



No. 11-133074- -00000-0000

Fecha: 2011-10-07 15:10:44 Dep. 2020 DIR.NUEVASCR
Tra. 11 PATENTEIYII Eve: 378 FASENACIONALI
Act. 411 PRESENTACION Folios: 156



Industria y Comercio

SUPERINTENDENCIA

DELEGATURA PROPIEDAD INDUSTRIAL

SOLICITUD
REGISTRO DE PATENTE DE INVENCION
PCT

EXPEDIENTE No _____

TITULO AGENTES TENSOACTIVOS
VISCOELÁSTICOS Y MÉTODOS PARA LA
ELABORACIÓN Y USO DE LOS MISMOS.

CLASIFICACION INTERNACIONAL _____

SOLICITANTE HALLIBURTON ENERGY
SERVICES, INC

DOMICILIO TEXAS, ESTADOS UNIDOS DE
AMERICA

APODERADO DARIO CARDENAS NAVAS

BOGOTA D.C. _____

PETITORIO



SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO



No. 11-133074- -00000-0000

Fecha: 2011-10-07 15:10:44 Dep. 2020 DIR.NUEVASCR
Tra. 11 PATENTEIYII Eve: 378 FASENACIONALI
Act. 411 PRESENTACION Folios: 156

FORMULARIO UNICO DE SOLICITUD DE PATENTE PCT ENTRADA EN FASE NACIONAL

①

SOLICITUD DE:

☒ X

Patente de Invención

☐

Patente de Modelo de Utilidad

☒ X

Capítulo I

☐

Capítulo II

②

SOLICITANTE

Nombre: **HALLIBURTON ENERGY SERVICES, INC**

Dirección: PO Box 1431, Duncan, Oklahoma 73536

Nacionalidad o Domicilio: Estados Unidos de América

Lugar de Constitución: Estados Unidos de América

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IDENTIFICACION

☐ NIT

☐ NIT

☐ Otro

☒ X Otro

Cual
Número

③

REPRESENTANTE
O APODERADO

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Teléfono: 313 7800 Fax: 312 3600

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IDENTIFICACION

☒ X NIT

☐ NIT

☐ Otro

☐ Otro

Cual
Número 170666629 TP 1250
BTA C.S.J.

④

INVENTOR(ES)
(72)

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Nacionalidad o Domicilio:
1. Norteamericano
2. Norteamericano

⑤ PCT (86)

Solicitud Internacional No. WO 2010/116117 A1 Fecha 14.10.2010
Publicación Internacional No. PCT/GB2010/000473 Fecha 17.03.2010

⑥

Título(54):
**AGENTES TENSOACTIVOS VISCOELÁSTICOS Y MÉTODOS PARA LA ELABORACIÓN Y
USO DE LOS MISMOS.**

⑦

Clasificación Internacional (51):

⑧

Prioridad

(33)País de Origen

(32)Fecha

(31)N° de Solicitud

US

07.04.2009

12/419,893

SI ☒ X NO ☐

⑨

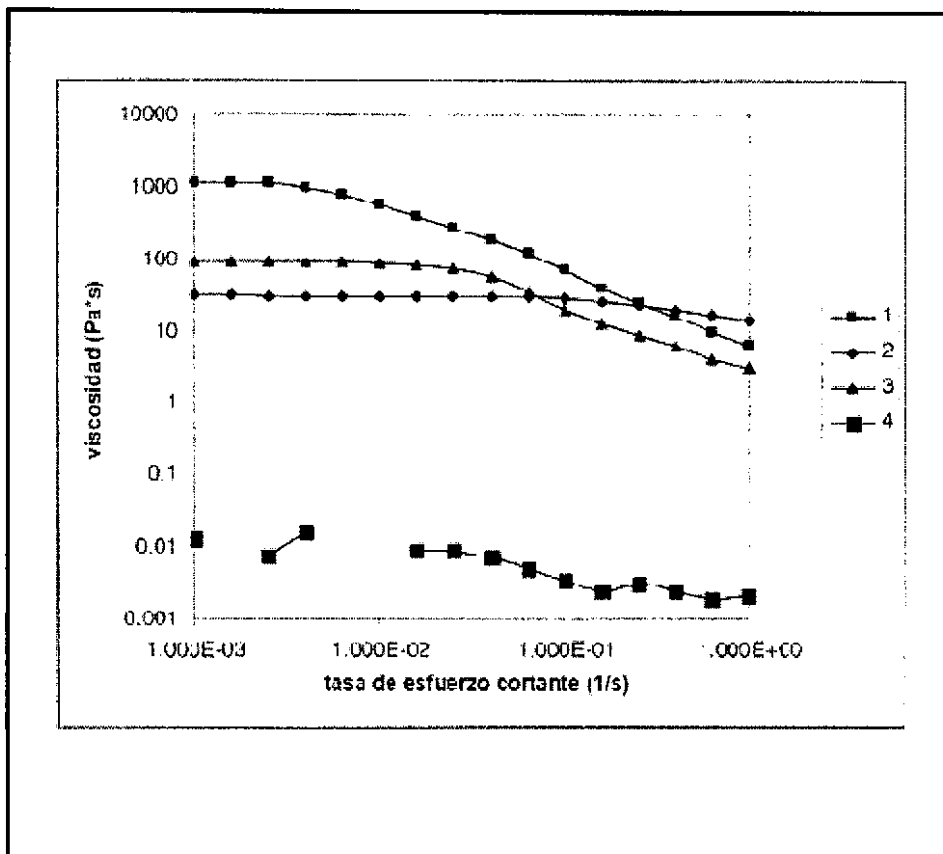
Comprobante de Pago No.:

Fecha

10 ANEXOS

- ☒ Comprobante de pago de la tasa de presentación de la solicitud.
- ☐ Documento que acredita la existencia y representación legal cuando el solicitante sea persona jurídica.
- ☐ Poderes, si fuere el caso.
- ☐ Documento de cesión del inventor al solicitante o a su causante.
- ☒ Traducción de la solicitud internacional al castellano (Resumen, descripción, reivindicaciones, dibujos)
- ☐ Copia del examen preliminar internacional efectuado por la Autoridad Internacional de Examen Preliminar (IPEA)
- ☐ Traducción del examen preliminar internacional efectuado por la IPEA.
- ☐ De ser el caso, copia del contrato de acceso.
- ☐ De ser el caso, documento que acredite la licencia o autorización de uso de conocimientos tradicionales de las comunidades indígenas.
- ☐ De ser el caso, certificado de depósito del material biológico.
- ☒ Arte final 12x12.
- ☐ De ser el caso, información sobre otras solicitudes de patente o títulos obtenidos en el extranjero por el mismo titular o su causante, relacionadas parcial o totalmente con la invención de esta solicitud.
- ☒ Recibo Reivindicaciones adicionales No _____
- ☒ Prioridad
<http://www.wipo.int/patentscope/search/en/detail.jsf?docId=WO2010116117&recNum=1&tab=PCTDocuments&maxRec=&office=&prevFilter=&sortOption=&queryString=>

11 FIGURA CARACTERISTICA



12 Solicito la Concesión de la patente

NOMBRE: DARIO CARDENAS NAVAS

FIRMA: _____

C.C. 17066629 BTA TP. 1250 CSJ *W*

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO
NIT : 800.176.089-2
- / -

Industria y Comercio SUPERINTENDENCIA	RECIBO DE CAJA	No. 11 - 0094717
		Bogotá D.C., Septiembre 27 de 2011 - 12:23:55

RECIBIDO DE : CARDENAS & CARDENAS ABOGADOS PI LTDA	NI 830.083.491
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*** Soporte del Pago ***					
TIPO PAGO	BANCO	CUENTA	No. PAGO	FECHA PAGO	VR. PAGO
CONSIGNACION	BANCO DE BOGOTA	062754387	186851372	27/09/2011	22.584.000.00

*** Conceptos Pagados ***			
CANT. RENTISTICO	CONCEPTO	Vr. UNIDITARIO	Vr. CONCEPTO
1 50005-01-01 SOLICITUDES	110 PTC SOLICITUD DE PATENTE DE INVENCIÓN	571.000.00	571.000.00
			\$571.000.00

SON: **QUINIENTOS SETENTA Y UN MIL PESOS MONEDA CORRIENTE***

Responsable: _____
Recibo de Caja Aplicado al Expediente No. _____

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO
No. 11-133074- -00000-0000
Fecha: 2011-10-07 15:10:44 Dep. 2020 DIR.NUEVASCR
Tra. 11 PATENTEIYII Eve: 378 FASENACIONALI
Act. 411 PRESENTACION Folios: 156

CARDENAS & CARDENAS

ABOGADOS

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO
NIT : 800.176.089-2
-/-

Industria y Comercio
SUPERINTENDENCIA

RECIBO DE CAJA

No. 11 - 0094724

Bogotá D.C., Septiembre 27 de 2011 - 12:23:55

RECIBIDO DE : CARDENAS & CARDENAS ABOGADOS PI LTDA

NI 830.083.491

*** Soporte del Pago ***

TIPO PAGO	BANCO	CUENTA	No. PAGO	FECHA PAGO	VR. PAGO
CONSIGNACION	BANCO DE BOGOTA	062754387	186851372	27/09/2011	22.584.000.00

*** Conceptos Pagados ***

CANT. RENTISTICO	CONCEPTO	Vr. UNDITARIO	Vr. CONCEPTO
16 50005-01-01 SOLICITUDES	1607 REIVINDICACION UNITARIA ADICIONAL A LAS 10 INICIALES	27.000.00	432.000.00
			\$432.000.00

SON: **CUATROCIENTOS TREINTA Y DOS MIL PESOS MONEDA CORRIENTE***

Responsable. _____

Recibo de Caja Aplicado al Expediente No. _____

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO



No. 11-133074- -00000-0000

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CARDENAS & CARDENAS
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Septiembre 27 de 2011 - 12:23:59

7



Industria y Comercio

SUPERINTENDENCIA

(21) N° de solicitud: (22) Fecha de solicitud:

(51) Clasificación Internacional :

(71) Solicitante(s) **HALLIBURTON ENERGY SERVICES, INC**

(72) Inventor(es) **Ryan Van Zanten, Douglas J Harrison**

(74) Apoderado: **DARIO CARDENAS NAVAS**

(30) Prioridad	(31) No. Prioridad	32) Fecha	(33) País
	12/419,893	07.04.2009	US

(85) Fecha inicio fase nacional: 07.11.2011

(86) Datos relativos a la presentación de la solicitud PCT

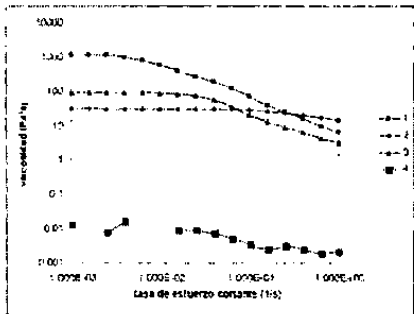
Fecha de presentación de la solicitud: 17.03.2010

No. de solicitud **PCT/GB2010/000473**

(54) Título **AGENTES TENSOACTIVOS VISCOELÁSTICOS Y MÉTODOS PARA LA ELABORACIÓN Y USO DE LOS MISMOS**



(21) N° de solicitud:		(22) Fecha de solicitud:	
(51) Clasificación Internacional :			
(71) Solicitante(s) HALLIBURTON ENERGY SERVICES, INC			
(72) Inventor(es) Ryan Van Zanten, Douglas J Harrison			
(74) Apoderado: DARIO CARDENAS NAVAS			
(30) Prioridad	(31) No. Prioridad	32) Fecha	(33) País
	12/419,893	07.04.2009	US
(85) Fecha límite inicio fase nacional: 07.11.2011		(87) Publicación internacional:	
(86) Datos relativos a la presentación de la solíc. PCT		Fecha: 14.10.2010	
Fecha de presentación de la solicitud: 17.03.2010		No. Publicación WO2010/116117 A1	
No. de solicitud PCT/GB2010/000473			



(54) Título:	AGENTES TENSOACTIVOS VISCOELÁSTICOS Y MÉTODOS PARA LA ELABORACIÓN Y USO DE LOS MISMOS
(57) Resumen:	

Un método para el mantenimiento de perforaciones de pozo que comprende la colocación barreno abajo de una composición que comprende un conjunto de agentes tensoactivos comprendiendo un agente tensoactivo catiónico y un agente tensoactivo aniónico, en donde el conjunto de agentes tensoactivos cuando entra en contacto con una solución acuosa forma una composición viscosificada en presencia de menos de aproximadamente 30% en peso de un hidrótrofo.

(21) N° de solicitud:					(51) Int Cl:	
22) Fecha de solicitud:					(71) Solicitante(s) HALLIBURTON ENERGY SERVICES, INC	
(30) Prioridad	(31) No. Prioridad	32) Fecha	(33) País	(72) Inventor(es) Ryan Van Zanten, Douglas J Harrison		
	12/419,893	07.04.2009	US	(74) Apoderado: DARIO CARDENAS NAVAS		
(54) Título: AGENTES TENSOACTIVOS VISCOELÁSTICOS Y MÉTODOS PARA LA ELABORACIÓN Y USO DE LOS MISMOS						

Resumen:

Un método para el mantenimiento de perforaciones de pozo que comprende la colocación barreno abajo de una composición que comprende un conjunto de agentes tensoactivos comprendiendo un agente tensoactivo catiónico y un agente tensoactivo aniónico, en donde el conjunto de agentes tensoactivos cuando entra en contacto con una solución acuosa forma una composición viscosificada en presencia de menos de aproximadamente 30% en peso de un hidrótrofo.

ESPAÑOL
DESCRIPCIÓN

AGENTES TENSOACTIVOS VISCOELÁSTICOS Y MÉTODOS PARA LA ELABORACIÓN Y USO DE LOS MISMOS

ANTECEDENTES

Campo Técnico

[0001] La presente revelación se relaciona de manera general con fluidos para mantenimiento de perforaciones de pozos. Más específicamente, esta revelación se relaciona con agentes tensoactivos viscoelásticos así como con los métodos para elaborar y utilizar los mismos.

Antecedentes

[0002] Los recursos naturales tales como el gas, petróleo y agua que residen en una zona o formación subterránea se recuperan usualmente al taladrar una perforación de pozo hacia la formación subterránea mientras se hace circular un fluido de perforación en la perforación de pozo. Durante el taladrado de una perforación de pozo se puede hacer circular un fluido de perforación hacia abajo a través del interior de la sarta de perforación, a través de la broca de barrena, y hacia la superficie a través del anillo entre las paredes de la perforación de pozo y la sarta de perforación. La sarta de perforación puede ser una tubería de perforación, una sarta de tubería de revestimiento o cualquier otro conducto apropiado. Entre otras cosas, el fluido de perforación circulante lubrica la broca de barrena, lleva los detritos de la perforación hacia la superficie y balancea la presión de la formación ejercida sobre la perforación de pozo.

Un problema asociado con el taladrado de una perforación de pozo puede ser una pérdida no deseable de grandes cantidades del fluido de perforación hacia la formación subterránea. Se puede hacer referencia a este problema como una "circulación perdida" y las secciones de la formación hacia las cuales se pierde el fluido de perforación son referidas como "zonas de circulación perdida". En adición a los fluidos de perforación, los problemas con la circulación perdida también se pueden encontrar con otros fluidos, por ejemplo fluidos de separación, fluidos de completación (por ejemplo, salmueras) así como fluidos de reacondicionamiento que pueden ser hechos circular en una perforación de pozo. En la presente, fluido de separación se refiere a cualquier líquido que se utiliza para separar físicamente un líquido de propósito especial de otro; un fluido de completación se refiere a un líquido libre de sólidos que se utiliza para facilitar las operaciones finales antes de iniciar la producción; y un fluido de reacondicionamiento se refiere a un fluido de control de pozo, que se utiliza durante el desarrollo de los tratamientos de mantenimiento o correctivos en un pozo que produce hidrocarburos. Una variedad de factores pueden ser responsables por la circulación pérdida. Por ejemplo, la formación subterránea penetrada por la perforación de pozo puede ser altamente permeable o puede contener fracturas o grietas en la misma. Asimismo, la formación puede resquebrajarse bajo la presión hidrostática aplicada por el fluido, permitiendo de esta manera que el fluido se pierda en la formación. Por ejemplo, las fracturas en la formación subterránea pueden ser creadas o incrementadas debido a la presión hidrostática del fluido de

perforación con la pérdida resultante de fluido de perforación en esas fracturas.

[0003] Se ha desarrollado una cantidad de métodos para controlar la circulación perdida. Un método que se utiliza comúnmente para controlar la circulación perdida involucra la colocación de los materiales de circulación perdida en la zona de circulación perdida. Estos materiales de circulación perdida se pueden colocar en la formación, por ejemplo, como píldoras de circulación perdida en un intento por controlar y/o prevenir la circulación perdida. Las píldoras de circulación perdida convencionales pueden tener una variedad de desventajas tales como la gran cantidad de materiales necesarios para alcanzar las propiedades deseadas (por ejemplo, viscosidades, etc.) así como a las dificultades asociadas con la remoción de los materiales componentes de la píldora una vez que el tratamiento ha sido completado. Por consiguiente, puede ser deseable desarrollar composiciones mejoradas para el control de la circulación perdida.

RESUMEN

[0004] Se revela en la presente un método para el mantenimiento de una perforación de pozo que comprende la colocación barreno abajo de una composición que comprende un conjunto de agentes tensoactivos que comprende un agente tensoactivo catiónico y un agente tensoactivo aniónico, en donde el conjunto de agentes tensoactivos cuando se pone en contacto con una solución acuosa forma una composición viscosificada en

presencia de menos de aproximadamente 30% en peso de un hidrótropo.

BREVE DESCRIPCIÓN DE LOS DIBUJOS

[0005] Para una comprensión más cabal de la presente revelación y de las ventajas de la misma, se hace ahora referencia a la siguiente breve descripción, tomada en conjunto con los dibujos anexos y la descripción detallada:

[0006] Las Figuras 1 y 2 son gráficos de la viscosidad como función de la tasa de esfuerzo cortante para las muestras del Ejemplo 1.

[0007] La Figura 3 es un gráfico de la viscosidad como función de porcentaje del agente tensoactivo para las muestras del Ejemplo 2.

[0008] Las Figuras 4 a 5 son gráficos de la viscosidad compleja, módulo de almacenamiento y módulo de pérdida como función de la frecuencia para las muestras del Ejemplo 3.

[0009] Las Figuras 6 a 7 son gráficos de la viscosidad de esfuerzo cortante cero como función de la temperatura para las muestras del Ejemplo 4.

[0010] La Figura 8 es un gráfico de la viscosidad de esfuerzo cortante cero como función de la temperatura para las muestras del Ejemplo 5.

[0011] La Figura 9 es un gráfico de la viscosidad compleja, módulo de almacenamiento y módulo de pérdida como función de la frecuencia para las muestras del Ejemplo 6.

[0012] La Figura 10 es un gráfico de la viscosidad y del esfuerzo cortante como función de la tasa de esfuerzo cortante para las muestras del Ejemplo 6.

[0013] La Figura 11 es un gráfico de la viscosidad como función del porcentaje de agente tensoactivo catiónico para las muestras del Ejemplo 6.

[0014] La Figura 12 es un gráfico de la viscosidad de esfuerzo cortante cero como función del porcentaje en peso de SDBS para las muestras del Ejemplo 7.

[0015] La Figura 13 es un gráfico de la viscosidad y del esfuerzo cortante como función de la tasa de esfuerzo cortante para las muestras del Ejemplo 8.

DESCRIPCIÓN DETALLADA

[0016] Para comenzar, se debe entender que aunque a continuación se provee una implementación ilustrativa de una o más de las configuraciones, los sistemas y/o métodos revelados en la presente se pueden implementar utilizando cualquier cantidad de técnicas, ya sea actualmente conocidas o en existencia. La revelación en ningún sentido está limitada a las implementaciones ilustrativas, dibujos y técnicas ilustradas a continuación, incluyendo los diseños e implementaciones ejemplares que se ilustran y describen en la presente, pero puede ser modificada dentro del alcance de las reivindicaciones anexas junto con todo el alcance de sus equivalentes.

[0017] En la presente se revelan composiciones (por ejemplo, composiciones para mantenimiento de perforaciones de pozos) que

comprenden por lo menos un agente tensoactivo catiónico y por lo menos un agente tensoactivo aniónico. Se dice que dichas composiciones contienen un conjunto de agentes tensoactivos catiónico-aniónico (CASP). En una de las configuraciones, el CASP puede reaccionar con uno o más de los componentes del fluido de mantenimiento de perforaciones de pozos formando una composición viscosificada que se denota de aquí en adelante como CASP-VC. Una CASP-VC del tipo que se describe en la presente puede ser útil en varias operaciones de mantenimiento de perforaciones de pozos. Por ejemplo, la CASP-VC puede ser útil en el tratamiento de perforaciones de pozos que experimentan circulación perdida. Los componentes del CASP y CASP-VC así como también los métodos para elaborar y utilizar los mismos se describirán con mayor detalle más adelante en la presente.

[0018] En una de las configuraciones, el CASP comprende un agente tensoactivo catiónico. Los agentes tensoactivos en general son agentes humectantes que reducen la tensión superficial de un líquido en el cual ellos se disuelven, permitiendo una dispersión más fácil y disminuyendo la tensión interfacial entre dos líquidos. Cada uno de los agentes tensoactivos tiene una cabeza hidrofílica que es atraída por las moléculas de agua y una cola hidrofóbica que repele el agua y se enlaza en sí misma a los materiales hidrofóbicos tal como el aceite y la grasa. En la presente, un agente tensoactivo catiónico tiene un cabezal cargado positivamente y una cola hidrofóbica que comprende una cadena de carbonos. Un agente tensoactivo catiónico adecuado para su uso en esta revelación puede tener una cadena de carbonos que tiene una longitud desde

aproximadamente 8 hasta aproximadamente 24, de manera alternativa desde aproximadamente 8 hasta aproximadamente 18, alternativamente desde aproximadamente 12 hasta aproximadamente 22, de manera alternativa desde aproximadamente 16 hasta aproximadamente 24. Los ejemplos de agentes tensoactivos catiónicos adecuados para su uso en esta revelación incluyen sin limitación sales de amonio cuaternario, sales de amonio cuaternario etoxiladas, óxidos de amina o una combinación de los mismos. En una de las configuraciones, el agente tensoactivo catiónico comprende cloruro de esteariltrimetilamonio, tosilato de cetiltrimetilamonio, cloruro de cetiltrimetilamonio, bromuro de cetiltrimetilamonio, cloruro de miristiltrimetilamonio, bromuro de miristiltrimetilamonio, cloruro de dodeciltrimetilamonio, bromuro de dodeciltrimetilamonio, cloruro de deciltrimetilamonio, bromuro de deciltrimetilamonio, cloruro de octiltrimetilamonio, cloruro de erucil bis-(hidroxi etil) metilamonio, cloruro de eruciltrimetilamonio, o una combinación de los mismos. En una de las configuraciones, el agente tensoactivo catiónico puede estar presente en el CASP en una cantidad desde aproximadamente 0,01 por ciento en peso (% en p.) sobre la base del peso total del CASP hasta aproximadamente 99,99% en peso, de manera alternativa desde aproximadamente 0,1% en peso hasta aproximadamente 99,9% en peso, alternativamente desde aproximadamente 1% en peso hasta aproximadamente 99% en peso.

[0019] En una de las configuraciones, el CASP comprende un agente tensoactivo aniónico. En la presente, un agente tensoactivo aniónico tiene un cabezal cargado negativamente y una

cola hidrofóbica que comprende una cadena de carbonos. Un agente tensoactivo aniónico adecuado para su uso en esta revelación puede tener una cadena de carbonos que tiene una longitud desde aproximadamente 8 hasta aproximadamente 24, de manera alternativa desde aproximadamente 8 hasta aproximadamente 18, alternativamente desde aproximadamente 12 hasta aproximadamente 22, de manera alternativa desde aproximadamente 18 hasta aproximadamente 24. Los ejemplos de agentes tensoactivos aniónicos adecuados para su uso en esta revelación incluyen sin limitación sales álcalis de ácidos, sales álcali de ácidos grasos, sales alcalinas de ácidos, sales sódicas de ácido, sales sódicas de ácido graso, sulfatos de alquilo, etoxilato de alquilo, sulfatos, sulfonatos, jabones o una combinación de los mismos. En una de las configuraciones el agente tensoactivo aniónico comprende oleato de sodio, estearato de sodio, dodecylbencenosulfonato de sodio, miristato de sodio, laurato de sodio, decanoato de sodio, caprilato de sodio, cetil sulfato de sodio, miristil sulfato de sodio, lauril sulfato de sodio, decil sulfato de sodio, octil sulfato de sodio o una combinación de los mismos.

[0020] En una de las configuraciones, el agente tensoactivo aniónico puede estar presente en el CASP en una cantidad desde aproximadamente 0,01 por ciento en peso (% en p.) sobre la base del peso total del CASP hasta aproximadamente 99,99% en peso, de manera alternativa desde aproximadamente 0,1% en peso hasta aproximadamente 99,9% en peso, alternativamente desde aproximadamente 1% en peso hasta aproximadamente 99% en peso.

[0021] En una de las configuraciones, la cantidad de agente tensoactivo catiónico presente en el CASP es mayor que la cantidad de agente tensoactivo aniónico y dicha composición es denominada un CASP rico en agente tensoactivo catiónico. De manera alternativa, la cantidad de agente tensoactivo aniónico presente en el CASP es mayor que la cantidad de agente tensoactivo catiónico y dicha composición se denomina un CASP rico en agente tensoactivo aniónico.

[0022] En una de las configuraciones, la proporción de agente tensoactivo catiónico: agente tensoactivo aniónico (CAR) puede ser seleccionada por una persona con los conocimientos habituales en la técnica con los beneficios de esta revelación para mitigar los efectos no deseados que normalmente se asocian con la puesta en contacto de un conjunto de agentes tensoactivos con otros materiales. Por ejemplo, la CAR se puede seleccionar para reducir o eliminar la separación de las fases cuando el CASP se pone en contacto con una solución acuosa. Además, la CAR se puede seleccionar para reducir o eliminar la precipitación de uno o ambos componentes del CASP cuando se pone en contacto con una solución acuosa. Por ejemplo, la CAR puede ser desde aproximadamente 1:100 hasta aproximadamente 100:1; de manera alternativa desde aproximadamente 90:1 hasta aproximadamente 1:90; alternativamente desde aproximadamente 80:1 hasta aproximadamente 1:80; de manera alternativa desde aproximadamente 70:1 hasta aproximadamente 1:70; alternativamente desde aproximadamente 60:1 hasta aproximadamente 1:60; de manera alternativa desde aproximadamente 1:50 hasta aproximadamente 50:1; alternativamente desde aproximadamente 40:1 hasta

aproximadamente 1:40; de manera alternativa desde aproximadamente 30:1 hasta aproximadamente 1:30; alternativamente desde aproximadamente 20:1 hasta aproximadamente 1:20; de manera alternativa desde aproximadamente 10:1 hasta aproximadamente 1:10; alternativamente desde aproximadamente 1:9 hasta aproximadamente 9:1.

[0023] En una de las configuraciones, un CASP (por ejemplo, un CASP rico en agente tensoactivo catiónico, un CASP rico en agente tensoactivo aniónico) puede ser puesto en contacto con una solución acuosa para formar una CASP-VC. La solución acuosa puede comprender agua dulce o agua salada, por ejemplo, una solución salina acuosa no saturada o una solución salina acuosa saturada tan como salmuera o agua de mar. La solución acuosa y el CASP pueden ser puestos en contacto mediante cualquier manera conocida por una persona con conocimientos en la técnica con los beneficios de la presente revelación. En una de las configuraciones, la solución acuosa comprende una salmuera. La salmuera puede ser cualquier solución adecuada de agua salada saturada o casi saturada. Por ejemplo, la salmuera puede ser cualquier solución salina saturada o casi saturada adecuada que comprende agua y un porcentaje en peso de sal mayor que aproximadamente 90, 95, 99 ó 99,9. Los ejemplos no limitativos de salmuera adecuada por su uso en la presente revelación incluyen cloruro de amonio, cloruro de potasio, cloruro de sodio, bromuro de zinc, cloruro de calcio, bromuro de calcio, bromuro de sodio, formiato de potasio, formiato de sodio, formiato de cesio o una combinación de los mismos. En una de las configuraciones, el CASP puede ser puesto en contacto con la solución acuosa en

una cantidad desde aproximadamente 0,01g hasta aproximadamente 20g de CASP por 80g de solución acuosa, de manera alternativa desde aproximadamente 0,1g hasta aproximadamente 15g de CASP por 80g de solución acuosa, de manera alternativa desde aproximadamente 1g hasta aproximadamente 10g de CASP por 80g de solución acuosa.

[0024] La CASP-VC que se describe en la presente puede exhibir comportamiento viscoelástico. Los materiales viscoelásticos exhiben tanto características viscosas como elásticas cuando son objeto de deformación. En una de las configuraciones, la viscoelasticidad de la CASP-VC puede ser ajustada para satisfacer una necesidad deseada del proceso o del usuario mediante el ajuste de la CAR o la concentración total del agente tensoactivo. La habilidad para ajustar o afinar la viscoelasticidad de la CASP-VC puede permitir a un usuario seleccionar una CASP-VC apropiada en base a las necesidades de una perforación de pozo y sus requerimientos de procesamiento. Por ejemplo, la CAR puede ser optimizada para producir una CASP-VC que tiene una viscosidad adecuada para su uso en zonas de circulación perdida a mayor profundidad o a una temperatura elevada.

[0025] En una de las configuraciones, la CASP-VC puede exhibir una viscosidad en un rango desde aproximadamente 0,001 Pa*s hasta aproximadamente 100.000 Pa*s, de manera alternativa desde aproximadamente 1 Pa*s hasta aproximadamente 100.000 Pa*s, de manera alternativa desde aproximadamente 100 Pa*s hasta aproximadamente 100.000 Pa*s sobre un rango de temperatura desde aproximadamente 10 °C hasta aproximadamente 200 °C, de manera

alternativa desde aproximadamente 25 °C hasta aproximadamente 200 °C, de manera alternativa desde aproximadamente 50 °C hasta aproximadamente 200 °C. La viscosidad es una medida de la resistencia de un fluido que está siendo deformado por el esfuerzo cortante. En otras palabras, es la resistencia de un líquido a fluir. La determinación de las propiedades que se describen en la presente se puede realizar utilizando cualquier metodología adecuada conocida por una persona con conocimientos en la técnica. Por ejemplo, el módulo de almacenamiento, el módulo de pérdida y la viscosidad se pueden determinar por medio de la aplicación de una tasa de esfuerzo cortante constante a la CASP-VC y la lectura del esfuerzo cortante utilizando una geometría de copa en cilindro estacionario de separación angosta tal como se describe en Rheology: Principles, Measurements and Applications, por C.W. Macosko, Wiley-VCH, Nueva York (1994) la cual se incorpora en la presente como referencia en su totalidad.

[0026] En una de las configuraciones, la CASP-VC puede exhibir una viscosidad de esfuerzo cortante cero desde aproximadamente 0,001 Pa*s hasta aproximadamente 100.000 Pa*s, de manera alternativa desde aproximadamente 1 Pa*s hasta aproximadamente 100.000 Pa*s, de manera alternativa desde aproximadamente 100 Pa*s hasta aproximadamente 100.000 Pa*s sobre un rango de temperatura desde aproximadamente 10 °C hasta aproximadamente 200 °C, de manera alternativa desde aproximadamente 25 °C hasta aproximadamente 200 °C, de manera alternativa desde aproximadamente 50 °C hasta aproximadamente 200 °C. La viscosidad de esfuerzo cortante cero se refiere a la viscosidad en el límite de la tasa de esfuerzo cortante menor.

La viscosidad de esfuerzo cortante cero es la viscosidad que un producto finalmente alcanzará cuando está en reposo y tranquilo. La viscosidad de esfuerzo cortante cero se determinó conforme se describe líneas antes en la presente con la excepción de que los datos fueron extrapolados a esfuerzo cortante "cero" y la viscosidad se leyó en dicho esfuerzo cortante.

[0027] En una de las configuraciones, la CASP-VC tiene una viscosidad compleja desde aproximadamente 10 Pa*s hasta aproximadamente 100.000 Pa*s, de manera alternativa desde aproximadamente 100 Pa*s hasta aproximadamente 100.000 Pa*s, de manera alternativa desde aproximadamente 1.000 Pa*s hasta aproximadamente 100.000 Pa*s para un rango de frecuencias desde aproximadamente 0.00001 Hz hasta aproximadamente 1.000 Hz, de manera alternativa desde aproximadamente 0.01 Hz hasta aproximadamente 1.000 Hz, de manera alternativa desde aproximadamente 1 Hz hasta aproximadamente 1.000 Hz. La viscosidad compleja se refiere a la función de la viscosidad dependiente de la frecuencia determinada durante la oscilación armónica forzada de esfuerzo cortante. Está en relación con el módulo de esfuerzo cortante complejo y representa el ángulo entre el esfuerzo cortante viscoso y el esfuerzo cortante. La función de la viscosidad compleja es igual a la diferencia entre la viscosidad dinámica y la viscosidad fuera de fase, o parte imaginaria de la viscosidad compleja:

$$\eta^*(i\omega) = \eta'(\omega) - i\eta''(\omega)$$

en donde

η^* = viscosidad compleja

η' = viscosidad dinámica

η'' = viscosidad fuera de fase

La viscosidad compleja se determinó tal como se describe previamente en la presente con la excepción de que la frecuencia se mantuvo constante.

[0028] El módulo de almacenamiento en los materiales viscoelásticos mide la energía almacenada y representa la porción elástica del material. El módulo de pérdida se relaciona con la energía disipada como calor y representa la porción viscosa relacionada con la cantidad de energía perdida debido al flujo viscoso. En una de las configuraciones, la CASP-VC tiene un módulo de almacenamiento desde aproximadamente 0,001 Pa hasta aproximadamente 1.000 Pa, de manera alternativa desde aproximadamente 0,1 Pa hasta aproximadamente 1.000 Pa, de manera alternativa desde aproximadamente 1 Pa hasta aproximadamente 1.000 Pa, para un rango de frecuencias desde aproximadamente 0,00001 Hz hasta aproximadamente 1.000 Hz, de manera alternativa desde aproximadamente 0,01 Hz hasta aproximadamente 1.000 Hz, de manera alternativa desde aproximadamente 1 Hz hasta aproximadamente 1.000 Hz. En otra de las configuraciones, la CASP-VC tiene un módulo de pérdida desde aproximadamente 0,001 Pa hasta aproximadamente 1.000 Pa, de manera alternativa desde aproximadamente 0,1 Pa hasta aproximadamente 1.000 Pa, de manera alternativa desde aproximadamente 1 Pa hasta aproximadamente 1.000 Pa, para un rango de frecuencias desde aproximadamente 0,00001 Hz hasta aproximadamente 1.000 Hz, de manera alternativa desde aproximadamente 0,01 Hz hasta aproximadamente 1.000 Hz, de manera alternativa desde aproximadamente 1 Hz hasta

aproximadamente 1.000 Hz. El módulo de almacenamiento y el módulo de pérdida se determinaron tal como se describe anteriormente en la presente.

[0029] En una de las configuraciones, la CASP-VC está libre de sólidos. En la presente, libre de sólidos se refiere a la cantidad de sólidos que es igual a o menor que aproximadamente 3% en peso, de manera alternativa igual a o menor que aproximadamente 2% en peso, de manera alternativa igual a o menor que aproximadamente 1% en peso sobre la base del peso total del CASP. Los ejemplos de sólidos incluyen sin limitación partículas, arenas, materiales de la formación o una combinación de los mismos.

[0030] En una de las configuraciones, la CASP-VC puede soportar gradientes de presión alta. La viscoelasticidad elevada generada por medio del CASP permite que el fluido resista gradientes de presión alta.

[0031] En una de las configuraciones, los CASP del tipo que se describen en la presente pueden ser introducidos en un fluido de mantenimiento de perforación de pozo o a una perforación de pozo y llevar a cabo su función proyectada ante la ausencia sustancial de un hidrótropo y/o exceso de sal (por ejemplo, el CASP está libre, sustancialmente libre o no contiene una cantidad material de un hidrótropo y/o exceso de sal). Ambos hidrótropo y el exceso de sal se utilizan para estabilizar el crecimiento micelar. En la presente, un hidrótropo se refiere a un compuesto que solubiliza los compuestos hidrofóbicos en soluciones acuosas. Por lo general, los hidrótropos consisten de una parte hidrofílica y una parte hidrofóbica (como los agentes

tensoactivos) pero la parte hidrofóbica es generalmente muy pequeña para generar la auto-agregación espontánea. Los ejemplos de hidrótropos incluyen, por ejemplo y sin limitación, p-tolueno sulfonato de sodio, xilen sulfonato de sodio, salicilato de sodio, alcoholes alquílicos o una combinación de los mismos. En las configuraciones alternativas, los CASP son introducidos en un fluido de mantenimiento de perforación de pozo o a una perforación de pozo y llevan a cabo su función proyectada ante la presencia de un hidrótropo. En una de las configuraciones, el CASP comprende menos que o igual a aproximadamente 30; 20; 10; 9; 8; 7; 6; 5; 4; 3; 2; 1; 0,1; 0,01 ó 0,001% en peso de uno o más hidrótropos basado en el peso total del CASP. En una de las configuraciones, el CASP comprende una cantidad de sal igual a o menor que la cantidad de saturación. En una de las configuraciones, el CASP comprende una cantidad en exceso de sal igual a o menor que aproximadamente 1,0; 0,1; 0,01; 0,001 ó 0,0001 de porcentaje en peso sobre la cantidad de saturación (es decir, $\leq 1,0$; 0,1; 0,001 ó 0,0001% en peso de exceso de sal).

[0032] Sin desear estar limitados por la teoría, la viscoelasticidad ajustable de la CASP-VC que se revela en la presente se puede atribuir al mecanismo de crecimiento de las micelas en estas composiciones. Un mecanismo para la formación y crecimiento de micelas puede involucrar las interacciones electrostáticas de un agente tensoactivo catiónico y un agente tensoactivo aniónico (por ejemplo, CASP). En este mecanismo, el CASP interactúa para formar un agente tensoactivo zwitteriónico de pseudo cola doble que se auto acopla en una bicapa de agente tensoactivo en forma de hojas lamelares de micelas en forma de

gusano o vesículas. La presencia de sal (por ejemplo, hidrótrofo) puede facilitar el crecimiento de micelas o la creación de vesículas multilamelares debido a la interacción entre los agentes tensoactivos catiónicos y aniónicos, agentes tensoactivos catiónico/ aniónico e hidrótrofo, y agentes tensoactivo catiónico/ aniónico y sal inorgánica.

[0033] Además, la longitud de la cadena del agente tensoactivo catiónico y aniónico puede afectar las micelas resultantes. Cuando los agentes tensoactivos catiónicos y aniónicos son de longitud de cadena similar, hay un amplio espacio de la fase en donde los agregados de bicapa están estables. Sin embargo, cuando existe una diferencia en las longitudes de las cadenas, el espacio de la fase de bicapa será más pequeño, estabilizando de este modo las micelas sobre un rango de concentración más amplio. Para generar la diferencia de longitud de cadena entre los agentes tensoactivos catiónicos y aniónicos, la cantidad de agente tensoactivo catiónico puede ser mucho mayor cuando se compara con el agente tensoactivo aniónico o vice versa. Además, incluso en cantidades equimolares de agentes tensoactivos catiónicos y aniónicos en donde la diferencia de longitud de cadena entre los agentes tensoactivos catiónicos y aniónicos es suficientemente grande, una fase de micelas será estable. Sin embargo, una fase de micelas no estará estable si los agentes tensoactivos catiónicos y aniónicos tienen longitudes de cadenas similares.

[0034] El segundo mecanismo propuesto involucra una transición del CASP de una fase vesicular de baja viscosidad (por ejemplo, cerca de aquella del agua con 1% en volumen de esferas)

a una fase viscoelástica de alta viscosidad por medio de un incremento en la temperatura. En la presente, una fase viscoelástica de alta viscosidad se refiere a una cantidad mayor que aquélla de la fase vesicular a la vez que a la misma concentración general de agente tensoactivo. En este mecanismo, una fase de bicapa vesicular unilamelar se genera mediante la mezcla del agente tensoactivo catiónico y el agente tensoactivo aniónico. En contraste con el primer mecanismo en donde una diferencia en la longitud de cadena de carbonos ayuda en la formación de las micelas, la cantidad del agente tensoactivo catiónico puede ser similar al agente tensoactivo aniónico en la fase vesicular, por ejemplo una CAR 1:1. Conforme se incrementa la temperatura, la tasa de intercambio de agente tensoactivo entre la vesícula y el agua se incrementará. El aumento ocurre de forma más rápida para un agente tensoactivo de cadena corta que para un agente tensoactivo de cadena larga, conduciendo a una menor concentración (por ejemplo, conforme se determina por medio de la resonancia magnética nuclear) de un agente tensoactivo en la bicapa, de este modo posiblemente promoviendo el crecimiento de micelas.

[0035] El tercer mecanismo propuesto involucra el desarrollo de una curvatura espontánea por medio de la mezcla de los agentes tensoactivos y la generación de una fase lamelar con muchos defectos con cualidades similares al gel como visualizado utilizando técnicas de formación de imágenes. En este mecanismo, se forma un gel catiónico/ aniónico por medio de una fase de defecto lamelar. A una elevada concentración de agente tensoactivo de doble cola (por ejemplo, bajos contenidos de agua,

igual a o mayor que aproximadamente 50% en peso de agente tensoactivo), a menudo se forma una fase de hoja lamelar (L_{α}). Conforme se incrementa el contenido de agua a una cantidad desde aproximadamente 60% en peso hasta aproximadamente 80% en peso, la separación de bicapa generalmente se hincha hasta una cierta separación que expelle cualquier exceso de agua que se añada. La separación puede ser determinada mediante el uso de cualquier técnica adecuada tal como una técnica de dispersión de rayos x de ángulo pequeño. En el caso de las bicapas catiónicas/ aniónicas (agentes tensoactivos de "seudo" cola doble), existe una curvatura espontánea que conduce a emplazamientos con defectos de vesícula mulilamelar (MLV) que existen con la fase de hoja lamelar conforme se agrega más agua. La formación de los emplazamientos con defectos MLV dentro de la fase de hoja lamelar conduce además a hojas lamelares entrecruzadas con los emplazamientos con defectos MLV, generando de este modo un gel altamente viscoelástico con una viscosidad mayor que 1.000 centipoise.

[0036] En una de las configuraciones, una CASP-VC del tipo que se describe en la presente se puede utilizar para controlar la circulación perdida en una formación subterránea. Se deberá entender que "formación subterránea" abarca tanto las áreas por debajo de la tierra expuesta así como las áreas por debajo de la tierra cubierta por agua tal como el océano o agua dulce. En el proceso de perforación de un pozo, a menudo se enfrentan zonas con bajas gradientes de fractura, zonas fracturadas, etc. y la pérdida de todo el fluido de perforación a la formación se vuelve un problema. Las pérdidas del fluido de perforación pueden

dificultar el progreso de la perforación del pozo, agregar costos a la perforación del pozo, impedir la perforación del pozo a la profundidad objetivo y/o ocasionar la pérdida total de la sección perforada a pozo abierto. En dicha configuración, el CASP se puede introducir en una sarta de perforación, ser bombeado hacia abajo a una zona de circulación perdida tales como vacíos, zonas vugulares y fracturas normales o inducidas mientras se perfora. El CASP puede luego entrar en contacto con un fluido en la zona de circulación perdida y formar una CASP-VC que sustancialmente sella la zona de circulación perdida con poca o ninguna interrupción de las operaciones de perforación y reducción en la pérdida del fluido de perforación a la zona de circulación perdida.

[0037] En otra de las configuraciones, se puede bombear un CASP hacia abajo hacia una zona de circulación perdida, se puede introducir un fluido de mantenimiento de perforación de pozo desde la perforación de pozo hacia la zona de circulación perdida en donde el CASP entra en contacto con el fluido de mantenimiento de la perforación de pozo y forma una CASP-VC que sustancialmente sella la zona de circulación perdida. Tal como se utiliza en la presente, un "fluido de mantenimiento" se refiere a un fluido que se utiliza para perforar, completar, reacondicionar, fracturar, reparar o de cualquier manera preparar una perforación de pozo para la recuperación de materiales que permanecen en una formación subterránea penetrada por la formación de pozo. Los ejemplos de fluidos de mantenimiento incluyen, pero no están limitados a, papillas de cemento, fluidos de perforación o lodos, fluidos de separación, fluidos de fracturamiento, fluidos de

empaque de grava o fluidos de completación, todos los cuales son conocidos en la técnica. Los métodos para la introducción de composiciones en una perforación de pozo para sellar las zonas subterráneas se describen en las patentes estadounidenses Nos. 5.913.364, 6.167.967 y 6.258.757, cada una de las cuales se incorpora en la presente como referencia en su totalidad.

[0038] La CASP-VC puede formar una masa intacta que no fluye de elevada viscosidad dentro de la zona de circulación perdida que taponar la zona e inhibe la pérdida del fluido posteriormente bombeado. En una de las configuraciones, la CAR es ajustada a fin de producir una CASP-VC de elevada viscosidad que taponar una zona a temperaturas elevadas, tales como aquéllas que se encuentran a mayores profundidades dentro de una perforación de pozo.

[0039] En otra de las configuraciones, las CASP-VC forman píldoras de circulación perdida para su uso en salmueras de completación. Las CASP-VC que se divulgan en la presente pueden formar píldoras posteriores a la perforación libre de sólidos y/o píldoras de pérdida de fluido posteriores al empaque de grava que son útiles en el mantenimiento de una perforación de pozo durante las operaciones de completación.

[0040] En una de las configuraciones, se utiliza una CASP-VC para el mantenimiento de una perforación de pozo. Posteriormente, se puede romper la viscoelasticidad de una CASP-VC (es decir, la viscosidad de la CASP-VC puede ser reducida) poniendo en contacto la CASP-VC con una cantidad efectiva de un rompedor de viscosidad tal como hidrocarburo o un rompedor interno. La habilidad para romper la viscosidad de una CASP-VC

puede ser útil por ejemplo para la limpieza de una perforación de pozo. Los ejemplos de rompedores internos adecuados para su uso en la presente revelación incluyen sin limitación rompedor SP, rompedor VICON NF, rompedor OXOL II, rompedor GBW-40 y rompedor HT, los cuales están comercialmente disponibles de Halliburton. Los ejemplos de hidrocarburos adecuados para su uso en la presente revelación incluyen, por ejemplo, y sin limitación, petróleo crudo, gas natural e hidratos de gas. Las cantidades efectivas de hidrocarburos y rompedores internos pueden ser determinadas por una persona con conocimientos en la técnica con la ayuda de la presente revelación.

EJEMPLOS

[0041] Habiéndose descrito de manera general la revelación, los siguientes ejemplos se proporcionan como configuraciones particulares de la divulgación y para demostrar la práctica y ventajas de la misma. Se debe entender que los ejemplos se proporcionan de manera ilustrativa y no tienen la intención de limitar la memoria descriptiva o las reivindicaciones de manera alguna.

EJEMPLO 1

[0042] Se investigó el comportamiento reológico de las CASP-VC del tipo que se describen en la presente. Se prepararon ocho muestras, designadas Muestras 1 a 8. Las Muestras 1 a 4 se prepararon utilizando oleato de sodio (NaOle), que está comercialmente disponible de TCI America como el agente tensoactivo aniónico y cloruro de octil trimetil amonio (C_8TAC),

que está comercialmente disponible de TCI America como el agente tensoactivo catiónico. Las Muestras 1 a 4 se prepararon utilizando una relación $C_8TAC:NaO$ de 3:7, 4:6, 2:8 y 1:9, respectivamente. Las muestras fueron luego disueltas en agua desionizada ($DI\ H_2O$) en una cantidad suficiente para formar una solución al 3% en peso. Puesto que las Muestras 1 a 4 tenían una mayor relación aniónica a catiónica, las CASP-VC resultantes fueron ricas en agentes tensoactivos aniónicos.

[0043] Las Muestras 5 a 8 se prepararon utilizando octoato de sodio (NaCap) que está comercialmente disponible de TCI America como el agente tensoactivo aniónico y cloruro de estearil trimeil amonio ($C_{18}TAC$), que está comercialmente disponible de TCI America como el agente tensoactivo catiónico. Las Muestras 5 a 8 se prepararon utilizando una relación de $C_{18}TAC:NaCap$ de 7:3, 6:4, 8:2 y 9:1, respectivamente. Las muestras luego fueron disueltas en agua desionizada ($DI\ H_2O$) en una cantidad suficiente para formar una solución al 3% en peso. Puesto que las Muestras 1 a 5 tenían una mayor relación catiónica a aniónica, las CASP-VC resultantes fueron ricas en agentes tensoactivos catiónicos. La Tabla 1 tabula los tipos de agente tensoactivo catiónico y aniónico y las relaciones para cada muestra.

TABLA 1

Muestra	Agente tensoactivo catiónico	Agente tensoactivo aniónico	CAR	% en Peso
1	C_8TAC	NaO	3:7	3
2	C_8TAC	NaO	4:6	3
3	C_8TAC	NaO	2:8	3

4	C ₈ TAC	NaO	1:9	3
5	C ₁₈ TAC	NaCap	7:3	3
6	C ₁₈ TAC	NaCap	6:4	3
7	C ₁₈ TAC	NaCap	8:2	3
8	C ₁₈ TAC	NaCap	9:1	3

[0044] Las mediciones reológicas se llevaron a cabo utilizando un MCR 501 con un cilindro concéntrico de 27 mm, que es un reómetro comercialmente disponible de Anton Paar a una temperatura de 25 °C.

[0045] La Figura 1 es un gráfico de la viscosidad como una función de la tasa de esfuerzo cortante para las Muestras 1 a 4. La Figura 2 es un gráfico de la viscosidad como una función de la tasa de esfuerzo cortante para las Muestras 5 a 8. Las viscosidades de esfuerzo cortante cero de las Muestras 1 a 4 se pueden determinar extrapolando la viscosidad nuevamente al punto de esfuerzo cortante teórico cero y fueron 1200, 93, 33 y 0,006 Pa*s, respectivamente. Las viscosidades de esfuerzo cortante cero de las Muestras 5 a 8 se pueden determinar extrapolando la viscosidad nuevamente al punto de esfuerzo cortante teórico cero y fueron 542, 196, 0,4 y 0,001 Pa*s, respectivamente. Los resultados demostraron que la viscosidad de esfuerzo cortante cero es altamente dependiente de la relación catiónica/ aniónica y puede ser ajustada variando la misma. Asimismo, se puede generar un incremento de un millón de veces en la viscosidad mediante la adición de agente tensoactivo con carga opuesta independiente de sal o concentración de hidrógeno.

EJEMPLO 2

[0046] Se investigó la viscosidad de esfuerzo cortante cero de una CASP-VC rica en agentes tensoactivos catiónicos y rica en agentes tensoactivos aniónicos. Las Muestras 1 a 8, que se describen en el Ejemplo 1, se utilizaron nuevamente en este ejemplo. Además, cinco muestras más, designadas como Muestras 9 a 13, fueron preparadas tal como se describe en el Ejemplo 1. La Tabla 2 tabula las CARS y tipos de agentes tensoactivos catiónicos y aniónicos para las Muestras 9 a 13.

TABLA 2

Muestra	Agente tensoactivo catiónico	Agente tensoactivo aniónico	CAR	% en Peso
9	C ₈ TAC	NaO	5:5	3
10	C ₈ TAC	NaO	6:4	3
11	C ₈ TAC	NaO	0:10	3
12	C ₁₈ TAC	NaCap	5:5	3
13	C ₁₈ TAC	NaCap	4:6	3

[0047] La Figura 3 es un gráfico de la viscosidad como una función de la fracción en peso del componente menor para las Muestras 1 a 13. Para las Muestras 1 a 4 y 9 a 11, el componente menor fue el agente tensoactivo catiónico. Para las Muestras 5 a 8 y 12 a 13, el componente menor fue el agente tensoactivo aniónico. Los resultados demostraron que la CAR que generó la viscosidad máxima fue aproximadamente 70:30 y 30:70, tal como se muestra por los picos para las CASP-VC ricas en agentes tensoactivos aniónicos y ricas en agentes tensoactivos catiónicos en la Figura 3. Además, tanto las CASP-VC ricas en agentes tensoactivos catiónicos y ricas en agentes tensoactivos aniónicos

exhibieron incrementos pronunciados en la viscoelasticidad hasta 300.000 veces cuando se compara con los componentes individuales de los agentes tensoactivos. Este incremento en la viscoelasticidad también se observó de forma visual colocando las Muestras 1 y 5 en frascos separados e invirtiendo ambos frascos. En ambos frascos, las muestras de gel viscoelástico permanecieron suspendidas durante 10 segundos.

EJEMPLO 3

[0048] Se investigaron las propiedades dinámicas de las CASP-VC del tipo que se describen en la presente. De manera específica, se determinó la viscosidad compleja, módulo de almacenamiento y módulo de pérdida como una función de la frecuencia para las Muestras 1 a 3 y 5 a 7 del Ejemplo 1. Las Figuras 4 y 5 son gráficos de la viscosidad compleja, módulo de almacenamiento y módulo de pérdida como una función de la frecuencia para las Muestras 1 a 3 y 5 a 7, respectivamente. Los resultados demostraron que estos fluidos presentaron tanto un módulo de pérdida como un módulo de almacenamiento significativo, demostrando por consiguiente su viscoelasticidad.

EJEMPLO 4

[0049] Se investigó el efecto de la temperatura en la viscosidad de las CASP-VC. Las viscosidades de esfuerzo cortante cero de las Muestras 1 y 5 del Ejemplo 1 se probaron en un rango de temperatura de 70 °F a 190 °F. Los resultados para ambas CASP-VC rica en agentes tensoactivos aniónicos (Muestra 1) y una

CASP-VC rica en agentes tensoactivos catiónicos (Muestra 5) se muestran en las Figuras 6 y 7, respectivamente.

[0050] Los resultados demuestran que hubo un decrecimiento en la viscosidad en varios órdenes de magnitud en cada muestra conforme aumentó la temperatura. Sin embargo, la viscosidad para las CASP-VC ricas en agentes tensoactivos catiónicos y ricas en agentes tensoactivos aniónicos fue incluso aproximadamente 10 y 30 veces mayor respectivamente que aquélla del agua (viscosidad del agua a 194 °F es aproximadamente 0,000315 Pa*s). De este modo, incluso a elevada temperatura, hay un incremento apreciable de la viscosidad cuando se compara con el agua.

[0051] Sin desear estar limitados por la teoría, la disminución observada en la viscosidad conforme la temperatura aumentó puede ser el resultado de la solubilidad de los CASP en el incremento del agua (es decir, aumentó la concentración crítica de micelas). La solubilidad incrementada del CASP puede conducir a una cinética más rápida y micelas más cortas y más pequeñas. La presencia de estas micelas más cortas y más pequeñas puede contribuir al decrecimiento observado en la viscosidad.

[0052] Una persona con conocimientos en la técnica y con los beneficios de la presente revelación podrá ajustar los CASP, de tal manera que la viscosidad de la CASP-VC tiene una respuesta reducida a la temperatura. Por ejemplo, una técnica consiste en utilizar agentes tensoactivos de cadena de alquilo tales como agentes tensoactivos catiónicos C_{22} y agentes tensoactivos zwitteriónicos C_{22} . Además, se pueden explotar los cambios en el comportamiento en la fase de agentes tensoactivos con la

temperatura (es decir, transición de vesícula a micelas en forma de gusano). El enfoque final consiste en incrementar la concentración de los agentes tensoactivos en el CASP. Mediante el incremento de la concentración, se puede alcanzar el entrelazamiento o concentración cruzada incluso con micelas de longitud mucho más cortas. En otras palabras, la respuesta viscoelástica ocurre cuando hay un incremento en la concentración, longitud o ambas.

[0053] También se investigó la estabilidad de la CASP-VC. Se preparó una solución de agente tensoactivo aniónico que comprende la Muestra 1 y se observó durante un periodo de tiempo de 7 días a una temperatura de 25 °C. Se observó que el agente tensoactivo aniónico se degrada con el tiempo, conforme la solución de componente único se volvió algo turbia en unas pocas semanas. Sin desear estar limitado por la teoría, el enlace doble en la cadena de alquil oleato puede ser oxidado, causando que el agente tensoactivo se vuelva igual que el jabón de sodio y ácido esteárico. El jabón de sodio y ácido esteárico tiene una solubilidad mucho menor en agua y puede no formar micelas en forma de gusanos tan fácilmente como jabón de sodio y ácido oleico.

[0054] Igualmente se preparó una CASP-VC rica en agentes tensoactivos aniónicos y se observó durante un periodo de tiempo de 7 días a una temperatura de 25 °C. La CASP-VC rica en agentes tensoactivos aniónicos también se volvió turbia, mostró viscosidad reducida y comenzó a separar las fases después de unas cuantas semanas. Este comportamiento puede ser explotado ya que puede ser útil para la degradación del material viscoelástico sin

la utilización de ningún componente agregado. A temperaturas elevadas, puede ocurrir dicha descomposición de la viscosidad en el orden de días, lo cual puede ser útil para una píldora de circulación perdida, puesto que permitirá que el material de circulación perdida se disuelva y permitirá que comience la producción. Se observó que una CASP-VC rica en agentes tensoactivos catiónicos permanece estable por un periodo de tiempo mayor de 30 días a una temperatura de 25 °C.

EJEMPLO 5

[0055] Se investigó la estabilidad de temperatura de una CASP-VC rica en agentes tensoactivos catiónicos y se comparó con un agente tensoactivo solamente catiónico. La CASP-VC rica en agentes tensoactivos catiónicos, designada Muestra 14, fue tosilato de cetil trimetil amonio/ dodecilbenceno sulfonato de sodio (CTAT/SDBS) de 97:3 que se preparó como una solución al 3% en peso. El agente tensoactivo solamente catiónico, designado Muestra 15, fue CTAT que se preparó como una solución al 3% en peso. Las viscosidades de esfuerzo cortante cero para las Muestras 14 y 15 se midieron para un rango de temperatura desde 75 °F hasta 190 °F. Los resultados se muestran en la Figura 8.

[0056] Haciendo referencia a la Figura 8, la viscosidad de esfuerzo cortante cero disminuyó conforme aumentó la temperatura para ambas muestras. Sin embargo, la caída en la viscosidad de esfuerzo cortante cero a temperatura elevada (aproximadamente por encima de los 150 °F) para la Muestra 14 fue menor que la Muestra 15 debido a la adición del agente tensoactivo aniónico. Sin

desea estar limitados por la teoría, la menor caída en la viscosidad de esfuerzo cortante cero se puede deber al mayor enlace de un agente tensoactivo versus un hidrótrofo simple o debido a la menor solubilidad de los agentes tensoactivos versus los hidrótrofos. De este modo, dichos CAP ofrecen mayor estabilidad a la temperatura que los agentes tensoactivos tradicionales.

EJEMPLO 6

[0057] Se investigó la tolerancia de las CASP-VC ricas en agentes tensoactivos catiónicos y ricas en agentes tensoactivos aniónicos a la sal. Se seleccionó la Muestra 5 del Ejemplo 1 para la CASP-VC rica en agentes tensoactivos catiónicos. Se preparó una muestra comparativa de CASP-VC rica en agentes tensoactivos catiónicos en salmuera, designada Muestra 16, a partir de C18TAC/NaCap que tiene una relación 7:3 la cual se preparó como una solución al 3% en peso (similar a la Muestra 5) y 0,15M de salmuera de bromuro de sodio (NaBr). La viscosidad compleja, módulo de almacenamiento, módulo de pérdida y viscosidad de esfuerzo cortante cero de las Muestras 5 y 16 se midieron y los resultados se muestran en las Figuras 9 y 10. Los resultados demostraron que la CASP-VC era capaz de mantener su viscosidad con la adición de sal. Sin desear estar limitado por la teoría, esto sugiere que las interacciones electrostáticas no son la fuerza dominante en la formación de la viscoelasticidad.

[0058] Se seleccionó la Muestra 1 para el CASP rico en agentes tensoactivos aniónicos. Se preparó una muestra

comparativa de CASP-VC rica en agentes tensoactivos aniónicos en salmuera, designada Muestra 17 a partir de una relación de $\text{NaO}:\text{C}_8\text{TAC}$ de 7:3 y 0,15M de salmuera de bromuro de sodio (NaBr). Se midió la viscosidad compleja, módulo de almacenamiento, módulo de pérdida y viscosidad de esfuerzo cortante cero de las Muestras 1 y 17. Los resultados se muestran en la Figura 11. Los resultados demostraron que la CASP-VC rica en agentes tensoactivos aniónicos experimentó una gran caída en sus propiedades viscoelásticas sin la adición de la sal, lo que sugiere que las interacciones electrostáticas están formando la viscosidad de esfuerzo cortante cero. Esta viscosidad puede ser recuperada variando la CAR para cambiar la carga total en la micela.

EJEMPLO 7

[0059] Se investigó la viscosidad de esfuerzo cortante cero de la CASP-VC del tipo que se describe en la presente. Se prepararon cuatro muestras, designadas Muestras 18 a 21. La Muestra 18 fue una solución acuosa al 3% en peso de tosilato de cetil trimetil amonio (CTAT). Las Muestras 19 a 21 fueron CTAT/dodecilbenceno sulfonato de sodio (SDBS) con una CAR de 99:1, 97:3 y 95:5 respectivamente y se preparó como una solución acuosa al 3% en peso. Las viscosidades de esfuerzo cortante cero de las Muestras 18 a 21 se determinaron que eran 126, 205, 255 y 207 $\text{Pa}\cdot\text{s}$ respectivamente y se muestran en la Figura 12. El CTAT forma soluciones micelares en forma de gusanos viscoelásticos con elevadas viscosidades de esfuerzo cortante cero. Mediante la

adición de una pequeña cantidad de SDBS en las Muestras 19 a 21, las soluciones se volvieron altamente viscosas con viscosidades de esfuerzo cortante cero incrementadas en comparación con la Muestra 18. Además, la viscosidad de esfuerzo cortante cero de la Muestra 20 fue más del doble (256.000 centiPoise) cuando se comparó con la Muestra 18 (126.000 centiPoise).

[0060] Se preparó otra muestra, designada Muestra 22. La Muestra 22 fue CTAT/ octil sulfato de sodio (SOS) con una CAR de 94:6 y se preparó como una solución acuosa al 3% en peso. La viscosidad de esfuerzo cortante cero de la Muestra 22 se determinó que era 470.000 centiPoise, que fue más del triple cuando se comparó con la Muestra 18. Estos resultados demostraron la habilidad del CASP para incrementar la viscosidad de las soluciones.

EJEMPLO 8

[0061] Se investigó el efecto de utilizar agentes tensoactivos que contienen cadenas largas de alquilo en las propiedades de la CASP-VC. Se investigaron tres muestras, designadas Muestras 23 a 25. Las Muestras 23 y 24 que fueron el CASP rico en agentes tensoactivos catiónicos, se prepararon a partir de cloruro de erucil bis-(hidroxi etil) metilamonio (EHAC)/ sal sódica del ácido n-caprílico (NaCap) con una CAR de 8:2 y 9:1 respectivamente como una solución acuosa al 3% en peso. La Muestra 25, que fue el CASP rico en agentes tensoactivos catiónicos, se preparó a partir de cloruro de erucil bis-(hidroxi etil)metilamonio/ sal sódica de ácido decanoico con una relación

catiónica: aniónica de 9:1 como una solución acuosa al 3% en peso. Se determinaron las viscosidades de esfuerzo cortante cero para las Muestras 23 y 24 y los resultados se muestran en la Figura 13. Las viscosidades de las Muestras 23 y 24 estuvieron en un rango desde 200.000 hasta 800.000 centiPoise mientras que la viscosidad de la Muestra 25 fue aproximadamente 70.000 centiPoise. Los resultados demostraron que los agentes tensoactivos de cadena larga que generan viscosidad apreciable ($>10 \text{ Pa}\cdot\text{s}$) a temperaturas elevadas también forman estos agregados viscoelásticos catiónicos/aniónicos.

[0062] A continuación, se investigó la habilidad del hidrocarburo para reducir la viscosidad de la CASP-VC. Una porción de las Muestras 23 a 25 se colocó en frascos individuales y se introdujo un fluido hidrocarburo en cada frasco. El fluido hidrocarburo que se utilizó para la prueba fue diesel. Luego se agitó cada frasco para mezclar la CASP-VC con el diesel. Cada frasco fue luego invertida y se observó visualmente. Ante la ausencia del hidrocarburo, los CASP forman masas viscosas que permanecieron suspendidas durante segundos, ver Ejemplo 2. Sin embargo, con la adición de un hidrocarburo, luego de la inversión de los frascos la masa no estuvo completamente suspendida y se observó que el fluido fluyó por ambos CASP rico en agentes tensoactivos catiónicos y rico en agentes tensoactivos aniónicos.

[0063] Mientras que se han mostrado y descrito las configuraciones de la revelación, una persona experta en la técnica puede realizar modificaciones a la misma sin apartarse del alcance de la invención. Las configuraciones que se describen en la presente son solamente ejemplares y no tienen la

intención de ser limitativas. Muchas variaciones y modificaciones de la divulgación que se revela en la presente son posibles y están dentro del alcance de la divulgación. Cuando rangos numéricos o limitaciones son señalados de manera expresa, dichos rangos de expresión o limitaciones deberán ser entendidos que incluyen rangos iterativos o limitaciones de similar magnitud que caen dentro de los rangos o limitaciones señalados de manera expresa (por ejemplo, desde aproximadamente 1 hasta aproximadamente 10 incluye, 2, 3, 4, etc.; mayor que 0,10 incluye 0,11; 0,12; 0,13; etc.). Por ejemplo, cuando se divulga un rango numérico con un límite inferior R_L , y un límite superior R_U , cualquier número que cae dentro del rango es revelado de manera específica. En particular, los siguientes números dentro del rango son divulgados de manera específica: $R=R_L+k*(R_U-R_L)$, en donde k es una variable en un rango desde 1 por ciento hasta 100 por ciento con 1 por ciento de incremento, es decir, k es 1 por ciento, 2 por ciento, 3 por ciento, 4 por ciento, 5 por ciento, ..., 50 por ciento, 51 por ciento, 52 por ciento, ..., 95 por ciento, 96 por ciento, 97 por ciento, 98 por ciento, 99 por ciento o 100 por ciento. Además, cualquier rango numérico definido por dos números R tal como se define líneas antes también es igualmente divulgado de manera específica. El uso del término "de manera opcional" con relación a cualquier elemento de una reivindicación tiene la intención de significar que se requiere el elemento objeto, o de manera alternativa, no es requerido. Ambas alternativas están proyectadas para estar dentro del alcance de la reivindicación. El empleo de términos más amplios tales como comprende, incluye, tiene, etc., deberán

ser entendidos que proveen soporte para los términos más limitados tales como consiste de, consiste esencialmente de, compuesto sustancialmente de, etc.

[0064] Por consiguiente, el alcance de la protección no está limitado por la descripción planteada líneas antes sino solamente está limitada por las reivindicaciones que siguen, dicho alcance incluyendo todos los equivalentes de la materia de las reivindicaciones. Todas y cada una de las reivindicaciones se incorporan en la memoria descriptiva como una configuración de la presente revelación. De este modo, las reivindicaciones son una descripción adicional y son una adición a las configuraciones de la presente divulgación. La discusión de una referencia no es una aceptación de que constituye arte previo a la presente divulgación, de manera especial cualquier referencia que puede tener una fecha de publicación posterior a la fecha de prioridad de esta solicitud. Las revelaciones de todas las patentes, solicitudes de patentes y publicaciones que se citan en la presente, son por lo tanto incorporadas como referencia, en la medida en que las mismas proveen detalles ejemplares, de procedimiento u otros detalles suplementarios a aquéllos planteados en la presente.

ESPAÑOL
REIVINDICACIONES

REIVINDICACIONES

Lo que se reivindica es:

1. Un fluido para mantenimiento de perforaciones de pozos comprendiendo un conjunto de agentes tensoactivos que comprende un agente tensoactivo catiónico y agente tensoactivo aniónico; caracterizado porque el conjunto de agentes tensoactivos cuando es puesto en contacto con una solución acuosa forma una composición viscosificada en presencia de menos de aproximadamente 30% en peso de un hidrótopo.

2. Un fluido de acuerdo con la Reivindicación 1, caracterizado porque el agente tensoactivo catiónico tiene una longitud de cadena de carbonos desde aproximadamente 8 hasta aproximadamente 24.

3. Un fluido de acuerdo con la Reivindicación 1 ó la 2, caracterizado porque el agente tensoactivo catiónico comprende sales de amonio cuaternario, sales de amonio cuaternario etoxiladas, óxidos de amina o una combinación de los mismos.

4. Un fluido de acuerdo con la Reivindicación 1, 2 ó la 3, caracterizado porque el agente tensoactivo catiónico comprende cloruro de esteariltrimetilamonio, tosilato de cetiltrimetilamonio, cloruro de octiltrimetilamonio, cloruro de erucil bis-(hidroxí etil)metilamonio, cloruro de eruciltrimetilamonio, cloruro de cetiltrimetilamonio, bromuro de cetiltrimetilamonio, cloruro de miristiltrimetilamonio, bromuro de miristiltrimetilamonio, cloruro de dodeciltrimetilamonio, bromuro de dodeciltrimetilamonio, cloruro de deciltrimetilamonio, bromuro de deciltrimetilamonio, o una combinación de los mismos.

5. Un fluido de acuerdo con cualquiera de las reivindicaciones precedentes, caracterizado porque el agente tensoactivo catiónico está presente en el conjunto de agentes tensoactivos en una cantidad desde aproximadamente 0,01% en peso hasta aproximadamente 99,99% en peso basado en el peso total del conjunto de agentes tensoactivos.

6. Un fluido de acuerdo con cualquiera de las reivindicaciones precedentes, caracterizado porque el agente tensoactivo aniónico tiene una longitud de cadena de carbonos desde aproximadamente 8 hasta aproximadamente 24.

7. Un fluido de acuerdo con cualquiera de las reivindicaciones precedentes, caracterizado porque el agente tensoactivo aniónico comprende sales álcalis de ácidos, sales álcalis de ácidos grasos, sales alcalinas de ácidos, sales sódicas de ácido, sales sódicas de ácido graso, sulfatos de alquilo, etoxilato de alquilo, sulfatos, sulfonatos, jabones o una combinación de los mismos.

8. Un fluido de acuerdo con cualquiera de las reivindicaciones precedentes, caracterizado porque el agente tensoactivo aniónico comprende oleato de sodio, dodecilbencenosulfonato de sodio, decanoato de sodio, octil sulfato de sodio, caprilato de sodio, estearato de sodio, miristato de sodio, laurato de sodio, cetil sulfato de sodio, miristil sulfato de sodio, lauril sulfato de sodio, decil sulfato de sodio, o una combinación de los mismos.

9. Un fluido de acuerdo con cualquiera de las reivindicaciones precedentes, caracterizado porque el agente tensoactivo aniónico está presente en el conjunto de agentes

tensoactivos en una cantidad desde aproximadamente 0,01% en peso hasta aproximadamente 99,99% en peso en base al peso total del conjunto de agentes tensoactivos.

10. Un fluido de acuerdo con cualquiera de las reivindicaciones precedentes, caracterizado porque el conjunto de agentes tensoactivos tiene una relación de agente tensoactivo catiónico: agente tensoactivo aniónico desde 1:100 hasta 100:1.

11. Un fluido de acuerdo con cualquiera de las reivindicaciones precedentes, caracterizado porque el conjunto de agentes tensoactivos es puesto en contacto con la solución acuosa en una cantidad desde aproximadamente 0,01 gramos hasta aproximadamente 20 gramos por 80 gramos de la solución acuosa.

12. Un fluido de acuerdo con cualquiera de las reivindicaciones precedentes, caracterizado porque la solución acuosa comprende agua, salmuera, un fluido para mantenimiento de perforaciones de pozos o una combinación de los mismos.

13. Un fluido de acuerdo con la Reivindicación 12, caracterizado porque la salmuera comprende cloruro de amonio, cloruro de potasio, cloruro de sodio, bromuro de zinc, cloruro de calcio, bromuro de calcio, bromuro de sodio, formiato de potasio, formiato de sodio, formiato de cesio o una combinación de los mismos.

14. Un fluido de acuerdo con la Reivindicación 12 o la 13, caracterizado porque el fluido para mantenimiento de perforaciones de pozos comprende papillas de cemento, fluidos de perforación, fluidos de separación, fluidos de fracturamiento, fluidos de empaque de grava, fluidos de re-acondicionamiento, fluidos de completación o una combinación de los mismos.

15. Un fluido de acuerdo con cualquiera de las Reivindicaciones precedentes, caracterizado porque la composición viscosificada está libre de sólidos.

16. Un fluido de acuerdo con cualquiera de las Reivindicaciones precedentes, caracterizado porque la composición viscosificada tiene una viscosidad desde aproximadamente 0,001 Pa*s hasta aproximadamente 100.000 Pa*s a una temperatura desde aproximadamente 10 °C hasta aproximadamente 200 °C.

17. Un fluido de acuerdo con cualquiera de las Reivindicaciones precedentes, caracterizado porque la composición viscosificada tiene una viscosidad de esfuerzo cortante cero desde aproximadamente 0,001 Pa*s hasta aproximadamente 100.000 Pa*s a una temperatura desde aproximadamente 10 °C hasta aproximadamente 200 °C.

18. Un fluido de acuerdo con cualquiera de las Reivindicaciones precedentes, caracterizado porque la composición viscosificada tiene una viscosidad compleja desde aproximadamente 10 Pa*s hasta aproximadamente 10.000 Pa*s a un rango de frecuencia desde aproximadamente 0,00001 Hz hasta aproximadamente 1000 Hz.

19. Un fluido de acuerdo con cualquiera de las Reivindicaciones precedentes, caracterizado porque la composición viscosificada tiene un módulo de almacenamiento desde aproximadamente 0,001 Pa hasta aproximadamente 1.000 Pa a un rango de frecuencia desde aproximadamente 0,00001 Hz hasta aproximadamente 1000 Hz.

20. Un fluido de acuerdo con cualquiera de las Reivindicaciones precedentes, caracterizado porque la composición

viscosificada tiene un módulo de pérdida desde aproximadamente 0,001 Pa hasta aproximadamente 1.000 Pa a un rango de frecuencia desde aproximadamente 0,00001 Hz hasta aproximadamente 1000 Hz.

21. Un fluido de acuerdo con cualquiera de las Reivindicaciones precedentes, caracterizado porque la composición viscosificada comprende una píldora posterior a la perforación libre de sólidos o una píldora de pérdida de fluido de empaque de grava.

22. Un método para el mantenimiento de perforaciones de pozos que comprende: la colocación de un fluido de acuerdo con cualquier reivindicación precedente en la perforación de pozo.

23. Un método de acuerdo con la Reivindicación 22, que comprende además poner en contacto la composición viscosificada con un rompedor de la viscosidad.

24. Un método de acuerdo con la Reivindicación 23, caracterizado porque el rompedor de la viscosidad comprende un fluido hidrocarburo, un rompedor interno o una combinación de los mismos.

**AGENTES TENSOACTIVOS VISCOELÁSTICOS Y MÉTODOS PARA LA
ELABORACIÓN Y USO DE LOS MISMOS**

RESUMEN DE LO REVELADO

Un método para el mantenimiento de perforaciones de pozo que comprende la colocación barreno abajo de una composición que comprende un conjunto de agentes tensoactivos comprendiendo un agente tensoactivo catiónico y un agente tensoactivo aniónico, en donde el conjunto de agentes tensoactivos cuando entra en contacto con una solución acuosa forma una composición viscosificada en presencia de menos de aproximadamente 30% en peso de un hidrótrofo.

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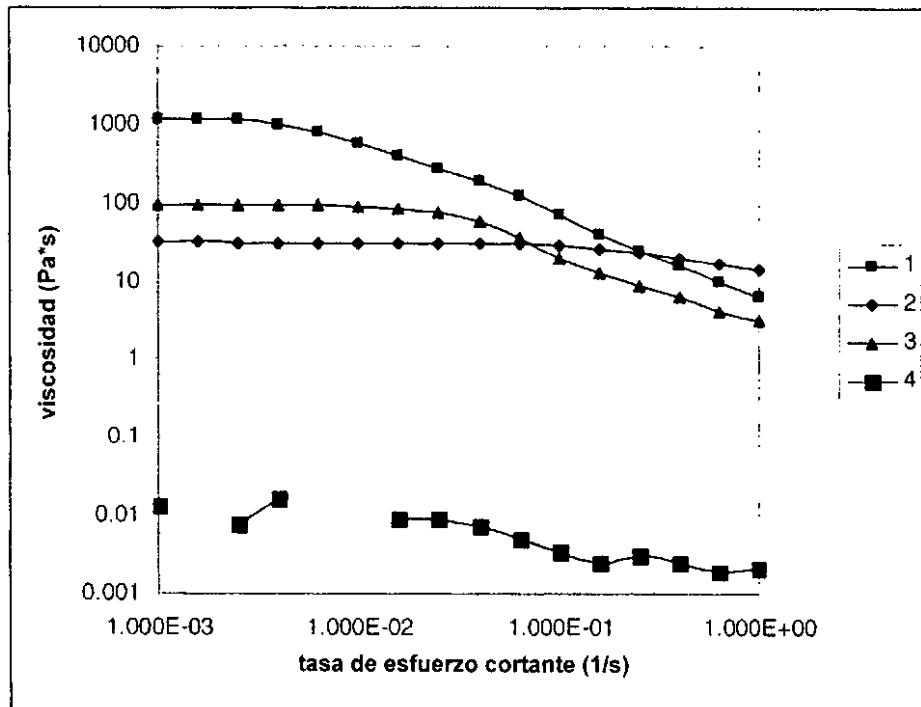


FIG. 1

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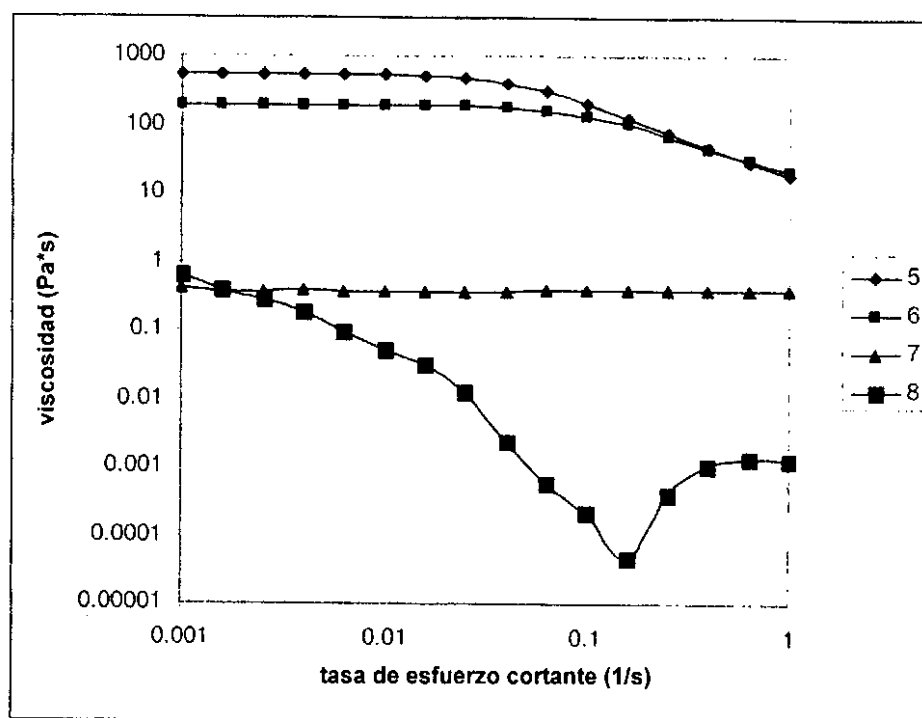


FIG. 2

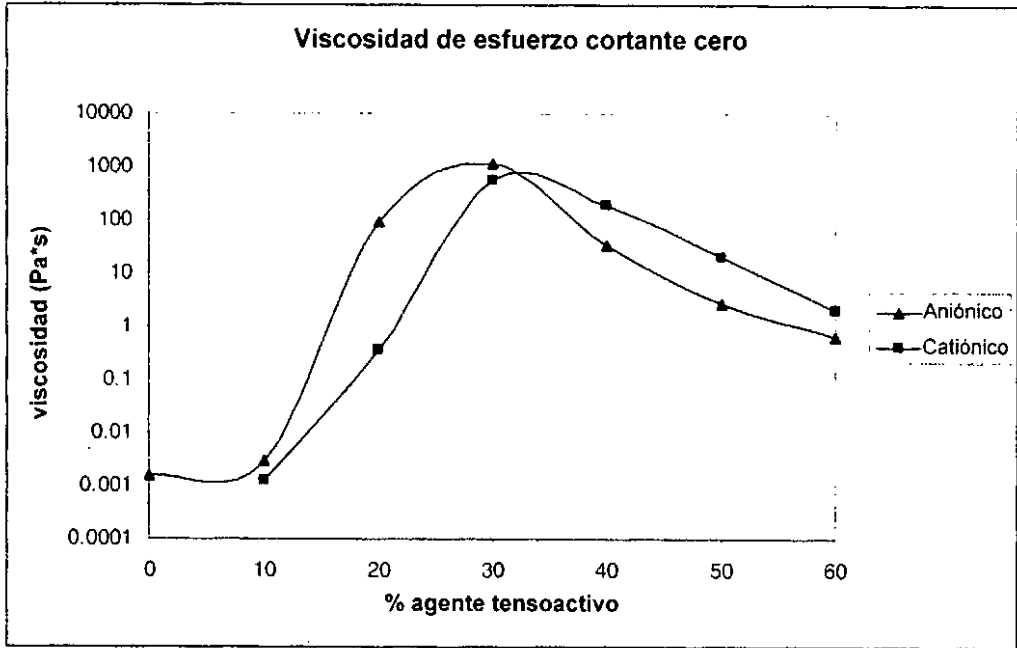


FIG. 3

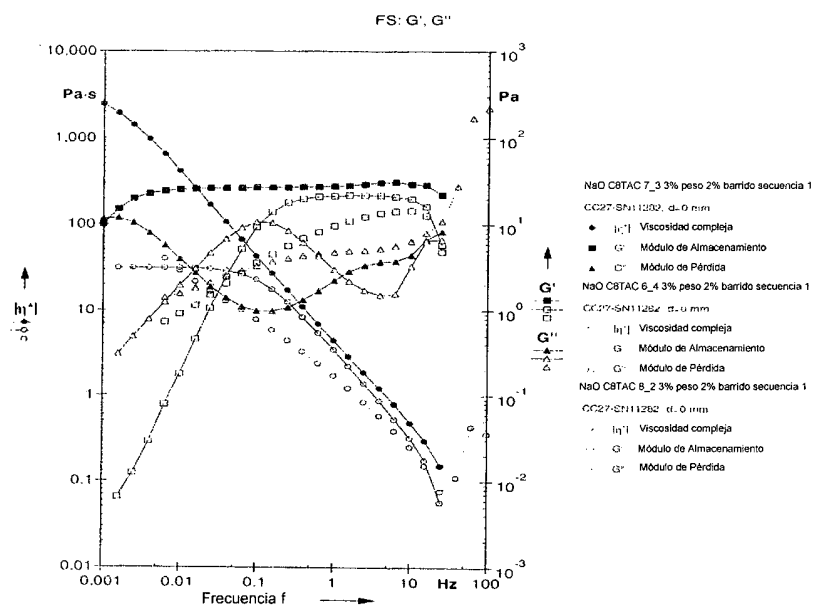


FIG. 4

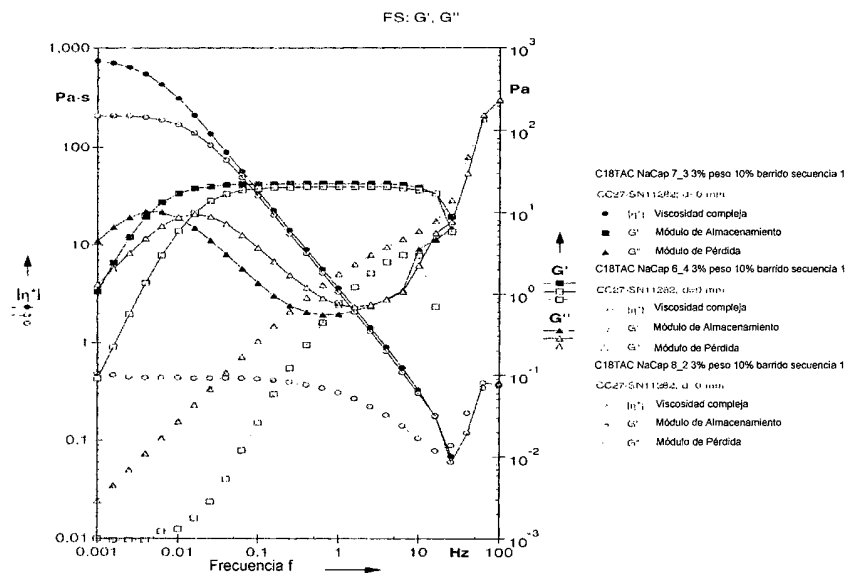


FIG. 5

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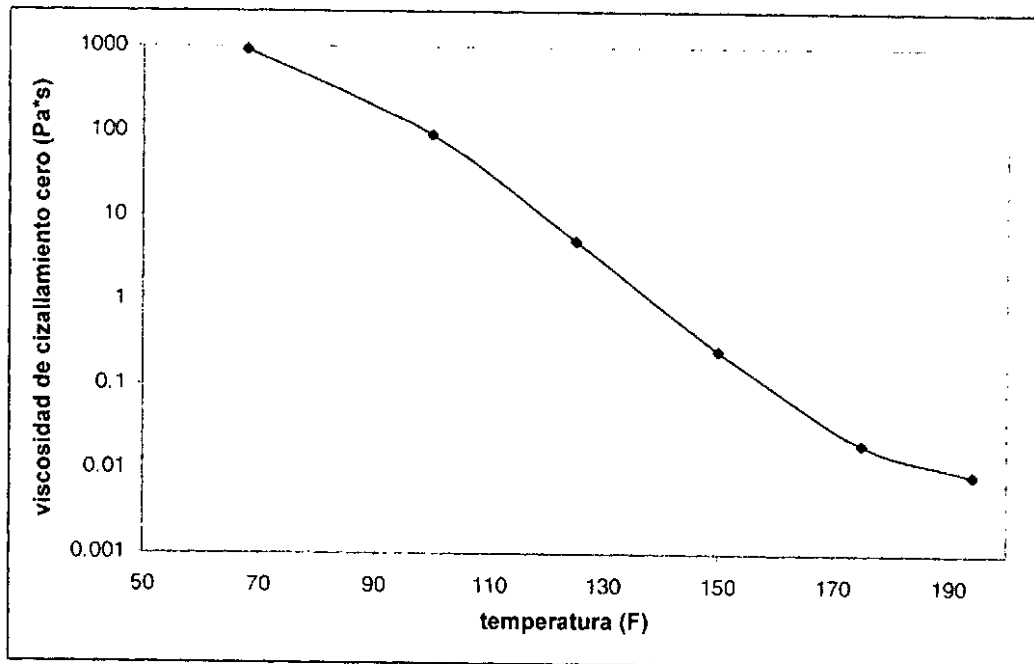


FIG. 6

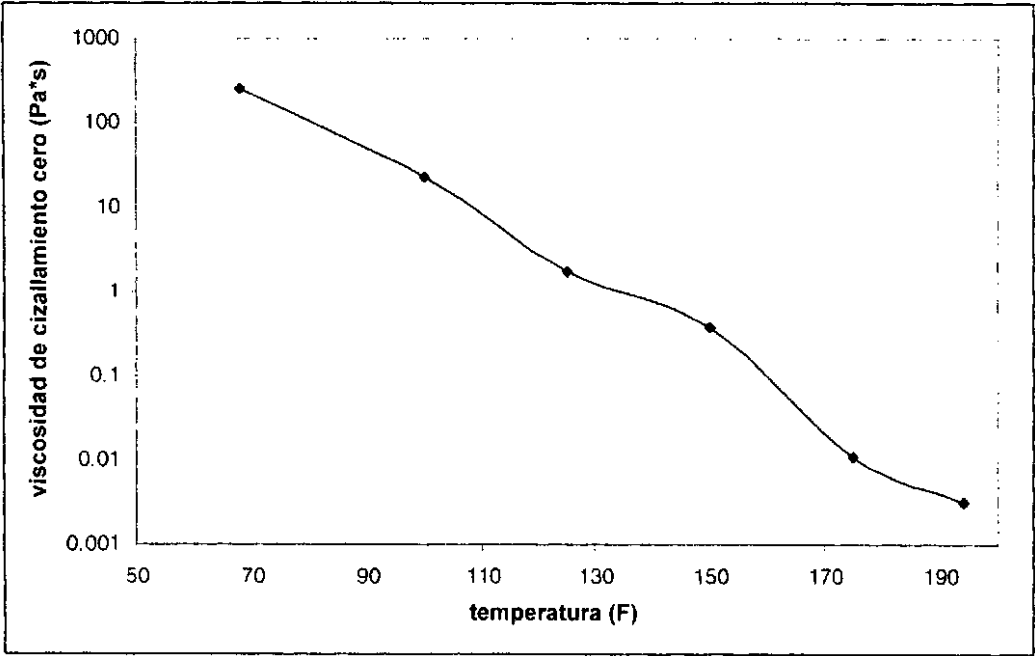


FIG. 7

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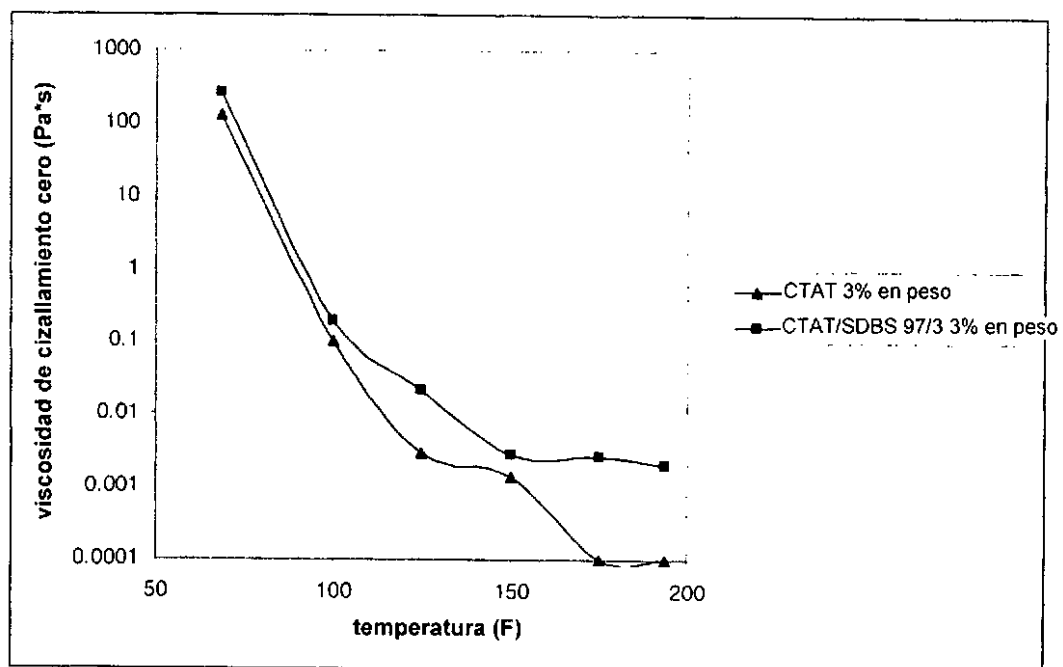


FIG. 8

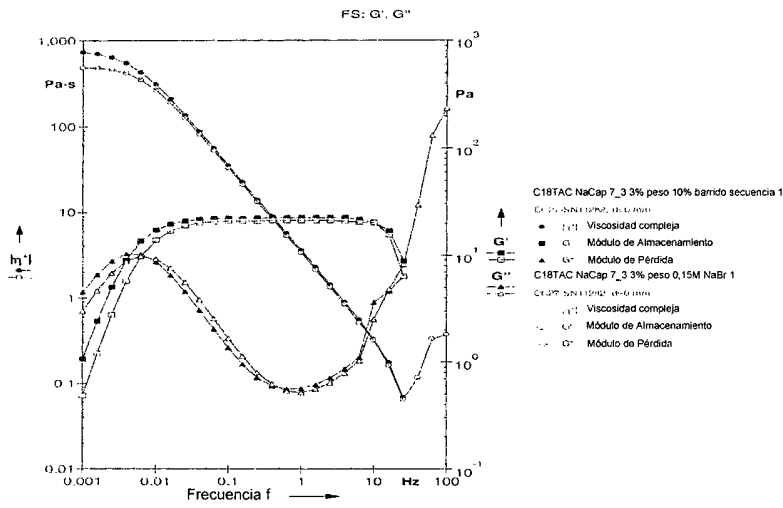


FIG. 9

10/13

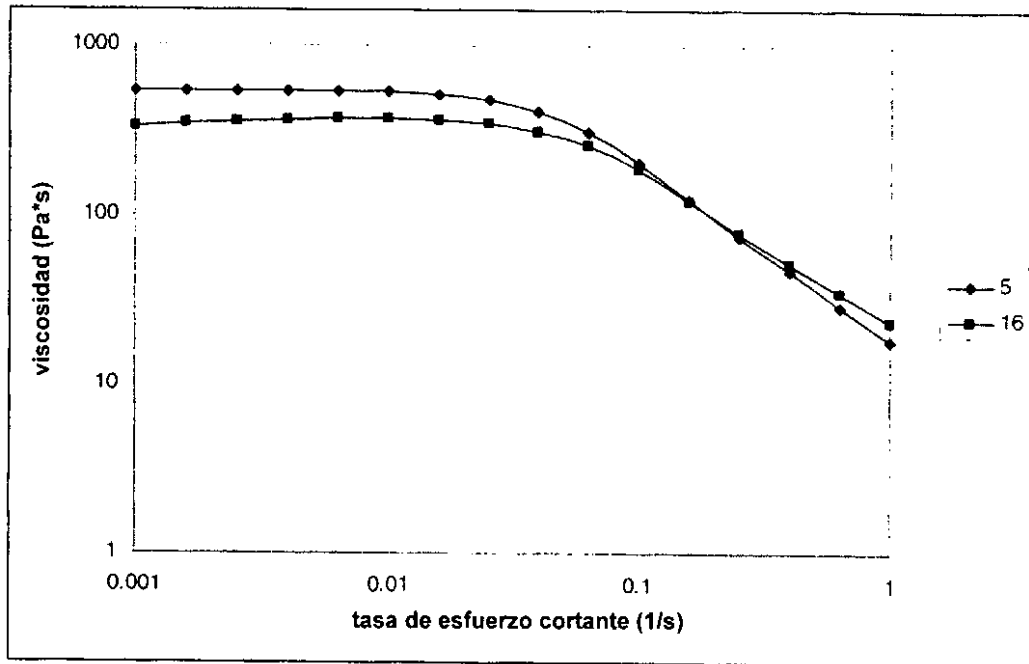


FIG. 10

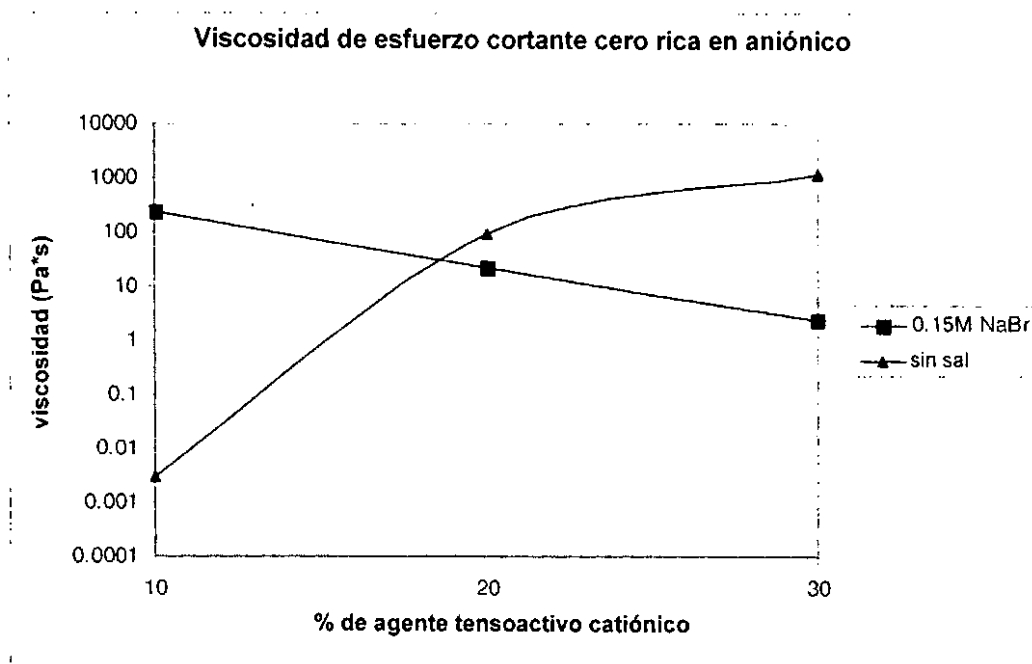


FIG. 11

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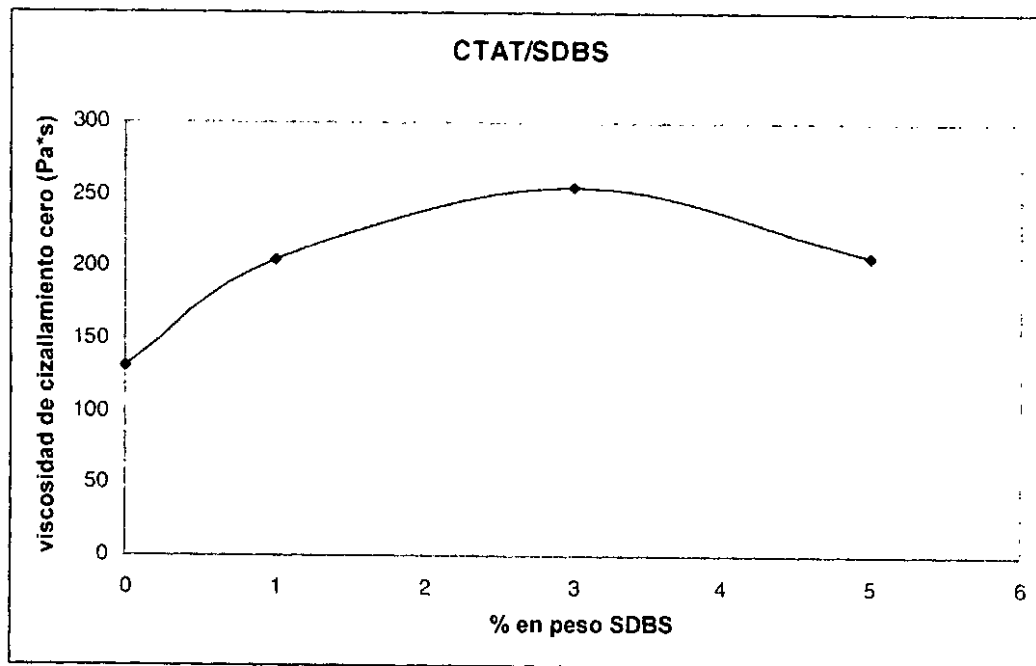


FIG. 12

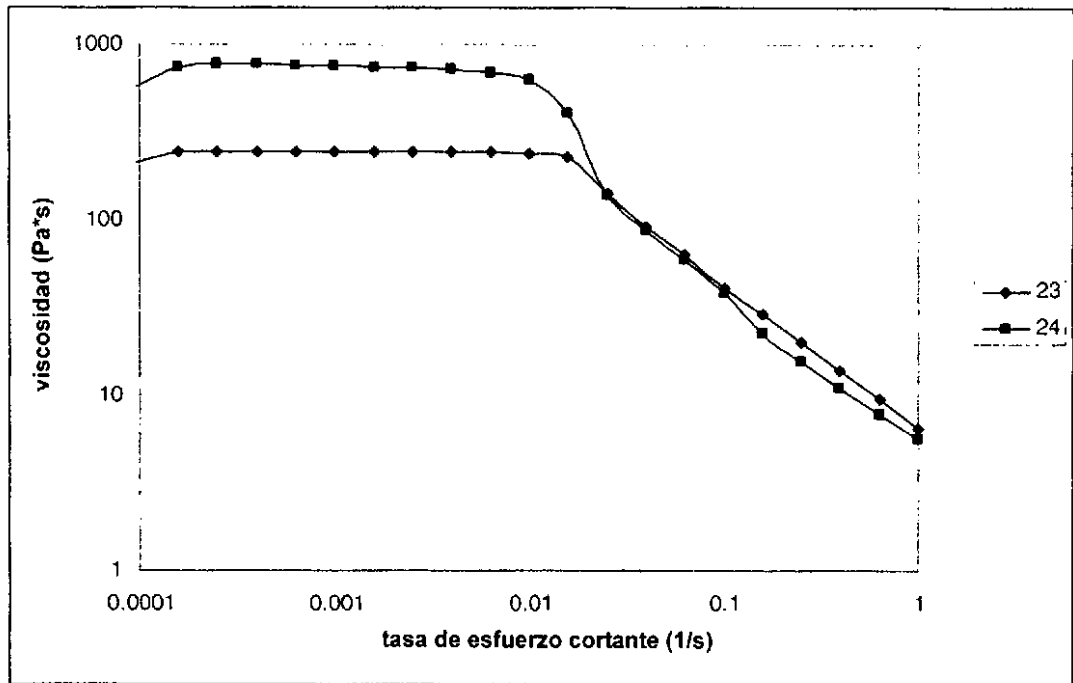


FIG. 13

VISCOELASTIC SURFACTANTS AND METHODS OF MAKING AND USING
SAME

BACKGROUND

Technical Field

[0001] The present disclosure generally relates to wellbore servicing fluids. More particularly, this disclosure relates to viscoelastic surfactants and methods of making and using same.

Background

[0002] Natural resources such as gas, oil, and water residing in a subterranean formation or zone are usually recovered by drilling a wellbore down to the subterranean formation while circulating a drilling fluid in the wellbore. During the drilling of a well bore a drilling fluid may be circulated down through the inside of the drill string, through the drill bit, and to the surface through the annulus between the walls of the well bore and the drill string. The drill string may be a drill pipe, a casing string, or any other suitable conduit. Among other things, the circulating drilling fluid lubricates the drill bit, carries drill cuttings to the surface, and balances the formation pressure exerted on the well bore. One problem associated with the drilling of a well bore may be the undesirable loss of large amounts of the drilling fluid into the subterranean formation. This problem may be referred to as "lost circulation" and the sections of the formation into which the drilling fluid is lost are referred to as "lost circulation zones." In addition to drilling fluids, problems with lost circulation may also be encountered with other fluids, for example, spacer fluids, completion fluids (e.g., brines) and workover fluids that may be circulated in a well bore. Herein a spacer fluid refers to any liquid used to physically separate one special-purpose liquid from another; a completion fluid refers to a solids-free liquid used to facilitate final operations prior to initiation of production; and a workover fluid refers to a well-control fluid, that is used during the performance of maintenance or remedial treatments on a hydrocarbon producing well. A variety of factors may be responsible for lost circulation. For example, the subterranean formation penetrated by the well bore may be highly permeable or may contain fractures or crevices therein. Furthermore, the formation may breakdown under the hydrostatic pressure applied by the fluid, thereby allowing the fluid to be lost into the formation. For instance, fractures in the subterranean formation may be created or

enhanced due to the hydrostatic pressure of the drilling fluid with the resulting loss of drilling fluid into those fractures.

[0003] A number of methods have been developed to control lost circulation. One method commonly used to control lost circulation involves the placement of lost circulation materials into the lost circulation zone. These lost circulation materials may be placed into the formation for example as lost circulation pills in an attempt to control and/or prevent lost circulation. Conventional lost circulation pills may suffer from a variety of drawbacks such as the large amount of materials needed to achieve desired properties (e.g., viscosities, etc.) and difficulties associated with removing the component materials of the pill once the treatment has been completed. Thus, it would be desirable to develop improved compositions for controlling lost circulation.

SUMMARY

[0004] Disclosed herein is a method of servicing a wellbore comprising placing downhole a composition comprising a surfactant package comprising a cationic surfactant and anionic surfactant, wherein the surfactant package when contacted with an aqueous solution forms a viscosified composition in the presence of less than about 30 wt.% of a hydrotrope.

BRIEF DESCRIPTION OF THE DRAWINGS

[0005] For a more complete understanding of the present disclosure and the advantages thereof, reference is now made to the following brief description, taken in connection with the accompanying drawings and detailed description:

[0006] Figures 1 and 2 are plots of viscosity as a function of shear rate for the samples from Example 1.

[0007] Figure 3 is a plot of viscosity as a function of percent surfactant for the samples from Example 2.

[0008] Figures 4-5 are plots of complex viscosity, storage modulus, and loss modulus as a function of frequency for the samples from Example 3.

[0009] Figures 6-7 is a plot of zero shear viscosity as a function of temperature for the samples from Example 4.

[0010] Figure 8 is a plot of zero shear viscosity as a function of temperature for the samples from Example 5.

[0011] Figure 9 is a plot of complex viscosity, storage modulus, and loss modulus as a function of frequency for the samples from Example 6.

[0012] Figure 10 is a plot of viscosity and shear stress as a function of shear rate for the samples from Example 6.

[0013] Figure 11 is a plot of viscosity as a function of percentage of cationic surfactant for the samples from Example 6.

[0014] Figure 12 is a plot of zero shear viscosity as a function of weight percentage of SDBS for the samples from Example 7.

[0015] Figure 13 is a plot of viscosity and shear stress as a function of shear rate for the samples from Example 8.

DETAILED DESCRIPTION

[0016] It should be understood at the outset that although an illustrative implementation of one or more embodiments are provided below, the disclosed systems and/or methods may be implemented using any number of techniques, whether currently known or in existence. The disclosure should in no way be limited to the illustrative implementations, drawings, and techniques illustrated below, including the exemplary designs and implementations illustrated and described herein, but may be modified within the scope of the appended claims along with their full scope of equivalents.

[0017] Disclosed herein are compositions (e.g., wellbore servicing compositions) comprising at least one cationic surfactant and at least one anionic surfactant. Such compositions are said to contain a cationic anionic surfactant package (CASP). In an embodiment, the CASP may react with one or more components of the wellbore servicing fluid to form a viscosified composition hereinafter denoted CASP-VC. A CASP-VC of the type described herein may be useful in various wellbore servicing operations. For example, the CASP-VC may be useful in the treatment of wellbores experiencing lost circulation. The components of the CASP and CASP-VC as well as methods of making and using same will be described in more detail later herein.

[0018] In an embodiment, the CASP comprises a cationic surfactant. Surfactants in general are wetting agents that lower the surface tension of a liquid in which they are dissolved, allowing easier spreading and decreasing the interfacial tension between two liquids. Each surfactant has a hydrophilic head that is attracted to water molecules and a hydrophobic tail that repels water and attaches itself to hydrophobic materials such as oil and grease. Herein a cationic surfactant has a positively charged head and a hydrophobic tail comprising a carbon chain. A cationic surfactant suitable for use in this disclosure may have a carbon chain having

a length of from about 8 to about 24, alternatively from about 8 to about 18, alternatively from about 12 to about 22, alternatively from about 16 to about 24. Examples of cationic surfactants suitable for use in this disclosure include without limitation quaternary ammonium salts, ethoxylated quaternary ammonium salts, amine oxides, or a combination thereof. In an embodiment, the cationic surfactant comprises stearyltrimethylammonium chloride, cetyltrimethylammonium tosylate, cetyltrimethylammonium chloride, cetyltrimethylammonium bromide, myristyltrimethylammonium chloride, myristyltrimethylammonium bromide, dodecyltrimethylammonium chloride, dodecyltrimethylammonium bromide, decyltrimethylammonium chloride, decyltrimethylammonium bromide, octyltrimethylammonium chloride, erucyl bis-(hydroxy ethyl)methylammonium chloride, erucyltrimethylammonium chloride, or a combination thereof. In an embodiment, the cationic surfactant may be present in the CASP in an amount of from about 0.01 weight percent (wt.%) based on the total weight of the CASP to about 99.99 wt.%, alternatively from about 0.1 wt.% to about 99.9 wt.%, alternatively from about 1 wt.% to about 99 wt.%.

[0019] In an embodiment, the CASP comprises an anionic surfactant. Herein an anionic surfactant has a negatively charged head and a hydrophobic tail comprising a carbon chain. An anionic surfactant suitable for use in this disclosure may have carbon chain having a length of from about 8 to about 24, alternatively from about 8 to about 18, alternatively from about 12 to about 22, alternatively from about 18 to about 24. Examples of anionic surfactants suitable for use in this disclosure include without limitation alkali salts of acids, alkali salts of fatty acids, alkaline salts of acids, sodium salts of acid, sodium salts of fatty acid, alkyl sulphates, alkyl ethoxylate, sulphates, sulfonates, soaps, or a combination thereof. In an embodiment, the anionic surfactant comprises sodium oleate, sodium stearate, sodium dodecylbenzenesulfonate, sodium myristate, sodium laurate, sodium decanoate, sodium caprylate, sodium cetyl sulfate, sodium myristyl sulfate, sodium lauryl sulfate, sodium decyl sulfate, sodium octyl sulfate, or a combination thereof.

[0020] In an embodiment, the anionic surfactant may be present in the CASP in an amount of from about 0.01 weight percent (wt.%) based on the total weight of the CASP to about 99.99 wt.%, alternatively from about 0.1 wt.% to about 99.9 wt.%, alternatively from about 1 wt.% to about 99 wt.%.

[0021] In an embodiment the amount of cationic surfactant present in the CASP is greater than the amount of anionic surfactant and such a composition is termed a cationic rich CASP. Alternatively, the amount of anionic surfactant present in the CASP is greater than the amount of cationic surfactant and such a composition is termed an anionic rich CASP.

[0022] In an embodiment, the cationic surfactant:anionic surfactant ratio (CAR) may be chosen by one of ordinary skill in the art with the benefits of this disclosure so as to mitigate unwanted effects normally associated with the contacting of a surfactant package with other materials. For example, the CAR may be chosen so as to reduce or eliminate phase separation when the CASP is contacted with an aqueous solution. Further, the CAR may be chosen so as to reduce or eliminate precipitation of one or both components of the CASP when contacted with an aqueous solution. For example, the CAR may be from about 1:100 to about 100:1; alternatively from about 90:1 to about 1:90; alternatively from about 80:1 to about 1:80; alternatively from about 70:1 to about 1:70; alternatively from about 60:1 to about 1:60; alternatively from about 1:50 to about 50:1; alternatively from about 40:1 to about 1:40; alternatively from about 30:1 to about 1:30; alternatively from about 20:1 to about 1:20; alternatively from about 10:1 to about 1:10; alternatively from about 1:9 to about 9:1.

[0023] In an embodiment, a CASP (e.g., a cationic rich CASP, an anionic rich CASP) may be contacted with an aqueous solution to form a CASP-VC. The aqueous solution may comprise fresh water or salt water, e.g., an unsaturated aqueous salt solution or a saturated aqueous salt solution such as brine or seawater. The aqueous solution and CASP may be contacted in any manner known to one of ordinary skill in the art with the benefits of this disclosure. In an embodiment the aqueous solution comprises a brine. The brine may be any suitable saturated or a nearly saturated saltwater solution. For example, the brine may be any suitable saturated or a nearly saturated salt solution comprising water and greater than about 90, 95, 99, or 99.9 wt.% salt. Nonlimiting examples of brines suitable for use in this disclosure include ammonium chloride, potassium chloride, sodium chloride, zinc bromide, calcium chloride, calcium bromide, sodium bromide, potassium formate, sodium formate, cesium formate or a combination thereof. In an embodiment, the CASP may be contacted with the aqueous solution in an amount of from about 0.01g to about 20g CASP per 80g aqueous solution, alternatively from about 0.1g to about 15g CASP per 80g aqueous solution, alternatively from about 1g to about 10g CASP per 80g aqueous solution.

[0024] The CASP-VC described herein may exhibit viscoelastic behavior. Viscoelastic materials exhibit both viscous and elastic characteristics when undergoing deformation. In an embodiment, the viscoelasticity of the CASP-VC may be adjusted to meet a user or process-desired need by adjustment of the CAR or the total concentration of surfactant. The ability to adjust or tune the viscoelasticity of the CASP-VC may allow a user to select an appropriate CASP-VC based on the needs of a wellbore and its processing requirements. For example, the CAR may be optimized to produce a CASP-VC having a viscosity suitable for use in lost circulation zones at higher depth or at an elevated temperature.

[0025] In an embodiment, the CASP-VC may exhibit a viscosity ranging from about 0.001 Pa*s to about 100,000 Pa*s, alternatively from 1 Pa*s to about 100,000 Pa*s, alternatively from about 100 Pa*s to about 100,000 Pa*s over a temperature range of from about 10°C to about 200°C, alternatively from about 25°C to about 200°C, alternatively from about 50°C to about 200°C. Viscosity is a measure of the resistance of a fluid which is being deformed by shear stress. In other words, it is the resistance of a liquid to flow. Determination of the properties described herein may be made using any suitable methodology known to one of ordinary skill in the art. For example, the storage modulus, loss modulus and viscosity may be determined by applying a constant shear rate to the CASP-VC and reading the shear stress using a narrow gap cup in bob geometry as described in Rheology: Principles, Measurements and Applications, by C.W. Macosko, Wiley-VCH, New York (1994) which is incorporated by reference herein in its entirety.

[0026] In an embodiment, the CASP-VC may exhibit a zero shear viscosity of from about 0.001 Pa*s to about 100,000 Pa*s, alternatively from about 1 Pa*s to about 100,000 Pa*s, alternatively from about 100 Pa*s to about 100,000 Pa*s over a temperature range of from about 10°C to about 200°C, alternatively from about 25°C to about 200°C, alternatively from about 50°C to about 200°C. Zero shear viscosity refers to the viscosity at the limit of low shear rate. The zero shear viscosity is the viscosity a product will ultimately attain when at rest and undisturbed. The zero shear viscosity was determined as described previously herein with the exception that the data was extrapolated to "zero" shear and the viscosity read at that shear.

[0027] In an embodiment, the CASP-VC has a complex viscosity of from about 10 Pa*s to about 100,000 Pa*s, alternatively from about 100 Pa*s to about 100,000 Pa*s, alternatively from about 1,000 Pa*s to about 100,000 Pa*s for a range of frequencies of from about 0.00001 Hz to about 1,000 Hz, alternatively from about 0.01 Hz to about 1,000 Hz, alternatively from

about 1 Hz to about 1,000 Hz. Complex viscosity refers a frequency-dependent viscosity function determined during forced harmonic oscillation of shear stress. It is related to the complex shear modulus and represents the angle between the viscous stress and the shear stress. The complex viscosity function is equal to the difference between the dynamic viscosity and the out-of-phase viscosity, or imaginary part of the complex viscosity:

$$\eta^*(i\omega) = \eta'(\omega) - i\eta''(\omega)$$

where

η^* = complex viscosity

η' = dynamic viscosity

η'' = out-of-phase viscosity

The complex viscosity was determined as described previously herein with the exception that the frequency was kept constant.

[0028] The storage modulus in viscoelastic materials measures the stored energy and represents the elastic portion of the material. The loss modulus relates to the energy dissipated as heat and represents the viscous portion related to the amount of energy lost due to viscous flow. In an embodiment, the CASP-VC has a storage modulus of from about 0.001 Pa to about 1,000 Pa, alternatively from about 0.1 Pa to about 1,000 Pa, alternatively from about 1 Pa to about 1,000 Pa for a range of frequencies of from about 0.00001 Hz to about 1,000 Hz, alternatively from about 0.01 Hz to about 1,000 Hz, alternatively from about 1 Hz to about 1,000 Hz. In another embodiment, the CASP-VC has a loss modulus of from about 0.001 Pa to about 1,000 Pa, alternatively from about 0.1 Pa to about 1,000 Pa, alternatively from about 1 Pa to about 1,000 Pa for a range of frequencies of from about 0.00001 Hz to about 1,000 Hz, alternatively from about 0.01 Hz to about 1,000 Hz, alternatively about 1 Hz to about 1,000 Hz. The storage modulus and loss modulus were determined as described previously herein.

[0029] In an embodiment, the CASP-VC is solids free. Herein, solids free refers to the amount of solid being equal to or less than about 3 wt.%, alternatively equal to or less than about 2 wt.%, alternatively equal to or less than about 1 wt.% based on the total weight of the CASP. Examples of solids include without limitation particles, sands, formation materials, or a combination thereof.

[0030] In an embodiment, the CASP-VC can withstand high pressure gradients. The high viscoelasticity generated by the CASP allows the fluid to resist high pressure gradients.

[0031] In an embodiment, CASPs of the type described herein may be introduced to a wellbore servicing fluid or to a wellbore and carry out its intended function in the substantial absence of a hydrotrope and/or excess salt (e.g., the CASP is free, substantially free, or does not contain a material amount of a hydrotrope and/or excess salt). Both hydrotropes and excess salt are used to stabilize micellar growth. Herein a hydrotrope refers to a compound that solubilises hydrophobic compounds in aqueous solutions. Typically, hydrotropes consist of a hydrophilic part and a hydrophobic part (like surfactants) but the hydrophobic part is generally too small to cause spontaneous self-aggregation. Examples of hydrotropes include for example and without limitation sodium p-toluenesulfonate, sodium xylene sulfonate, sodium salicylate, alkyl alcohols, or a combination thereof. In alternative embodiments, the CASPs are introduced to a wellbore servicing fluid or to a wellbore and carry out its intended function in the presence of a hydrotrope. In an embodiment, the CASP comprises less than or equal to about 30, 20, 10, 9, 8, 7, 6, 5, 4, 3, 2, 1, 0.1, 0.01, or 0.001 wt% of one or more hydrotropes based upon the total weight of the CASP. In an embodiment, the CASP comprises an amount of salt equal to or less than the saturation amount. In an embodiment, the CASP comprises an excess amount of salt equal to or less than about 1.0, 0.1, 0.01, 0.001, or 0.0001 weight percent over the saturation amount (i.e., $\leq 1.0, 0.1, 0.01, 0.001, \text{ or } 0.0001 \text{ wt \% excess salt}$).

[0032] Without wishing to be limited by theory, the tunable viscoelasticity of the CASP-VC disclosed herein may be attributed to the mechanism of micelle growth in these compositions. One mechanism for the formation and growth of micelles may involve the electrostatic interactions of a cationic surfactant and an anionic surfactant (e.g., CASP). In this mechanism, the CASP interacts to form a pseudo-double tailed zwitterionic surfactant that self assembles into a surfactant bilayer in the form of lamellar sheets of vesicles or wormlike micelles. The presence of salt (e.g. hydrotrope) may facilitate the growth of micelles or the creation of multilamellar vesicles because of interaction between cationic and anionic surfactant, cationic/anionic surfactant and hydrotrope, and cationic/anionic surfactant and inorganic salt.

[0033] In addition, the chain length of the cationic and anionic surfactant may affect the resulting micelles. When the cationic and anionic surfactants are of similar chain length, there is a wider phase space where the bilayer aggregates are stable. However, when there is a difference in chain lengths, the bilayer phase space will be smaller, thus stabilizing the micelles over a wider concentration range. To generate chain length difference between the cationic and

anionic surfactants, the amount of cationic surfactant may be much larger when compared to the anionic surfactant or vice versa. Further, even at equimolar amounts of cationic and anionic surfactants wherein the chain length difference between the cationic and anionic surfactants is sufficiently large, a micelle phase will be stable. However, a micelle phase will not be stable if the cationic and anionic surfactants have similar chain lengths.

[0034] The second proposed mechanism involves a phase transition of the CASP from a low viscosity vesicle phase (e.g., near that of water with 1 vol.% spheres) to a higher viscosity viscoelastic phase by an increase in temperature. Herein, a higher viscosity viscoelastic phase refers to an amount higher than that of the vesicle phase while at the same overall concentration of surfactant. In this mechanism, a unilamellar vesicle bilayer phase is created by mixing the cationic surfactant and the anionic surfactant. In contrast to the first mechanism where a difference in carbon chain length aids in micelles formation, the amount of the cationic surfactant may be similar to the anionic surfactant in the vesicle phase, for example a 1:1 CAR. As temperature increases, the surfactant exchange rate between the vesicle and water will increase. The increase occurs more rapidly for a shorter chain surfactant than for a longer chain surfactant, leading to a lower concentration (e.g., as determined by nuclear magnetic resonance) of one surfactant in the bilayer, thus possibly promoting the growth of micelles.

[0035] The third proposed mechanism involves development of a spontaneous curvature by mixing surfactants and creating a defect ridden lamellar phase with gel-like qualities as visualized using standard imaging techniques. In this mechanism, a cationic/anionic gel is formed by a lamellar defect phase. At high double-tailed surfactant concentration (e.g., low water contents, equal to or greater than about 50 wt.% surfactant), a lamellar sheet (L_{α}) phase is often formed. As the water content is increased to an amount of from about 60 wt.% to about 80 wt.%, the bilayer spacing generally swells to a certain spacing that expel any excess water that is added. This spacing may be determined using any suitable technique such as small angle x-ray scattering technique. In the case of cationic/anionic bilayers ("pseudo" double tailed surfactants), a spontaneous curvature exists that leads to multilamellar vesicle (MLV) defect sites existing with the lamellar sheet phase as more water is added. The formation of MLV defect sites within the lamellar sheet phase further leads to lamellar sheets entangled with MLV defect sites, thereby creating a highly viscoelastic gel with a viscosity greater than 1,000 centipoise.

[0036] In an embodiment, a CASP-VC of the type described herein may be used to control lost circulation in a subterranean formation. It is to be understood that "subterranean formation" encompasses both areas below exposed earth and areas below earth covered by water such as ocean or fresh water. In the process of drilling a well, low fracture gradients zones, fractured zones, etc. are often encountered and loss of whole drilling fluid to the formation becomes a problem. Losses of drilling fluid can impede the progress of drilling the well, add cost to the drilling of the well, prevent the drilling of the well to target depth, and/or cause the total loss of the drilled open hole section. In such an embodiment, the CASP may be introduced into a drill string, pumped down to a lost circulation zone such as voids, vugular zones, and natural or induced fractures while drilling. The CASP may then contact a fluid in the lost circulation zone and form a CASP-VC that substantially seals the lost circulation zone with little or no interruption of drilling operations and reduction in loss of drilling fluid to the lost circulation zone.

[0037] In another embodiment, a CASP may be pumped down to a lost circulation zone, a wellbore servicing fluid may be introduced from the wellbore to the lost circulation zone wherein the CASP contacts the wellbore servicing fluid and forms a CASP-VC that substantially seals the lost circulation zone. As used herein, a "servicing fluid" refers to a fluid used to drill, complete, work over, fracture, repair, or in any way prepare a wellbore for the recovery of materials residing in a subterranean formation penetrated by the wellbore. Examples of servicing fluids include, but are not limited to, cement slurries, drilling fluids or muds, spacer fluids, fracturing fluids, gravel pack fluids, or completion fluids, all of which are well known in the art. Methods for introducing compositions into a wellbore to seal subterranean zones are described in U.S. Patent Nos. 5,913,364; 6,167,967; and 6,258,757, each of which is incorporated by reference herein in its entirety.

[0038] The CASP-VC may form a non-flowing, intact mass of high viscosity inside the lost circulation zone which plugs the zone and inhibits loss of subsequently pumped fluid. In an embodiment, the CAR is adjusted so as to produce a high viscosity CASP-VC that plugs a zone at elevated temperatures, such as those found at higher depths within a wellbore.

[0039] In another embodiment, the CASP-VCs form lost circulation pills for use in completion brines. The CASP-VCs disclosed herein may form solids free post perforation pills and/or post gravel pack fluid loss pills that are useful in servicing a wellbore during completion operations.

[0040] In an embodiment, a CASP-VC is used to service a wellbore. Subsequently, the viscoelasticity of a CASP-VC may be broken (i.e., the viscosity of the CASP-VC may be reduced) by contacting the CASP-VC with an effective amount of a viscosity breaker such as a hydrocarbon or an internal breaker. The ability to break the viscosity of a CASP-VC may be useful for example for wellbore cleanup. Examples of internal breakers suitable for use in this disclosure include without limitation SP breaker, VICON NF breaker, OXOL II breaker, GBW-40 breaker, and HT breaker, which are commercially available from Halliburton. Examples of hydrocarbons suitable for use in this disclosure include for example and without limitation crude oil, natural gas and gas hydrates. Effective amounts of hydrocarbons and internal breakers may be determined by one of ordinary skill in the art with the aid of this disclosure.

EXAMPLES

[0041] The disclosure having been generally described, the following examples are given as particular embodiments of the disclosure and to demonstrate the practice and advantages thereof. It is understood that the examples are given by way of illustration and are not intended to limit the specification or the claims in any manner.

EXAMPLE 1

[0042] The rheological behavior of CASP-VCs of the type described herein was investigated. Eight samples, designated Samples 1-8, were prepared. Samples 1-4 were prepared using sodium oleate (NaOle), which is commercially available from TCI America as the anionic surfactant and octyl trimethyl ammonium chloride (C₈TAC), which is commercially available from TCI America as the cationic surfactant. Samples 1-4 were prepared using a C₈TAC:NaO ratio of 3:7, 4:6, 2:8, and 1:9 respectively. The samples were then dissolved in deionized water (DI H₂O) in sufficient quantity to form a 3 wt.% solution. Since Samples 1-4 had larger anionic ratio to cationic, the resulting CASP-VCs were anionic rich.

[0043] Sample 5-8 were prepared using sodium octoate (NaCap), which is commercially available from TCI America as the anionic surfactant and stearyltrimethylammonium chloride (C₁₈TAC), which is commercially available from TCI America as the cationic surfactant. Samples 5-8 were prepared using a C₁₈TAC:NaCap ratio of 7:3, 6:4, 8:2, and 9:1 respectively. The samples were then dissolved in deionized water (DI H₂O) in sufficient quantity to form a 3 wt.% solution. Since Samples 5-8 had larger cationic ratio to anionic, the resulting CASP-VCs were cationic rich. Table 1 tabulates the cationic and anionic surfactant types, and ratios for each sample.

Table 1

Sample	Cationic Surfactant	Anionic Surfactant	CAR	Weight %
1	C ₈ TAC	NaO	3:7	3
2	C ₈ TAC	NaO	4:6	3
3	C ₈ TAC	NaO	2:8	3
4	C ₈ TAC	NaO	1:9	3
5	C ₁₈ TAC	NaCap	7:3	3
6	C ₁₈ TAC	NaCap	6:4	3
7	C ₁₈ TAC	NaCap	8:2	3
8	C ₁₈ TAC	NaCap	9:1	3

[0044] Rheological measurements were performed using an MCR 501 with a concentric cylinder of 27mm, which is a commercially available rheometer from Anton Paar at a temperature of 25°C.

[0045] Figure 1 is a plot of viscosity as a function of shear rate for Samples 1-4. Figure 2 is a plot of viscosity as a function of shear rate for Samples 5-8. The zero shear viscosities of Samples 1-4 may be determined by extrapolating the viscosity back to the theoretical zero-shear point and were 1200, 93, 33, and 0.006 Pa*s respectively. The zero shear viscosities of Samples 5-8 may be determined by extrapolating the viscosity back to the theoretical zero-shear point and were 542, 196, 0.4, and 0.001 respectively. The results demonstrated that the zero-shear viscosity is highly dependent on the cationic/anionic ratio and can be tuned by varying it. Also, over a million fold increase in viscosity can be generated by adding an oppositely charged surfactant independent of salt or hydrotrope concentration.

EXAMPLE 2

[0046] The zero shear viscosity of an anionic rich and a cationic rich CASP-VCs were investigated. Samples 1-8, described in Example 1, were used again in this example. In addition, five more samples, designated Samples 9-13, were prepared as described in Example 1. Table 2 tabulates the cationic and anionic surfactant types and CARs for Samples 9-13.

Table 2

Sample	Cationic Surfactant	Anionic Surfactant	CAR	Weight %
9	C ₈ TAC	NaO	5:5	3
10	C ₈ TAC	NaO	6:4	3
11	C ₈ TAC	NaO	0:10	3
12	C ₁₈ TAC	NaCap	5:5	3
13	C ₁₈ TAC	NaCap	4:6	3

[0047] Figure 3 is a plot of viscosity as a function of weight fraction of minor component for Samples 1-13. For Samples 1-4 and 9-11, the minor component was the cationic surfactant. For Samples 5-8 and 12-13, the minor component was the anionic surfactant. The results demonstrated that the CAR that created the maximum viscosity was about 70:30 and 30:70, as shown by the peaks for the anionic rich and the cationic rich CASP-VCs on Figure 3. In addition, both the cationic rich and the anionic rich CASP-VCs exhibited pronounced increases in viscoelasticity up to 300,000 fold when compared to the individual surfactant components. This increase in viscoelasticity was also observed visually by placing Sampled 1 and 5 in separate vials and inverting both vials. In both vials, the viscoelastic gel samples remained suspended for over 10 seconds.

EXAMPLE 3

[0048] The dynamic properties of CASP-VCs of the type described herein were investigated. Specifically, the complex viscosity, storage modulus, and loss modulus as a function of frequency for Samples 1-3 and 5-7 from Example 1 were determined. Figures 4 and 5 are plots of complex viscosity, storage modulus, and loss modulus as a function of frequency for Samples 1-3 and Samples 5-7 respectively. The results demonstrated that these fluids displayed both a significant loss modulus and storage modulus, thereby proving their viscoelasticity.

EXAMPLE 4

[0049] The effect of temperature on the viscosity of CASP-VCs was investigated. The zero shear viscosities of Samples 1 and 5 from Example 1 were tested over the temperature range of 70°F to 190°F. The results for both an anionic rich CASP-VC (Sample 1) and a cationic rich CASP-VC (Sample 5) are shown in Figures 6 and 7 respectively.

[0050] The results demonstrated that for there was a decrease in viscosity by several orders of magnitude in each sample as the temperature increased. However, the viscosity for the cationic and anionic rich CASP-VCs was still about 10 and 30 times greater respectively than that of water (viscosity of water at 194°F is about 0.000315 Pa*s). Thus, even at high temperature, there is an appreciable viscosity increase when compared to water.

[0051] Without wishing to be limited by theory the observed decrease in viscosity as the temperature increased may be a result of the solubility of the CASPs in water increasing (i.e., the critical micelle concentration increased). The increased solubility of the CASP may lead to faster kinetics and shorter and smaller micelles. The presence of these shorter and smaller micelles may contribute to the observed decrease in viscosity.

[0052] One of ordinary skill in the art with the benefits of this disclosure may adjust the CASPs such that the viscosity of the CASP-VC has a reduced response to temperature. For example, one technique is to use alkyl chain surfactants such as C₂₂ cationic surfactants and C₂₂ zwitterionic surfactants. In addition, changes in surfactant phase behavior with temperature may be exploited (i.e., vesicle to wormlike micelle transition). The final approach is to increase the concentration of the surfactants in the CASP. By increasing the concentration, one may achieve the entanglement or crossover concentration even with much shorter length micelles. In other words, the viscoelastic response occurs when there is either an increase in concentration, length, or both.

[0053] The stability of the CASP-VC was also investigated. An anionic surfactant solution comprising sample 1 was prepared and observed over a time period of 7 days at a temperature of 25°C. The anionic surfactant was observed to degrade with time, as the single component solution became somewhat cloudy in a few weeks. Without wishing to be limited by theory, the double bond in the oleate alkyl chain may be oxidized, causing the surfactant to become the same as stearic acid sodium soap. Stearic acid sodium soap has a much lower solubility in water and may not form wormlike micelles as readily as oleic acid sodium soap.

[0054] An anionic-rich CASP-VC was also prepared and observed over a time period of 7 days at a temperature of 25°C. The anionic rich CASP-VC also became cloudy, displayed reduced viscosity and began to phase separate after a few weeks. This behavior may be exploited in that it may be useful for degradation of the viscoelastic material without the utilization of any added components. At higher temperatures, such break down of viscosity may occur on the order of days, which may be useful for a lost circulation pill, as it will allow the lost circulation material to dissolve and allow production to begin. A cationic rich CASP-VC was observed to remain stable for a time period of greater than 30 days at a temperature of 25°C.

EXAMPLE 5

[0055] The temperature stability of a cationic rich CASP-VC was investigated and compared to a cationic only surfactant. The cationic rich CASP-VC, designated Sample 14, was cetyl trimethylammonium tosylate/sodium dodecylbenzene sulfonate (CTAT/SDBS) of 97:3 which was prepared as a 3 wt.% solution. The cationic only surfactant, designated Sample 15, was CTAT which was prepared as a 3 wt.% solution. The zero shear viscosities for Samples 14 and 15 were measured for a range of temperature of from 75°F to 190°F. The results are shown in Figure 8.

[0056] Referring to Figure 8, the zero shear viscosity decreased as the temperature increased for both samples. However, the drop in zero shear viscosity at high temperature (about above 150°F) for Sample 14 was less than Sample 15 because of the addition of the anionic surfactant. Without wishing to be limited by theory, the lesser drop in zero shear viscosity may be due to the greater binding of a surfactant versus a simple hydrotrope or due to the lower solubility of surfactants versus hydrotropes. Thus, these CASPs offer greater temperature stability than traditional surfactants.

EXAMPLE 6

[0057] The tolerance of cationic rich and anionic rich CASP-VCs to salt was investigated. Sample 5 from Example 1 was selected for the cationic rich CASP-VC. A comparative sample of cationic rich CASP-VC in brine, designated Sample 16, was prepared from C18TAC/NaCap having 7:3 ratio which was prepared as a 3 wt.% solution (similar to Sample 5) and 0.15M sodium bromide (NaBr) brine. The complex viscosity, storage modulus, loss modulus, and zero shear viscosity of Samples 5 and 16 were measured and the results are shown in Figures 9 and 10. The results demonstrated that the CASP-VC was able to maintain its viscosity with the

addition of salt. Without wishing to be limited by theory, this suggests that electrostatic interactions are not the dominant force in the creation of the viscoelasticity.

[0058] Sample 1 was selected for the anionic rich CASP. A comparative sample of anionic rich CASP-VC in brine, designated Sample 17 was prepared from NaO:C₈TAC ratio of 7:3 and 0.15M sodium bromide (NaBr) brine. The complex viscosity, storage modulus, loss modulus, and zero shear viscosity of Samples 1 and 17 were measured. The results are shown in Figure 11. The results demonstrated that the anionic rich CASP-VC suffered a large drop in its viscoelastic properties with the addition of salt, which suggests that electrostatic interactions are creating the large zero shear viscosity. This viscosity can be regained by varying CAR to change the overall charge on the micelle.

EXAMPLE 7

[0059] The zero shear viscosity of CASP-VCs of the type described herein was investigated. Four samples, designated Samples 18-21, were prepared. Sample 18 was a 3 wt.% aqueous solution of cetyl trimethylammonium tosylate (CTAT). Samples 19-21 were CTAT/sodium dodecylbenzene sulfonate (SDBS) with a CAR of 99:1, 97:3, and 95:5 respectively and was prepared as a 3 wt.% aqueous solution. The zero shear viscosities of Samples 18-21 were determined to be 126, 205, 255, and 207 Pa*s respectively and are shown in Figure 12. CTAT forms viscoelastic wormlike micellar solutions with high zero shear viscosities. By adding a small amount of SDBS in Samples 19-21, the solutions became highly viscous with increased zero shear viscosities when compared to Sample 18. Furthermore, the zero shear viscosity of Sample 20 was more than doubled (256,000 centiPoise) when compared to Sample 18 (126,000 centiPoise).

[0060] Another sample, designated Sample 22, was prepared. Sample 22 was CTAT/sodium octyl sulfate (SOS) with a CAR of 94:6 and was prepared as a 3 wt.% aqueous solution. The zero shear viscosity of Sample 22 was determined to be 470,000 centiPoise, which was more than tripled when compared to sample 18. These results demonstrated the ability of CASPs to increase the viscosity of solutions.

EXAMPLE 8

[0061] The effect of using surfactants containing longer alkyl chains on the properties of the CASP-VC was investigated. Three samples, designated Samples 23-25, were investigated. Samples 23 and 24, which were the cationic rich CASP, were prepared from erucyl bis-(hydroxy ethyl)methylammonium chloride (EHAC)/ n-caprylic acid sodium salt (NaCap) with

a CAR of 8:2 and 9:1 respectively as a 3 wt.% aqueous solution. Sample 25, which was the cationic rich CASP was prepared from erucyl bis-(hydroxy ethyl)methylammonium chloride/decanoic acid sodium salt with a cationic:anionic ratio of 9:1 as a 3 wt.% aqueous solution. The zero shear viscosities for Samples 23 and 24 were determined and the results are shown in Figure 13. The viscosities of Samples 23-24 ranged from 200,000 to 800,000 centiPoise while the viscosity of Sample 25 was about 70,000 centiPoise. The results demonstrate that the long chain surfactants that generate appreciable viscosity (>10 Pa*s) at elevated temperatures also form these cationic/anionic viscoelastic aggregates.

[0062] Next, the ability of hydrocarbon to reduce the viscosity of CASP-VC was investigated. A portion of samples 23-25 were placed in individual vials and a hydrocarbon fluid was introduced to each vial. The hydrocarbon fluid used for the test was diesel. Each vial was then shaken to mix the CASP-VC with diesel. Each vial was then inverted and visually observed. In the absence of the hydrocarbon, the CASPs form viscous masses that remained suspended for seconds, see Example 2. However, with the addition of a hydrocarbon, upon inversion of the vials the mass was not completely suspended and fluid was observed to flow for both the cationic rich and anionic rich CASPs.

[0063] While embodiments of the disclosure have been shown and described, modifications thereof can be made by one skilled in the art without departing from the scope of the invention. The embodiments described herein are exemplary only, and are not intended to be limiting. Many variations and modifications of the disclosure disclosed herein are possible and are within the scope of the disclosure. Where numerical ranges or limitations are expressly stated, such express ranges or limitations should be understood to include iterative ranges or limitations of like magnitude falling within the expressly stated ranges or limitations (e.g., from about 1 to about 10 includes, 2, 3, 4, etc.; greater than 0.10 includes 0.11, 0.12, 0.13, etc.). For example, whenever a numerical range with a lower limit, R_l , and an upper limit, R_u , is disclosed, any number falling within the range is specifically disclosed. In particular, the following numbers within the range are specifically disclosed: $R=R_l+k*(R_u-R_l)$, wherein k is a variable ranging from 1 percent to 100 percent with a 1 percent increment, i.e., k is 1 percent, 2 percent, 3 percent, 4 percent, 5 percent, ..., 50 percent, 51 percent, 52 percent, ..., 95 percent, 96 percent, 97 percent, 98 percent, 99 percent, or 100 percent. Moreover, any numerical range defined by two R numbers as defined in the above is also specifically disclosed. Use of the term "optionally" with respect to any element

of a claim is intended to mean that the subject element is required, or alternatively, is not required. Both alternatives are intended to be within the scope of the claim. Use of broader terms such as comprises, includes, having, etc. should be understood to provide support for narrower terms such as consisting of, consisting essentially of, comprised substantially of, etc.

[0064] Accordingly, the scope of protection is not limited by the description set out above but is only limited by the claims which follow, that scope including all equivalents of the subject matter of the claims. Each and every claim is incorporated into the specification as an embodiment of the present disclosure. Thus, the claims are a further description and are an addition to the embodiments of the present disclosure. The discussion of a reference is not an admission that it is prior art to the present disclosure, especially any reference that may have a publication date after the priority date of this application. The disclosures of all patents, patent applications, and publications cited herein are hereby incorporated by reference, to the extent that they provide exemplary, procedural, or other details supplementary to those set forth herein.

INGLES
REIVINDICACIONES

CLAIMS:

1. A wellbore servicing fluid comprising a surfactant package comprising a cationic surfactant and anionic surfactant: wherein the surfactant package when contacted with an aqueous solution forms a viscosified composition in the presence of less than about 30 wt.% of a hydrotrope.
2. A fluid according to claim 1, wherein the cationic surfactant has a carbon chain length of from about 8 to about 24.
3. A fluid according to claim 1 or 2, wherein the cationic surfactant comprises quaternary ammonium salt, ethoxylated quaternary ammonium salts, amine oxides, or a combination thereof.
4. A fluid according to claim 1, 2 or 3, wherein the cationic surfactant comprises stearyltrimethylammonium chloride, cetyltrimethylammonium tosylate, octyltrimethylammonium chloride, erucyl bis-(hydroxyethyl)methylammonium chloride, erucyl trimethylammonium chloride, cetyltrimethylammonium chloride, cetyltrimethylammonium bromide, myristyltrimethylammonium chloride, myristyltrimethylammonium bromide, dodecyltrimethylammonium chloride, dodecyltrimethylammonium bromide, decyltrimethylammonium chloride, decyltrimethylammonium bromide, or a combination thereof.
5. A fluid according to any preceding claim, wherein the cationic surfactant is present in the surfactant package in an amount of from about 0.01 wt.% to about 99.99 wt.% based on the total weight of the surfactant package.
6. A fluid according to any preceding claim, wherein the anionic surfactant has a carbon chain length of from about 8 to about 24.
7. A fluid according to any preceding claim, wherein the anionic surfactant comprises alkali salts of acids, alkali salts of fatty acids, alkaline salts of acids, sodium salts of acid, sodium salts of fatty acid, alkyl sulphates, alkyl ethoxylate, sulphates, sulfonates, soaps, or a combination thereof.
8. A fluid according to any preceding claim, wherein the anionic surfactant comprises sodium oleate, sodium dodecylbenzenesulfonate, sodium decanoate, sodium octyl sulfate, sodium caprylate, sodium stearate, sodium myristate, sodium laurate, sodium cetyl sulfate, sodium myristyl sulfate, sodium lauryl sulfate, sodium decyl sulfate, or a combination thereof.

9. A fluid according to any preceding claim, wherein the anionic surfactant is present in the surfactant package in an amount of from about 0.01 wt.% to about 99.99 wt.% based on the total weight of the surfactant package.
10. A fluid according to any preceding claim, wherein the surfactant package has cationic surfactant:anionic surfactant ratio of from 1:100 to 100:1.
11. A fluid according to any preceding claim, wherein the surfactant package is contacted with the aqueous solution in an amount of from about 0.01 grams to about 20 grams per 80 grams of the aqueous solution.
12. A fluid according to any preceding claim, wherein the aqueous solution comprises water, brine, a wellbore servicing fluid, or a combination thereof.
13. A fluid according to claim 12, wherein the brine comprises ammonium chloride, potassium chloride, sodium chloride, zinc bromide, calcium chloride, calcium bromide, sodium bromide, potassium formate, sodium formate, cesium formate or a combination thereof.
14. A fluid according to claim 12 or 13, wherein the wellbore servicing fluid comprises cement slurries, drilling fluids, spacer fluids, fracturing fluids, gravel pack fluids, workover fluids, completion fluids, or a combination thereof.
15. A fluid according to any preceding claim 1, wherein the viscosified composition is solids free.
16. A fluid according to any preceding claim, wherein the viscosified composition has a viscosity of from about 0.001 Pa*s to about 100,000 Pa*s at a temperature of from about 10°C to about 200°C.
17. A fluid according to any preceding claim, wherein the viscosified composition has a zero shear viscosity of from about 0.001 Pa*s to about 100,000 Pa*s at a temperature of from about 10°C to about 200°C.
18. A fluid according to any preceding claim, wherein the viscosified composition has a complex viscosity of from about 10 Pa*s to about 10,000 Pa*s at a frequency range of from about 0.00001 Hz to about 1000 Hz.
19. A fluid according to any preceding claim, wherein the viscosified composition has a storage modulus of from about 0.001 Pa to about 1,000 Pa at a frequency range of from about 0.00001 Hz to about 1000 Hz.

20. A fluid according to any preceding claim, wherein the viscosified composition has a loss modulus of from about 0.001 Pa to about 1.000 Pa at a frequency range of from about 0.00001 Hz to about 1000 Hz.
21. A fluid according to any preceding claim, wherein the viscosified composition comprises a solids free post perforation pill or a gravel pack fluid loss pill.
22. A method of servicing a wellbore comprising: placing a fluid according to any preceding claim in the wellbore.
23. A method according to claim 22, further comprising contacting the viscosified composition with a viscosity breaker.
24. A method according to claim 23, wherein the viscosity breaker comprises a hydrocarbon fluid, an internal breaker, or a combination thereof.

ABSTRACT

A method of servicing a wellbore comprising placing downhole a composition comprising a surfactant package comprising a cationic surfactant and anionic surfactant, wherein the surfactant package when contacted with an aqueous solution forms a viscified composition in the presence of less than about 30 wt.% of a hydrotrope.

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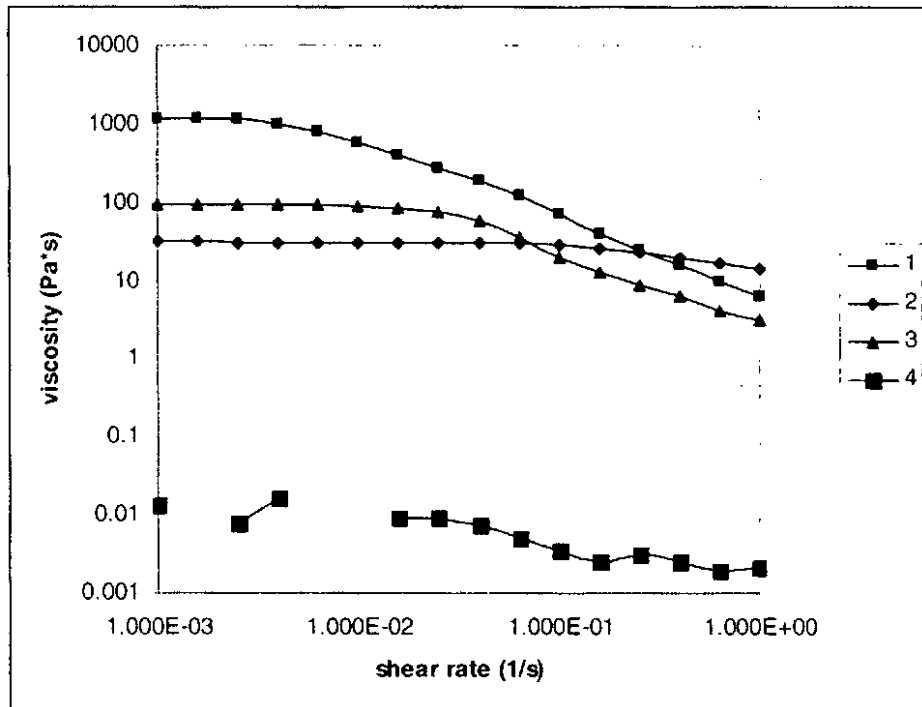


FIG. 1

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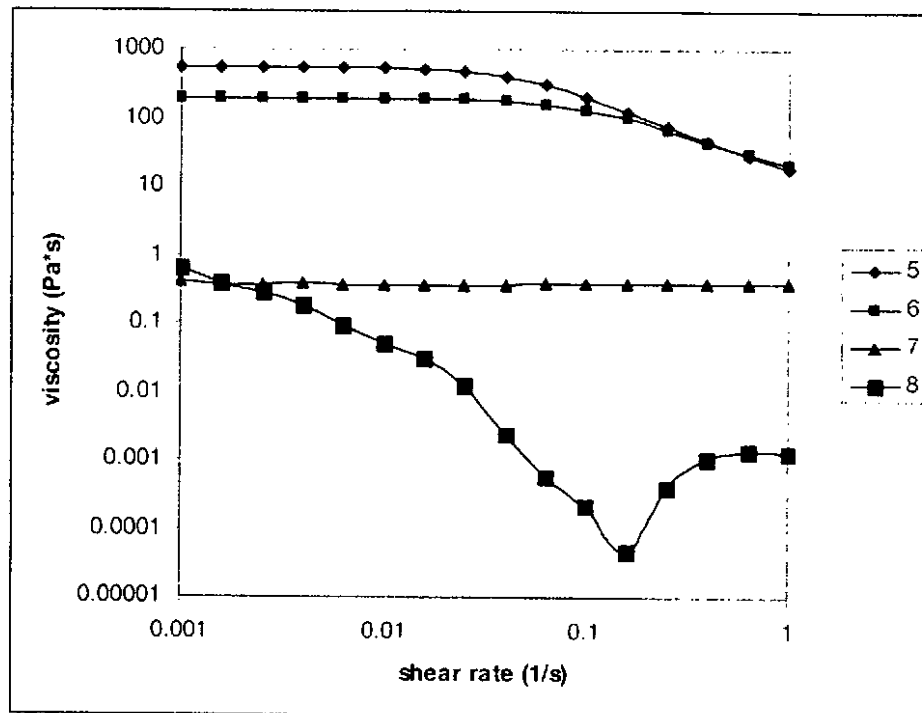


FIG. 2

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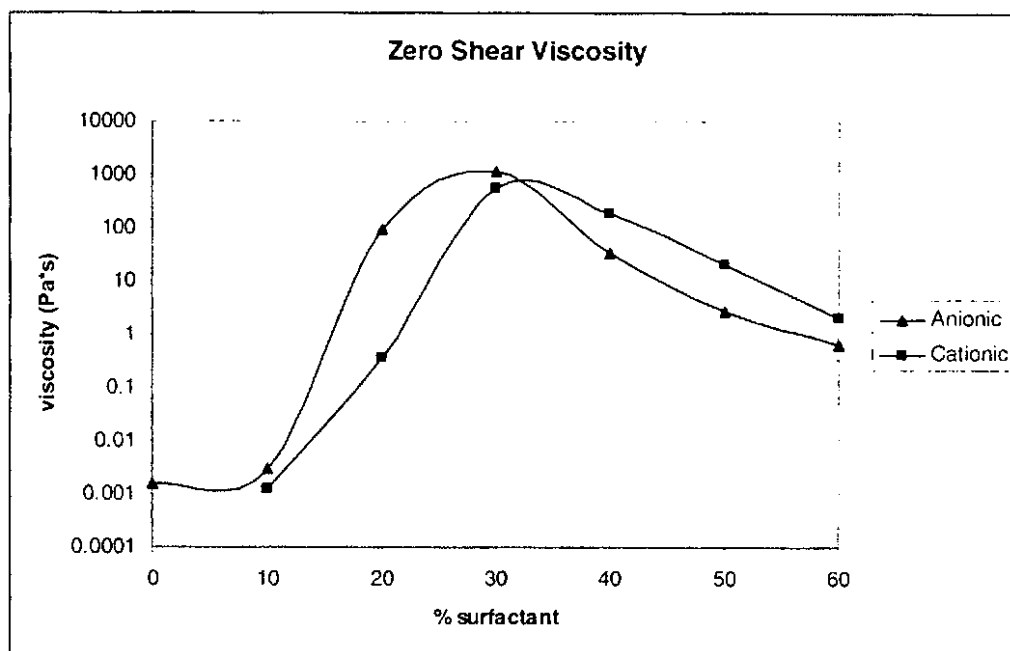


FIG. 3

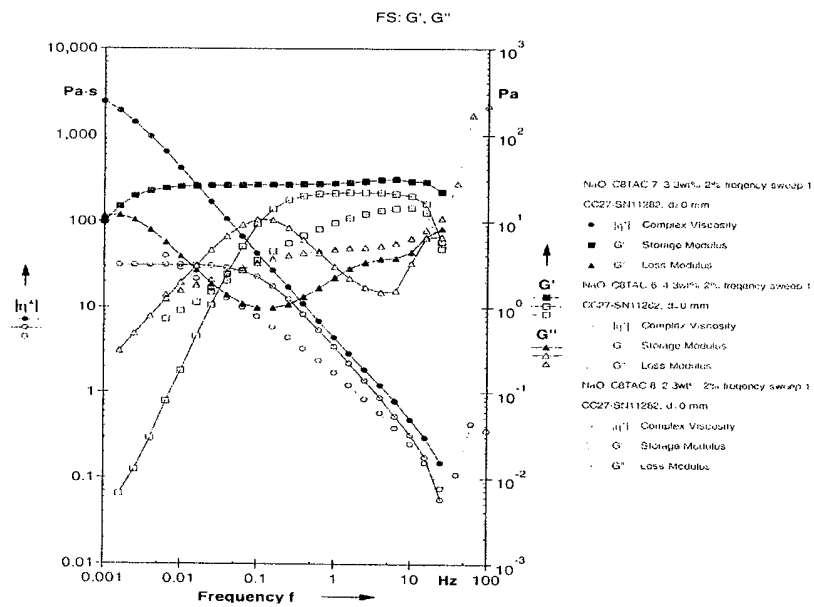


FIG. 4

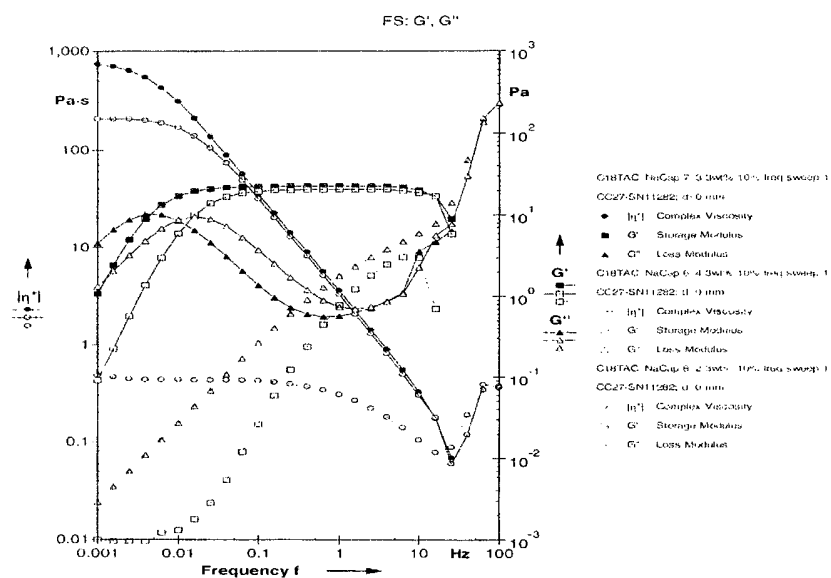


FIG. 5

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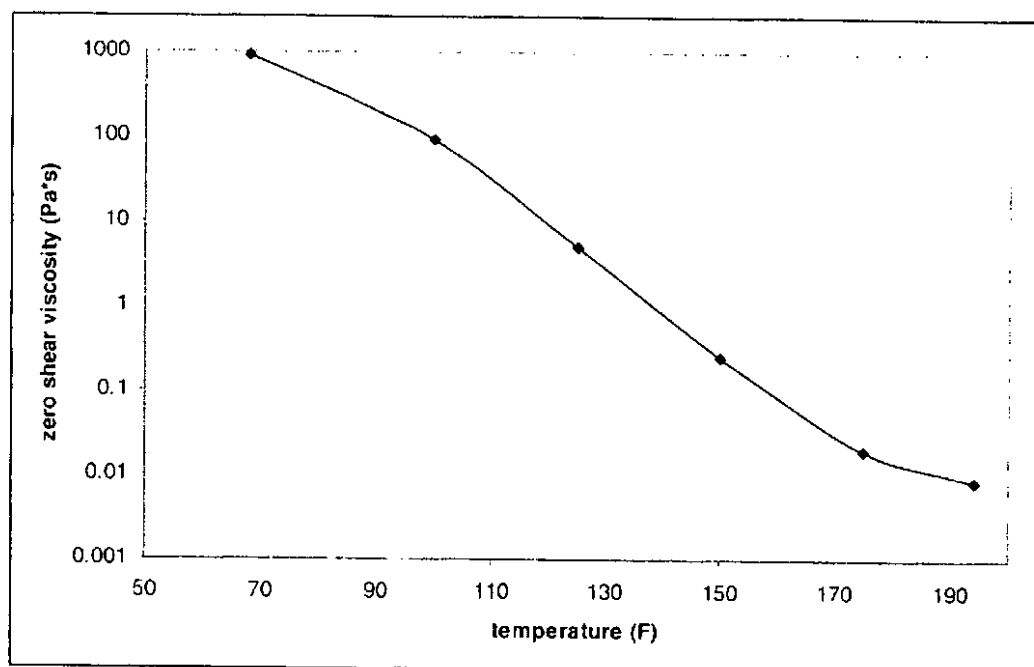


FIG. 6

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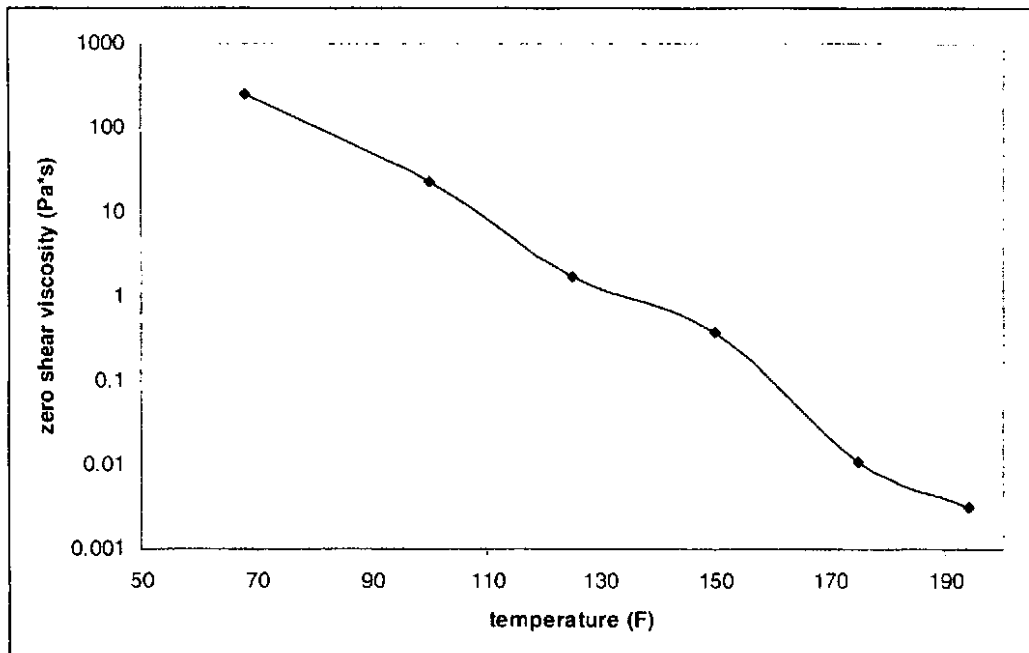


FIG. 7

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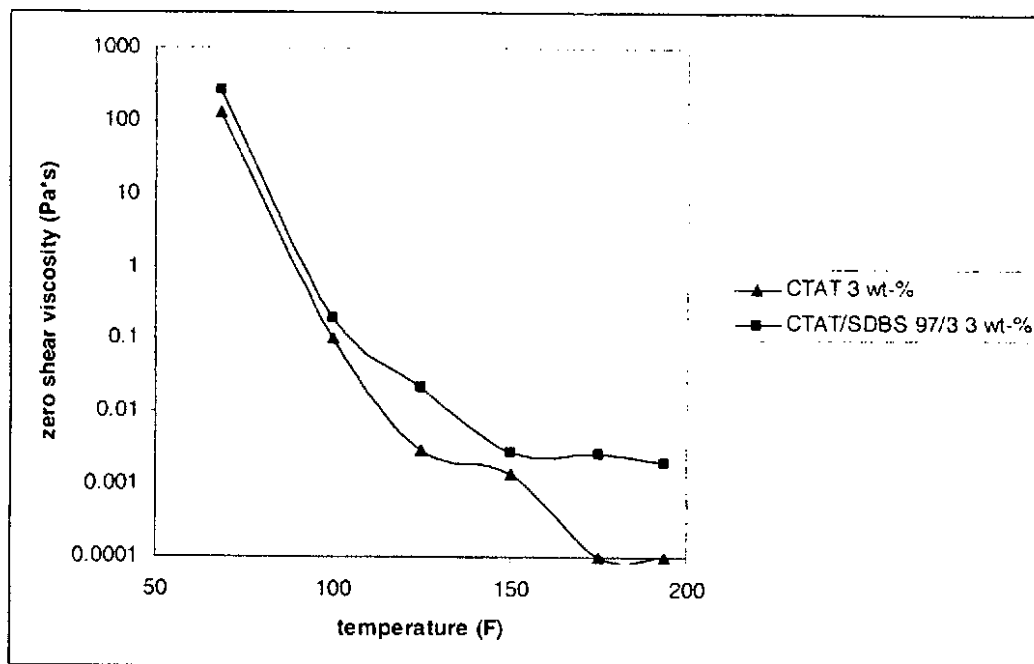


FIG. 8



FIG. 9

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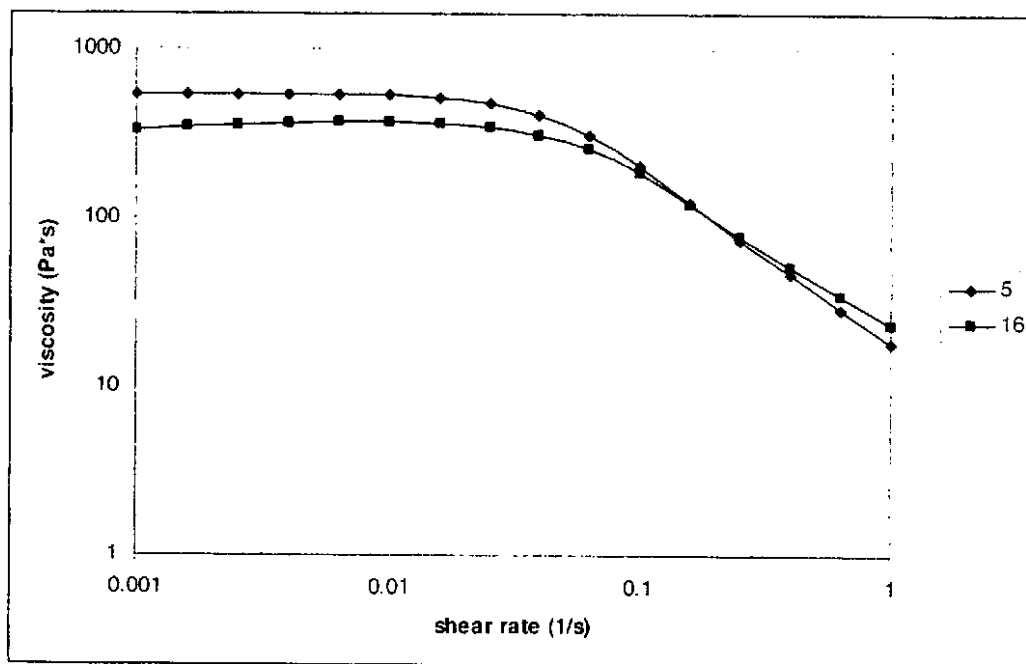


FIG. 10

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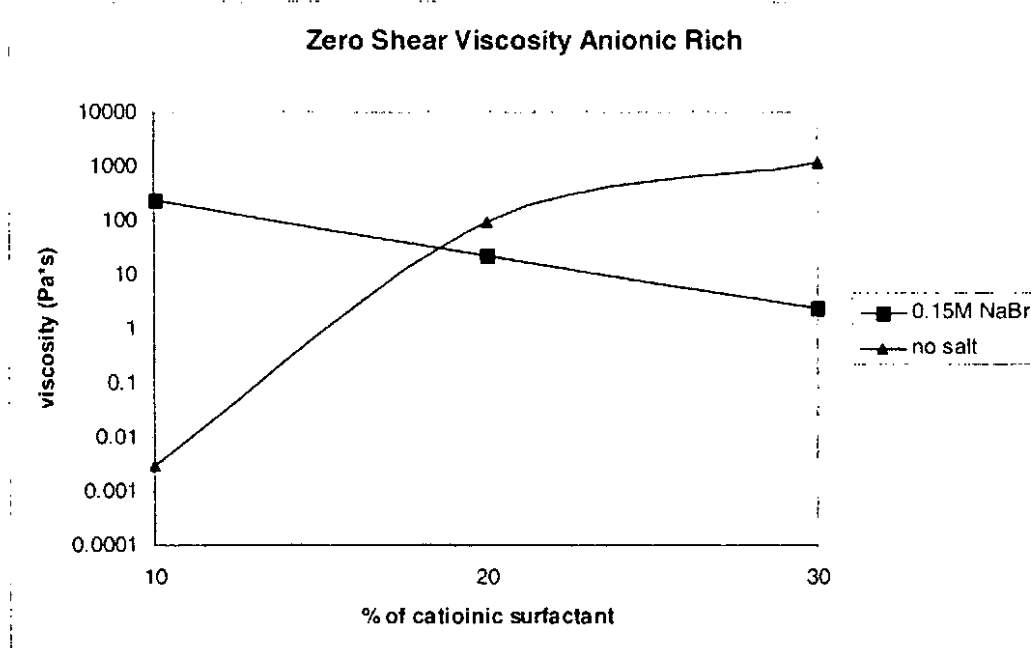


FIG. 11

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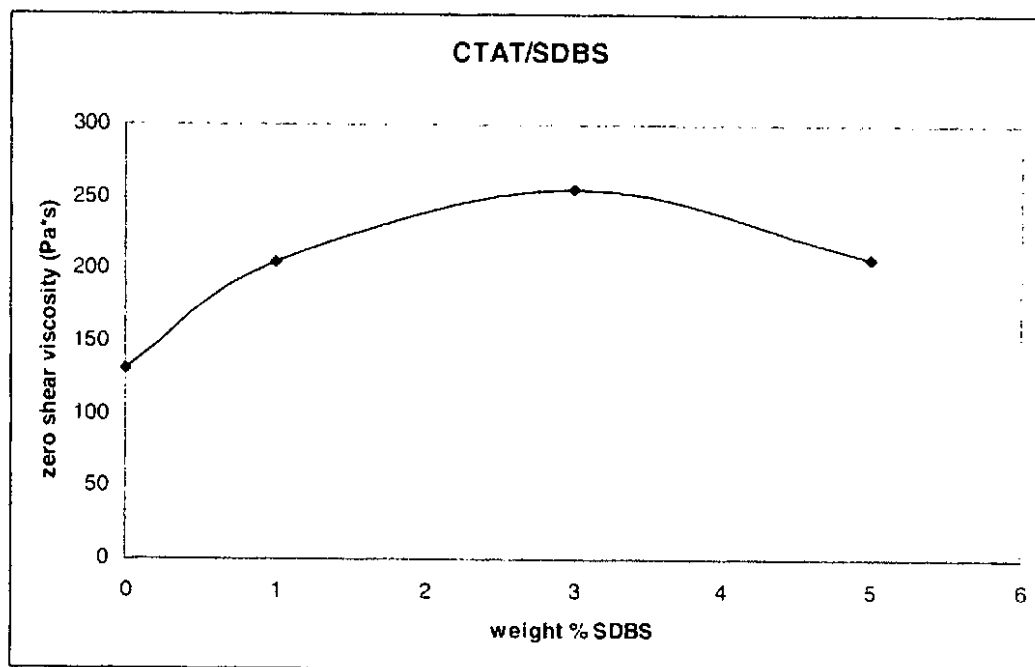


FIG. 12

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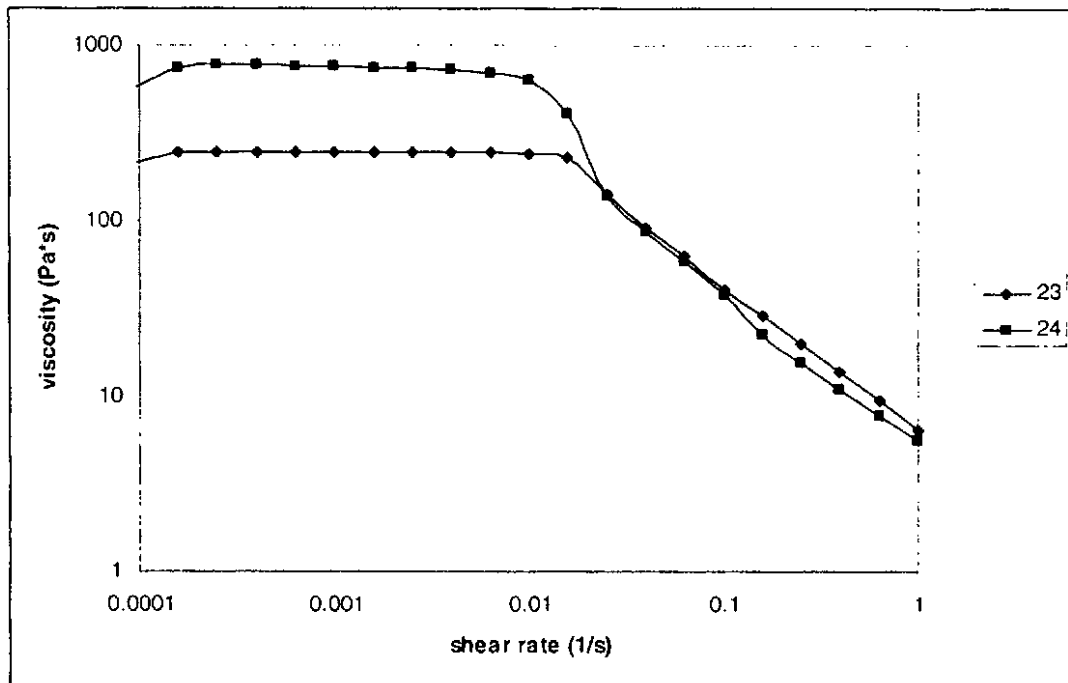


FIG. 13

DOC.
PRESENTACION
SOLICITUD
INTERNACIONAL

PATENT COOPERATION TREATY

From the RECEIVING OFFICE

To: A A Thornton & Co 235 High Holborn London WC1V 7LE	RECEIVED 24 MAR 2010
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PCT

**NOTIFICATION OF THE INTERNATIONAL
APPLICATION NUMBER AND OF THE
INTERNATIONAL FILING DATE**

(PCT Rule 20.2(c))

Date of mailing <i>(day/month/year)</i>		19 MAR 2010
Applicant's or agent's file reference PC/P/N/27846		IMPORTANT NOTIFICATION
International application No. PCT/GB2010/000473	International filing date <i>(day/month/year)</i> 17/03/2010	Priority date <i>(day/month/year)</i> 07/04/2009
Applicant Halliburton Energy Services Inc et al		
Title of the invention Viscoelastic surfactants and methods of making and using same		

1. The applicant is hereby notified that the international application has been accorded the international application number and the international filing date indicated above.	
2. The applicant is further notified that the record copy of the international application:	
☒	was transmitted to the International Bureau on 19 MAR 2010
☐	has not yet been transmitted to the International Bureau for the reason indicated below and a copy of this notification has been sent to the International Bureau*:
☐	because the necessary national security clearance has not yet been obtained.
☐	because <i>(reason to be specified):</i>
* The International Bureau monitors the transmittal of the record copy by the receiving Office and will notify the applicant (with Form PCT/IB/301) of its receipt. Should the record copy not have been received by the expiration of 14 months from the priority date, the International Bureau will notify the applicant (Rule 22.1(c)).	

Name and mailing address of the receiving Office Intellectual Property Office Cardiff Road, Newport South Wales NP10 8QQ	Authorized officer Steve Bevan
Facsimile No.	Telephone No. 01633 814588

Form PCT/RO/105 (July 2008)

Intellectual Property Office is an operating name of the Patent Office

PCT

REQUEST

The undersigned requests that the present international application be processed according to the Patent Cooperation Treaty.

For receiving Office use only

International Application No.

International Filing Date

Name of receiving Office and "PCT International Application"

Applicant's or agent's file reference
(if desired) (12 characters maximum) PC/P/N/27846

Box No. I TITLE OF INVENTION	
VISCOELASTIC SURFACTANTS AND METHODS OF MAKING AND USING SAME	
Box No. II APPLICANT ☐ This person is also inventor	
Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)	
HALLIBURTON ENERGY SERVICES, INC. P O Box 1431 Duncan Oklahoma 73536 US	
Telephone No.	
Facsimile No.	
Applicant's registration No. with the Office	
State (that is, country) of nationality: US	
State (that is, country) of residence: US	
This person is applicant for the purposes of: ☐ all designated States ☒ all designated States except the United States of America ☐ the United States of America only ☐ the States indicated in the Supplemental Box	
Box No. III FURTHER APPLICANT(S) AND/OR (FURTHER) INVENTOR(S)	
☒ Further applicants and or (further) inventors are indicated on a continuation sheet.	
Box No. IV AGENT OR COMMON REPRESENTATIVE; OR ADDRESS FOR CORRESPONDENCE	
The person identified below is hereby has been appointed to act on behalf of the applicant(s) before the competent International Authorities as: ☒ agent ☐ common representative	
Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.)	
CURTIS, Philip, Anthony, A A Thornton & Co 235 High Holborn London WC1V 7LE GB	
Telephone No. +44 20 7405 4044	
Facsimile No. +44 20 7405 3580	
Agent's registration No. with the Office	
☐ Address for correspondence: Mark this check-box where no agent or common representative is has been appointed and the space above is used instead to indicate a special address to which correspondence should be sent.	

Box No. III FURTHER APPLICANT(S) AND/OR (FURTHER) INVENTOR(S)	
<i>If none of the following sub-boxes is used, this sheet should not be included in the request.</i>	
Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.) VAN ZANTEN, Ryan, 4335 Tylergate Drive Spring Texas 77373 US	This person is: ☐ applicant only ☒ applicant and inventor ☐ inventor only (If this check-box is marked, do not fill in below.) Applicant's registration No. with the Office
State (that is, country) of nationality: US	State (that is, country) of residence: US
This person is applicant for the purposes of: ☐ all designated States ☐ all designated States except the United States of America ☒ the United States of America only ☐ the States indicated in the Supplemental Box	
Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.) HARRISON, Douglas, J, 11823 Brantley Haven Drive Tomball Texas 77375 US	This person is: ☐ applicant only ☒ applicant and inventor ☐ inventor only (If this check-box is marked, do not fill in below.) Applicant's registration No. with the Office
State (that is, country) of nationality: US	State (that is, country) of residence: US
This person is applicant for the purposes of: ☐ all designated States ☐ all designated States except the United States of America ☒ the United States of America only ☐ the States indicated in the Supplemental Box	
Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.) CURTIS, Philip, Anthony, A A Thornton & Co 235 High Holborn London WC1V 7LE GB	This person is: ☒ applicant only ☐ applicant and inventor ☐ inventor only (If this check-box is marked, do not fill in below.) Applicant's registration No. with the Office
State (that is, country) of nationality: GB	State (that is, country) of residence: GB
This person is applicant for the purposes of: ☐ all designated States ☐ all designated States except the United States of America ☐ the United States of America only ☒ the States indicated in the Supplemental Box	
Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)	This person is: ☐ applicant only ☐ applicant and inventor ☐ inventor only (If this check-box is marked, do not fill in below.) Applicant's registration No. with the Office
State (that is, country) of nationality:	State (that is, country) of residence:
This person is applicant for the purposes of: ☐ all designated States ☐ all designated States except the United States of America ☐ the United States of America only ☐ the States indicated in the Supplemental Box	
☐ Further applicants and or (further) inventors are indicated on another continuation sheet	

Supplemental Box
If the Supplemental Box is not used, this sheet should not be included in the request.

1. *If, in any of the Boxes, except Boxes Nos. VIII(i) to (iv) for which a special continuation box is provided, the space is insufficient to furnish all the information: in such case, write "Continuation of Box No. ..." (indicate the number of the Box) and furnish the information in the same manner as required according to the captions of the Box in which the space was insufficient, in particular:*

(i) *if more than one person is to be indicated as applicant and/or inventor and no "continuation sheet" is available: in such case, write "Continuation of Box No. III" and indicate for each additional person the same type of information as required in Box No. III. The country of the address indicated in this Box is the applicant's State (that is, country of residence if no State of residence is indicated below;*

(ii) *if, in Box No. II or in any of the sub-boxes of Box No. III, the indication "the States indicated in the Supplemental Box" is checked: in such case, write "Continuation of Box No. II" or "Continuation of Box No. III" or "Continuation of Boxes No. II and No. III" (as the case may be), indicate the name of the applicant(s) involved and, next to each such name, the State(s) (and or, where applicable, ARIPO, Eurasian, European or OAPI patent) for the purposes of which the named person is applicant;*

(iii) *if, in Box No. II or in any of the sub-boxes of Box No. III, the inventor or the inventor/applicant is not inventor for the purposes of all designated States or for the purposes of the United States of America: in such case, write "Continuation of Box No. II" or "Continuation of Box No. III" or "Continuation of Boxes No. II and No. III" (as the case may be), indicate the name of the inventor(s) and, next to each such name, the State(s) (and or, where applicable, ARIPO, Eurasian, European or OAPI patent) for the purposes of which the named person is inventor;*

(iv) *if, in addition to the agents indicated in Box No. IV, there are further agents: in such case, write "Continuation of Box No. IV" and indicate for each further agent the same type of information as required in Box No. IV;*

(v) *if, in Box No. VI, there are more than three earlier applications whose priority is claimed: in such case, write "Continuation of Box No. VI" and indicate for each additional earlier application the same type of information as required in Box No. VI.*

2. *If the applicant intends to make an indication of the wish that the international application be treated, in certain designated States, as an application for a patent of addition, certificate of addition, inventor's certificate of addition or utility certificate of addition: in such a case, write the name or two-letter code of each designated State concerned and the indication "patent of addition," "certificate of addition," "inventor's certificate of addition" or "utility certificate of addition," the number of the parent application or parent patent or other parent grant and the date of grant of the parent patent or other parent grant or the date of filing of the parent application (Rules 4.1 I (a)(iii) and 49bis.1(a) or (b)).*

3. *If the applicant intends to make an indication of the wish that the international application be treated, in the United States of America, as a continuation or continuation-in-part of an earlier application: in such a case, write "United States of America" or "US" and the indication "continuation" or "continuation-in-part" and the number and the filing date of the parent application (Rules 4.1 I (a)(iv) and 49bis.1(d)).*

CONTINUATION OF BOX III

P A Curtis is applicant for Malawi (MW) only.

CONTINUATION OF BOX NO IV

Further agents of A A Thornton & Co., 235 High Holborn, London, WC1V 7LE, United Kingdom, who have been appointed to act on behalf of the applicants before the competent International Authorities are:

LERWILL, John,
GILL, Ian Stephen,
HEDGES, Martin Nicholas,
TURNER, Craig Robert,
BENNETT, Adrian Robert James,
SOUTH, Nicholas Geoffrey
JENNINGS, Michael John
COTTRILL, Emily Elizabeth Helen
PATEL, Nimesh Prakash
AMERY, Marcus James

Box No. V DESIGNATIONS

The filing of this request constitutes under Rule 4.9(a), the designation of all Contracting States bound by the PCT on the international filing date, for the grant of every kind of protection available and, where applicable, for the grant of both regional and national patents. However,

- ☐ DE Germany is not designated for any kind of national protection
☐ JP Japan is not designated for any kind of national protection
☐ KR Republic of Korea is not designated for any kind of national protection
☐ RU Russian Federation is not designated for any kind of national protection

(The check-boxes above may only be used to exclude irrevocably the designations concerned if, at the time of filing or subsequently under Rule 26bis.1, the international application contains in Box No. VI a priority claim to an earlier national application filed in the particular State concerned, in order to avoid the ceasing of the effect, under the national law, of this earlier national application.)

Box No. VI PRIORITY CLAIM

The priority of the following earlier application(s) is hereby claimed:

Filing date of earlier application (day month year)	Number of earlier application	Where earlier application is:		
		national application: country or Member of WTO	regional application: regional Office	international application: receiving Office
item (1) 07/04/09 (07 April 2009)	12/419,893	US		
item (2)				
item (3)				

☐ Further priority claims are indicated in the Supplemental Box.

Transmit certified copy: the receiving Office is requested to prepare and transmit to the International Bureau a certified copy of the earlier application(s) *(only if the earlier application was filed with the Office which for the purposes of this international application is the receiving Office)* identified above as:

- ☐ all items ☐ item (1) ☐ item (2) ☐ item (3) ☐ other, see Supplemental Box

Restore the right of priority: the receiving Office is requested to restore the right of priority for the earlier application(s) identified above or in the Supplemental Box as item(s) (). *(See also the Notes to Box No. VI; further information must be provided to support a request to restore the right of priority.)*

Incorporation by reference: where an element of the international application referred to in Article 11(1)(ii)(d) or (e) or a part of the description, claims or drawings referred to in Rule 20.5(a) is not otherwise contained in this international application but is completely contained in an earlier application whose priority is claimed on the date on which one or more elements referred to in Article 11(1)(ii) were first received by the receiving Office, that element or part is, subject to confirmation under Rule 20.6, incorporated by reference in this international application for the purposes of Rule 20.6.

Box No. VII INTERNATIONAL SEARCHING AUTHORITY

Choice of International Searching Authority (ISA) (if two or more International Searching Authorities are competent to carry out the international search, indicate the Authority chosen; the two-letter code may be used):

ISA / EP

Request to use results of earlier search: reference to that search (if an earlier search has been carried out by or requested from the International Searching Authority):

Date (day month year) Number Country (or regional Office)

Box No. VIII DECLARATIONS

The following declarations are contained in Boxes Nos. VIII (i) to (v) mark the applicable check-boxes below and indicate in the right column the number of each type of declaration:

- ☐ Box No. VIII (i) Declaration as to the identity of the inventor
☐ Box No. VIII (ii) Declaration as to the applicant's entitlement, as at the international filing date, to apply for and be granted a patent
☐ Box No. VIII (iii) Declaration as to the applicant's entitlement, as at the international filing date, to claim the priority of the earlier application
☐ Box No. VIII (iv) Declaration of inventorship (only for the purposes of the designation of the United States of America)
☐ Box No. VIII (v) Declaration as to non-prejudicial disclosures or exceptions to lack of novelty

Number of
declarations

Box No. IX CHECK LIST: LANGUAGE OF FILING		
This international application contains: (a) on paper, the following number of sheets: request (including declaration and supplemental sheets) : 5 description (excluding sequence listing and/or tables related thereto) : 18 claims : 3 abstract : 1 drawings : 13 Sub-total number of sheets : 40 sequence listing tables related thereto <i>(for both, actual number of sheets if filed on paper, whether or not also filed in electronic form; see (c) below)</i> Total number of sheets : 40 (b) ☐ only in electronic form (Section 801(a)(i)) (i) ☐ sequence listing (ii) ☐ tables related thereto (c) ☐ also in electronic form (Section 801(a)(ii)) (i) ☐ sequence listing (ii) ☐ tables related thereto Type and number of carriers (diskette, CD-ROM, CD-R or other) on which are contained the ☐ sequence listing: ☐ tables related thereto: <i>additional copies to be indicated under items 9(ii) and/or 10(ii), in right column)</i>	This international application is accompanied by the following item(s) <i>mark the applicable check-boxes below and indicate in right column the number of each item:</i> 1. ☒ fee calculation sheet : 1 2. ☐ original separate power of attorney 3. ☐ original general power of attorney 4. ☐ copy of general power of attorney; reference number, if any: 5. ☐ statement explaining lack of signature 6. ☒ priority documents identified in Box No. VI as item(s): USSN 12/419,893 : 1 7. ☐ translation of international application into <i>language</i>: 8. ☐ separate indications concerning deposited microorganism or other biological material 9. ☐ sequence listing in electronic form <i>(indicate type and number of carriers)</i> (i) ☐ copy submitted for the purposes of international search under Rule 13ter only (and not as part of the international application) : (ii) ☐ <i>(only where check-box (b)(i) or (c)(ii) is marked in left column)</i> additional copies including, where applicable, the copy for the purposes of international search under Rule 13ter : (iii) ☐ together with relevant statement as to the identity of the copy or copies with the sequence listing mentioned in left column : 10. ☐ tables in electronic form related to sequence listing <i>(indicate type and number of carriers)</i> (i) ☐ copy submitted for the purposes of international search under Section 802(b-quater) only (and not as part of the international application) (ii) ☐ <i>(only where check-box (b)(ii) or (c)(iii) is marked in left column)</i> additional copies including, where applicable, the copy for the purposes of international search under Section 802(b-quater) (iii) ☐ together with relevant statement as to the identity of the copy or copies with the tables mentioned in left column 11. ☒ other <i>specify</i>: Letter : 1	
Figure of the drawings which should accompany the abstract: Fig 1	Language of filing of the international application: English	
Box No. X SIGNATURE OF APPLICANT, AGENT OR COMMON REPRESENTATIVE <i>Next to each signature indicate the name of the person signing and the capacity in which the person signs (if such capacity is not obvious from reading the request)</i> CURTIS, Philip, Anthony, 17 MARCH 2010		

For receiving Office use only	
1. Date of actual receipt of the purported international application:	2. Drawings: ☐ received:
3. Corrected date of actual receipt due to later but timely received papers or drawings completing the purported international application:	☐ not received:
4. Date of timely receipt of the required corrections under PCT Article 17(2):	6. ☐ Transmittal of search copy delayed until search fee is paid
5. International Searching Authority (if two or more are competent) ISA /	

For International Bureau use only
Date of receipt of the record copy by the International Bureau:

PATENT COOPERATION TREATY

01 JUN 2010

From the INTERNATIONAL SEARCHING AUTHORITY

PCT

To: A.A. Thornton & Co. Attn. Curtis, Philip Anthony 235 High Holborn London WC1V 7LE GRANDE BRETAGNE Initials: GPV Date: 27/5/2010 due 7/8/2010	RECEIVED 25 MAY 2010 NOTICE OF TRANSMITTAL NOTIFICATION OF TRANSMITTAL OF THE INTERNATIONAL SEARCH REPORT AND THE WRITTEN OPINION OF THE INTERNATIONAL SEARCHING AUTHORITY, OR THE DECLARATION (PCT Rule 44.1)
Applicant's or agent's file reference PC/P/N/27846	Date of mailing (day/month/year) 26/05/2010
International application No. PCT/GB2010/000473	International filing date (day/month/year) 17/03/2010
Applicant HALLIBURTON ENERGY SERVICES, INC.	

1. ☒ The applicant is hereby notified that the international search report and the written opinion of the International Searching Authority have been established and are transmitted herewith.

Filing of amendments and statement under Article 19:
The applicant is entitled, if he so wishes, to amend the claims of the International Application (see Rule 46):

When? The time limit for filing such amendments is normally two months from the date of transmittal of the International Search Report.

Where? Directly to the International Bureau of WIPO, 34 chemin des Colombettes
1211 Geneva 20, Switzerland, Facsimile No.: (41-22) 338.82.70

For more detailed instructions, see the notes on the accompanying sheet.

2. ☐ The applicant is hereby notified that no international search report will be established and that the declaration under Article 17(2)(a) to that effect and the written opinion of the International Searching Authority are transmitted herewith.

3. ☐ **With regard to any protest** against payment of (an) additional fee(s) under Rule 40.2, the applicant is notified that:

☐ the protest together with the decision thereon has been transmitted to the International Bureau together with the applicant's request to forward the texts of both the protest and the decision thereon to the designated Offices.

☐ no decision has been made yet on the protest; the applicant will be notified as soon as a decision is made.

4. **Reminders**

Shortly after the expiration of **18 months** from the priority date, the international application will be published by the International Bureau. If the applicant wishes to avoid or postpone publication, a notice of withdrawal of the international application, or of the priority claim, must reach the International Bureau as provided in Rules 90bis.1 and 90bis.3, respectively, before the completion of the technical preparations for international publication.

The applicant may submit comments on an informal basis on the written opinion of the International Searching Authority to the International Bureau. The International Bureau will send a copy of such comments to all designated Offices unless an International preliminary examination report has been or is to be established. These comments would also be made available to the public but not before the expiration of 30 months from the priority date.

Within **19 months** from the priority date, but only in respect of some designated Offices, a demand for international preliminary examination must be filed if the applicant wishes to postpone the entry into the national phase **until 30 months** from the priority date (in some Offices even later); otherwise, the applicant must, **within 20 months** from the priority date, perform the prescribed acts for entry into the national phase before those designated Offices.

In respect of other designated Offices, the time limit of **30 months** (or later) will apply even if no demand is filed within 19 months.

See the Annex to Form PCT/IB/301 and, for details about the applicable time limits, Office by Office, see the *PCT Applicant's Guide*, National Chapters.

Name and mailing address of the International Searching Authority European Patent Office, P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk Tel. (+31-70) 340-2040 Fax: (+31-70) 340-3016	Authorized officer Arne Nielsen-Hannerup
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NOTES TO FORM PCT/ISA/220

These Notes are intended to give the basic instructions concerning the filing of amendments under article 19. The Notes are based on the requirements of the Patent Cooperation Treaty, the Regulations and the Administrative Instructions under that Treaty. In case of discrepancy between these Notes and those requirements, the latter are applicable. For more detailed information, see also the *PCT Applicant's Guide*.

In these Notes, "Article", "Rule"; and "Section" refer to the provisions of the PCT, the PCT Regulations and the PCT Administrative Instructions, respectively.

INSTRUCTIONS CONCERNING AMENDMENTS UNDER ARTICLE 19

The applicant has, after having received the international search report and the written opinion of the International Searching Authority, one opportunity to amend the claims of the international application. It should however be emphasized that, since all parts of the international application (claims, description and drawings) may be amended during the international preliminary examination procedure, there is usually no need to file amendments of the claims under Article 19 except where, e.g. the applicant wants the latter to be published for the purposes of provisional protection or has another reason for amending the claims before international publication. Furthermore, it should be emphasized that provisional protection is available in some States only (see *PCT Applicant's Guide*, Annex B).

The attention of the applicant is drawn to the fact that amendments to the claims under Article 19 are not allowed where the International Searching Authority has declared, under Article 17(2), that no international search report would be established (see *PCT Applicant's Guide*, International Phase, paragraph 296).

What parts of the international application may be amended?

Under Article 19, only the claims may be amended.

During the international phase, the claims may also be amended (or further amended) under Article 34 before the International Preliminary Examining Authority. The description and drawings may only be amended under Article 34 before the International Examining Authority.

Upon entry into the national phase, all parts of the international application may be amended under Article 28 or, where applicable, Article 41.

When?

Within 2 months from the date of transmittal of the international search report or 16 months from the priority date, whichever time limit expires later. It should be noted, however, that the amendments will be considered as having been received on time if they are received by the International Bureau after the expiration of the applicable time limit but before the completion of the technical preparations for international publication (Rule 46.1).

Where not to file the amendments?

The amendments may only be filed with the International Bureau and not with the receiving Office or the International Searching Authority (Rule 46.2).

Where a demand for international preliminary examination has been/is filed, see below.

How?

Either by cancelling one or more entire claims, by adding one or more new claims or by amending the text of one or more of the claims as filed.

A replacement sheet or sheets containing a complete set of claims in replacement of all the claims previously filed must be submitted.

Where a claim is cancelled, no renumbering of the other claims is required. In all cases where claims are renumbered, they must be renumbered consecutively in Arabic numerals (Section 205(a)).

The amendments must be made in the language in which the international application is to be published.

What documents must/may accompany the amendments?

Letter (Section 205(b)):

The amendments must be submitted with a letter.

The letter will not be published with the international application and the amended claims. It should not be confused with the "Statement under Article 19(1)" (see below, under "Statement under Article 19(1)").

The letter must be in English or French, at the choice of the applicant. However, if the language of the international application is English, the letter must be in English; if the language of the international application is French, the letter must be in French.

NOTES TO FORM PCT/ISA/220 (continued)

The letter must indicate the differences between the claims as filed and the claims as amended. It must, in particular, indicate, in connection with each claim appearing in the international application (it being understood that identical indications concerning several claims may be grouped), whether

- (i) the claim is unchanged;
- (ii) the claim is cancelled;
- (iii) the claim is new;
- (iv) the claim replaces one or more claims as filed;
- (v) the claim is the result of the division of a claim as filed.

The following examples illustrate the manner in which amendments must be explained in the accompanying letter:

1. [Where originally there were 48 claims and after amendment of some claims there are 51]:
"Claims 1 to 29, 31, 32, 34, 35, 37 to 48 replaced by amended claims bearing the same numbers; claims 30, 33 and 36 unchanged; new claims 49 to 51 added."
2. [Where originally there were 15 claims and after amendment of all claims there are 11]:
"Claims 1 to 15 replaced by amended claims 1 to 11."
3. [Where originally there were 14 claims and the amendments consist in cancelling some claims and in adding new claims]:
"Claims 1 to 6 and 14 unchanged; claims 7 to 13 cancelled; new claims 15, 16 and 17 added." or
"Claims 7 to 13 cancelled; new claims 15, 16 and 17 added; all other claims unchanged."
4. [Where various kinds of amendments are made]:
"Claims 1–10 unchanged; claims 11 to 13, 18 and 19 cancelled; claims 14, 15 and 16 replaced by amended claim 14; claim 17 subdivided into amended claims 15, 16 and 17; new claims 20 and 21 added."

"Statement under article 19(1)" (Rule 46.4)

The amendments may be accompanied by a statement explaining the amendments and indicating any impact that such amendments might have on the description and the drawings (which cannot be amended under Article 19(1)).

The statement will be published with the international application and the amended claims.

It must be in the language in which the international application is to be published.

It must be brief, not exceeding 500 words if in English or if translated into English.

It should not be confused with and does not replace the letter indicating the differences between the claims as filed and as amended. It must be filed on a separate sheet and must be identified as such by a heading, preferably by using the words "Statement under Article 19(1)."

It may not contain any disparaging comments on the international search report or the relevance of citations contained in that report. Reference to citations, relevant to a given claim, contained in the international search report may be made only in connection with an amendment of that claim.

Consequence if a demand for international preliminary examination has already been filed

If, at the time of filing any amendments and any accompanying statement, under Article 19, a demand for international preliminary examination has already been submitted, the applicant must preferably, at the time of filing the amendments (and any statement) with the International Bureau, also file with the International Preliminary Examining Authority a copy of such amendments (and of any statement) and, where required, a translation of such amendments for the procedure before that Authority (see Rules 55.3(a) and 62.2, first sentence). For further information, see the Notes to the demand form (PCT/IPEA/401).

If a demand for international preliminary examination is made, the written opinion of the International Searching Authority will, except in certain cases where the International Preliminary Examining Authority did not act as International Searching Authority and where it has notified the International Bureau under Rule 66.1 bis(b), be considered to be a written opinion of the International Preliminary Examining Authority. If a demand is made, the applicant may submit to the International Preliminary Examining Authority a reply to the written opinion together, where appropriate, with amendments before the expiration of 3 months from the date of mailing of Form PCT/ISA/220 or before the expiration of 22 months from the priority date, whichever expires later (Rule 43 bis.1(c)).

Consequence with regard to translation of the international application for entry into the national phase

The applicant's attention is drawn to the fact that, upon entry into the national phase, a translation of the claims as amended under Article 19 may have to be furnished to the designated/elected Offices, instead of, or in addition to, the translation of the claims as filed.

For further details on the requirements of each designated/elected Office, see the *PCT Applicant's Guide*, National Chapters.

PATENT COOPERATION TREATY

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference PC/P/N/27846	FOR FURTHER ACTION see Form PCT/ISA/220 as well as, where applicable, item 5 below.	
International application No. PCT/GB2010/000473	International filing date (day/month/year) 17/03/2010	(Earliest) Priority Date (day/month/year) 07/04/2009
Applicant HALLIBURTON ENERGY SERVICES, INC.		

This international search report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This international search report consists of a total of 4 sheets.



It is also accompanied by a copy of each prior art document cited in this report.

1. Basis of the report

a. With regard to the language, the international search was carried out on the basis of:



the international application in the language in which it was filed



a translation of the international application into _____, which is the language of a translation furnished for the purposes of international search (Rules 12.3(a) and 23.1(b))

b. ☐

This international search report has been established taking into account the rectification of an obvious mistake authorized by or notified to this Authority under Rule 91 (Rule 43.6bis(a)).

c. ☐

With regard to any nucleotide and/or amino acid sequence disclosed in the international application, see Box No. I.

2. ☐

Certain claims were found unsearchable (See Box No. II)

3. ☐

Unity of invention is lacking (see Box No. III)

4. With regard to the title,



the text is approved as submitted by the applicant



the text has been established by this Authority to read as follows:

5. With regard to the abstract,



the text is approved as submitted by the applicant



the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box No. IV. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority

6. With regard to the drawings,

a. the figure of the drawings to be published with the abstract is Figure No. 1



as suggested by the applicant



as selected by this Authority, because the applicant failed to suggest a figure



as selected by this Authority, because this figure better characterizes the invention

b. ☐

none of the figures is to be published with the abstract

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2010/000473

A. CLASSIFICATION OF SUBJECT MATTER

INV. C09K8/035 C09K8/40 C09K8/42 C09K8/60 C09K8/68
E21B43/04

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 C11D

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 practical, 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 2003/019627 A1 (QU QI [US] ET AL SAMUEL MATHEW M [US] ET AL) 30 January 2003 (2003-01-30) claims 1,5; examples 20,21 -----	1-24
X	US 6 468 945 B1 (ZHANG KEWEI [CA]) 22 October 2002 (2002-10-22) column 1, line 54 - line 65; claims 1,7; figure 1; table 1 -----	1-3,5-7, 9-22
X	WO 01/83946 A1 (TRICAN WELL SERVICE LTD [CA]; ZHANG KEWEI [CA]; ONEIL BILL [CA]) 8 November 2001 (2001-11-08) page 1, line 1 - line 5 page 4, line 6 - line 9 page 7, line 3 - line 15; examples 1,4,7; table 1 ----- -/--	1-3,5-22

☒ Further documents are listed in the continuation of Box C.☒ See patent family annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *&* document member of the same patent family

Date of the actual completion of the international search

11 May 2010

Date of mailing of the international search report

26/05/2010

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

Redecker, Michael

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INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2010/000473

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 01/29369 A1 (SCHLUMBERGER TECHNOLOGY CORP [US]) 26 April 2001 (2001-04-26) page 20, line 8 - line 12; claim 1; figure 1 -----	1-3, 5-23
X	US 3 985 686 A (BARRAT CHRISTIAN) 12 October 1976 (1976-10-12) column 5, line 22 - line 39; claim 1; examples 1,2 -----	1-21
X	US 2008/305157 A1 (ENGLISH DOUGLAS S [US] ET AL) 11 December 2008 (2008-12-11) paragraphs [0002], [0004]; example 1 -----	1-21
A	C. TONDRE, C. CAILLET: "Properties of the amphiphilic films in mixed cationic/anionic vesicles: a comprehensive view from a literature analysis" ADV. COLL. INTERF. SCI, vol. 93, 31 December 2001 (2001-12-31), pages 115-134, XP002581807 tables 1,2 -----	1-24

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/GB2010/000473

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2003019627	A1	30-01-2003	NONE
US 6468945	B1	22-10-2002	CA 2257699 A1 30-06-2000
WO 0183946	A1	08-11-2001	AU 5602301 A 12-11-2001 US 2003168217 A1 11-09-2003
WO 0129369	A1	26-04-2001	AT 353947 T 15-03-2007 AU 8011500 A 30-04-2001 CA 2387248 A1 26-04-2001 DE 60033419 T2 29-11-2007 DK 1230468 T3 11-06-2007 EP 1230468 A1 14-08-2002 MX PA02003618 A 14-10-2003 NO 20021684 A 14-06-2002 US 2002132741 A1 19-09-2002 US 6399546 B1 04-06-2002
US 3985686	A	12-10-1976	CA 990666 A1 08-06-1976 DE 2261849 A1 28-06-1973 FR 2164700 A1 03-08-1973 GB 1375450 A 27-11-1974 LU 64487 A1 16-07-1973 NL 7217258 A 22-06-1973 US B310740 I5 28-01-1975
US 2008305157	A1	11-12-2008	NONE

PATENT COOPERATION TREATY

From the
INTERNATIONAL SEARCHING AUTHORITY

PCT

To:

see form PCT/ISA/220

WRITTEN OPINION OF THE
INTERNATIONAL SEARCHING AUTHORITY
(PCT Rule 43bis.1)

Date of mailing
(day/month/year) see form PCT/ISA/210 (second sheet)

Applicant's or agent's file reference
see form PCT/ISA/220

FOR FURTHER ACTION
See paragraph 2 below

International application No.
PCT/GB2010/000473

International filing date (day/month/year)
17.03.2010

Priority date (day/month/year)
07.04.2009

International Patent Classification (IPC) or both national classification and IPC
INV. C09K8/035 C09K8/40 C09K8/42 C09K8/60 C09K8/68 E21B43/04

Applicant
HALLIBURTON ENERGY SERVICES, INC.

1. This opinion contains indications relating to the following items:

- ☒ Box No. I Basis of the opinion
- ☐ Box No. II Priority
- ☐ Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- ☐ Box No. IV Lack of unity of invention
- ☒ Box No. V Reasoned statement under Rule 43bis.1(a)(i) with regard to novelty, inventive step and industrial applicability; citations and explanations supporting such statement
- ☐ Box No. VI Certain documents cited
- ☒ Box No. VII Certain defects in the international application
- ☒ Box No. VIII Certain observations on the international application

2. **FURTHER ACTION**

If a demand for international preliminary examination is made, this opinion will usually be considered to be a written opinion of the International Preliminary Examining Authority ("IPEA") except that this does not apply where the applicant chooses an Authority other than this one to be the IPEA and the chosen IPEA has notified the International Bureau under Rule 66.1bis(b) that written opinions of this International Searching Authority will not be so considered.

If this opinion is, as provided above, considered to be a written opinion of the IPEA, the applicant is invited to submit to the IPEA a written reply together, where appropriate, with amendments, before the expiration of 3 months from the date of mailing of Form PCT/ISA/220 or before the expiration of 22 months from the priority date, whichever expires later.

For further options, see Form PCT/ISA/220.

3. For further details, see notes to Form PCT/ISA/220.

Name and mailing address of the ISA:



European Patent Office

D-80298 Munich
Tel. +49 89 2399 - 0
Fax: +49 89 2399 - 4465

Date of completion of
this opinion

see form
PCT/ISA/210

Authorized Officer

Redecker, Michael

Telephone No. +49 89 2399-2286



WRITTEN OPINION OF THE
INTERNATIONAL SEARCHING AUTHORITY

International application No.
PCT/GB2010/000473

Box No. I Basis of the opinion

1. With regard to the **language**, this opinion has been established on the basis of:
- ☒ the international application in the language in which it was filed
 - ☐ a translation of the international application into , which is the language of a translation furnished for the purposes of international search (Rules 12.3(a) and 23.1 (b)).
2. ☐ This opinion has been established taking into account the **rectification of an obvious mistake** authorized by or notified to this Authority under Rule 91 (Rule 43bis.1(a))
3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, this opinion has been established on the basis of a sequence listing filed or furnished:
- a. (means)
- ☐ on paper
 - ☐ in electronic form
- b. (time)
- ☐ in the international application as filed
 - ☐ together with the international application in electronic form
 - ☐ subsequently to this Authority for the purposes of search
4. ☐ In addition, in the case that more than one version or copy of a sequence listing has been filed or furnished, the required statements that the information in the subsequent or additional copies is identical to that in the application as filed or does not go beyond the application as filed, as appropriate, were furnished.
5. Additional comments:

Box No. V Reasoned statement under Rule 43bis.1(a)(i) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes: Claims	
	No: Claims	<u>1-24</u>
Inventive step (IS)	Yes: Claims	
	No: Claims	<u>1-24</u>
Industrial applicability (IA)	Yes: Claims	<u>1-24</u>
	No: Claims	

2. Citations and explanations

see separate sheet

**WRITTEN OPINION OF THE
INTERNATIONAL SEARCHING AUTHORITY**

International application No.
PCT/GB2010/000473

Box No. VII Certain defects in the international application

The following defects in the form or contents of the international application have been noted:

see separate sheet

Box No. VIII Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

see separate sheet

Re Item V

Reasoned statement with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

Reference is made to the following documents:

- D1 US 2003/019627 A1 (QU QI [US] ET AL SAMUEL MATHEW M [US] ET AL) 30 January 2003 (2003-01-30)
- D2 US 6 468 945 B1 (ZHANG KEWEI [CA]) 22 October 2002 (2002-10-22)
- D3 WO 01/83946 A1 (TRICAN WELL SERVICE LTD [CA]; ZHANG KEWEI [CA]; ONEIL BILL [CA]) 8 November 2001 (2001-11-08)
- D4 WO 01/29369 A1 (SCHLUMBERGER TECHNOLOGY CORP [US]) 26 April 2001 (2001-04-26)
- D5 US 3 985 686 A (BARRAT CHRISTIAN) 12 October 1976 (1976-10-12)
- D6 US 2008/305157 A1 (ENGLISH DOUGLAS S [US] ET AL) 11 December 2008 (2008-12-11)

1. Novelty

Furthermore, the severe lack of clarity mentioned in section VIII notwithstanding, the subject-matter of claims 1-24 is not new in the sense of Article 33(2) PCT, and the criteria of Article 33(1) PCT are therefore not met.

1.1 The document D1 discloses (the references in parentheses applying to this document) a method of reducing fluid loss of a fracturing fluid by providing a fluid comprising a thickening amount of a surfactant forming viscosifying micelles (cl. 1). The viscosity of the fluid is reduced by contact with hydrocarbons (cl. 5).

Example 20 discloses a viscosified fluid comprising erucyl amine oxide and sodium behenyl sulfate, whereas example 21 discloses a fluid comprising erucyl quaternary ammonium chloride and laureth carboxylate.

Therefore, the disclosure of document D1 seems to anticipate the subject matter of independent claims 1 and 22, which are not considered to be novel over D1 in the sense of Article 33(2) PCT.

Dependent claims 2-8, 9-21 (see also the corresponding clarity objection VIII-1), 23, 24 do not contain any features which, in combination with the features of any claim to which they refer, meet the requirements of the PCT in respect of novelty since the respective technical features are disclosed by D1 as cited above.

1.2 The subject matter of claims 1-23 is anticipated by the disclosure of documents D2-D6, see the corresponding passages cited in the search report.

Re Item VII

Certain defects in the international application

1. The unit "Fahrenheit", used throughout the description and the figures, is not recognised in international practice and should be replaced by the appropriate SI unit (Art. 5 and Rule 10 PCT).
2. The origin of the data shown in Fig. 11 is not clear, since the corresponding passage in § 58 refers only to 2 samples, namely samples 1 and 17, while figure 11 shows results for 3 different concentrations of cationic surfactant.

Re Item VIII

Certain observations on the international application

The application does not meet the requirements of Article 6 PCT, because claims 1, 2, 5-7, 9, 11-21 are not clear.

1. The feature of forming a viscosified composition after contact with an aqueous solution in product claim 1 as well as the features disclosed in the product claims 11-21 relate to a method of using the product rather than clearly defining the product per se - said product being represented by the wellbore fluid comprising the surfactant package before it has been contacted with an aqueous solution - in terms of its technical features. The intended limitations are therefore not clear from this claim, contrary to the requirements of Article 6 PCT.

Therefore, said feature disclosed in claim 1 as well as the subject matter of claims 11-21 is considered to be non limiting.

2. Claims 1, 15-20 do not meet the requirements of Article 6 PCT because the matter for which protection is sought is not clearly defined. The claim attempts to define the subject-matter in terms of the result to be achieved, which merely amounts to a statement of the underlying problem, without providing the technical features necessary for achieving this result.

3. An essential feature seems to be missing in claim 1, since said claim discloses a fluid, while the only limiting technical features of said claim are the presence of a surfactant package (see also clarity objection VIII-1), i.e. a definition of the used base fluid is missing. Furthermore, it appears from the disclosure of the description and the examples that all fluids according to the invention are water-based (Art. 6 PCT).

4. The term "wherein the anionic surfactant comprises alkali salts of acids/alkaline salts of acids/sodium salts of acid" used in claim 7 is unclear since said salts in their broad definition are not known in the art as representing surfactants (Art. 6 PCT).

5. The term "about" used in claims 2, 5, 6, 9, 11, 16-20 is vague and leaves the reader in doubt as to the meaning of the technical feature to which it refers, thereby rendering the definition of the subject-matter of said claims unclear (Article 6 PCT).

6. Claim 3 is unclear in defining an amine oxide as a cationic surfactant (Art. 6 PCT)

7. The expression "incorporated herein by reference" used throughout the description is unclear (Art. 5 PCT and GL 4.26) and should be deleted.

8. The definition of the scope of legal protection by elements inside ranges in § 63 of the description is unclear (Art. 5 PCT) and should be deleted.

Possible steps after receipt of the international search report (ISR) and written opinion of the International Searching Authority (WO-ISA)

General information

For all international applications filed on or after 01/01/2004 the competent ISA will establish an ISR. It is accompanied by the WO-ISA. Unlike the former written opinion of the IPEA (Rule 66.2 PCT), the WO-ISA is not meant to be responded to, but to be taken into consideration for further procedural steps. This document explains about the possibilities.

Amending claims under Art. 19 PCT

Within 2 months after the date of mailing of the ISR and the WO-ISA the applicant may file amended claims under Art. 19 PCT directly with the International Bureau of WIPO. The PCT reform of 2004 did not change this procedure. For further information please see Rule 46 PCT as well as form PCT/ISA/220 and the corresponding Notes to form PCT/ISA/220.

Filing a demand for international preliminary examination

In principle, the WO-ISA will be considered as the written opinion of the IPEA. This should, in many cases, make it unnecessary to file a demand for international preliminary examination. If the applicant nevertheless wishes to file a demand this must be done before expiry of 3 months after the date of mailing of the ISR/ WO-ISA or 22 months after priority date, whichever expires later (Rule 54bis PCT). Amendments under Art. 34 PCT can be filed with the IPEA as before, normally at the same time as filing the demand (Rule 66.1 (b) PCT).

If a demand for international preliminary examination is filed and no comments/amendments have been received the WO-ISA will be transformed by the IPEA into an IPRP (International Preliminary Report on Patentability) which would merely reflect the content of the WO-ISA. The demand can still be withdrawn (Art. 37 PCT).

Filing informal comments

After receipt of the ISR/WO-ISA the applicant may file informal comments on the WO-ISA directly with the International Bureau of WIPO. These will be communicated to the designated Offices together with the IPRP (International Preliminary Report on Patentability) at 30 months from the priority date. Please also refer to the next box.

End of the international phase

At the end of the international phase the International Bureau of WIPO will transform the WO-ISA or, if a demand was filed, the written opinion of the IPEA into the IPRP, which will then be transmitted together with possible informal comments to the designated Offices. The IPRP replaces the former IPER (international preliminary examination report).

Relevant PCT Rules and more information

Rule 43 PCT, Rule 43bis PCT, Rule 44 PCT, Rule 44bis PCT, PCT Newsletter 12/2003, OJ 11/2003, OJ 12/2003

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
14 October 2010 (14.10.2010)

PCT

(10) International Publication Number
WO 2010/116117 A1

(51) International Patent Classification:

C09K 8/035 (2006.01) C09K 8/60 (2006.01)
C09K 8/40 (2006.01) C09K 8/68 (2006.01)
C09K 8/42 (2006.01) E21B 43/04 (2006.01)

(21) International Application Number:

PCT/GB2010/000473

(22) International Filing Date:

17 March 2010 (17.03.2010)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

12/419,893 7 April 2009 (07.04.2009) US

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(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

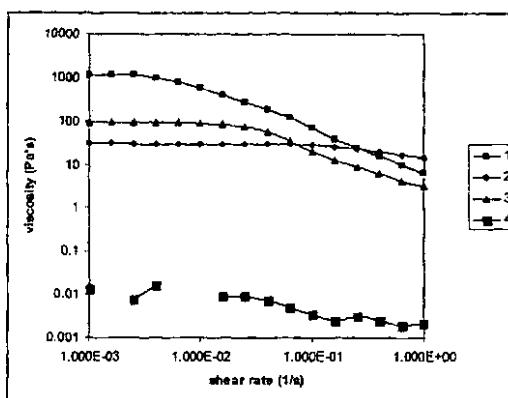
(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT,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

Published:

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

(54) Title: VISCOELASTIC SURFACTANTS AND METHODS OF MAKING AND USING SAME

FIG. 1



(57) Abstract: A method of servicing a wellbore comprising placing downhole a composition comprising a surfactant package comprising a cationic surfactant and anionic surfactant, wherein the surfactant package when contacted with an aqueous solution forms a viscosified composition in the presence of less than about 30 wt.% of a hydrotrope.

**VISCOELASTIC SURFACTANTS AND METHODS OF MAKING AND USING
SAME**

BACKGROUND

Technical Field

[0001] The present disclosure generally relates to wellbore servicing fluids. More particularly, this disclosure relates to viscoelastic surfactants and methods of making and using same.

Background

[0002] Natural resources such as gas, oil, and water residing in a subterranean formation or zone are usually recovered by drilling a wellbore down to the subterranean formation while circulating a drilling fluid in the wellbore. During the drilling of a well bore a drilling fluid may be circulated down through the inside of the drill string, through the drill bit, and to the surface through the annulus between the walls of the well bore and the drill string. The drill string may be a drill pipe, a casing string, or any other suitable conduit. Among other things, the circulating drilling fluid lubricates the drill bit, carries drill cuttings to the surface, and balances the formation pressure exerted on the well bore. One problem associated with the drilling of a well bore may be the undesirable loss of large amounts of the drilling fluid into the subterranean formation. This problem may be referred to as "lost circulation" and the sections of the formation into which the drilling fluid is lost are referred to as "lost circulation zones." In addition to drilling fluids, problems with lost circulation may also be encountered with other fluids, for example, spacer fluids, completion fluids (e.g., brines) and workover fluids that may be circulated in a well bore. Herein a spacer fluid refers to any liquid used to physically separate one special-purpose liquid from another; a completion fluid refers to a solids-free liquid used to facilitate final operations prior to initiation of production; and a workover fluid refers to a well-control fluid, that is used during the performance of maintenance or remedial treatments on a hydrocarbon producing well. A variety of factors may be responsible for lost circulation. For example, the subterranean formation penetrated by the well bore may be highly permeable or may contain fractures or crevices therein. Furthermore, the formation may breakdown under the hydrostatic pressure applied by the fluid, thereby allowing the fluid to be lost into the formation. For instance, fractures in the subterranean formation may be created or

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enhanced due to the hydrostatic pressure of the drilling fluid with the resulting loss of drilling fluid into those fractures.

[0003] A number of methods have been developed to control lost circulation. One method commonly used to control lost circulation involves the placement of lost circulation materials into the lost circulation zone. These lost circulation materials may be placed into the formation for example as lost circulation pills in an attempt to control and/or prevent lost circulation. Conventional lost circulation pills may suffer from a variety of drawbacks such as the large amount of materials needed to achieve desired properties (e.g., viscosities, etc.) and difficulties associated with removing the component materials of the pill once the treatment has been completed. Thus, it would be desirable to develop improved compositions for controlling lost circulation.

SUMMARY

[0004] Disclosed herein is a method of servicing a wellbore comprising placing downhole a composition comprising a surfactant package comprising a cationic surfactant and anionic surfactant, wherein the surfactant package when contacted with an aqueous solution forms a viscosified composition in the presence of less than about 30 wt.% of a hydrotrope.

BRIEF DESCRIPTION OF THE DRAWINGS

[0005] For a more complete understanding of the present disclosure and the advantages thereof, reference is now made to the following brief description, taken in connection with the accompanying drawings and detailed description:

[0006] Figures 1 and 2 are plots of viscosity as a function of shear rate for the samples from Example 1.

[0007] Figure 3 is a plot of viscosity as a function of percent surfactant for the samples from Example 2.

[0008] Figures 4-5 are plots of complex viscosity, storage modulus, and loss modulus as a function of frequency for the samples from Example 3.

[0009] Figures 6-7 is a plot of zero shear viscosity as a function of temperature for the samples from Example 4.

[0010] Figure 8 is a plot of zero shear viscosity as a function of temperature for the samples from Example 5.

[0011] Figure 9 is a plot of complex viscosity, storage modulus, and loss modulus as a function of frequency for the samples from Example 6.

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[0012] Figure 10 is a plot of viscosity and shear stress as a function of shear rate for the samples from Example 6.

[0013] Figure 11 is a plot of viscosity as a function of percentage of cationic surfactant for the samples from Example 6.

[0014] Figure 12 is a plot of zero shear viscosity as a function of weight percentage of SDBS for the samples from Example 7.

[0015] Figure 13 is a plot of viscosity and shear stress as a function of shear rate for the samples from Example 8.

DETAILED DESCRIPTION

[0016] It should be understood at the outset that although an illustrative implementation of one or more embodiments are provided below, the disclosed systems and/or methods may be implemented using any number of techniques, whether currently known or in existence. The disclosure should in no way be limited to the illustrative implementations, drawings, and techniques illustrated below, including the exemplary designs and implementations illustrated and described herein, but may be modified within the scope of the appended claims along with their full scope of equivalents.

[0017] Disclosed herein are compositions (e.g., wellbore servicing compositions) comprising at least one cationic surfactant and at least one anionic surfactant. Such compositions are said to contain a cationic anionic surfactant package (CASP). In an embodiment, the CASP may react with one or more components of the wellbore servicing fluid to form a viscosified composition hereinafter denoted CASP-VC. A CASP-VC of the type described herein may be useful in various wellbore servicing operations. For example, the CASP-VC may be useful in the treatment of wellbores experiencing lost circulation. The components of the CASP and CASP-VC as well as methods of making and using same will be described in more detail later herein.

[0018] In an embodiment, the CASP comprises a cationic surfactant. Surfactants in general are wetting agents that lower the surface tension of a liquid in which they are dissolved, allowing easier spreading and decreasing the interfacial tension between two liquids. Each surfactant has a hydrophilic head that is attracted to water molecules and a hydrophobic tail that repels water and attaches itself to hydrophobic materials such as oil and grease. Herein a cationic surfactant has a positively charged head and a hydrophobic tail comprising a carbon chain. A cationic surfactant suitable for use in this disclosure may have a carbon chain having

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a length of from about 8 to about 24, alternatively from about 8 to about 18, alternatively from about 12 to about 22, alternatively from about 16 to about 24. Examples of cationic surfactants suitable for use in this disclosure include without limitation quaternary ammonium salts, ethoxylated quaternary ammonium salts, amine oxides, or a combination thereof. In an embodiment, the cationic surfactant comprises stearyltrimethylammonium chloride, cetyltrimethylammonium tosylate, cetyltrimethylammonium chloride, cetyltrimethylammonium bromide, myristyltrimethylammonium chloride, myristyltrimethylammonium bromide, dodecyltrimethylammonium chloride, dodecyltrimethylammonium bromide, decyltrimethylammonium chloride, decyltrimethylammonium bromide, octyltrimethylammonium chloride, erucyl bis-(hydroxy ethyl)methylammonium chloride, erucyltrimethylammonium chloride, or a combination thereof. In an embodiment, the cationic surfactant may be present in the CASP in an amount of from about 0.01 weight percent (wt.%) based on the total weight of the CASP to about 99.99 wt.%, alternatively from about 0.1 wt.% to about 99.9 wt.%, alternatively from about 1 wt.% to about 99 wt.%.

[0019] In an embodiment, the CASP comprises an anionic surfactant. Herein an anionic surfactant has a negatively charged head and a hydrophobic tail comprising a carbon chain. An anionic surfactant suitable for use in this disclosure may have carbon chain having a length of from about 8 to about 24, alternatively from about 8 to about 18, alternatively from about 12 to about 22, alternatively from about 18 to about 24. Examples of anionic surfactants suitable for use in this disclosure include without limitation alkali salts of acids, alkali salts of fatty acids, alkaline salts of acids, sodium salts of acid, sodium salts of fatty acid, alkyl sulphates, alkyl ethoxylate, sulphates, sulfonates, soaps, or a combination thereof. In an embodiment, the anionic surfactant comprises sodium oleate, sodium stearate, sodium dodecylbenzenesulfonate, sodium myristate, sodium laurate, sodium decanoate, sodium caprylate, sodium cetyl sulfate, sodium myristyl sulfate, sodium lauryl sulfate, sodium decyl sulfate, sodium octyl sulfate, or a combination thereof.

[0020] In an embodiment, the anionic surfactant may be present in the CASP in an amount of from about 0.01 weight percent (wt.%) based on the total weight of the CASP to about 99.99 wt.%, alternatively from about 0.1 wt.% to about 99.9 wt.%, alternatively from about 1 wt.% to about 99 wt.%.

[0021] In an embodiment the amount of cationic surfactant present in the CASP is greater than the amount of anionic surfactant and such a composition is termed a cationic rich CASP. Alternatively, the amount of anionic surfactant present in the CASP is greater than the amount of cationic surfactant and such a composition is termed an anionic rich CASP.

[0022] In an embodiment, the cationic surfactant:anionic surfactant ratio (CAR) may be chosen by one of ordinary skill in the art with the benefits of this disclosure so as to mitigate unwanted effects normally associated with the contacting of a surfactant package with other materials. For example, the CAR may be chosen so as to reduce or eliminate phase separation when the CASP is contacted with an aqueous solution. Further, the CAR may be chosen so as to reduce or eliminate precipitation of one or both components of the CASP when contacted with an aqueous solution. For example, the CAR may be from about 1:100 to about 100:1; alternatively from about 90:1 to about 1:90; alternatively from about 80:1 to about 1:80; alternatively from about 70:1 to about 1:70; alternatively from about 60:1 to about 1:60; alternatively from about 1:50 to about 50:1; alternatively from about 40:1 to about 1:40; alternatively from about 30:1 to about 1:30; alternatively from about 20:1 to about 1:20; alternatively from about 10:1 to about 1:10; alternatively from about 1:9 to about 9:1.

[0023] In an embodiment, a CASP (e.g., a cationic rich CASP, an anionic rich CASP) may be contacted with an aqueous solution to form a CASP-VC. The aqueous solution may comprise fresh water or salt water, e.g., an unsaturated aqueous salt solution or a saturated aqueous salt solution such as brine or seawater. The aqueous solution and CASP may be contacted in any manner known to one of ordinary skill in the art with the benefits of this disclosure. In an embodiment the aqueous solution comprises a brine. The brine may be any suitable saturated or a nearly saturated saltwater solution. For example, the brine may be any suitable saturated or a nearly saturated salt solution comprising water and greater than about 90, 95, 99, or 99.9 wt.% salt. Nonlimiting examples of brines suitable for use in this disclosure include ammonium chloride, potassium chloride, sodium chloride, zinc bromide, calcium chloride, calcium bromide, sodium bromide, potassium formate, sodium formate, cesium formate or a combination thereof. In an embodiment, the CASP may be contacted with the aqueous solution in an amount of from about 0.01g to about 20g CASP per 80g aqueous solution, alternatively from about 0.1g to about 15g CASP per 80g aqueous solution, alternatively from about 1g to about 10g CASP per 80g aqueous solution.

[0024] The CASP-VC described herein may exhibit viscoelastic behavior. Viscoelastic materials exhibit both viscous and elastic characteristics when undergoing deformation. In an embodiment, the viscoelasticity of the CASP-VC may be adjusted to meet a user or process-desired need by adjustment of the CAR or the total concentration of surfactant. The ability to adjust or tune the viscoelasticity of the CASP-VC may allow a user to select an appropriate CASP-VC based on the needs of a wellbore and its processing requirements. For example, the CAR may be optimized to produce a CASP-VC having a viscosity suitable for use in lost circulation zones at higher depth or at an elevated temperature.

[0025] In an embodiment, the CASP-VC may exhibit a viscosity ranging from about 0.001 Pa*s to about 100,000 Pa*s, alternatively from 1 Pa*s to about 100,000 Pa*s, alternatively from about 100 Pa*s to about 100,000 Pa*s over a temperature range of from about 10°C to about 200°C, alternatively from about 25°C to about 200°C, alternatively from about 50°C to about 200°C. Viscosity is a measure of the resistance of a fluid which is being deformed by shear stress. In other words, it is the resistance of a liquid to flow. Determination of the properties described herein may be made using any suitable methodology known to one of ordinary skill in the art. For example, the storage modulus, loss modulus and viscosity may be determined by applying a constant shear rate to the CASP-VC and reading the shear stress using a narrow gap cup in bob geometry as described in Rheology: Principles, Measurements and Applications, by C.W. Macosko, Wiley-VCH, New York (1994) which is incorporated by reference herein in its entirety.

[0026] In an embodiment, the CASP-VC may exhibit a zero shear viscosity of from about 0.001 Pa*s to about 100,000 Pa*s, alternatively from about 1 Pa*s to about 100,000 Pa*s, alternatively from about 100 Pa*s to about 100,000 Pa*s over a temperature range of from about 10°C to about 200°C, alternatively from about 25°C to about 200°C, alternatively from about 50°C to about 200°C. Zero shear viscosity refers to the viscosity at the limit of low shear rate. The zero shear viscosity is the viscosity a product will ultimately attain when at rest and undisturbed. The zero shear viscosity was determined as described previously herein with the exception that the data was extrapolated to "zero" shear and the viscosity read at that shear.

[0027] In an embodiment, the CASP-VC has a complex viscosity of from about 10 Pa*s to about 100,000 Pa*s, alternatively from about 100 Pa*s to about 100,000 Pa*s, alternatively from about 1,000 Pa*s to about 100,000 Pa*s for a range of frequencies of from about 0.00001 Hz to about 1,000 Hz, alternatively from about 0.01 Hz to about 1,000 Hz, alternatively from

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about 1 Hz to about 1,000 Hz. Complex viscosity refers a frequency-dependent viscosity function determined during forced harmonic oscillation of shear stress. It is related to the complex shear modulus and represents the angle between the viscous stress and the shear stress. The complex viscosity function is equal to the difference between the dynamic viscosity and the out-of-phase viscosity, or imaginary part of the complex viscosity:

$$\eta^*(i\omega) = \eta'(\omega) - i\eta''(\omega)$$

where

η^* = complex viscosity

η' = dynamic viscosity

η'' = out-of-phase viscosity

The complex viscosity was determined as described previously herein with the exception that the frequency was kept constant.

[0028] The storage modulus in viscoelastic materials measures the stored energy and represents the elastic portion of the material. The loss modulus relates to the energy dissipated as heat and represents the viscous portion related to the amount of energy lost due to viscous flow. In an embodiment, the CASP-VC has a storage modulus of from about 0.001 Pa to about 1,000 Pa, alternatively from about 0.1 Pa to about 1,000 Pa, alternatively from about 1 Pa to about 1,000 Pa for a range of frequencies of from about 0.00001 Hz to about 1,000 Hz, alternatively from about 0.01 Hz to about 1,000 Hz, alternatively from about 1 Hz to about 1,000 Hz. In another embodiment, the CASP-VC has a loss modulus of from about 0.001 Pa to about 1,000 Pa, alternatively from about 0.1 Pa to about 1,000 Pa, alternatively from about 1 Pa to about 1,000 Pa for a range of frequencies of from about 0.00001 Hz to about 1,000 Hz, alternatively from about 0.01 Hz to about 1,000 Hz, alternatively about 1 Hz to about 1,000 Hz. The storage modulus and loss modulus were determined as described previously herein.

[0029] In an embodiment, the CASP-VC is solids free. Herein, solids free refers to the amount of solid being equal to or less than about 3 wt.%, alternatively equal to or less than about 2 wt.%, alternatively equal to or less than about 1 wt.% based on the total weight of the CASP. Examples of solids include without limitation particles, sands, formation materials, or a combination thereof.

[0030] In an embodiment, the CASP-VC can withstand high pressure gradients. The high viscoelasticity generated by the CASP allows the fluid to resist high pressure gradients.

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[0031] In an embodiment, CASPs of the type described herein may be introduced to a wellbore servicing fluid or to a wellbore and carry out its intended function in the substantial absence of a hydrotrope and/or excess salt (e.g., the CASP is free, substantially free, or does not contain a material amount of a hydrotrope and/or excess salt). Both hydrotropes and excess salt are used to stabilize micellar growth. Herein a hydrotrope refers to a compound that solubilises hydrophobic compounds in aqueous solutions. Typically, hydrotropes consist of a hydrophilic part and a hydrophobic part (like surfactants) but the hydrophobic part is generally too small to cause spontaneous self-aggregation. Examples of hydrotropes include for example and without limitation sodium p-toluenesulfonate, sodium xylene sulfonate, sodium salicylate, alkyl alcohols, or a combination thereof. In alternative embodiments, the CASPs are introduced to a wellbore servicing fluid or to a wellbore and carry out its intended function in the presence of a hydrotrope. In an embodiment, the CASP comprises less than or equal to about 30, 20, 10, 9, 8, 7, 6, 5, 4, 3, 2, 1, 0.1, 0.01, or 0.001 wt% of one or more hydrotropes based upon the total weight of the CASP. In an embodiment, the CASP comprises an amount of salt equal to or less than the saturation amount. In an embodiment, the CASP comprises an excess amount of salt equal to or less than about 1.0, 0.1, 0.01, 0.001, or 0.0001 weight percent over the saturation amount (i.e., $\leq 1.0, 0.1, 0.001, \text{ or } 0.0001 \text{ wt \% excess salt}$).

[0032] Without wishing to be limited by theory, the tunable viscoelasticity of the CASP-VC disclosed herein may be attributed to the mechanism of micelle growth in these compositions. One mechanism for the formation and growth of micelles may involve the electrostatic interactions of a cationic surfactant and an anionic surfactant (e.g., CASP). In this mechanism, the CASP interacts to form a pseudo-double tailed zwitterionic surfactant that self assembles into a surfactant bilayer in the form of lamellar sheets of vesicles or wormlike micelles. The presence of salt (e.g. hydrotrope) may facilitate the growth of micelles or the creation of multilamellar vesicles because of interaction between cationic and anionic surfactant, cationic/anionic surfactant and hydrotrope, and cationic/anionic surfactant and inorganic salt.

[0033] In addition, the chain length of the cationic and anionic surfactant may affect the resulting micelles. When the cationic and anionic surfactants are of similar chain length, there is a wider phase space where the bilayer aggregates are stable. However, when there is a difference in chain lengths, the bilayer phase space will be smaller, thus stabilizing the micelles over a wider concentration range. To generate chain length difference between the cationic and

anionic surfactants, the amount of cationic surfactant may be much larger when compared to the anionic surfactant or vice versa. Further, even at equimolar amounts of cationic and anionic surfactants wherein the chain length difference between the cationic and anionic surfactants is sufficiently large, a micelle phase will be stable. However, a micelle phase will not be stable if the cationic and anionic surfactants have similar chain lengths.

[0034] The second proposed mechanism involves a phase transition of the CASP from a low viscosity vesicle phase (e.g., near that of water with 1 vol.% spheres) to a higher viscosity viscoelastic phase by an increase in temperature. Herein, a higher viscosity viscoelastic phase refers to an amount higher than that of the vesicle phase while at the same overall concentration of surfactant. In this mechanism, a unilamellar vesicle bilayer phase is created by mixing the cationic surfactant and the anionic surfactant. In contrast to the first mechanism where a difference in carbon chain length aids in micelles formation, the amount of the cationic surfactant may be similar to the anionic surfactant in the vesicle phase, for example a 1:1 CAR. As temperature increases, the surfactant exchange rate between the vesicle and water will increase. The increase occurs more rapidly for a shorter chain surfactant than for a longer chain surfactant, leading to a lower concentration (e.g., as determined by nuclear magnetic resonance) of one surfactant in the bilayer, thus possibly promoting the growth of micelles.

[0035] The third proposed mechanism involves development of a spontaneous curvature by mixing surfactants and creating a defect ridden lamellar phase with gel-like qualities as visualized using standard imaging techniques. In this mechanism, a cationic/anionic gel is formed by a lamellar defect phase. At high double-tailed surfactant concentration (e.g., low water contents, equal to or greater than about 50 wt.% surfactant), a lamellar sheet (L_{α}) phase is often formed. As the water content is increased to an amount of from about 60 wt.% to about 80 wt.%, the bilayer spacing generally swells to a certain spacing that expel any excess water that is added. This spacing may be determined using any suitable technique such as small angle x-ray scattering technique. In the case of cationic/anionic bilayers ("pseudo" double tailed surfactants), a spontaneous curvature exists that leads to multilamellar vesicle (MLV) defect sites existing with the lamellar sheet phase as more water is added. The formation of MLV defect sites within the lamellar sheet phase further leads to lamellar sheets entangled with MLV defect sites, thereby creating a highly viscoelastic gel with a viscosity greater than 1,000 centipoise.

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[0036] In an embodiment, a CASP-VC of the type described herein may be used to control lost circulation in a subterranean formation. It is to be understood that "subterranean formation" encompasses both areas below exposed earth and areas below earth covered by water such as ocean or fresh water. In the process of drilling a well, low fracture gradients zones, fractured zones, etc. are often encountered and loss of whole drilling fluid to the formation becomes a problem. Losses of drilling fluid can impede the progress of drilling the well, add cost to the drilling of the well, prevent the drilling of the well to target depth, and/or cause the total loss of the drilled open hole section. In such an embodiment, the CASP may be introduced into a drill string, pumped down to a lost circulation zone such as voids, vugular zones, and natural or induced fractures while drilling. The CASP may then contact a fluid in the lost circulation zone and form a CASP-VC that substantially seals the lost circulation zone with little or no interruption of drilling operations and reduction in loss of drilling fluid to the lost circulation zone.

[0037] In another embodiment, a CASP may be pumped down to a lost circulation zone, a wellbore servicing fluid may be introduced from the wellbore to the lost circulation zone wherein the CASP contacts the wellbore servicing fluid and forms a CASP-VC that substantially seals the lost circulation zone. As used herein, a "servicing fluid" refers to a fluid used to drill, complete, work over, fracture, repair, or in any way prepare a wellbore for the recovery of materials residing in a subterranean formation penetrated by the wellbore. Examples of servicing fluids include, but are not limited to, cement slurries, drilling fluids or muds, spacer fluids, fracturing fluids, gravel pack fluids, or completion fluids, all of which are well known in the art. Methods for introducing compositions into a wellbore to seal subterranean zones are described in U.S. Patent Nos. 5,913,364; 6,167,967; and 6,258,757, each of which is incorporated by reference herein in its entirety.

[0038] The CASP-VC may form a non-flowing, intact mass of high viscosity inside the lost circulation zone which plugs the zone and inhibits loss of subsequently pumped fluid. In an embodiment, the CAR is adjusted so as to produce a high viscosity CASP-VC that plugs a zone at elevated temperatures, such as those found at higher depths within a wellbore.

[0039] In another embodiment, the CASP-VCs form lost circulation pills for use in completion brines. The CASP-VCs disclosed herein may form solids free post perforation pills and/or post gravel pack fluid loss pills that are useful in servicing a wellbore during completion operations.

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[0040] In an embodiment, a CASP-VC is used to service a wellbore. Subsequently, the viscoelasticity of a CASP-VC may be broken (i.e., the viscosity of the CASP-VC may be reduced) by contacting the CASP-VC with an effective amount of a viscosity breaker such as a hydrocarbon or an internal breaker. The ability to break the viscosity of a CASP-VC may be useful for example for wellbore cleanup. Examples of internal breakers suitable for use in this disclosure include without limitation SP breaker, VICON NF breaker, OXOL II breaker, GBW-40 breaker, and HT breaker, which are commercially available from Halliburton. Examples of hydrocarbons suitable for use in this disclosure include for example and without limitation crude oil, natural gas and gas hydrates. Effective amounts of hydrocarbons and internal breakers may be determined by one of ordinary skill in the art with the aid of this disclosure.

EXAMPLES

[0041] The disclosure having been generally described, the following examples are given as particular embodiments of the disclosure and to demonstrate the practice and advantages thereof. It is understood that the examples are given by way of illustration and are not intended to limit the specification or the claims in any manner.

EXAMPLE 1

[0042] The rheological behavior of CASP-VCs of the type described herein was investigated. Eight samples, designated Samples 1-8, were prepared. Samples 1-4 were prepared using sodium oleate (NaOle), which is commercially available from TCI America as the anionic surfactant and octyl trimethyl ammonium chloride (C₈TAC), which is commercially available from TCI America as the cationic surfactant. Samples 1-4 were prepared using a C₈TAC:NaO ratio of 3:7, 4:6, 2:8, and 1:9 respectively. The samples were then dissolved in deionized water (DI H₂O) in sufficient quantity to form a 3 wt.% solution. Since Samples 1-4 had larger anionic ratio to cationic, the resulting CASP-VCs were anionic rich.

[0043] Sample 5-8 were prepared using sodium octoate (NaCap), which is commercially available from TCI America as the anionic surfactant and stearyltrimethylammonium chloride (C₁₈TAC), which is commercially available from TCI America as the cationic surfactant. Samples 5-8 were prepared using a C₁₈TAC:NaCap ratio of 7:3, 6:4, 8:2, and 9:1 respectively. The samples were then dissolved in deionized water (DI H₂O) in sufficient quantity to form a 3 wt.% solution. Since Samples 5-8 had larger cationic ratio to anionic, the resulting CASP-VCs were cationic rich. Table 1 tabulates the cationic and anionic surfactant types, and ratios for each sample.

Table 1

Sample	Cationic Surfactant	Anionic Surfactant	CAR	Weight %
1	C ₈ TAC	NaO	3:7	3
2	C ₈ TAC	NaO	4:6	3
3	C ₈ TAC	NaO	2:8	3
4	C ₈ TAC	NaO	1:9	3
5	C ₁₈ TAC	NaCap	7:3	3
6	C ₁₈ TAC	NaCap	6:4	3
7	C ₁₈ TAC	NaCap	8:2	3
8	C ₁₈ TAC	NaCap	9:1	3

[0044] Rheological measurements were performed using an MCR 501 with a concentric cylinder of 27mm, which is a commercially available rheometer from Anton Paar at a temperature of 25°C.

[0045] Figure 1 is a plot of viscosity as a function of shear rate for Samples 1-4. Figure 2 is a plot of viscosity as a function of shear rate for Samples 5-8. The zero shear viscosities of Samples 1-4 may be determined by extrapolating the viscosity back to the theoretical zero-shear point and were 1200, 93, 33, and 0.006 Pa*s respectively. The zero shear viscosities of Samples 5-8 may be determined by extrapolating the viscosity back to the theoretical zero-shear point and were 542, 196, 0.4, and 0.001 respectively. The results demonstrated that the zero-shear viscosity is highly dependent on the cationic/anionic ratio and can be tuned by varying it. Also, over a million fold increase in viscosity can be generated by adding an oppositely charged surfactant independent of salt or hydrotrope concentration.

EXAMPLE 2

[0046] The zero shear viscosity of an anionic rich and a cationic rich CASP-VCs were investigated. Samples 1-8, described in Example 1, were used again in this example. In addition, five more samples, designated Samples 9-13, were prepared as described in Example 1. Table 2 tabulates the cationic and anionic surfactant types and CARs for Samples 9-13.

Table 2

Sample	Cationic Surfactant	Anionic Surfactant	CAR	Weight %
9	C ₈ TAC	NaO	5:5	3
10	C ₈ TAC	NaO	6:4	3
11	C ₈ TAC	NaO	0:10	3
12	C ₁₈ TAC	NaCap	5:5	3
13	C ₁₈ TAC	NaCap	4:6	3

[0047] Figure 3 is a plot of viscosity as a function of weight fraction of minor component for Samples 1-13. For Samples 1-4 and 9-11, the minor component was the cationic surfactant. For Samples 5-8 and 12-13, the minor component was the anionic surfactant. The results demonstrated that the CAR that created the maximum viscosity was about 70:30 and 30:70, as shown by the peaks for the anionic rich and the cationic rich CASP-VCs on Figure 3. In addition, both the cationic rich and the anionic rich CASP-VCs exhibited pronounced increases in viscoelasticity up to 300,000 fold when compared to the individual surfactant components. This increase in viscoelasticity was also observed visually by placing Sample 1 and 5 in separate vials and inverting both vials. In both vials, the viscoelastic gel samples remained suspended for over 10 seconds.

EXAMPLE 3

[0048] The dynamic properties of CASP-VCs of the type described herein were investigated. Specifically, the complex viscosity, storage modulus, and loss modulus as a function of frequency for Samples 1-3 and 5-7 from Example 1 were determined. Figures 4 and 5 are plots of complex viscosity, storage modulus, and loss modulus as a function of frequency for Samples 1-3 and Samples 5-7 respectively. The results demonstrated that these fluids displayed both a significant loss modulus and storage modulus, thereby proving their viscoelasticity.

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EXAMPLE 4

[0049] The effect of temperature on the viscosity of CASP-VCs was investigated. The zero shear viscosities of Samples 1 and 5 from Example 1 were tested over the temperature range of 70°F to 190°F. The results for both an anionic rich CASP-VC (Sample 1) and a cationic rich CASP-VC (Sample 5) are shown in Figures 6 and 7 respectively.

[0050] The results demonstrated that for there was a decrease in viscosity by several orders of magnitude in each sample as the temperature increased. However, the viscosity for the cationic and anionic rich CASP-VCs was still about 10 and 30 times greater respectively than that of water (viscosity of water at 194°F is about 0.000315 Pa*s). Thus, even at high temperature, there is an appreciable viscosity increase when compared to water.

[0051] Without wishing to be limited by theory the observed decrease in viscosity as the temperature increased may be a result of the solubility of the CASPs in water increasing (i.e., the critical micelle concentration increased). The increased solubility of the CASP may lead to faster kinetics and shorter and smaller micelles. The presence of these shorter and smaller micelles may contribute to the observed decrease in viscosity.

[0052] One of ordinary skill in the art with the benefits of this disclosure may adjust the CASPs such that the viscosity of the CASP-VC has a reduced response to temperature. For example, one technique is to use alkyl chain surfactants such as C₂₂ cationic surfactants and C₂₂ zwitterionic surfactants. In addition, changes in surfactant phase behavior with temperature may be exploited (i.e., vesicle to wormlike micelle transition). The final approach is to increase the concentration of the surfactants in the CASP. By increasing the concentration, one may achieve the entanglement or crossover concentration even with much shorter length micelles. In other words, the viscoelastic response occurs when there is either an increase in concentration, length, or both.

[0053] The stability of the CASP-VC was also investigated. An anionic surfactant solution comprising sample 1 was prepared and observed over a time period of 7 days at a temperature of 25°C. The anionic surfactant was observed to degrade with time, as the single component solution became somewhat cloudy in a few weeks. Without wishing to be limited by theory, the double bond in the oleate alkyl chain may be oxidized, causing the surfactant to become the same as stearic acid sodium soap. Stearic acid sodium soap has a much lower solubility in water and may not form wormlike micelles as readily as oleic acid sodium soap.

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[0054] An anionic- rich CASP-VC was also prepared and observed over a time period of 7 days at a temperature of 25°C. The anionic rich CASP-VC also became cloudy, displayed reduced viscosity and began to phase separate after a few weeks. This behavior may be exploited in that it may be useful for degradation of the viscoelastic material without the utilization of any added components. At higher temperatures, such break down of viscosity may occur on the order of days, which may be useful for a lost circulation pill, as it will allow the lost circulation material to dissolve and allow production to begin. A cationic rich CASP-VC was observed to remain stable for a time period of greater than 30 days at a temperature of 25°C.

EXAMPLE 5

[0055] The temperature stability of a cationic rich CASP-VC was investigated and compared to a cationic only surfactant. The cationic rich CASP-VC, designated Sample 14, was cetyl trimethylammonium tosylate/sodium dodecylbenzene sulfonate (CTAT/SDBS) of 97:3 which was prepared as a 3 wt.% solution. The cationic only surfactant, designated Sample 15, was CTAT which was prepared as a 3 wt.% solution. The zero shear viscosities for Samples 14 and 15 were measured for a range of temperature of from 75°F to 190°F. The results are shown in Figure 8.

[0056] Referring to Figure 8, the zero shear viscosity decreased as the temperature increased for both samples. However, the drop in zero shear viscosity at high temperature (about above 150°F) for Sample 14 was less than Sample 15 because of the addition of the anionic surfactant. Without wishing to be limited by theory, the lesser drop in zero shear viscosity may be due to the greater binding of a surfactant versus a simple hydrotrope or due to the lower solubility of surfactants versus hydrotropes. Thus, these CASPs offer greater temperature stability than traditional surfactants.

EXAMPLE 6

[0057] The tolerance of cationic rich and anionic rich CASP-VCs to salt was investigated. Sample 5 from Example 1 was selected for the cationic rich CASP-VC. A comparative sample of cationic rich CASP-VC in brine, designated Sample 16, was prepared from C18TAC/NaCap having 7:3 ratio which was prepared as a 3 wt.% solution (similar to Sample 5) and 0.15M sodium bromide (NaBr) brine. The complex viscosity, storage modulus, loss modulus, and zero shear viscosity of Samples 5 and 16 were measured and the results are shown in Figures 9 and 10. The results demonstrated that the CASP-VC was able to maintain its viscosity with the

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addition of salt. Without wishing to be limited by theory, this suggests that electrostatic interactions are not the dominant force in the creation of the viscoelasticity.

[0058] Sample 1 was selected for the anionic rich CASP. A comparative sample of anionic rich CASP-VC in brine, designated Sample 17 was prepared from NaO:C₈TAC ratio of 7:3 and 0.15M sodium bromide (NaBr) brine. The complex viscosity, storage modulus, loss modulus, and zero shear viscosity of Samples 1 and 17 were measured. The results are shown in Figure 11. The results demonstrated that the anionic rich CASP-VC suffered a large drop in its viscoelastic properties with the addition of salt, which suggests that electrostatic interactions are creating the large zero shear viscosity. This viscosity can be regained by varying CAR to change the overall charge on the micelle.

EXAMPLE 7

[0059] The zero shear viscosity of CASP-VCs of the type described herein was investigated. Four samples, designated Samples 18-21, were prepared. Sample 18 was a 3 wt.% aqueous solution of cetyl trimethylammonium tosylate (CTAT). Samples 19-21 were CTAT/sodium dodecylbenzene sulfonate (SDBS) with a CAR of 99:1, 97:3, and 95:5 respectively and was prepared as a 3 wt.% aqueous solution. The zero shear viscosities of Samples 18-21 were determined to be 126, 205, 255, and 207 Pa*s respectively and are shown in Figure 12. CTAT forms viscoelastic wormlike micellar solutions with high zero shear viscosities. By adding a small amount of SDBS in Samples 19-21, the solutions became highly viscous with increased zero shear viscosities when compared to Sample 18. Furthermore, the zero shear viscosity of Sample 20 was more than doubled (256,000 centiPoise) when compared to Sample 18 (126,000 centiPoise).

[0060] Another sample, designated Sample 22, was prepared. Sample 22 was CTAT/sodium octyl sulfate (SOS) with a CAR of 94:6 and was prepared as a 3 wt.% aqueous solution. The zero shear viscosity of Sample 22 was determined to be 470,000 centiPoise, which was more than tripled when compared to sample 18. These results demonstrated the ability of CASPs to increase the viscosity of solutions.

EXAMPLE 8

[0061] The effect of using surfactants containing longer alkyl chains on the properties of the CASP-VC was investigated. Three samples, designated Samples 23-25, were investigated. Samples 23 and 24, which were the cationic rich CASP, were prepared from erucyl bis-(hydroxy ethyl)methylammonium chloride (EHAC)/ n-caprylic acid sodium salt (NaCap) with

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a CAR of 8:2 and 9:1 respectively as a 3 wt.% aqueous solution. Sample 25, which was the cationic rich CASP was prepared from erucyl bis-(hydroxy ethyl)methylammonium chloride/decanoic acid sodium salt with a cationic:anionic ratio of 9:1 as a 3 wt.% aqueous solution. The zero shear viscosities for Samples 23 and 24 were determined and the results are shown in Figure 13. The viscosities of Samples 23-24 ranged from 200,000 to 800,0000 centiPoise while the viscosity of Sample 25 was about 70,000 centiPoise. The results demonstrate that the long chain surfactants that generate appreciable viscosity ($>10 \text{ Pa}\cdot\text{s}$) at elevated temperatures also form these cationic/anionic viscoelastic aggregates.

[0062] Next, the ability of hydrocarbon to reduce the viscosity of CASP-VC was investigated. A portion of samples 23-25 were placed in individual vials and a hydrocarbon fluid was introduced to each vial. The hydrocarbon fluid used for the test was diesel. Each vial was then shaken to mix the CASP-VC with diesel. Each vial was then inverted and visually observed. In the absence of the hydrocarbon, the CASPs form viscous masses that remained suspended for seconds, see Example 2. However, with the addition of a hydrocarbon, upon inversion of the vials the mass was not completely suspended and fluid was observed to flow for both the cationic rich and anionic rich CASPs.

[0063] While embodiments of the disclosure have been shown and described, modifications thereof can be made by one skilled in the art without departing from the scope of the invention. The embodiments described herein are exemplary only, and are not intended to be limiting. Many variations and modifications of the disclosure disclosed herein are possible and are within the scope of the disclosure. Where numerical ranges or limitations are expressly stated, such express ranges or limitations should be understood to include iterative ranges or limitations of like magnitude falling within the expressly stated ranges or limitations (e.g., from about 1 to about 10 includes, 2, 3, 4, etc.; greater than 0.10 includes 0.11, 0.12, 0.13, etc.). For example, whenever a numerical range with a lower limit, R_L , and an upper limit, R_U , is disclosed, any number falling within the range is specifically disclosed. In particular, the following numbers within the range are specifically disclosed: $R = R_L + k \cdot (R_U - R_L)$, wherein k is a variable ranging from 1 percent to 100 percent with a 1 percent increment, i.e., k is 1 percent, 2 percent, 3 percent, 4 percent, 5 percent, ..., 50 percent, 51 percent, 52 percent, ..., 95 percent, 96 percent, 97 percent, 98 percent, 99 percent, or 100 percent. Moreover, any numerical range defined by two R numbers as defined in the above is also specifically disclosed. Use of the term "optionally" with respect to any element

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of a claim is intended to mean that the subject element is required, or alternatively, is not required. Both alternatives are intended to be within the scope of the claim. Use of broader terms such as comprises, includes, having, etc. should be understood to provide support for narrower terms such as consisting of, consisting essentially of, comprised substantially of, etc.

[0064] Accordingly, the scope of protection is not limited by the description set out above but is only limited by the claims which follow, that scope including all equivalents of the subject matter of the claims. Each and every claim is incorporated into the specification as an embodiment of the present disclosure. Thus, the claims are a further description and are an addition to the embodiments of the present disclosure. The discussion of a reference is not an admission that it is prior art to the present disclosure, especially any reference that may have a publication date after the priority date of this application. The disclosures of all patents, patent applications, and publications cited herein are hereby incorporated by reference, to the extent that they provide exemplary, procedural, or other details supplementary to those set forth herein.

CLAIMS:

1. A wellbore servicing fluid comprising a surfactant package comprising a cationic surfactant and anionic surfactant; wherein the surfactant package when contacted with an aqueous solution forms a viscosified composition in the presence of less than about 30 wt.% of a hydrotrope.
2. A fluid according to claim 1, wherein the cationic surfactant has a carbon chain length of from about 8 to about 24.
3. A fluid according to claim 1 or 2, wherein the cationic surfactant comprises quaternary ammonium salt, ethoxylated quaternary ammonium salts, amine oxides, or a combination thereof.
4. A fluid according to claim 1, 2 or 3, wherein the cationic surfactant comprises stearyltrimethylammonium chloride, cetyltrimethylammonium tosylate, octyltrimethylammonium chloride, erucyl bis-(hydroxyethyl)methylammonium chloride, erucyl trimethylammonium chloride cetyltrimethylammonium chloride, cetyltrimethylammonium bromide, myristyltrimethylammonium chloride, myristyltrimethylammonium bromide, dodecyltrimethylammonium chloride, dodecyltrimethylammonium bromide, decyltrimethylammonium chloride, decyltrimethylammonium bromide, or a combination thereof.
5. A fluid according to any preceding claim, wherein the cationic surfactant is present in the surfactant package in an amount of from about 0.01 wt.% to about 99.99 wt.% based on the total weight of the surfactant package.
6. A fluid according to any preceding claim, wherein the anionic surfactant has a carbon chain length of from about 8 to about 24.
7. A fluid according to any preceding claim, wherein the anionic surfactant comprises alkali salts of acids, alkali salts of fatty acids, alkaline salts of acids, sodium salts of acid, sodium salts of fatty acid, alkyl sulphates, alkyl ethoxylate, sulphates, sulfonates, soaps, or a combination thereof.
8. A fluid according to any preceding claim, wherein the anionic surfactant comprises sodium oleate, sodium dodecylbenzenesulfonate, sodium decanoate, sodium octyl sulfate, sodium caprylate sodium stearate, sodium myristate, sodium laurate, sodium cetyl sulfate, sodium myristyl sulfate, sodium lauryl sulfate, sodium decyl sulfate, or a combination thereof.

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9. A fluid according to any preceding claim, wherein the anionic surfactant is present in the surfactant package in an amount of from about 0.01 wt.% to about 99.99 wt.% based on the total weight of the surfactant package.
10. A fluid according to any preceding claim, wherein the surfactant package has cationic surfactant:anionic surfactant ratio of from 1:100 to 100:1.
11. A fluid according to any preceding claim, wherein the surfactant package is contacted with the aqueous solution in an amount of from about 0.01 grams to about 20 grams per 80 grams of the aqueous solution.
12. A fluid according to any preceding claim, wherein the aqueous solution comprises water, brine, a wellbore servicing fluid, or a combination thereof.
13. A fluid according to claim 12, wherein the brine comprises ammonium chloride, potassium chloride, sodium chloride, zinc bromide, calcium chloride, calcium bromide, sodium bromide, potassium formate, sodium formate, cesium formate or a combination thereof.
14. A fluid according to claim 12 or 13, wherein the wellbore servicing fluid comprises cement slurries, drilling fluids, spacer fluids, fracturing fluids, gravel pack fluids, workover fluids, completion fluids, or a combination thereof.
15. A fluid according to any preceding claim 1, wherein the viscosified composition is solids free.
16. A fluid according to any preceding claim, wherein the viscosified composition has a viscosity of from about 0.001 Pa*s to about 100,000 Pa*s at a temperature of from about 10°C to about 200°C.
17. A fluid according to any preceding claim, wherein the viscosified composition has a zero shear viscosity of from about 0.001 Pa*s to about 100,000 Pa*s at a temperature of from about 10°C to about 200°C.
18. A fluid according to any preceding claim, wherein the viscosified composition has a complex viscosity of from about 10 Pa*s to about 10,000 Pa*s at a frequency range of from about 0.00001 Hz to about 1000 Hz.
19. A fluid according to any preceding claim, wherein the viscosified composition has a storage modulus of from about 0.001 Pa to about 1,000 Pa at a frequency range of from about 0.00001 Hz to about 1000 Hz.

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20. A fluid according to any preceding claim, wherein the viscosified composition has a loss modulus of from about 0.001 Pa to about 1,000 Pa at a frequency range of from about 0.00001 Hz to about 1000 Hz.
21. A fluid according to any preceding claim, wherein the viscosified composition comprises a solids free post perforation pill or a gravel pack fluid loss pill.
22. A method of servicing a wellbore comprising: placing a fluid according to any preceding claim in the wellbore.
23. A method according to claim 22, further comprising contacting the viscosified composition with a viscosity breaker.
24. A method according to claim 23, wherein the viscosity breaker comprises a hydrocarbon fluid, an internal breaker, or a combination thereof.

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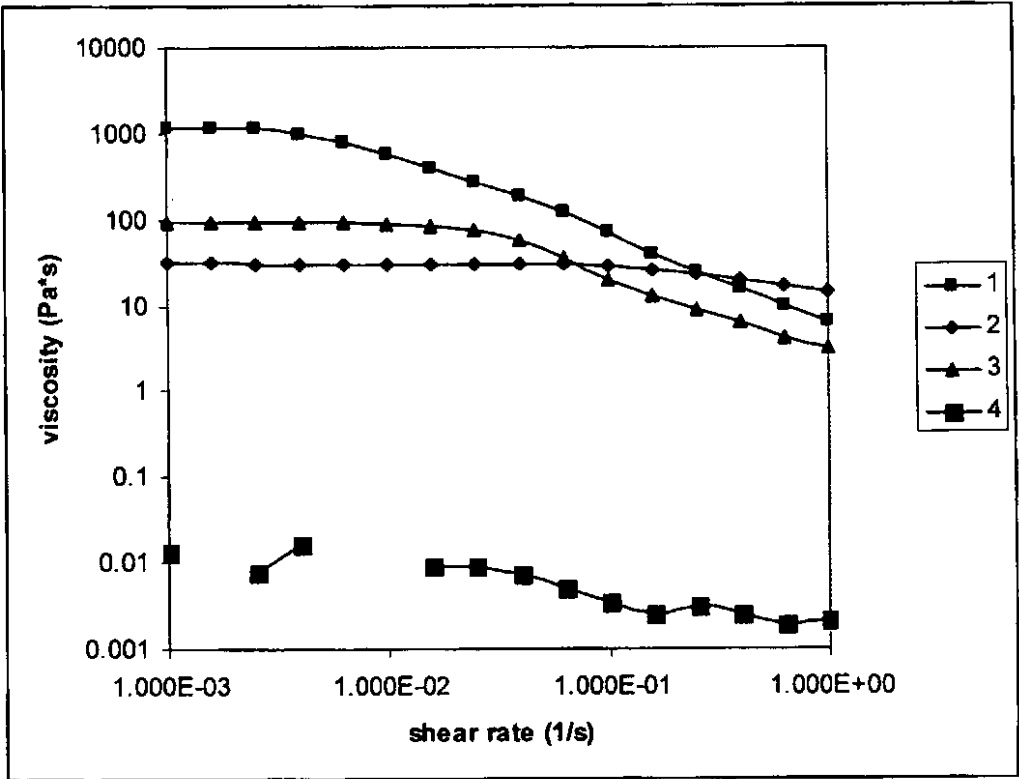


FIG. 1

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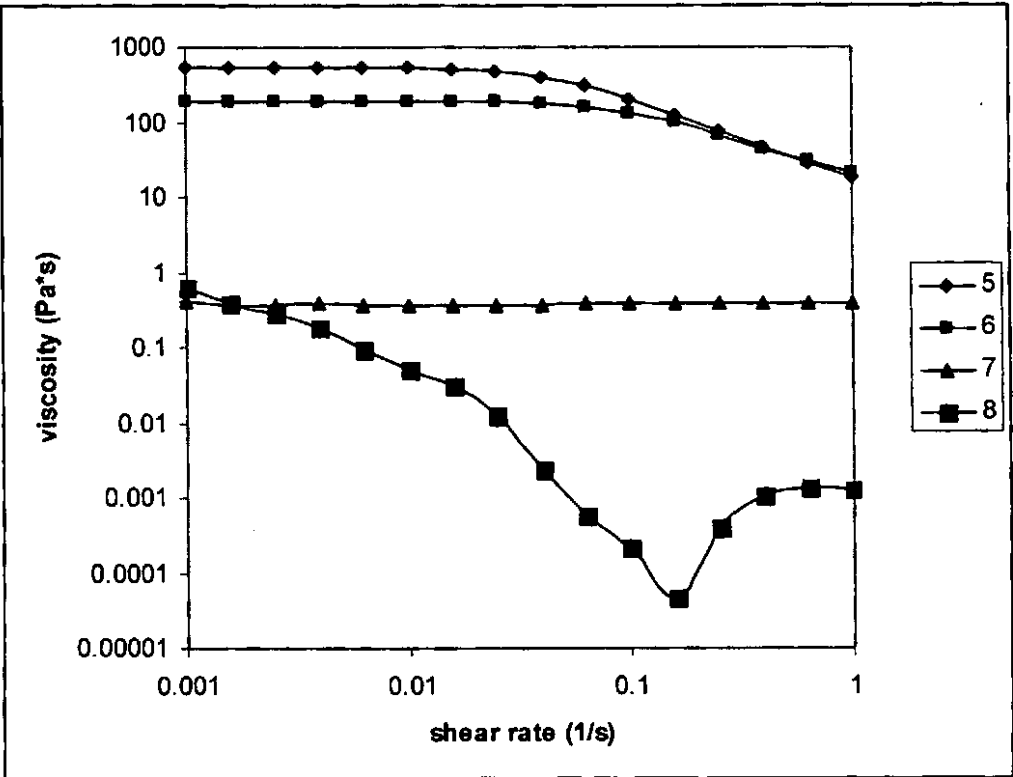


FIG. 2

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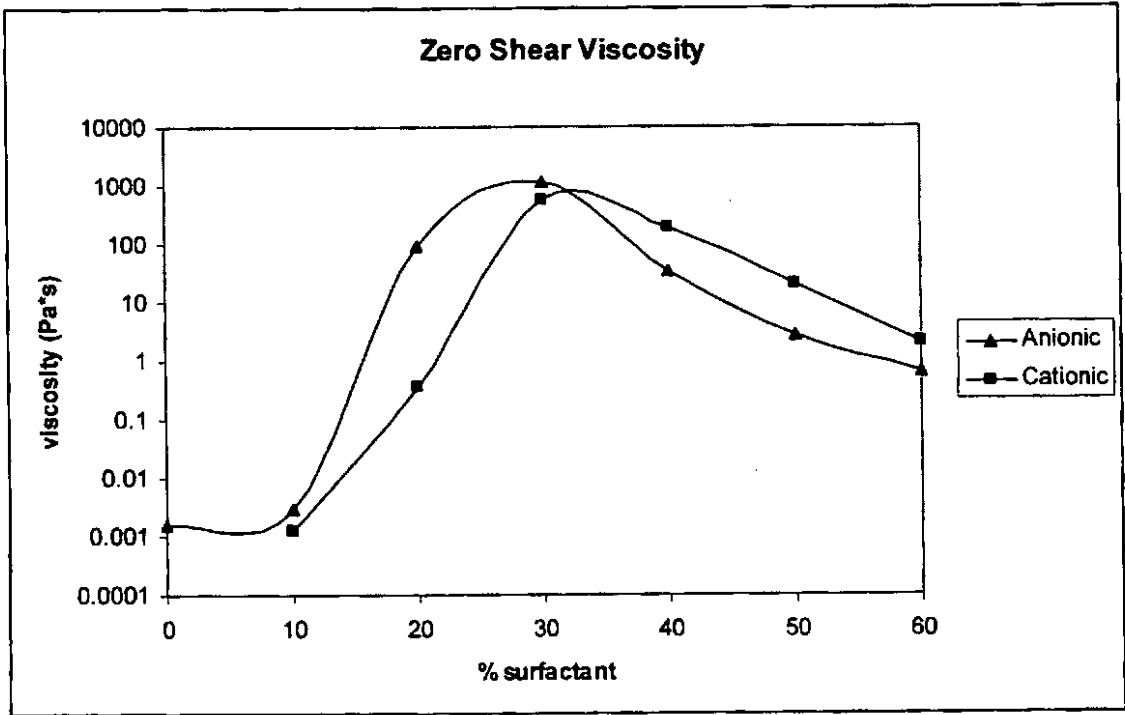


FIG. 3

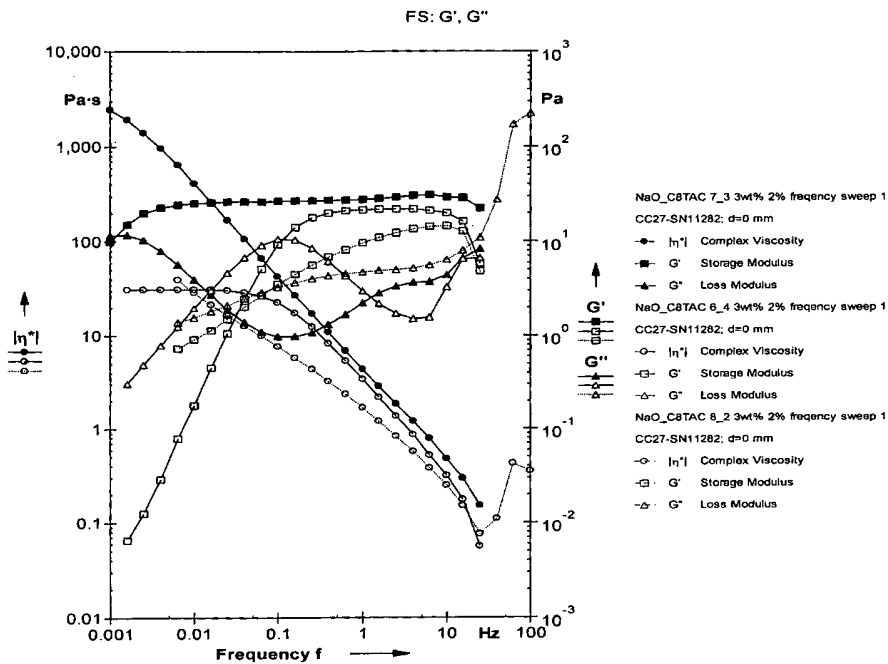


FIG. 4

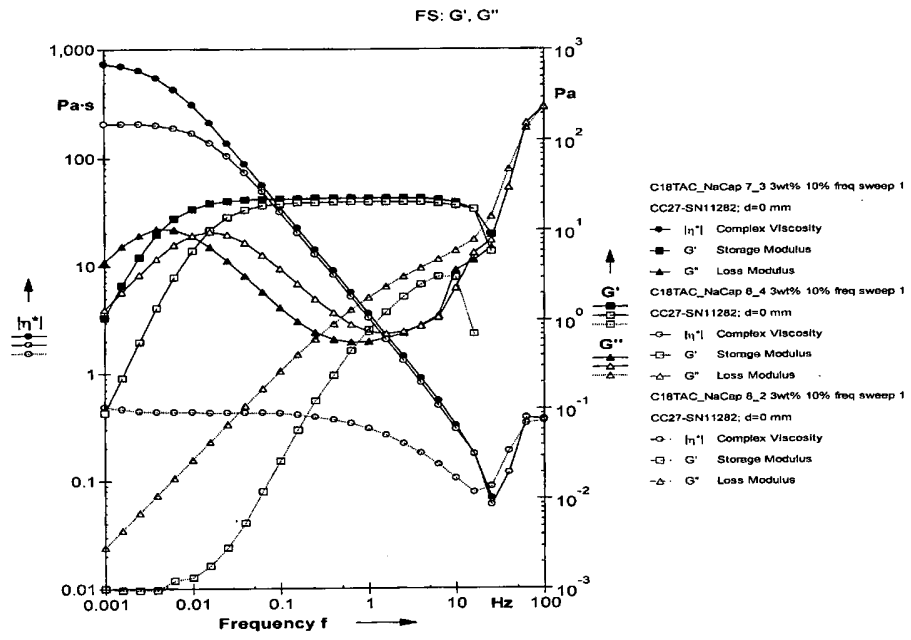


FIG. 5

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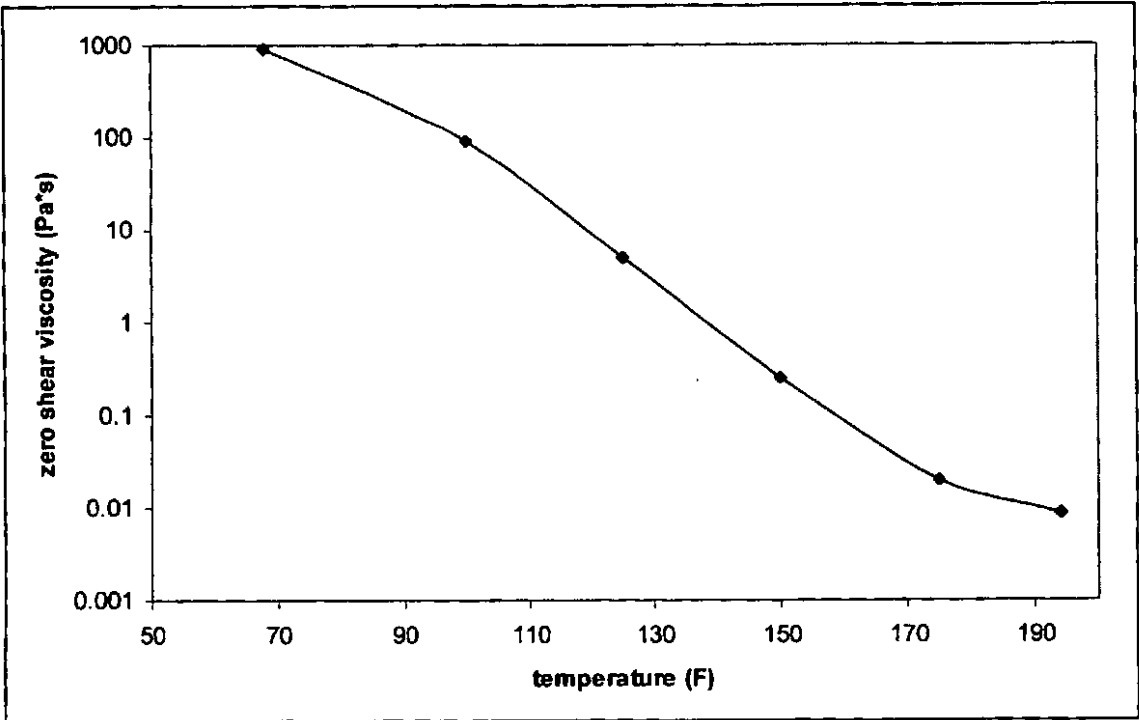


FIG. 6

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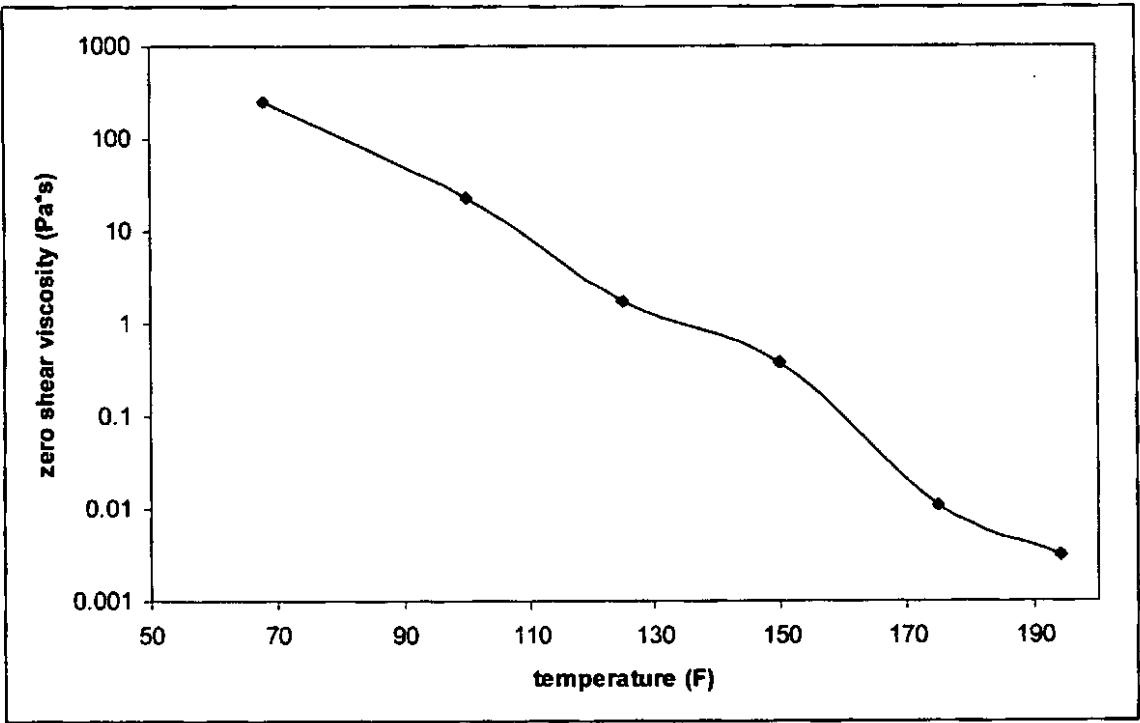


FIG. 7

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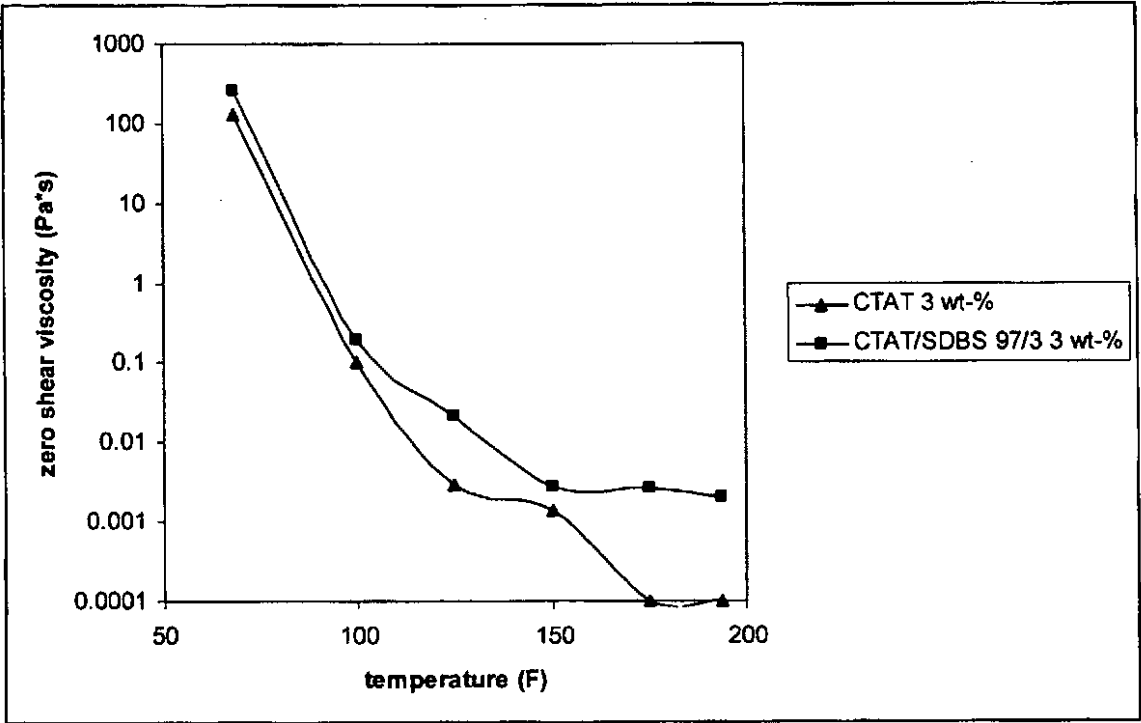


FIG. 8

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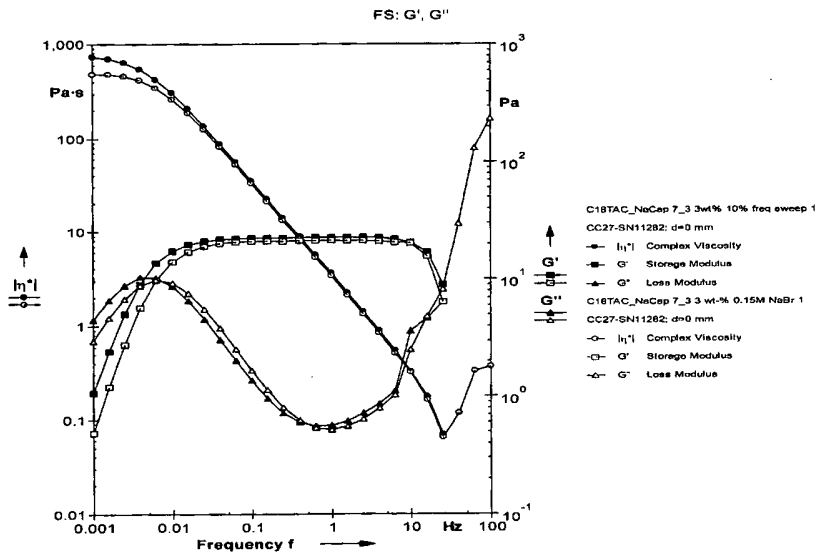


FIG. 9

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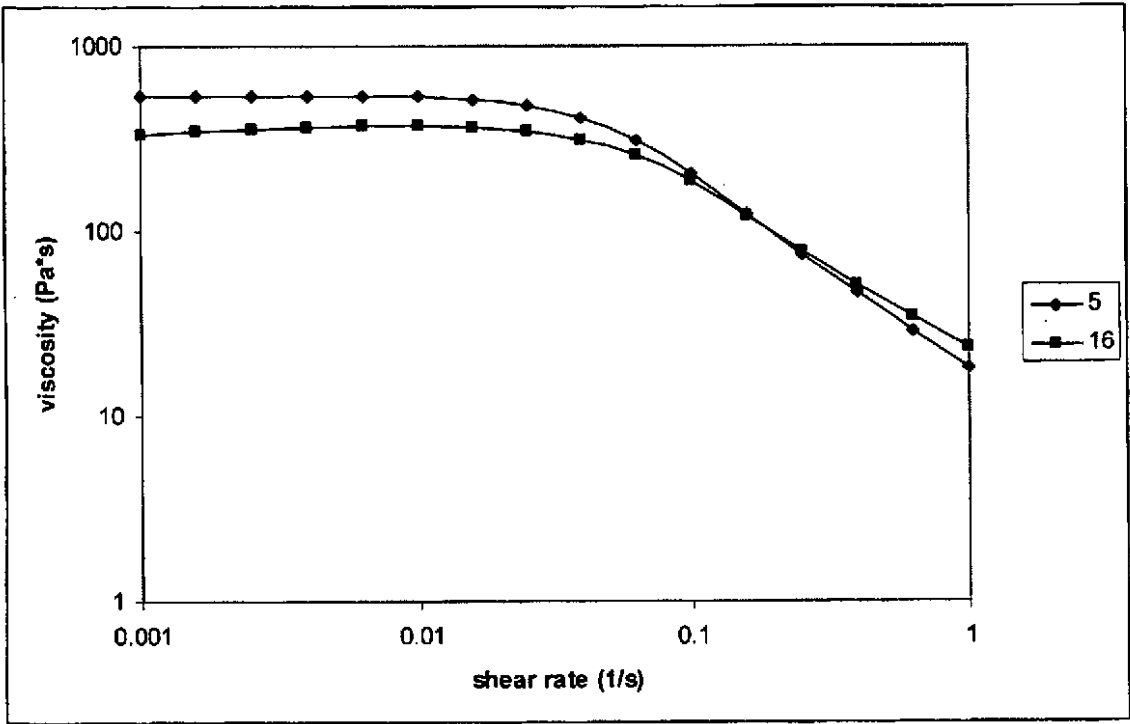


FIG. 10

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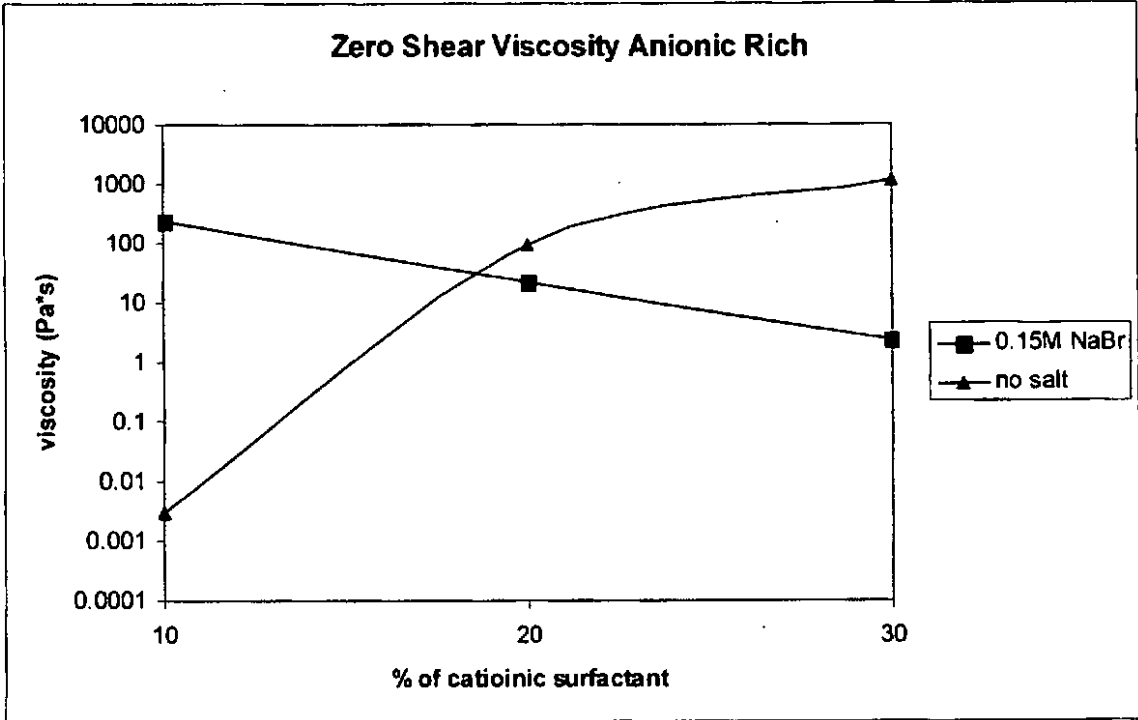


FIG. 11

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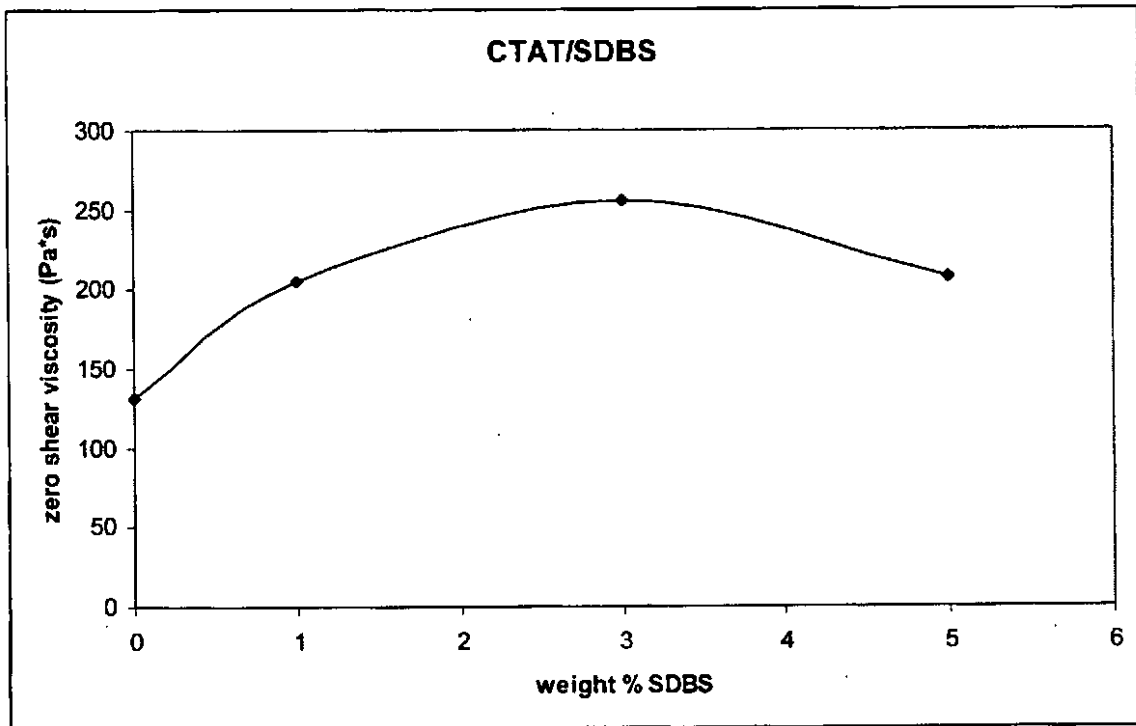


FIG. 12

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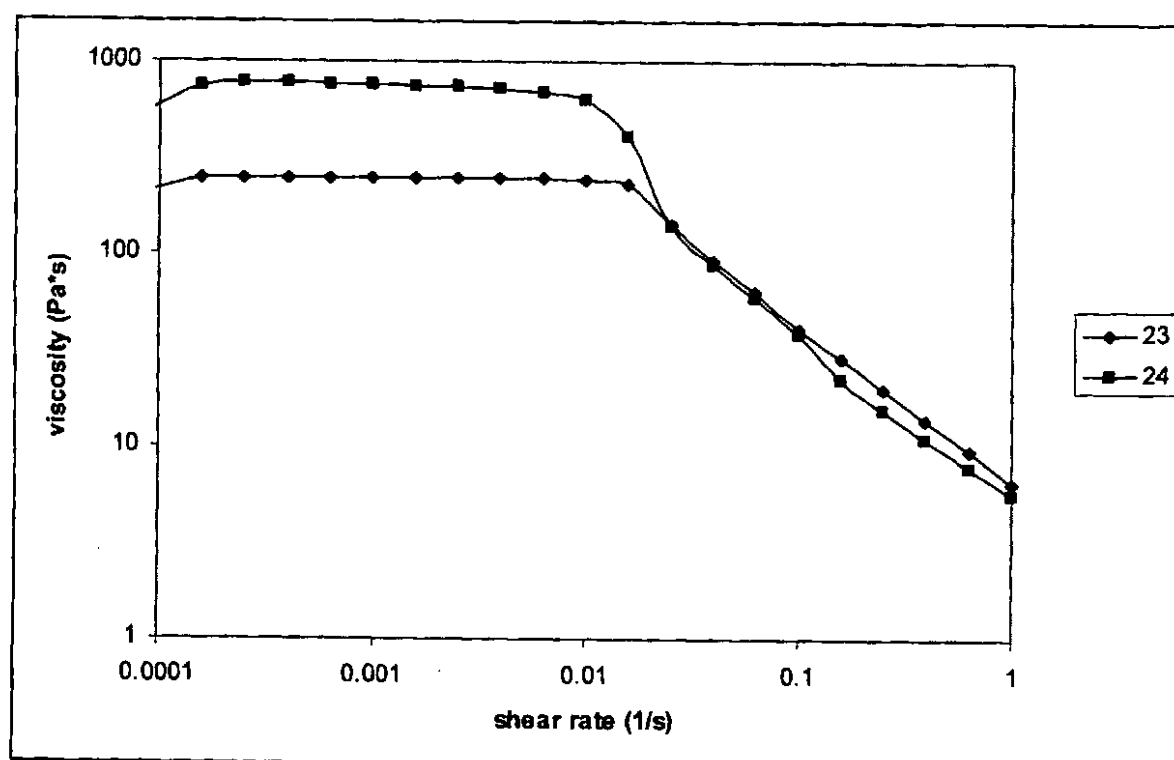


FIG. 13

INTERNATIONAL SEARCH REPORT

International application No

PCT/GB2010/000473

A. CLASSIFICATION OF SUBJECT MATTER

INV. C09K8/035 C09K8/40 C09K8/42 C09K8/60 C09K8/68
E21B43/04

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 C11D

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 practical, 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 2003/019627 A1 (QU QI [US] ET AL SAMUEL MATHEW M [US] ET AL) 30 January 2003 (2003-01-30) claims 1,5; examples 20,21	1-24
X	US 6 468 945 B1 (ZHANG KEWEI [CA]) 22 October 2002 (2002-10-22) column 1, line 54 - line 65; claims 1,7; figure 1; table 1	1-3,5-7, 9-22
X	WO 01/83946 A1 (TRICAN WELL SERVICE LTD [CA]; ZHANG KEWEI [CA]; ONEIL BILL [CA]) 8 November 2001 (2001-11-08) page 1, line 1 - line 5 page 4, line 6 - line 9 page 7, line 3 - line 15; examples 1,4,7; table 1	1-3,5-22
	-/-	

☒ Further documents are listed in the continuation of Box C.☒ See patent family annex.

* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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- "&" document member of the same patent family

Date of the actual completion of the international search

11 May 2010

Date of mailing of the international search report

26/05/2010

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Authorized officer

Redecker, Michael

INTERNATIONAL SEARCH REPORT

International application No

PCT/GB2010/000473

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 01/29369 A1 (SCHLUMBERGER TECHNOLOGY CORP [US]) 26 April 2001 (2001-04-26) page 20, line 8 - line 12; claim 1; figure 1 -----	1-3,5-23
X	US 3 985 686 A (BARRAT CHRISTIAN) 12 October 1976 (1976-10-12) column 5, line 22 - line 39; claim 1; examples 1,2 -----	1-21
X	US 2008/305157 A1 (ENGLISH DOUGLAS S [US] ET AL) 11 December 2008 (2008-12-11) paragraphs [0002], [0004]; example 1 -----	1-21
A	C. TONDRE, C. CAILLET: "Properties of the amphiphilic films in mixed cationic/anionic vesicles: a comprehensive view from a literature analysis" ADV. COLL. INTERF. SCI, vol. 93, 31 December 2001 (2001-12-31), pages 115-134, XP002581807 tables 1,2 -----	1-24

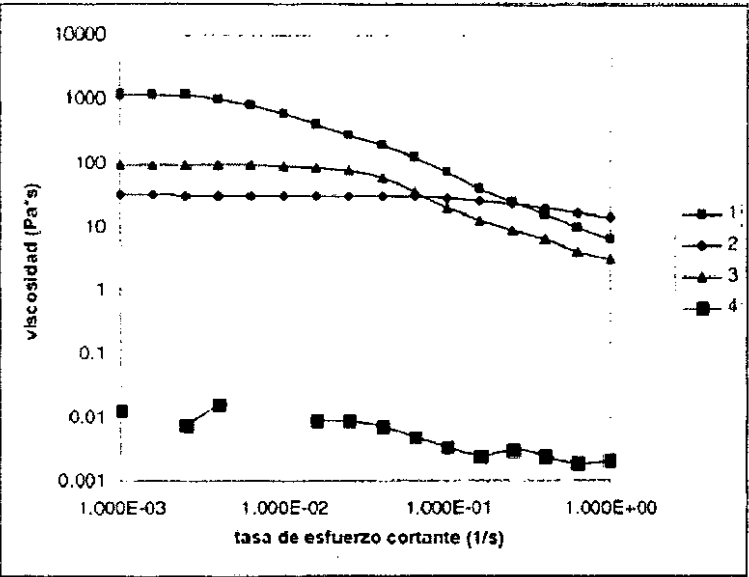
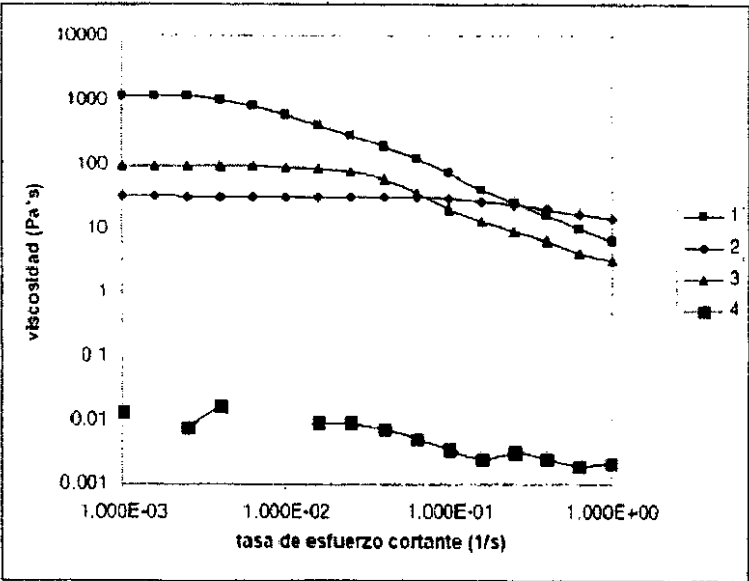
INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/GB2010/000473

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US 2008305157 A1	11-12-2008	NONE	



PATENTE DE INVENCION ☐

MODELO DE

☐

Indicación que se solicita una patente.

☐

Datos de identificación del solicitante o de la persona que presenta la solicitud

☐

Descripción de la invención

☐

Dibujos de ser estos pertinentes

☐

Comprobante de pago de las tasas establecidas (De ser el caso formato de descuento)

Completa ☐

Incompleta ☐

PATENTE DE INVENCION PCT ☒

MODELO DE UTILIDAD PCT ☐

Art.33 Decisión 486/00, Circular Única

☒

Indicación que se solicita una PCT

☒

Copia de la solicitud en español, tal como fue presentada inicialmente (capítulo descriptivo, reivindicatorio, resumen)

☒

Dibujos de ser estos pertinentes

☒

Comprobante de pago de las tasas establecidas (de ser el caso formato de descuento)

Completa ☒

Incompleta ☐

DISEÑO INDUSTRIAL ☐

(Art. 119 Decisión 486/00)

☐

Indicación que se solicita Diseño industrial

☐

Datos de identificación del solicitante o de la persona que presenta la solicitud

☐

Representación gráfica y fotográfica del Diseño industrial o muestra del material que incorpora el diseño

☐

Comprobante de pago de las tasas establecidas

Completa ☐

Incompleta ☐

ESQUEMA DE TRAZADO ☐

(Art. 92 Decisión 486/00)

☐

Indicación que se solicita un esquema de trazado

☐

Datos de identificación del solicitante o de la persona que presenta la solicitud

☐

Representación gráfica de un esquema de trazado

☐

Comprobante de pago de las tasas establecidas

Completa ☐

Incompleta ☐