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DIVISIÓN DE NUEVAS CREACIONES
SUPERINTENDENCIA DE INDUSTRIA Y COM
Bogotá, D.C.

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Act. 444 RESPUESTAREQUE Folios: 7

Re.: Código 011-379-444
Expediente No. 03-69.557
Fase nacional de Solicitud
de Patente PCT
SCHLUMBERGER TECHNOLOGY B.V.

En relación con el expediente de la referencia y dando cumplimiento a la última providencia recaída sobre este asunto por medio del presente escrito me permito manifestarles lo siguiente:

1. Se modifican y se adjuntan las páginas 8 y 12 con el fin de hacer mayor claridad en algunos términos.
2. Igualmente se acompaña un nuevo capítulo reivindicatorio revisado y modificado.
3. Haciendo referencia al punto 3 del concepto técnico, el examinador parece pensar que existe un error en la ortografía de los términos que se resaltaron en negrilla. No se trata de un error de ortografía, la explicación más detallada es la siguiente:

Existe un sistema de nomenclatura que se utiliza en algunas industrias y que emplea "laureth" para referirse a "lauril poly(oxietileno)". El compuesto que se muestra en la primera fórmula de la página 3 contenía un grupo lauril tri(oxietileno). La página 12 y la reivindicación 15 han sido modificadas para emplear este término.

Las dos fórmulas en la página 12 estaban incorrectas ya que mostraban un $-CH_{11}-$ que no tiene sentido y que debe corregirse por $-(CH_2)_{11}-$ tal como se muestra en la versión corregida en la página 12 adjunta.

El término “esterquat” es un nombre abreviado de un compuesto que es un éster de un compuesto de nitrógeno cuaternario. Esto es aparente de la explicación en las páginas 9 y 10. La palabra Esterquat es aún parte del título de un libro que se menciona en la línea 25 de la página 12 del texto PCT. Se ha insertado un paréntesis como explicación cuando se emplea esterquat por primera vez, tal como se muestra en la página 8, y se solicita al examinador que permita el uso subsiguiente de los términos esterquat y quat, ya que ellos están explicados en el texto.

4. El propósito de las modificaciones a las reivindicaciones es superar las objeciones del examinador en el concepto técnico. La reivindicación 1 modificada ahora define el primer surfactante viscoelástico por medio de una fórmula y definiciones copiadas de la reivindicación 2 anterior, salvo el texto final “que posiblemente comprende un grupo hidroxilo terminal” de la reivindicación 2 anterior. Esta propiedad opcional es el objeto de la reivindicación 2 modificada. La reivindicación 1 modificada define el segundo surfactante por medio de una fórmula y definiciones copiadas de la reivindicación 8, con algún cambio. El texto final “que posiblemente comprende un grupo hidroxilo terminal” de la reivindicación 8 es el objeto de la reivindicación 8 modificada.
5. En la reivindicación 1 modificada, X se refiere a un *grupo* y no a un enlace. Segundo, la longitud de la cadena del grupo R en el segundo surfactante ha sido cambiada a “al menos 3 átomos de carbono”. Esto se encuentra apoyado en la página 12 del texto PCT original que explica que la hendidura hidrolítica del segundo surfactante en el grupo X libera un compuesto que contiene el grupo R de este surfactante, donde R es al menos 3 átomos de carbono, posiblemente 8 a 18 átomos de carbono, o posiblemente más.

Las reivindicaciones 17 y 18 anteriores concordaban con esto. Los compuestos que se nombran en la página 17 son ejemplos de compuestos en los que R contiene 12 átomos de carbono.

6. Las reivindicaciones 12 y 15 han sido modificadas. La reivindicación 16 anterior ha sido eliminada. Las reivindicaciones 17, 18 y 19 han sido reenumeradas y modificadas para que sean dependientes de las reivindicaciones de la composición. Las reivindicaciones 20 y 21 han sido eliminadas. A las reivindicaciones dependientes se le han dado múltiples subdependencias.
7. El documento D1 (WO 94/09852) divulga composiciones acuosas que contienen un surfactante viscoelástico. Sin embargo, este documento no menciona un segundo surfactante que contenga un grupo X éster, amida o acetal hendible. Por lo tanto, las reivindicaciones son novedosas, y nada en la técnica anterior sugiere los requerimientos de la reivindicación 1 según ha sido modificada.
8. Teniendo en cuenta lo dispuesto por el Consejo de Estado en sentencia proferida dentro del Expediente No. 7684 el 22 de Octubre de 2004 y acogida por esa Superintendencia mediante memorando interno de fecha 22 de Diciembre de 2004 dirigido a los funcionarios de la Delegatura de Propiedad Industrial, no se hace necesario acompañar comprobante de pago por concepto de modificación de la solicitud por cuanto el nuevo pliego reivindicatorio se presenta a instancia de la Superintendencia en cumplimiento de lo ordenado por el artículo 45 de la Decisión 486.

Renuncio al término faltante de traslado, y les solicito conceder el privilegio de patente de invención aquí tramitado.

De ustedes Atentamente,


LUIS FELIPE CASTILLO GIBSONE
T. P. No. 68.995 del C.S.J.

viscoelásticos cuando están en una solución alcalina en la presencia de sales agregadas tales como cloruro de potasio o cloruro de sodio. Las micelas en forma de lombriz de dicho gel se degradan a micelas esféricas cuando el hidrocarburo rompe el gel.

El fluido de la invención comprende un segundo surfactante. Este surfactante es viscoelástico o no. Es fragmentable. Como tal, se descompone en condiciones pozo abajo para liberar los productos de degradación. Los surfactantes fragmentables para la implementación de la invención se divulgan en la solicitud de patente radicada el 13 de febrero de 2001 bajo el No. GB 0103449-5. Estos surfactantes son viscoelásticos de la siguiente fórmula:



donde R es la cola hidrofóbica del surfactante, el cual es una cadena de hidrocarburos, total o parcialmente saturada, lineal o ramificada de al menos 18 átomos de carbono, X es el grupo fragmentable o degradable del surfactante el cual es un enlace de acetal, amida, éter o éster, Y es un grupo espaciador el cual es constituido por una cadena corta saturada o parcialmente saturada de hidrocarburos de n átomos de carbono, donde n es al menos igual a 1, preferiblemente 2 y, cuando n es ≥ 3 , puede ser una cadena de alquilo recta o ramificada, y Z es el grupo delantero hidrofílico del surfactante el cual puede ser $NR_1R_2R_3^+$, $-SO_3^-$, $-COO^-$ o, en el caso en que el surfactante sea zwitteriónico, $-N^+(R_1R_2R_3)-COO^-$, donde R_1 , R_2 y R_3 son cada uno independientemente hidrógeno o una cadena alifática total o parcialmente saturada, lineal o ramificada de al menos un átomo de carbono, que comprende posiblemente un grupo terminal.

Por lo tanto, los segundos surfactantes típicos son carboxilatos de éster, sulfonatos de éster, por ejemplo, donde $Y = CH_2CH_2$, isetionatos, y quats de ésteres (de compuestos que contienen nitrógeno cuaternario). Los surfactantes equivalentes de amida inversa y delantera, es decir, carboxilatos de amida inversos, carboxilatos de amida delanteros, por ejemplo sarcosinatos ($RCON(CH_3)CH_2COO^-$), sulfonatos de amida inversos, sulfonatos de amida delanteros, por ejemplo tauratos ($RCON(R')CH_2CH_2SO_3^-$), quats de amida inversa y quats de amida delantera también son típicos segundos surfactantes según la invención.

Debido en particular a la presencia del grupo delantero hidrofílico, las concentraciones peso/porcentaje de los surfactantes R-X-Y-Z son compatibles con el gel del surfactante viscoelástico aún cuando R sea una cadena saturada o parcialmente insaturada con 18 átomos de carbono o más.

Por ejemplo, cuando X es un grupo éster, el surfactante fragmentable puede descomponerse en condiciones pozo abajo para liberar un separador de alcohol de acuerdo con la siguiente reacción:

104
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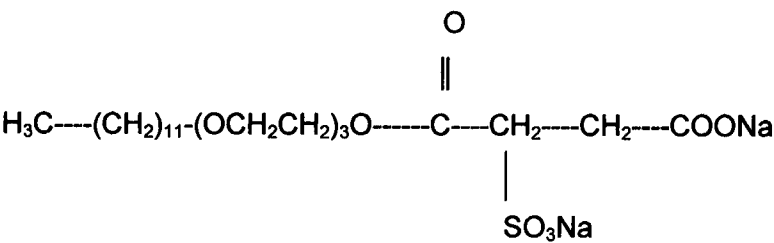
Sin embargo, otros surfactantes fragmentables pueden ser indicados para romper geles del surfactante de oleato o geles dimeros/trimeros de carboxilato. Estos se basan en surfactantes de sulfosuccinato y sulfoacetato.

Por ejemplo, los sulfosuccinatos de alquilo son mono o di-ésteres de ácido sulfosuccínico: $\text{HOOCCH}_2\text{CH}(\text{SO}_3\text{H})\text{COOH}$. La fórmula de estos mono y di-ésteres de ácido sulfosuccínico son las siguientes:

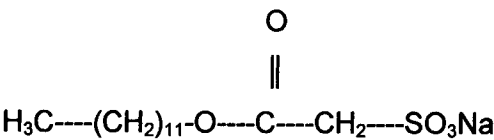


donde R es una cadena de alquilo.

Dos segundos surfactantes diferentes indicados para la implementación de la invención se consiguen de la Compañía StepanTM. El primero es lauril tri(oxietileno) sulfosuccinato disódico:



El Segundo es un surfactante de sulfoacetato, lauril sulfoacetato sódico:



STEPAN-MILD LSMTM es un producto líquido que contiene tanto surfactantes de laureth sulfosuccinato disódico como de lauril sulfoacetato sódico en agua, siendo 25%/peso la actividad total del surfactante. Este surfactante tolera agua dura y es fácilmente biodegradable. La temperatura recomendada de almacenamiento es entre 7°C y 43°C. STEPAN.MILD SL3TM es también un líquido que contiene 30%/peso de laureth sulfosuccinato disódico. Ambos surfactantes se pueden descomponer para liberar alcoholes de cadena larga tal como se ilustra en las Figuras 3 y 4. Esta descomposición viene acompañada por una reducción en el pH del fluido debido al consumo del ión OH⁻. Además, la presencia del grupo sulfonato acelera la velocidad de la hidrólisis de éster de modo que $\text{ROOCH}_2\text{CH}(\text{SO}_3\text{Na})\text{COONa}$ se degrada más fácilmente que su equivalente no sulfonato: $\text{ROOCCH}_2\text{CH}_2\text{COONa}$ y $\text{ROOCCH}_2\text{SO}_3\text{Na}$ se degradará más rápidamente que ROOCH_3 . En ambos casos, la presencia del grupo sulfonato aumenta la hidrofilicidad y la solubilidad en agua del compuesto, y esto aumenta la compatibilidad con el gel.

REIVINDICACIONES

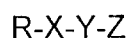
1. Un fluido viscoelástico acuoso para uso en la recuperación de hidrocarburos, que comprende:

un primer surfactante, siendo dicho surfactante viscoelástico, el cual es de las siguientes fórmulas:



en donde R es la cola hidrofóbica del surfactante, la cual es una cadena de hidrocarburos lineal o ramificada, total o parcialmente saturada, de al menos 18 átomos de carbono, y Z es el grupo delantero del surfactante el cual es $-NR_1R_2R_3^+$, $-SO_3^-$, $-COO^-$ o, en el caso en que el surfactante sea zwitteriónico, $-N^+(R_1R_2R_3-COO^-)$, donde R_1 , R_2 y R_3 son cada uno independientemente hidrógeno o una cadena alifática, lineal o ramificada, total o parcialmente saturada de al menos un átomo de carbono;

un segundo surfactante de las siguientes fórmulas:



donde R es la cola hidrofóbica del surfactante, la cual es una cadena de hidrocarburos lineal o ramificada, total o parcialmente saturada, de al menos 3 átomos de carbono, X es un grupo acetal, amida, éter o éster, Y es un grupo espaciador constituido por una cadena de hidrocarburos, saturada corta o saturada parcialmente, de átomos de carbono n donde n es al menos igual a 1, y cuando $n \geq 3$, puede ser una cadena de alquilo recta o ramificada, y Z es el grupo de cabeza hidrofílica del surfactante que puede ser $-NR_1R_2R_3^+$, $-SO_3^-$, $-COO^-$ o, en el caso en que el surfactante sea zwitteriónico, $-N^+(R_1R_2R_3-COO^-)$, donde R_1 , R_2 y R_3 son cada uno independientemente hidrógeno o una cadena alifática, lineal o ramificada, total o parcialmente saturada de al menos un átomo de carbono.

2. El fluido de la reivindicación 1, en donde:

R_2 y R_3 del primer surfactante son cada uno independientemente, una cadena alifática, lineal o ramificada, total o parcialmente saturada de al menos un átomo de carbono y que comprende un grupo hidroxilo terminal.

3. El fluido de la reivindicación 1, o la reivindicación 2, en donde el primer surfactante es hendible.

4. El fluido de la reivindicación 1 o la reivindicación 2, en donde el primer surfactante viscoelástico es N-erucil-N,N-bis(2-hidroxietil)-N-metil amonio cloruro.

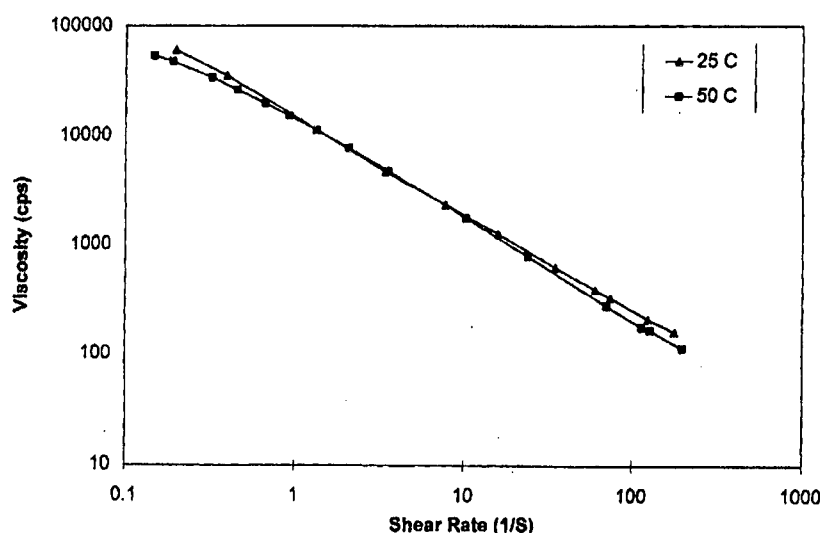
- 106
7
5. El fluido de la reivindicación 1 o la reivindicación 2, en donde el primer surfactante es un carboxilato mono-, di- u oligomérico.
 6. El fluido de la reivindicación 1 5, en donde el primer surfactante es oleato.
 7. El fluido según cualquiera de las reivindicaciones 1 a 6, en donde el segundo surfactante es un surfactante viscoelástico.
 8. El fluido según cualquiera de las reivindicaciones 1 a 76, en donde R_2 y R_3 del segundo surfactante son cada uno independientemente, una cadena alifática lineal o ramificada, total o parcialmente saturada de al menos un átomo de carbono, y comprende un grupo hidroxilo terminal.
 9. El fluido según cualquiera de las reivindicaciones 1 a 8 en donde el segundo surfactante es un éster carboxilato, un éster sulfonato, un carboxilato amida hacia atrás, un carboxilato amida hacia adelante, un sulfonato amida hacia atrás o un sulfonato amida hacia adelante.
 10. El fluido según cualquiera de las reivindicaciones 1 a 8, en donde el grupo cabeza Z en el segundo surfactante es $-NR_1R_2R_3+$ y X en el segundo surfactante es un grupo éster.
 11. El fluido según cualquiera de las reivindicaciones 1 a 8, en donde el segundo surfactante es éster de betaína.
 12. El fluido según cualquiera de las reivindicaciones 1 a 8, en donde el segundo surfactante es di(palmitoiletil) hidroxietilmetil-amonio o erucil éster metilen dimetil etil amonio.
 13. El fluido según la reivindicación 9, en donde el segundo surfactante es mono-oleil éster succinato.
 14. El fluido según la reivindicación 9, en donde el segundo surfactante es un surfactante sulfosuccinato o sufoacetato.
 15. El fluido según la reivindicación 14, en donde el segundo surfactante es lauril sulfosuccinato disódico o lauril sulfoacetato sódico.
 16. El fluido según cualquiera de las reivindicaciones 1 a 15, en donde el grupo R en el segundo surfactante es una cadena alquilo de al menos 3 átomos de carbono.
 17. El fluido según cualquiera de las reivindicaciones 1 a 15, en donde el grupo R en el segundo surfactante comprende de 8 a 18 átomos de carbono o más.
 18. El fluido según cualquiera de las reivindicaciones 1 a 15, en donde el grupo R en el segundo surfactante es oleil y X en el segundo surfactante es $-COC$.



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(21) International Application Number: PCT/US98/12067 (22) International Filing Date: 9 June 1998 (09.06.98) (30) Priority Data: 60/049,045 10 June 1997 (10.06.97) US 60/054,455 5 August 1997 (05.08.97) US (71) Applicant: RHODIA INC. [US/US]; 259 Prospect Plains Road, Cranbury, NJ 08512-7500 (US). (72) Inventors: DAHANAYAKE, Manilal, S.; 17 Reed Drive North, Princeton Junction, NJ 08550 (US). YANG, Jiang; 104 Marion Drive, Plainsboro, NJ 08536 (US). NIU, Joseph, H., Y.; 15722 T.C. Jester Boulevard, Houston, TX 77086 (US). DERIAN, Paul-Joel; 5 Wood Hollow Road, Lawrenceville, NJ 08648 (US). DINO, David; 23 Pinehurst Drive, Cranbury, NJ 08512 (US). LI, Ruoxin; 1415 Ravens Crest Drive, Plainsboro, NJ 08536 (US). (74) Agents: SHEDDEN, John, A. et al.; Rhodia Inc., 259 Prospect Plains Road, Cranbury, NJ 08512-7500 (US).		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, GW, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>

(54) Title: FLUIDS CONTAINING VISCOELASTIC SURFACTANT AND METHODS FOR USING THE SAME



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.



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108

(12) United States Patent
Dahayanake et al.**(10) Patent No.: US 6,258,859 B1**
(45) Date of Patent: Jul. 10, 2001**(54) VISCOELASTIC SURFACTANT FLUIDS AND RELATED METHODS OF USE****(75) Inventors:** Manilal S. Dahayanake, Princeton Junction; Jiang Yang, Plainsboro, both of NJ (US); Joseph H. Y. Niu, Houston, TX (US); Paul-Joel Derian, Lawrenceville, NJ (US); Ruoxin Li, Plainsboro, NJ (US); David Dino, Cranbury, NJ (US)**(73) Assignee:** Rhodia, Inc., Cranbury, NJ (US)**(*) Notice:** Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.**(21) Appl. No.:** 09/093,131**(22) Filed:** Jun. 8, 1998**Related U.S. Application Data****(60)** Provisional application No. 60/054,455, filed on Aug. 5, 1997, and provisional application No. 60/049,045, filed on Jun. 10, 1997.**(51) Int. Cl.⁷** B01J 17/22; B01J 17/28; C11D 1/10; C11D 1/90**(52) U.S. Cl.** 516/77; 252/77; 166/308; 405/128; 424/401; 507/922; 507/924; 510/480; 510/490; 510/502; 510/503**(58) Field of Search** 516/77; 507/922; 507/924; 252/77; 510/490; 502; 503; 480**(56) References Cited****U.S. PATENT DOCUMENTS**

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Primary Examiner—Richard D. Lovering*(74) Attorney, Agent, or Firm*—Ohlandt, Greeley, Ruggiero & Perle, L.L.P.**(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 amphoteric acetate or propionate, alkyl betaine, alkyl amidopropyl betaine and alkylimino 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.

5 Claims, 5 Drawing Sheets

1 VISCOELASTIC SURFACTANT FLUIDS AND RELATED METHODS OF USE

This application claims the benefit of the disclosure of U.S. Provisional Patent Application Serial No. 60/043,045, filed on Jun. 10, 1997, and Ser. No. 60/054,455, filed on Aug. 5, 1997.

FIELD OF THE INVENTION

This invention relates to viscoelastic fluids which contain a surfactant and 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 viscosity 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 fluid consists of an amphiphilic/zwitterionic surfactant and an inorganic salt and/or organic acid 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 amphiphilic 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 these 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 dispersing 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 method for forming a wellbore comprising a cleavage surface in a subterranean formation.

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 DRAWINGS

FIG. 1 shows viscosity versus shear rate for a viscoelastic surfactant solution prepared by adding 5 percent of disodium tallonimodipropionate (Miratane T2C09) and 2.25 percent of phthalic acid to water.

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

FIG. 3 shows the viscosity versus shear rate for a viscoelastic surfactant solution prepared by adding 5 percent of disodium tallonimodipropionate (Miratane T2C09), 4 percent of NH_4Cl and 1.75–2.0 percent of phthalic acid to water.

FIG. 4 shows the viscosity versus shear rate for viscoelastic surfactant solutions prepared by adding 4 or 5 percent of disodium oleamidopropyl betaine (Miratane HET-08), 3 percent of KCl and 0.5 percent of phthalic acid to water.

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

DETAILED DESCRIPTION OF THE INVENTION

The property of viscoelasticity in general is well known and reference is made to S. Gratch, *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", *Interfac. Surf. Sci.*, 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, more 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. Rheo-

logical 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., 1977, 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 micelles 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 surfactant solution is characterized by the following features. The present invention comprises an aqueous viscoelastic surfactant based on amphiphilic or zwitterionic surfactants. The amphiphilic 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). Zwitterionic surfactants have a permanently positively charged moiety and a permanently negatively charged moiety at all pH values.

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 is an emulsion of water and an organic surfactant. The emulsion contains a hydrophobic 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:

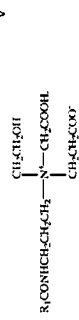


wherein R_1 represents a hydrophobic moiety of alkyl, alkylarylalkyl, alkoxyalkyl, alkylaminoalkyl and

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), octadecyl (stearyl), octadecyl (stearyl), decenyl (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.

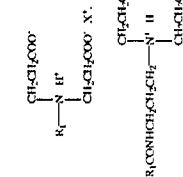
R_4 is a hydrocarbyl radical (e.g. alkylene) with chain length 1 to 4. Preferred are methylene or ethylene groups. Specific examples of zwitterionic surfactants include the following structures:



wherein R_1 has been previously defined herein. Examples of amphiphilic surfactants include those represented by formula VI:

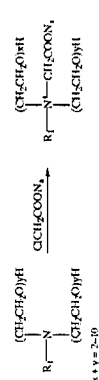


wherein R_1 , R_2 , R_3 , and R_4 are the same as defined above. Other specific examples of amphiphilic surfactants include the following structures:



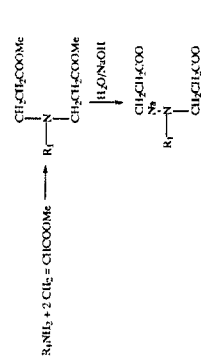
wherein R_1 has been previously defined herein, and X^- is an inorganic anion such as Na^+ , K^+ , NH_4^+ associated with a carboxylate group or hydrogen atom in an acidic medium.

A typical chemical process to synthesize dihydroxy ethoxyglycine starting from ethoxylated alkylamine is as follows:



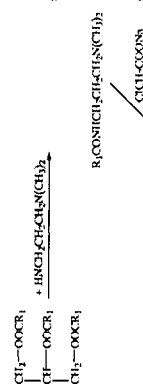
The final products may also include some unreacted starting dihydroxy ethyl alkyl amine, and small amounts of sodium glycolate, diglycolate and sodium chloride as by products. A similar process can be used to prepare propoxy-lated analogues.

A typical chemical process to synthesize alkylamino-dipropionate from alkyl amine is as follows:

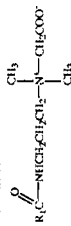


The final products will also include a small amount of methanol, unreacted acrylic acid, alkylamine and some oligomeric acrylate or acid as by products.

A typical chemical process to synthesize alkylamine from alkyl amine is as follows:



-continued



The final products will also include a small amount of sodium glycolate, diglycolate, sodium chloride and glycerine as by products.

To still another embodiment of the invention, the zwitterionic surfactant selected is an amine oxide. This material has the following structure:



where R_1 , R_2 and R_3 are as defined above.

The surfactants are used in an amount which in combination with the other ingredients is sufficient to form a viscoelastic fluid, which amount will typically be a minor amount by weight of the fluid (e.g. less than about 50% by weight). The concentration of surfactant can range from about 0.5% to about 10% percent by weight of the fluid, more typically from about 0.5% to about 8%, and even more typically from about 0.5% to about 6%. Optimum concentrations for any particular set of parameters can be determined experimentally.

The fluid also comprises one or more members from the group of organic acids, inorganic acid salts, and inorganic salts. Mixtures of the above members are specifically contemplated as falling within the scope of the invention. This member will typically be present in only a minor amount (e.g. less than about 20% by weight of the fluid).

The organic acid is typically acetic acid or a carboxylic acid and the anionic counter-ion of the organic acid salts are typically sulfonates or carboxylates. Representative of such organic molecules include various aromatic sulfonates and carboxylates such as p-toluene sulfonate, naphthalene sulfonate, chlorobenzoic acid, salicylic acid, phthalic acid and the like, where such counter-ions are water-soluble. Most preferred are salicylate, phthalate, p-toluene sulfonate, hydroxynaphthalene carboxylates, e.g., 5-hydroxy-1-naphthoic acid, 6-hydroxy-1-naphthoic acid, 7-hydroxy-1-naphthoic acid, 1-hydroxy-2-naphthoic acid, preferably 3-hydroxy-2-naphthoic acid, 5-hydroxy-2-naphthoic acid, 7-hydroxy-2-naphthoic acid, and 1,3-dihydroxy-2-naphthoic acid or salt thereof typically adds the development of increased viscosity which is characteristic of preferred fluids. Without wishing to be bound by any theory unless expressly noted otherwise in context, it is thought that association of the organic acid or salt thereof with the micelle decreases the aggregation curvature of the micelle and thus promotes the formation of a worm-like or rod-like micelle. The organic acid or salt thereof will typically be present in the viscoelastic fluid at a weight concentration of from about 0.1% to about 10%, more typically from about 0.1% to about 7%, and even more typically from about 0.1% to about 6%.

The inorganic salts that are particularly suitable for use in the viscoelastic fluid include water-soluble potassium, sodium, and ammonium salts, such as potassium chloride, calcium bromide and zinc halide salts may also be used. The inorganic salts may aid in the development of increased

viscosity which is characteristic of preferred fluids. Further, the inorganic salt may assist in maintaining the stability of a geologic formation to which the fluid is exposed. Formation stability and in particular clay stability (by inhibiting hydration of the clay) is achieved at a concentration level of a few percent by weight and as such the density of fluid is not significantly altered by the presence of the inorganic salt unless fluid density becomes an important consideration, at which point, heavier inorganic salts may be used. The inorganic salt will typically be present in the viscoelastic fluid at a weight concentration of from about 0.1% to about 30%, more typically from about 0.1% to about 10%, and even more typically from about 0.1% to about 8%. Organic salts, e.g., trimethylammonium hydrochloride and tetramethylammonium chloride, may also be useful in addition to, or as a replacement for, the inorganic salts.

As an alternative to the organic salts and inorganic salts, or as a partial substitute therefor, one can use a medium to long chain alcohol (preferably an alkanol), preferably having five to ten carbon atoms, or an alcohol ethoxylate (preferably an alkanol ethoxylate) preferably of a 12 to 16 carbon alcohol and having 1 to 6, preferably 1-4, oxyethylene units.

In the embodiment where the surfactant selected is an amine oxide, it is preferably used in combination with an anionic surfactant containing a hydrophobic having at least about 14 carbon atoms. Examples of suitable anionic surfactants include alkyl sulfates or sulfonates having an alkyl chain length of about 12 to about 24 carbon atoms, which may be branched or straight chain and which may be saturated or unsaturated, and more preferably contains between about 16 and about 22 carbon atoms.

For this embodiment (amine oxide/anionic surfactant) the weight ratio of the amine oxide to anionic surfactant is from about 100:1 to about 50:50.

In addition to the water-soluble salts and thickening agents described hereinbefore, the viscoelastic fluid used as a hydraulic fracturing fluid may contain other conventional constituents which perform specific desired functions, e.g., corrosion inhibitors, fluid-loss additives and the like. A proppant can be suspended in the fracturing fluid. The pH of the fluid will typically range from strongly acidic (e.g. less than a pH of about 3) to slightly alkaline (e.g. from a pH just greater than 7.0 to about 8.5, more typically about 8.0) or moderately alkaline (e.g. a pH of about 8.5 to about 9.5). Strongly alkaline pHs (e.g. above a pH of about 10) should be avoided.

It is also conceivable to combine the above amphoteric/zwitterionic surfactants with conventional anionic, cationic, and amphoteric surfactants to get desired viscoelastic fluid for a particular work. In typical embodiments, the amphoteric/zwitterionic surfactant is typically present in a major amount by weight of all surfactants, and more typically is essentially the only surfactant present. Typically, the viscoelastic fluid will be essentially free of anionic surfactants, e.g. it will contain less than about 0.5%, more typically less than about 0.2%, even more typically less than 0.1% by weight of anionic surfactants.

To prepare the aqueous fluids in accordance with the present invention, the surfactant is added to an aqueous solution in which has been dissolved a water-soluble inorganic salt, e.g. potassium chloride or ammonium chloride and/or at least one organic acid or water-soluble organic acid salt to provide selective control of the loss of particle suspension properties. In the embodiment wherein the fluid

is a mixture of water, and amine oxide surfactant, and an anionic surfactant, a simple mixture of the three components is utilized. Standard mixing procedures known in the art can be employed since heating of the solution and special agitation conditions are normally not necessary. Of course, if used under conditions of extreme cold such as found in Alaska, normal heating procedures should be employed. It has been found in some instances preferable to dissolve the thickener into a lower molecular weight alcohol prior to mixing it with the aqueous solution. The lower molecular weight alcohol, for instance isopropanol, functions as an aid to solubilize the thickener. Other similar agents may also be employed. Further, a defoaming agent such as a polyglycol may be employed to prevent undesirable foaming during the preparation of the viscoelastic fluid. It is a foam or gas-energized fluid is desired, any gas such as air, nitrogen, carbon dioxide and the like may be added.

The fluid of this invention is particularly useful in the handling of particles generated during the excavation of a geologic formation, e.g. digging, drilling, blasting, dredging, tunneling, and the like, for example, in the course of constructing roads, bridges, buildings, tunnels and the like. The particles are mixed with the viscoelastic fluid by means which are effective to disperse the particles in the fluid. The particles generally have a particle size ranging from a fine powder to coarse gravel, e.g. dust, sand, and gravel. Particle size affects the suspendability of excavation processing wastes. For example, small particles suspend better than large particles, and very fine particles suspend so well that the mixture may become too thick to transport by pump or similar means. The distribution of excavation processing waste sizes is also important, as waste which contains particles which span a wide range of sizes is more easily suspended than waste wherein the particles are of about the same size. Therefore, it may be preferred to screen the waste particles prior to applying the present method to a better particle size distribution.

The viscoelastic fluids of the present invention can be utilized to carry earth or materials excavated during boring, excavating and trenching operations in the deep foundation construction industry, the subterranean construction industry and in tunneling, in well drilling and in other applications of earth support fluids. The ability of the excavation tools or systems to build and remove increased loading of earth is improved by the suspending properties and lubricating properties of the surfactant viscoelastic fluids.

In one preferred embodiment of this invention, the surfactant can be combined with some fluid-loss control additives known in the industry like water-soluble or water-dispersible polymers (guar and guar derivatives, xanthan, polyacrylamide, starch and starch derivatives, cellulose derivatives, polyacrylates, polyDADMAC, [poly(diallyl dimethyl ammonium chloride) and combinations thereof], clay (bentonite and attapulgite) in order to give fluid-loss control properties to the excavating fluid and contribute to the stabilization of the wall of the excavation.

More comprehensive information can be found in 'The University of Houston, Department of Chemical Engineering, Publication No. UHCE 93-1 entitled, Effect of Mineral and Polymer Shrires on Permeate Loss Transfer in Drilled shafts, published in January 1993, and PCT WO 96/23849, the disclosures of which are incorporated by reference.

The above method for suspending solids has many applications, particularly in mining and the handling of mine

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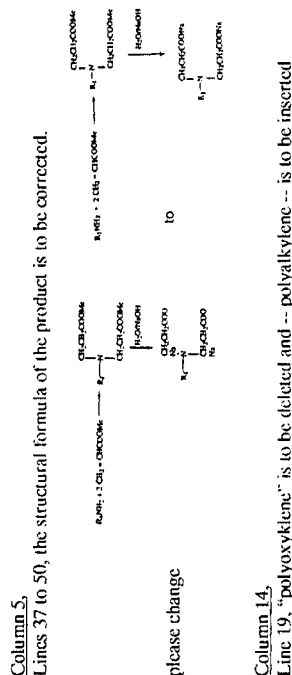
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UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 6,258,859 B1
DATED : July 10, 2001
INVENTOR(S) : Dahanayake et al.

Page 1 of 1

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below.



Signed and Sealed this
Ninth Day of July, 2002

JAMES E. ROGAN
Director of the United States Patent and Trademark Office

Attending Officer

Attest:

US 6,258,859 B1

14

2. A viscoelastic fluid comprising

- (1) an aqueous medium;
(2) a surfactant represented by the formula VI:



wherein R₁ is RCONHCH₂CH₂CH₂ and R is an alkyl group containing from about 14 to about 24 carbon atoms which may be branched or straight chained and which may be saturated or unsaturated;

R₂ is selected from the group of alkyl, alkenyl, acylalkyl, hydroxyalkyl, carboxyalkyl, and hydroxy-alkyl polyoxyethylene, each having from about 1 to about 10 carbon atoms; and

R₃ is a hydrocarbyl radical with chain length of about 1 to about 4;

(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

3. A viscoelastic fluid, comprising:

- (1) an aqueous medium;
(2) a surfactant comprising dihydroxyethyl tallow glycidate;

(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

4. The fluid of claim 3 wherein the surfactant is present at about 0.5% to about 10%; the member comprising one or more organic acids or salts thereof and being present at about 0.1% to about 30%.

5. A viscoelastic fluid comprising:

- (1) an aqueous medium;
(2) from about 0.5% to about 6% of a surfactant selected from the group consisting of dihydroxyethyl tallow glycidate, tallowaminodipropionate, and oleamidopropyl betaine; and

(3) from about 0.1% to about 6% of a combination of a member selected from the group consisting of p-toluenesulfonate, naphthalene sulfonate, chlorobenzoic acid, salicylic acid, and phthalic acid, with a member comprising one or more water-soluble ammonium salts;

wherein said fluid exhibits the property of viscoelasticity.

13

Example 10
A viscoelastic surfactant solution is prepared by mixing together in 94.8 parts of water 4.0 parts of curic amidepropyl amine oxide and 1.2 parts of sodium bisphenyl sulfate. The pH is adjusted to 9 by the addition of NaOH. Its temperature stability is determined by measuring its viscosity in cps (at shear rate of 100 sec⁻¹). The results are shown in Table 5.

TABLE 5

Temperature (° F.)	Viscosity Example 9	Viscosity Example 10
100	175	234
120	168	226
140	159	217
160	150	208
180	99	154
200	276	173
220	140	214
240	154	284
260	94	351
276	52	215
288	41	90
290	25	4
300	17	4

What is claimed is:

1. A viscoelastic fluid comprising:

- (1) an aqueous medium;
(2) a surfactant represented by the formula VI:



wherein R₁ represents alkyl, alkenyl, alkynyl, alkylarylalkylene, alkenylarylalkylene, alkylaminoalkylene, alkenylaminoalkylene, alkylamidoalkylene or alkylamidoalkylene 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, R₂ is beta-carboxyethyl, and R₃ is ethylene;

(2) 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.