for 30 minutes. Next, 34.3 g of glacial acetic acid was added to the same container, which was rolled for another hour. After the mixing was completed the product was a free flowing powder containing 50% of clay control agent by weight.

[0018] In some embodiments, substantially all the salt forming liquids may be adsorbed onto a solid carrier, such as the solid materials described above, before being blended into the liquid base material. In the case of JEFFAMINE<sup>®</sup> D-230 polyetheramine, the mixture carrying the polyetheramine component may be up to about 20% by weight of the JEFFAMINE<sup>®</sup> D-230 polyetheramine, before mixing with a co-reactive component.

[0019] While the foregoing is directed to embodiments of the present invention, other and further embodiments of the invention may be devised without departing from the basic scope thereof, and the scope thereof is determined by the claims that follow.

**Claims:**

1. A method of making a drilling fluid, comprising:  
mixing a first liquid component with a first solid component to form a first flowable solid mixant; and  
mixing the first flowable solid mixant with a liquid base to form the drilling fluid.
2. The method of claim 1, wherein the first liquid component is a reaction precursor.
3. The method of claim 1, wherein the liquid base is an oil-based mixture.
4. The method of claim 2, further comprising mixing a second liquid component with a second solid component to form a second flowable solid mixant and mixing the second flowable solid mixant with the liquid base.
5. The method of claim 4, wherein mixing the first and second flowable solid mixants with the liquid base comprises mixing the first flowable solid mixant with the second flowable solid mixant to form a flowable solid ingredient.
6. A composition, comprising:  
a drilling fluid solid component; and  
a drilling fluid liquid component, wherein the composition is a flowable solid material.
7. The composition of claim 6, wherein the drilling fluid liquid component is a reaction precursor.
8. The composition of claim 6, wherein the drilling fluid liquid component is a polyether diamine.
9. The composition of claim 7, wherein the drilling fluid solid component is a weighting component.

10. A method of making a drilling fluid, comprising:
  - forming a reverse emulsion base medium comprising water and an oil;
  - forming a first solid mixant by blending an acid with a first flowable solid;
  - forming a second solid mixant by blending a reaction precursor with a second flowable solid;
  - combining the first solid mixant and the second solid mixant into a dispersable solid ingredient; and
  - dispersing the dispersable solid ingredient into the reverse emulsion base medium.
11. The method of claim 10, wherein the dispersable solid ingredient comprises a drilling fluid weighting material.
12. The method of claim 11, wherein the reaction precursor comprises a polyetherdiamine.
13. The method of claim 12, wherein the acid is an amine reactive acid.
14. The method of claim 13, wherein the acid is acetic acid, hydrochloric acid, or sulfuric acid.
15. The method of claim 14, wherein the second solid mixant comprises at least about 7.5% by weight of the reaction precursor.
16. The method of claim 10, wherein at least one of the first flowable solid and the second flowable solid is a weighting material.
17. The method of claim 16, wherein blending the acid with the first flowable solid comprises coating the first flowable solid with the acid.
18. A method of making a drilling fluid, comprising:
  - forming a base medium comprising water and an oil;

forming a first flowable solid ingredient by mixing a first flowable solid with an acid;

forming a second flowable solid ingredient by mixing a second flowable solid with an amine;

forming a third flowable solid ingredient by mixing the first flowable solid ingredient with the second flowable solid ingredient; and

adding the third flowable solid ingredient to the base medium.

19. The method of claim 18, wherein the amine is a polyetherdiamine.

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 15/11103

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - C09K 8/02; C09K 8/32; C09K 8/36 (2015.01)

CPC - C09K 8/02; C09K 8/32; C09K 8/36

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)

IPC(8) - C09K 8/02; C09K 8/32; C09K 8/36 (2015.1)

CPC - C09K 8/02; C09K 8/32; C09K 8/36

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched  
USPC - 507/131; 507/133 Patents and NPL (classification, keyword; search terms below)Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)  
PubWest (US EP JP WO), Pat Base (AU BE BR CA CH CN DE DK EP ES FI FR GB IN JP KR SE TH TW US WO), Google Patent, Google Scholar, Free Patents Online; search terms: Flowable, pourable, pumpable, solid, powder, PEDAs, jeffamine, polyether diamine, polyalkylene oxide diamine, drill, wellbore, excavate, geotechnical, fluid, mud, coat, adsorb, absorb

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category*       | Citation of document, with indication, where appropriate, of the relevant passages                                               | Relevant to claim No.               |
|-----------------|----------------------------------------------------------------------------------------------------------------------------------|-------------------------------------|
| X<br>-----<br>Y | US 2010/0065269 A1 (BALLARD) 18 March 2010 (18.03.2010) para [0008], [0010], [0028], [0030], [0032]                              | 1-3, 6-9<br>-----<br>4-5, 11-15, 19 |
| X               | US 2,793,996 A1 (LUMMUS) 28 May 1957 (28.05.1957) col 1, ln 17; col 10, ln 64-73; col 11, ln 21-22                               | 1-3, 6-7                            |
| Y               | US 2014/0352963 A1 (MAHMOUDKHANI et al.) 04 December 2014 (04.12.2014) para [0005], [0025], [0033]                               | 4-5, 10-19                          |
| Y               | US 5,905,061 A (PATEL) 18 May 1999 (18.05.1999) col 1, ln 20-21 and 60-65; col 2, ln 43-33; col 3, ln 10-11, 26-27, 37 and 53-61 | 10-19                               |
| Y               | US 2007/0298976 A1 (BALLARD) 27 December 2007 (27.12.2007) para [0003]-[0048]                                                    | 1-19                                |
| Y               | US 2009/0294179 A1 (BALLARD) 03 December 2009 (03.12.2009) para [0003]-[0052]                                                    | 1-19                                |
| Y               | US 2008/0269079 A1 (BALLARD) 30 October 2008 (30.10.2008) para [0003]-[0055]                                                     | 1-19                                |
| Y               | US 3,002,923 A1 (BARKER et al.) 03 October 1961 (03.10.1961) col 1, ln 40 - col 6, ln 52                                         | 1-19                                |

☐ Further documents are listed in the continuation of Box C.

|                                                                                                                                                                         |                                                                                                                                                                                                                                                  |
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|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Date of the actual completion of the international search<br>16 March 2015 (16.03.2015)                                                                                         | Date of mailing of the international search report<br><b>06 APR 2015</b>                                                                                                         |
| Name and mailing address of the ISA/US<br>Mail Stop PCT, Attn: ISA/US, Commissioner for Patents<br>P.O. Box 1450, Alexandria, Virginia 22313-1450<br>Facsimile No. 571-273-3201 | Authorized officer:<br>Lee W. Young <br>PCT Helpdesk: 571-272-4300<br>PCT OSP: 571-272-7774 |