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NOTA: Dentro del plazo de los seis (6) meses siguientes a partir de la fecha de publicación en la gaceta de Propiedad Industrial, deberá solicitar y cancelar el examen de patentabilidad so pena de que la solicitud caiga en abandono, de acuerdo con lo establecido en el Artículo 44 de la Decisión 486/2000.

SE PRESENTARON OPOSICIONES POR PARTE DE TERCEROS.

SI _____ NO__ _**X**_ _____

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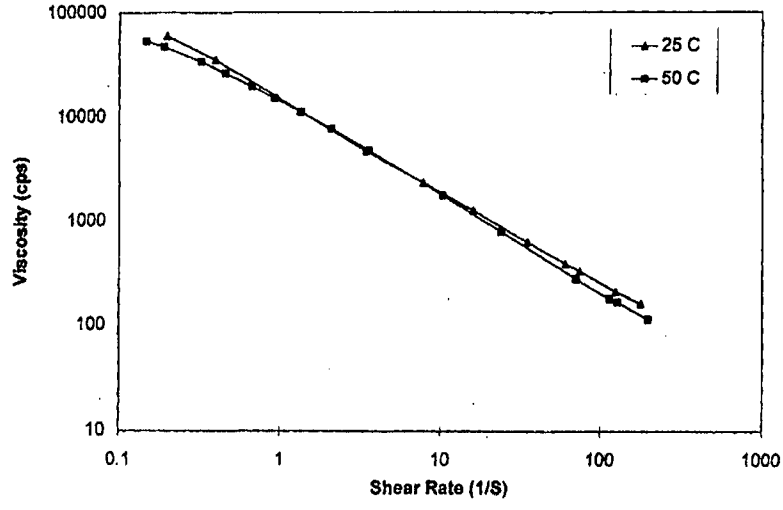


5% disodium tallowiminodipropionate with 2.25% phthalic acid at 25 and 50 degree C

(57) Abstract

Viscoelastic surfactant based aqueous fluid systems useful as thickening agents in various applications, e.g. to suspend particles produced during the excavation of geologic formations. The surfactants are zwitterionic/amphoteric surfactants such as dihydroxyl alkyl glycinate, alkyl ampho acetate or propionate, alkyl betaine, alkyl amidopropyl betaine and alkylamino mono- or di-propionates derived from certain waxes, fats and oils. The thickening agent is used in conjunction with an inorganic water-soluble salt or organic additive such as phthalic acid, salicylic acid or their salts.

FLUIDS CONTAINING VISCOELASTIC SURFACTANT AND METHODS FOR USING THE SAME

FIELD OF THE INVENTION

This invention relates to viscoelastic fluids which contain a surfactant and to methods of suspending particles using such viscoelastic fluids.

BACKGROUND OF THE INVENTION

It is known to thicken the aqueous phase of a suspension of solid particles or emulsified droplets. The addition of thickeners increases the viscosity of the aqueous phase and thereby retards settling of the particles or droplets. Such retardation is useful to maintain the particles or droplets in suspension during the storage, use, and/or transport of the suspension

Polymeric thickeners, e.g. starches, which thicken by entanglement of the polymeric chains, have been used to viscosify the aqueous phase of suspensions. Such thickeners can degrade under the influence of mechanical shear or chemical scission (e.g. by oxidation or hydrolysis) of the polymeric chains which results in a loss of viscosity and, thus, suspension stability.

Cationic surfactants have been found which form rod-like micelles under certain conditions. The presence of the rod-like micelles imparts to the fluid viscoelastic properties. However, cationic surfactants tend to have high toxicity and very low biodegradability.

SUMMARY OF THE INVENTION

The present invention provides a viscoelastic fluid useful as a thickener for the suspension of particles. The viscoelastic fluids consist of an amphoteric/zwitterionic surfactant and an organic acid/salt and/or inorganic salts.

Thus, this invention specifically relates to a viscoelastic fluid comprising:

(1) an aqueous medium;

(2) an amount of a surfactant selected from the group consisting of amphoteric surfactants, zwitterionic surfactants, and mixtures thereof, effective to render said aqueous medium viscoelastic; and

(3) a member selected from the group consisting of organic acids, organic acid salts, inorganic salts, and combinations of one or more organic acids or organic acid salts with one or more inorganic salts.

In yet another embodiment of the present invention, the invention relates to a viscoelastic fluid consisting essentially of:

(1) an aqueous medium;

(2) an amount of a surfactant comprising an amine oxide surfactant; and

(3) an anionic surfactant containing a hydrophobe having at least 14 carbon atoms.

The term "viscoelastic" refers to those viscous fluids having elastic properties, i.e., the liquid at least partially returns to its original form when an applied stress is released. The thickened aqueous viscoelastic fluids are useful as water-based hydraulic fluids in lubricant and hydraulic fracturing fluids to increase permeability in oil production.

The present invention also relates to a method for distributing suspended solid particles such as excavation by-products in a fluid comprised of the viscoelastic fluid of this invention, wherein the solid particles

remain suspended for an extended period of time to a side, by transporting the fluid to a site while the solid particles remain suspended in the fluid and depositing the fluid to such site.

This invention also relates to a method for fracturing a subterranean formation comprising pumping the inventive viscoelastic fluid through a wellbore and into a subterranean formation at a pressure sufficient to fracture the formation.

This invention also relates to a detergent formulation comprising a detersive surfactant in admixture with a viscoelastic fluid of this invention.

This invention also relates to the use of the viscoelastic fluid as a drift control agent for agricultural formulations. In this regard, this invention relates to an aqueous formulation of an agricultural chemical and an amount of the viscoelastic fluid of this invention sufficient to increase the average droplet size of a spray of said formulation.

BRIEF DESCRIPTION OF THE FIGURES

Figure 1 shows viscosity versus shear rate for a viscoelastic surfactant solution prepared by adding 5 percent of disodium tallowiminodipropionate (Mirataine T2C®) and 2.25 percent of phthalic acid to water.

Figure 2 shows the dynamic modulus G' (storage modulus) and G'' (loss modulus) at 25 °C and 50 °C of the same solution as Figure 1.

Figure 3 shows the viscosity versus shear rate for a viscoelastic surfactant solution prepared by adding 5 percent of disodium tallowiminodipropionate (Mirataine T2C®), 4 percent of NH_4Cl and 1.75~2.0 percent of phthalic acid to water.

Figure 4 shows the viscosity versus shear rate for viscoelastic surfactant solutions prepared by adding 4 or

5 percent of disodium oleamidopropyl betaine (Mirataine BET-O®), 3 percent of KCl and 0.5 percent of phthalic acid to water.

Figure 5 shows the dynamic modulus G'(storage modulus) and G'' (loss modulus) at 25 °C and 50 °C of the same solution as Figure 4.

DETAILED DESCRIPTION OF THE INVENTION

The property of viscoelasticity in general is well known and reference is made to S. Gravsholt, *Journal of Coll. And Interface Sci.*, 57(3), 575 (1976); Hoffmann et al., "Influence of Ionic Surfactants on the Viscoelastic Properties of Zwitterionic Surfactant Solutions", *Langmuir*, 8, 2140-2146 (1992); and Hoffmann et al., The Rheological Behaviour of Different Viscoelastic Surfactant Solutions, *Tenside Surf. Det.*, 31, 389-400, 1994. Of the test methods specified by these references to determine whether a liquid possesses viscoelastic properties, one test which has been found to be useful in determining the viscoelasticity of an aqueous solution consists of swirling the solution and visually observing whether the bubbles created by the swirling recoil after the swirling is stopped. Any recoil of the bubbles indicates viscoelasticity. Another useful test is to measure the storage modulus (G') and the loss modulus (G") at a given temperature. If G'> G" at some point or over some range of points below about 10 rad/sec, typically between about 0.001 to about 10 rad/sec, more typically between about 0.1 and about 10 rad/sec, at a given temperature and if G'> 10^{-2} Pascals, preferably 10^{-1} Pascals, the fluid is typically considered viscoelastic at that temperature. Rheological measurements such as G' and G" are discussed more fully in "Rheological Measurements", Encyclopedia of Chemical Technology, vol. 21, pp. 347-372, (John Wiley & Sons, Inc., N.Y., N.Y.,

1997, 4th ed.). To the extent necessary for completion, the above disclosures are expressly incorporated herein by reference.

Viscoelasticity is caused by a different type of micelle formation than the usual spherical micelles formed by most surfactants. Viscoelastic surfactant fluids form worm-like, rod-like or cylindrical micelles in solution. The formation of long, cylindrical micelles creates useful rheological properties. The viscoelastic surfactant solution exhibits shear thinning behavior, and remains stable despite repeated high shear applications. By comparison, the typical polymeric thickener will irreversibly degrade when subjected to high shear.

In the summary of the invention and this detailed description, each numerical value should be read once as modified by the term "about"(unless already expressly so modified), and then read again as not so modified, unless otherwise indicated in context.

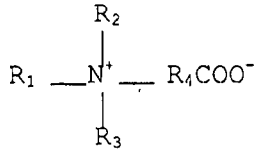
The viscoelastic surfactants can be either ionic or nonionic. The present invention comprises an aqueous viscoelastic surfactant based on amphoteric or zwitterionic surfactants. The amphoteric surfactant is a class of surfactant that has both a positively charged moiety and a negatively charged moiety over a certain pH range (e.g. typically slightly acidic), only a negatively charged moiety over a certain pH range (e.g. typically slightly alkaline) and only a positively charged moiety at a different pH range (e.g. typically moderately acidic), while a zwitterionic surfactant has a permanently positively charged moiety in the molecule regardless of pH and a negatively charged moiety at alkaline pH.

The viscoelastic fluid comprises water, surfactant, and a water-soluble compound selected from the group consisting of organic acids, organic acid salts, inorganic salts, and mixtures thereof. Alternatively,

the viscoelastic fluid can comprise water, an amine oxide surfactant and an anionic surfactant containing a hydrophobe having at least about 14 carbon atoms. The viscoelastic surfactant solution is useful as a fracturing fluid or water-based hydraulic fluid. The viscoelastic fluid used as a fracturing fluid may optionally contain a gas such as air, nitrogen or carbon dioxide to provide an energized fluid or a foam.

The component of the fluid which will be present in the greatest concentration is water, i.e. typically water will be a major amount by weight of the viscoelastic fluid. Water is typically present in an amount by weight greater than or equal to about 50% by weight of the fluid. The water can be from any source so long as the source contains no contaminants which are incompatible with the other components of the viscoelastic fluid (e.g., by causing undesirable precipitation). Thus, the water need not be potable and may be brackish or contain other materials typical of sources of water found in or near oil fields.

Examples of zwitterionic surfactants useful in the present invention are represented by the formula:



wherein R_1 represents a hydrophobic moiety of alkyl, alkylarylalkyl, alkoxyalkyl, alkylaminoalkyl and alkylamidoalkyl, wherein alkyl represents a group that contains from about 12 to about 24 carbon atoms which may be branched or straight chained and which may be saturated or unsaturated. Representative long chain alkyl groups include tetradecyl (myristyl), hexadecyl (cetyl), octadecentyl (oleyl), octadecyl (stearyl), docosenoic (erucyl) and the derivatives of tallow, coco,

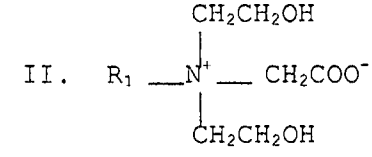
soya and rapeseed oils. The preferred alkyl and alkenyl groups are alkyl and alkenyl groups having from about 16 to about 22 carbon atoms. Representative of alkylamidoalkyl is alkylamidopropyl with alkyl being as described above.

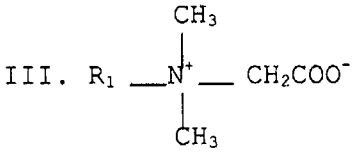
R_2 and R_3 are independently an aliphatic chain (i.e. as opposed to aromatic at the atom bonded to the quaternary nitrogen, e.g., alkyl, alkenyl, arylalkyl, hydroxyalkyl, carboxyalkyl, and hydroxyalkyl-polyoxyalkylene, e.g. hydroxyethyl-polyoxyethylene or hydroxypropyl-polyoxypropylene) having from 1 to about 30 atoms, preferably from about 1 to about 20 atoms, more preferably from about 1 to about 10 atoms and most preferably from about 1 to about 6 atoms in which the aliphatic group can be branched or straight chained, saturated or unsaturated. Preferred alkyl chains are methyl, ethyl, preferred arylalkyl is benzyl, and preferred hydroxyalkyls are hydroxyethyl or hydroxypropyl, while preferred carboxyalkyls are acetate and propionate.

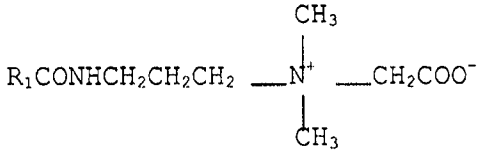
R_1 is a hydrocarbyl radical (e.g. alkylene) with chain length 1 to 4. Preferred are methylene or ethylene groups.

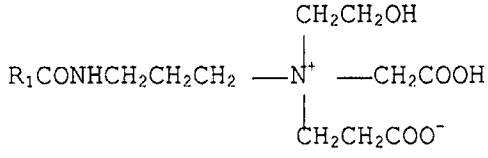
Specific examples of zwitterionic surfactants include the following structures:

II.



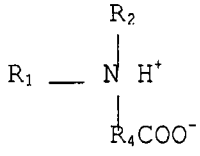
III. 

IV. 

V. 

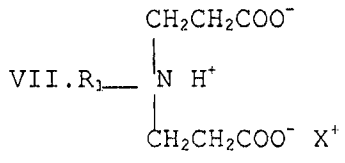
wherein R_1 has been previously defined herein.

Examples of amphoteric surfactants include those represented by formula VI:

VI. 

wherein R_1, R_2, and R_4 are the same as defined above.

Other specific examples of amphoteric surfactants include the following structures:

VII. 

What is claimed is:

1. A viscoelastic fluid consisting essentially of:

(1) an aqueous medium;

(2) a surfactant selected from the group consisting of amphoteric surfactants, zwitterionic surfactants, and mixtures thereof; and

(3) a member selected from the group consisting of organic acids, organic acid salts, inorganic salts, and combinations of one or more organic acids or organic acid salts with one or more inorganic salts;

wherein said fluid exhibits the property of viscoelasticity.

2. The fluid as claimed in claim 1 wherein said amount of said surfactant is from about 0.5% to about 6% by weight of said fluid.

3. The fluid as claimed in claim 1 wherein said member is selected from the group consisting of organic acids and organic acid salts.

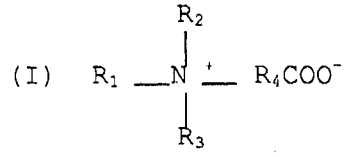
4. The fluid as claimed in claim 1 wherein said member is selected from the group of inorganic water-soluble salts.

5. The fluid as claimed in claim 1 wherein said surfactant is a zwitterionic surfactant comprising a quaternary ammonium hydrophilic moiety.

6. The fluid as claimed in claim 5 wherein the quaternary ammonium moiety of said zwitterionic surfactant is covalently bonded with an alkyl or a hydroxyalkyl group.

16. The fluid as claimed in claim 1 wherein said member is an organic acid or salt thereof and is present in an amount of from about 0.1% to about 8% by weight.

17. The fluid as claimed in claim 1 wherein said surfactant is represented by the formula (I):



(I)

wherein R_1 represents alkyl, alkenyl, alkylarylalkylene, alkenylarylalkylene, alkylaminoalkylene, alkenylamino-alkylene, alkylamidoalkylene, or alkenylamidoalkylene, wherein each of said alkyl groups contain from about 14 to about 24 carbon atoms and may be branched or straight chained and saturated or unsaturated, and wherein said alkylene groups have from about 1 to about 6 carbon atoms,

R_2 and R_3 are independently aliphatic chains having from about 1 to about 30 carbon atoms, and

R_4 is a hydrocarbyl radical with a chain length of about 1 to about 4.

18. The fluid of claim 17 wherein R_1 is selected from the group consisting of tetradecyl, hexadecyl, octadecentyl, and octadecyl.

19. The fluid of claim 17 wherein R_1 is an alkyl group derived from tallow, coco, soya bean, or rapeseed oil.

20. The fluid of claim 17 wherein said alkyl and alkenyl groups of R_1 are selected from alkyl groups and alkenyl groups respectively having from about 16 to about 22 carbon atoms.

wherein said fluid exhibits the property of viscoelasticity.

44. A method of suspending solid particles of excavation by-products in a viscoelastic fluid, wherein the solid particles remain suspended for an extended period of time in a site, comprising the steps of transporting the fluid to a site while the solid particles remain suspended in the fluid and depositing the fluid to such site, wherein said viscoelastic fluid comprises:

(1) an aqueous medium;

(2) a surfactant selected from the group consisting of amphoteric surfactants, zwitterionic surfactants, and mixtures thereof; and

(3) a member selected from the group consisting of organic acids and salts thereof, inorganic salts, and combinations of one or more organic acids or salts thereof, with one or more inorganic salts;

wherein said fluid exhibits the property of viscoelasticity.

45. A method of fracturing a subterranean formation comprising the step of pumping a viscoelastic fluid through a wellbore and into a subterranean formation at a pressure sufficient to fracture the formation, wherein said viscoelastic fluid comprises:

(1) an aqueous medium;

(2) a surfactant selected from the group consisting of amphoteric surfactants, zwitterionic surfactants, and mixtures thereof; and

(3) a member selected from the group consisting of organic acids, organic acid salts, inorganic salts, and combinations of one or more organic acids or organic acid salts with one or more inorganic salts;

wherein said fluid exhibits the property of viscoelasticity.

46. The method of fracturing as claimed in claim 44 wherein said viscoelastic fluid is further comprised of a particulate proppant suspended therein.

47. An aqueous formulation of an agricultural chemical and an amount of a viscoelastic fluid sufficient to increase the average droplet size of a spray of said formulation, wherein said viscoelastic fluid comprises:

(1) an aqueous medium;

(2) a surfactant selected from the group consisting of amphoteric surfactants, zwitterionic surfactants, and mixtures thereof; and

(3) a member selected from the group consisting of organic acids, organic acid salts, inorganic salts, and combinations of one or more organic acids or organic acid salts with one or more inorganic salts;

wherein said fluid exhibits the property of viscoelasticity.

48. A viscoelastic fluid consisting essentially of:

(1) an aqueous medium;

(2) an amount of a surfactant comprising an amine oxide surfactant; and

(3) an anionic surfactant containing a hydrophobe having at least 14 carbon atoms;

wherein said fluid exhibits the property of viscoelasticity.