

No. 12-002850- -00000-0000

Fecha: 2012-01-10 15:16:46

Dep. 2020 DIR NUEVASCR

Tra. 11 PATENTEIYII

Eve: 378 FASENACIONALI

Act. 411 PRESENTACION

Folios: 92

Act. 411 PRESENTACION

Folios: 91



Industria y Comercio

SUPERINTENDENCIA

DELEGATURA PROPIEDAD INDUSTRIAL

SOLICITUD REGISTRO DE PATENTE DE INVENCION PCT

EXPEDIENTE No _____

TITULO AGENTES ESTABILIZADORES DE EMULSIÓN
PARA FLUIDOS DE PERFORACIÓN Y TERMINACIÓN

CLASIFICACION INTERNACIONAL _____

SOLICITANTE HALLIBURTON ENERGY SERVICES, INC.

DOMICILIO Dunkan, Oklahoma

APODERADO JUANITA ACOSTA GOMEZ

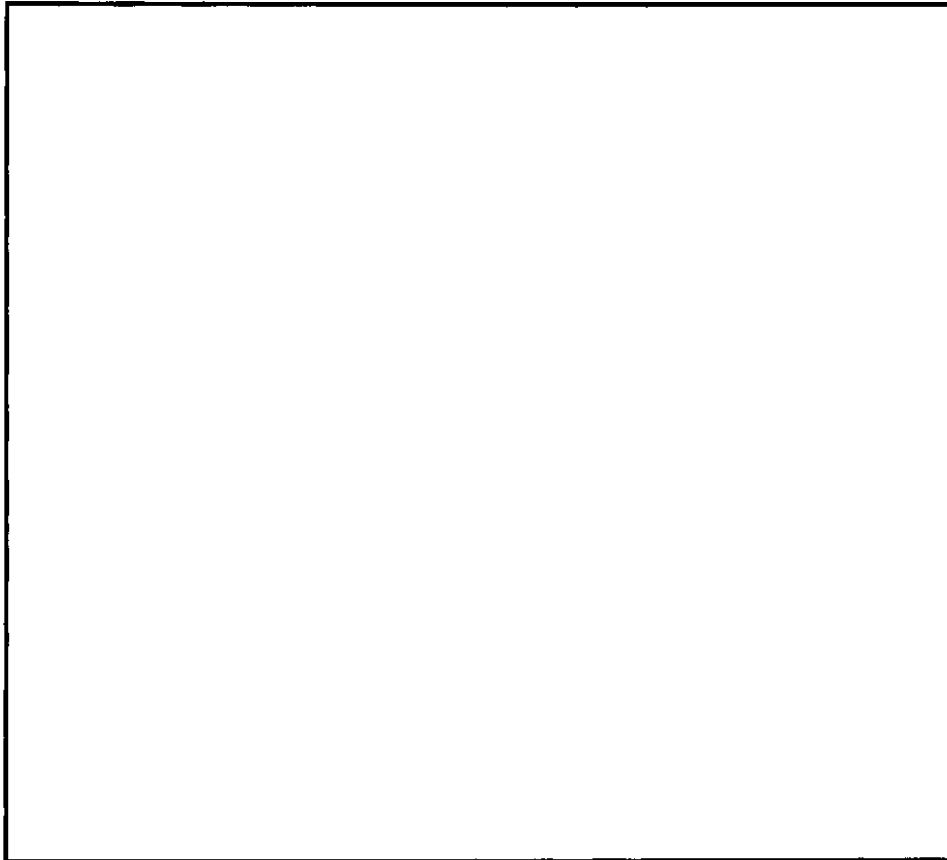
BOGOTA D.C. _____

0		PETITO		SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO	
				 No. 12-002850- -00000-0000	
		Fecha: 2012-01-10 15:16:46		Dep. 2020 DIR.NUEVASCR	
		Tra. 11 PATENTEIYII		Eve: 378 FASENACIONALI	
		Act. 411 PRESENTACION		Folios: 92	
		Act: 411 PRESENTACION		Folios: 91	
FORMULARIO UNICO DE SOLICITUD DE PATENTE PCT ENTRADA EN FASE NACIONAL					
① SOLICITUD DE:					
☒ Patente de Invención		☐ Patente de Modelo de Utilidad			
☒ Capítulo I		☐ Capítulo II			
② SOLICITANTE		Nombre: Halliburton Energy Services, Inc		IDENTIFICACION	
		Dirección: P.O. Box 1431, Duncan, OK 73536, Estados Unidos de América		☐ NIT ☐ NIT	
		Nacionalidad o Domicilio: Oklahoma, Estados Unidos de América		☐ Otro ☒ Otro	
		Lugar de Constitución: Estados Unidos de América		Cuál _____	
		Teléfono: 3137800 Fax: 3122410		Número _____	
		E-mail: general@cardenasycardenas.com			
③ REPRESENTANTE O APODERADO		Nombre: JUANITA ACOSTA GOMEZ		IDENTIFICACION	
		Dirección: Carrera 7 No 71-52 Torre B Piso 9		☐ NIT ☐ NIT	
		Teléfono: 312 3600 Fax: 312 2410		☒ CC ☐ Otro	
		E-Mail: general@cardenasycardenas.com		Cuál <u>52618636 BTA</u>	
				Número <u>14884 C.S.J.</u>	
④ INVENTOR(ES) (72)		Nombre: Ryan Van Zanten			
		Dirección: 4335 Tylergate Drive, Spring, Texas 77373, Estados Unidos de América			
		Nacionalidad o Domicilio: Estadounidense			
⑤ PCT (86)					
Solicitud Internacional No.		<u>WO/2011/004163 A1</u>		Fecha <u>13.01.2011</u>	
Publicación Internacional No.		<u>PCT/GB2010/001317</u>		Fecha <u>09.07.2010</u>	
⑥ Título(54): AGENTES ESTABILIZADORES DE EMULSIÓN PARA FLUIDOS DE PERFORACIÓN Y TERMINACIÓN					
⑦ Clasificación Internacional (51):					
⑧ Prioridad		(33) País de Origen	(32) Fecha	(31) N° de Solicitud	
SI ☒ NO ☐		<u>US</u>	<u>10.07.2009</u>	<u>12/501,267</u>	
⑨ Comprobante de Pago No.: _____ Fecha _____					
P-621					

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.
- ☐ De ser el caso, modificaciones efectuadas a la solicitud internacional.
- ☒ Prioridad
<http://www.wipo.int/patentscope/search/en/detail.jsf.jsessionid=09C85C9E72C0C1FAB89DB465AB5EA367.wap2?docId=WO2011004163&recNum=212&tab=PCTDocuments&maxRec=1546&office=&prevFilter=&sortOption=&queryString=%28PA%2FHalliburton+AND+PA%2FEnergy%29+>
- ☒ Recibo de Reivindicaciones adicionales No.

11 FIGURA CARACTERISTICA



12 Solicito la Concesión de la patente

NOMBRE: JUANITA ACOSTA GOMEZ

FIRMA:

Juanita Acosta

C.C. 52618636 BTA TP. 79686 C.S.J.

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

 Industria y Comercio SUPERINTENDENCIA	RECIBO DE CAJA	No. 12 - 002027
		Bogotá D.C., Enero 10 de 2012 - 15:03:19

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	181445320	10/01/2012	3.670.000.00

*** Conceptos Pagados ***			
CANT.	RENTISTICO	CONCEPTO	Vr.UNDITARIO Vr.CONCEPTO
1 50005-01-09	OTROS SERVICIOS DE PROPIEDAD INDUSTRIAL	99 OTROS SERVICIOS ADMINISTRATIVOS	210.000.00 210.000.00
			\$210.000.00
=====			

SON: **DOSCIENTOSDIEZ MIL PESOS MONEDA CORRIENTE**

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

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO

No. 12-002850- -00000-0000
Fecha: 2012-01-10 15:16:46 Dep. 2020 DIR.NUEVASCR
Tra. 11 PATENTEIYII Eve: 378 FASENACIONALI
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Act. 411 PRESENTACION Folios: 91

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



RECIBO DE CAJA

No. 12 - 002019

Bogotá D.C., Enero 10 de 2012 - 15:03:19

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	181445320	10/01/2012	3.670.000.00

*** Conceptos Pagados ***

CANT	RENTISTICO	CONCEPTO	Vr.UNDITARIO	Vr.CONCEPTO
1	50005-01-01 SOLICITUDES	1 TRAMITES DE SOL. DE PATENTE DE INVENCIÓN	590.000.00	590.000.00
				\$590.000.00

SON: **QUINIENTOS NOVENTA MIL PESOS MONEDA CORRIENTE**

Responsable: _____

Recibo de Caja Aplicado al Expediente No. _____

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO



No. 12-002850- -00000-0000

Fecha: 2012-01-10 15:16:46 Dep. 2020 DIR.NUEVASCR
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Act. 411 PRESENTACION Folios: 91

Sede Centro: Carrera 13 No. 27 - 00 Pisos 3,4,5 y 10 Bogotá, D.C.- Colombia

Web: www.sic.gov.co e-mail: info@sic.gov.co Conmutador: (571) 5870000 Fax: (571) 5870284 Línea: 018000-910165 Call Center: (571) 6513240

Enero 10 de 2012 - 15:03:20



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

(74) Apoderado: **JUANITA ACOSTA GOMEZ**

(30) Prioridad

(31) **No. Prioridad**

(32)

Fecha

(33) **País**

12/501,267

10.07.2009

US

(85) Fecha inicio fase nacional: **10.01.2012**

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

Fecha de presentación de la solicitud: **09.07.2010**

No. de solicitud **PCT/GB2010/001317**

(54) Título **AGENTES ESTABILIZADORES DE EMULSIÓN PARA FLUIDOS DE PERFORACIÓN Y TERMINACIÓN**



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			
(74) Apoderado: JUANITA ACOSTA GOMEZ			
(30) Prioridad	(31) No. Prioridad 12/501,267	(32) Fecha 10.07.2009	(33) País US
(85) Fecha límite inicio fase nacional: 10.01.2012		(87) Publicación internacional:	
(86) Datos relativos a la presentación de la solíc. PCT Fecha de presentación de la solicitud: 09.07.2010 No. de solicitud PCT/GB2010/001317		Fecha: 13.01.2011 No. Publicación WO2011/004163 A1	

(54) Título: **AGENTES ESTABILIZADORES DE EMULSIÓN PARA FLUIDOS DE PERFORACIÓN Y TERMINACIÓN**

(57) Resumen:

La presente invención proporciona una composición de emulsión estabilizada que comprende: un fluido oleaginoso; un fluido que es por lo menos parcialmente inmiscible con este último y un agente estabilizador de emulsión que comprende un primer compuesto iónico soluble en el fluido oleaginoso o el fluido que es por lo menos parcialmente inmiscible con este último; y un segundo compuesto iónico con una carga de signo opuesto al primer compuesto iónico y que es por lo menos parcialmente soluble en el fluido opuesto como el primer compuesto iónico. La presente invención proporciona también métodos que implican el uso de la composición de emulsión estabilizada y métodos para preparar a esta última.

(21) N° de solicitud:		(51) Int Cl:	
22) Fecha de solicitud:		(71) Solicitante(s) Halliburton Energy Services, Inc	
(30) Prioridad	(31) No. Prioridad 12/501,267	(32) Fecha 10.07.2009	(33) País US
		(72) Inventor(es) Ryan Van Zanten	
		(74) Apoderado: JUANITA ACOSTA GOMEZ	
(85)	Fecha limite inicio fase nacional: 10.01.2012		(87) Publicación internacional
(86)	Datos relativos a la presentación de la solicitud PCT		Fecha: 13.01.2011
	Fecha de presentación de la solicitud: 09.07.2010		N° publicación: WO 2011/004163
	No. de solicitud PCT/GB2010/001317		
(54) Título: AGENTES ESTABILIZADORES DE EMULSIÓN PARA FLUIDOS DE PERFORACIÓN Y TERMINACIÓN			

Resumen:

La presente invención proporciona una composición de emulsión estabilizada que comprende: un fluido oleaginoso; un fluido que es por lo menos parcialmente inmiscible con este último y un agente estabilizador de emulsión que comprende un primer compuesto iónico soluble en el fluido oleaginoso o el fluido que es por lo menos parcialmente inmiscible con este último; y un segundo compuesto iónico con una carga de signo opuesto al primer compuesto iónico y que es por lo menos parcialmente soluble en el fluido opuesto como el primer compuesto iónico. La presente invención proporciona también métodos que implican el uso de la composición de emulsión estabilizada y métodos para preparar a esta última.



000351

The State of Texas

Secretary of State

Requested for use in COLOMBIA

Not for use within the United States of America

This Apostille only certifies the signature, the capacity of the signer and the seal or stamp it bears. It does not certify the content of the document for which it was issued.

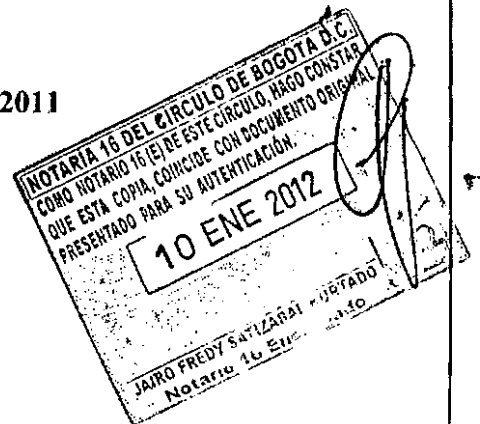
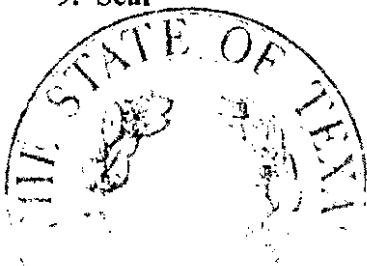
APOSTILLE

(Convention de La Haye du 5 Octobre 1961)

1. Country	United States of America
This public document	
2. has been signed by	VICKI KELLEY
3. acting in the capacity of	Notary Public, State of Texas
4. and bears the seal/stamp of	VICKI KELLEY, Notary Public, State of Texas, Commission Expires: 05-16-12

CERTIFIED

5. at Austin, Texas	6. on October 24, 2011
7. by the Secretary of State of Texas	
8. Certificate No. N-822556	
9. Seal	10. Signature:



Hope Andrade
Secretary of State

ST/tl

- Colombia -

POWER OF ATTORNEY

HALLIBURTON ENERGY SERVICES, INC., a company duly organized and existing under the laws of the State of Delaware, United States of America (hereinafter referred to as the "Company"), and domiciled at P.O.- Box 1431, Duncan, Oklahoma 73536, United States of America and acting through William E. Shull, the duly empowered Senior Vice President and Chief Patent Counsel does hereby appoint, authorize, designate and empower the following individuals as the true and lawful agents and Attorneys-In-Fact of the Company to act for and on behalf of the Company with respect to the following powers:

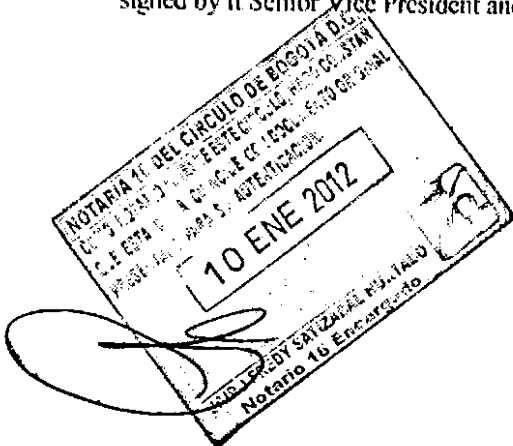
FIRST: DARIO CARDENAS-NAVAS and/or LUZ HELENA ADARVE-GOMEZ and/or EDUARDO CARDENAS-CABALLERO and/or BERNARDO P. CARDENAS-MARTINEZ and/or JUANITA ACOSTA GOMEZ and/or JULY GALINDO QUINTERO, registered lawyers of the firm CARDENAS & CARDENAS-LAWYERS, domiciled at Carrera 7 No. 71-52, Torre B, Piso 9 Bogotá, D.C., Colombia, to carry before the corresponding Colombian national Offices and authorities the proceedings to obtain trademarks, patents, utility models, industrial drawings and designs, deposits of commercial names and ensigns, as well as processing of renewals, assignments, change of name or domicile of the owner, waivers and licenses of the same for which purpose they are empowered to take before said authorities all necessary actions for the indicated purposes; to file applications, statements, claims, formulate descriptions, amendments, oppositions and appeals; pay all taxes and installments and make any other payments determined by law; to receive every document and values issuing the respective discharge; to fulfill any other requirements and take, in general, every measure that they shall deem opportune for the defense and protection of the Industrial Property of the company in the event of infringements, oppositions, proceedings for cancellation or annulment, imposition of fines, passing the antecedents to the courts; they are empowered to appear as plaintiff or defendant before the competent judges, being entitled to transact, submit to arbitration, waive, receive, resign, withdraw, appeal and all other legal powers which may be necessary, and it is hereby declared ever since now valid and good whatever such attorneys do for its benefit, granting them also power to substitute this proxy and if necessary to revoke such substitutions.

SECOND: That for purposes of articles 597 and 543 of the Colombian code of Commerce the agents and Attorneys-in-Fact are empowered to receive service of notice and designate judicial and extrajudicial attorneys.

IN WITNESS WHEREOF, HALLIBURTON ENERGY SERVICES, INC. has caused this to be signed by it Senior Vice President and Chief Patent Counsel on October 20, 2011.

HALLIBURTON ENERGY SERVICES, INC.

By: William E. Shull
William E. Shull
Senior Vice President and Chief Patent Counsel



SECRETARIAL CERTIFICATION

On this 21st day of October, 2011, the undersigned Secretary of Halliburton Energy Services, Inc.

CERTIFIES

1. That: **William E. Shull** of legal age and domiciled in Houston, Texas, United States of America, set his hand on the foregoing document.

2. That the grantor is to me personally known and that he has legal capacity to execute the instrument.

3. That the grantor has executed the foregoing document as Senior Vice President and Chief Patent Counsel of Halliburton Energy Services, Inc..

4. That the juridical person Halliburton Energy Services, Inc., having its office in the State of Texas, and an office in the State of Oklahoma, is duly organized, has present legal existence and that the present act is within the scope of its corporate purposes.

5. That the grantor has in fact the referred to authority and that his representation is legal.

6. That I have based certifications 3, 4 and 5 above on the following authentic documents for such purposes exhibited to me and which I mention specifically, giving their dates and their origin or source:

-Resolution dated February 1, 2006, appointing Mr. William E. Shull as Senior Vice President and Chief Patent Counsel of Halliburton Energy Services, Inc.;

-By-Laws for Halliburton Energy Services, Inc..

Bruce A. Metzinger
Bruce A. Metzinger, Secretary

CERTIFICADO DEL SECRETARIO

A los 21st días del mes de octubre de 2011, el suscrito Secretario de Halliburton Energy Services, Inc.

CERTIFICA

1. Que **William E. Shull** mayor y domiciliado en Houston, Texas, Estados Unidos de America, suscribió de su puño y letra el documento que antecede.

2. Que conozco al otorgante y que tiene capacidad legal para el otorgamiento del documento anterior.

3. Que el otorgante ha suscrito el referido documento en su carácter Vice Presidente Senior y Abogado Director de Patentes de Halliburton Energy Services, Inc.

4. Que la persona jurídica, Halliburton Energy Services, Inc., con oficina en el Estado de Texas, y una oficina en el estado de Oklahoma, está legalmente constituida, que tiene existencia legal actual y que el presente acto está comprendido entre los que constituyen su objeto social.

5. Que el otorgante tiene efectivamente la representación que ostenta, y que esta es legal.

6. Que he basado las certificaciones 3, 4 y 5 anteriores en los siguientes documentos auténticos que al efecto se me exhibieron y que menciono específicamente con expresión de sus fechas y de su origen o procedencia:

-Resolución de fecha 1 febrero de 2006, en la que se nombra al Sr. William E. Shull como Vice Presidente Senior y Abogado Director de Patentes de Halliburton Energy Services, Inc.;

- Estatutos de Constitución de la Halliburton Energy Services, Inc..

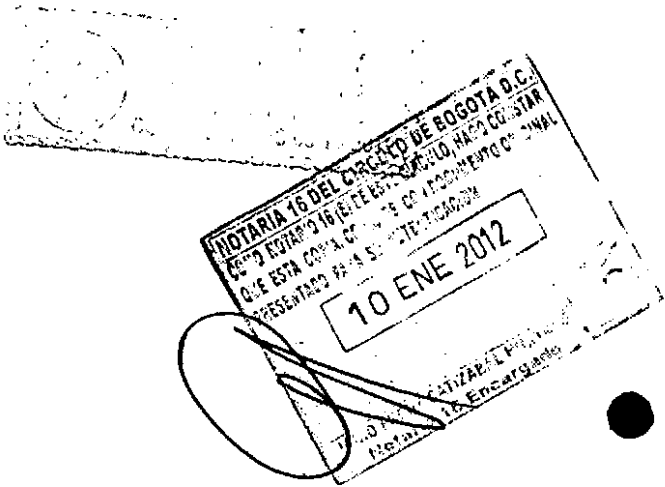
Bruce A. Metzinger
Bruce A. Metzinger, Secretario



UNITED STATES OF AMERICA §
STATE OF TEXAS §
COUNTY OF HARRIS §

BEFORE ME, the undersigned, a Notary Public in and for said State, on this day personally appeared Bruce A. Metzinger, Secretary of Halliburton Energy Services, Inc., a Delaware corporation, known to me to be the person and officer whose name is subscribed to the foregoing instrument and acknowledged to me that he executed the same for the purposes and consideration therein expressed, and in the capacity therein stated, this 21st day of October, 2011.

Victor Kelley
Notary Public, State of Texas





El Estado de Texas
Secretaría de Estado

Solicitado para uso en COLOMBIA

No es para uso dentro de los Estados Unidos de América.

Esta Apostilla solo certifica la firma, la calidad del firmante y el sello o timbre que lleva.

Esta no certifica el contenido del documento para el que se emite la misma.

APOSTILLA

(Convención de La Haya de Octubre 5 de 1961)

1. País: Estados Unidos de América

Este documento público

2. ha sido firmado por VICKI KELLEY

3. actuando en calidad de Notario Público, Estado de Texas

4. y lleva el sello/timbre de VICKI KELLEY, Notario Público, Estado de Texas

Comisión Expira: 05-16-12

CERTIFICA

5. en Austin, Texas

6. el 24 de octubre, 2011

7. por el Secretario del Estado de Texas

8. Certificado No. N-822556

9. Sello

10. Firma



Hope Andrade

Hope Andrade

Secretario de Estado
ST/tl

MINISTERIO DE
RELACIONES EXTERIORES
BOGOTÁ D.C.
2011 OCT 17 12:06

NO SE ASUME
RESPONSABILIDAD
POR ESTO
185980
Sergio / aforre

NOTARIA 16 DEL CIRCULO DE BOGOTÁ D.C.
COMO NOTARIO 16 DE ESTE CIRCULO, HAGO CONSTAR
QUE ESTA COPIA CONCORDA CON DOCUMENTO ORIGINAL
PRESENTADO PARA SU AUTENTICACIÓN
10 ENE 2012
JAIRÓ FREDY ESPARAL VILLALBA
Notario 16 del Circuito de Bogotá D.C.

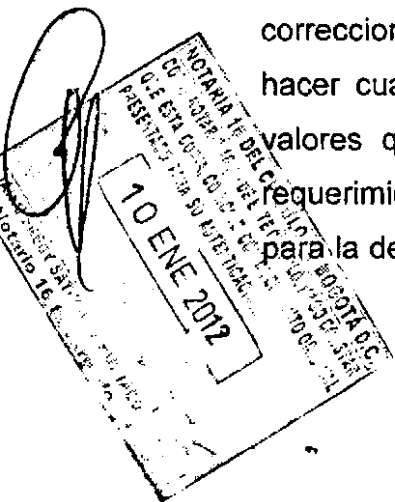
Sergio Cleuterio Lopez Mendoza
Traductor e Interpreté Oficial
Resol. No. 2839 Minjusticia 1991

Colombia-

PODER DE ABOGADO

HALLIBURTON ENERGY SERVICES, INC., una compañía debidamente constituida y en vigencia de conformidad con las leyes del Estado de Delaware, Estados Unidos de América (en lo sucesivo denominada como la "Compañía") y con domicilio en P.O. Box 1431, Duncan, Oklahoma 73536, Estados Unidos de América y que actúa a través de William E. Shull, el Vicepresidente Senior debidamente apoderado y Jefe de Abogados de Patentes por la presente nombra, autoriza, designa y faculta los siguientes individuos como los agentes legales y Apoderados de la Compañía para actuar para y en nombre de la compañía con respecto a las siguientes facultades:

PRIMERO: DARIO CARDENAS-NAVAS y/o LUZ HELENA ADARVE GOMEZ y/o EDUARDO CARDENAS-CABALLERO y/o BERNARDO P. CARDENAS-MARTINEZ y/o JUANITA ACOSTA GOMEZ y/o JULY GALINDO QUINTERO, abogados registrados de la firma CARDENAS & CARDENAS ABOGADOS, domiciliada en la carrera 7 No. 71-52, torre B, piso 9, Bogotá D.C., Colombia, para realizar ante las autoridades y las Oficinas nacionales Colombianas correspondientes los procesos para obtener marcas registradas, patentes, modelos de utilidad, diseños y dibujos industriales, depósitos de insignias y nombres comerciales, así como también procesar renovaciones, cesiones, cambios de nombre o domicilio del propietario, renunciaciones y licencias de las mismas para cuyo propósito ellos están facultados para tomar ante dichas autoridades todas las acciones necesarias para los propósitos indicados; para presentar solicitudes, declaraciones, reclamaciones, formular descripciones, correcciones, oposiciones y apelaciones; pagar todos los impuestos y cuotas y hacer cualquier otro pago determinado por ley; recibir todos los documentos y valores que emiten la respectiva cancelación; para cumplir cualesquier otros requerimientos y tomar, en general, todas las medidas que lleguen a ser oportunas para la defensa y protección de la Propiedad Industrial de la Compañía en el caso



Jorge Eluterio Latorre Mendoza
 Traductor e Interpreté Oficial
 Resol. No. 2889 Minjusticia 1991

de infracciones, oposiciones, procedimientos para cancelación o anulación, imposición de multas, paso de antecedentes a los tribunales; ellos están facultados para aparecer como demandante o defensor ante los jueces competentes, tienen derecho a transar, presentar arbitraje, renuncia, recibir, renunciar, retirar, apelar y todos los otros poderes legales que puedan ser necesarios, y por la presente declaro desde ahora válido y bueno todo lo que tales abogados hagan para su beneficio, otorgándoles también poder para sustituir este poder y si es necesario revocar tales sustituciones.

SEGUNDO: Que para propósitos de los artículos 597 y 543 del Código de Comercio Colombiano los abogados tienen facultad para recibir servicios de notificación y designar abogados judiciales y extrajudiciales.

EN FE DE LO CUAL, **HALLIBURTON ENERGY SERVICES, INC.** ha producido este documento para ser firmado por su Vicepresidente Senior y Jefe de Abogados de Patentes el 20 de octubre, 2011.

HALLIBURTON ENERGY SERVICES, INC.

POR: (aparece firma)

William E. Shull

Vicepresidente Senior y Jefe de Abogados de Patentes

Aparece Certificado del Secretario del 21 de octubre de 2011 de William E. Shull
Firmado por Bruce A. Metzinger, Secretario



Sergio Eleuterio Latorre Mendoza
Traductor e Interpreté Oficial
Resol. No. 2834 Minjusticia 1991

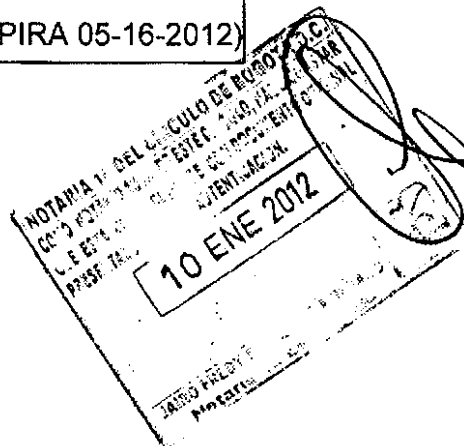
ESTADOS UNIDOS DE AMÉRICA §
 ESTADO DE TEXAS §
 CONDADO DE HARRIS §

ANTE MÍ, el abajo firmante, un Notario Público en y para dicho Estado, en este día compareció personalmente Bruce A. Metzinger, Secretario de Halliburton Energy Services, Inc., una corporación de Delaware, a quien conozco por ser la persona y funcionario cuyo nombre se suscribe al anterior instrumento y reconoció que el legalizó el mismo para los propósitos y consideración aquí expresadas, y en la calidad aquí establecida, el 21 de octubre, 2011.

(Aparece firma)

Notario Público, Estado de Texas

(Aparece sello:
 VICKY KELLEY
 NOTARIO PÚBLICO
 ESTADO DE TEXAS
 COMISIÓN EXPIRA 05-16-2012)



Sergio Eleuterio Latorre Mendoza
 Traductor e Interprete Oficial
 Resol. No. 2839 Minjusticia 1991

ANTECEDENTES

La presente invención se refiere a emulsiones y métodos para el uso de tales emulsiones. En forma más particular, la presente invención se refiere a agentes estabilizadores de emulsión y sus usos en aplicaciones subterráneas.

Las emulsiones comprenden generalmente dos fases inmiscibles. Las fases inmiscibles pueden incluir una fase continua (o externa) y una fase no continua (o interna). La fase no continua puede comprender al fluido secundario que existe generalmente en forma de gotas en la fase continua. Dos variedades de emulsiones son aceite en agua y agua en aceite. Las emulsiones de aceite en agua incluye generalmente un fluido por lo menos parcialmente inmiscible en un fluido oleaginoso (generalmente un fluido con base acuosa) como la fase continua y un fluido oleaginoso como la fase no continua. Las emulsiones agua en aceite son opuestas y tienen al fluido oleaginoso como la fase continua y un fluido por lo menos parcialmente inmiscible en el fluido oleaginoso (generalmente un fluido con base acuosa) como la fase no continua. Las emulsiones de agua en aceite pueden ser referidas también como emulsiones invertidas.

Se ha utilizado tales emulsiones en varias aplicaciones de petróleo y gas. Por ejemplo, las emulsiones pueden ser utilizadas en la industria del petróleo y el gas para aplicaciones de tratamiento

subterráneo, incluyendo operaciones de perforación, producción y terminación. Se puede utilizar emulsiones invertidas debido a que los fluidos de tratamiento con base oleaginosa (conocidos también como lodos) pueden tener características deseables de rendimiento cuando se los compara con lodos que tienen base de agua en algunas situaciones, por ejemplo, cuando existen abundancia de materiales reactivos en agua en un orificio de pozo. Estas características de rendimiento pueden incluir, por ejemplo, mejor lubricación de las sartas de perforación y herramientas de fondo de pozo, formación de torta de filtro más delgada y mejor estabilidad en el orificio.

Una emulsión del tipo agua en aceite que no tiene un agente emulsionador capaz de estabilizar al fluido que es por lo menos parcialmente inmiscible en el fluido oleaginoso, sufrirá típicamente procesos de degradación natural tales como aglutinación de gotas y maduración Ostwald, hasta que existen las dos fases que son parcialmente inmiscibles y separadas y la emulsión deja de existir. El tener una emulsión invertida inestable puede ser problemático debido a que si se desestabiliza la emulsión, entonces no puede tener propiedades confiables y consistentes. Este problema puede ser agravado por las fuerzas físicas que puede sufrir la emulsión cuando está siendo utilizada en aplicaciones subterráneas, tales como esfuerzos térmicos, mecánicos y químicos. Los agentes estabilizadores de emulsión,

referidos algunas veces como emulsionadores, pueden ser útiles en emulsiones como estabilizadores y especialmente cuando se utilizan en aplicaciones subterráneas. El término "agente estabilizador de emulsión" o emulsionador tal como se emplea aquí, puede referirse a cualquier compuesto capaz de reducir la tensión interfacial entre un fluido oleaginoso y un fluido por lo menos parcialmente inmiscible en este último.

Algunos agentes tradicionales estabilizadores de emulsión son agentes estabilizadores de emulsión basados en agente de actividad superficial. Estos agentes estabilizadores comprenden generalmente una parte hidrofóbica que interactúa con la fase aceite y una parte hidrofílica que interactúa con la fase no oleaginosa. Estas interacciones disminuyen generalmente la tensión superficial de la cara de contacto entre la gota de agua y el aceite, lo cual puede disminuir la tendencia natural de las dos fases inmiscibles a separarse.

RESUMEN

La presente invención se refiere a emulsiones y métodos para el uso de las mismas. En forma más particular, la presente invención se refiere a agentes estabilizadores de emulsión y sus usos en aplicaciones subterráneas.

De acuerdo con un primer aspecto de la presente invención, se proporciona una composición de emulsión estabilizada que comprende: un fluido oleaginoso; un

fluido que es por lo menos parcialmente inmisible con este último; y un agente estabilizador de emulsión, el cual comprende un primer compuesto iónico soluble en el fluido oleaginoso o el fluido que es por lo menos parcialmente inmisible con dicho fluido oleaginoso; y un segundo compuesto iónico con una carga de signo opuesto del primer compuesto iónico y que es por lo menos parcialmente soluble en el fluido opuesto como el primer compuesto iónico.

En una forma, el primer compuesto iónico, el segundo compuesto iónico o ambos comprenden un agente iónico de actividad superficial.

En una forma, el primer compuesto iónico, el segundo compuesto iónico o ambos comprenden un poli-electrolito iónico.

En una forma, uno del primer compuesto iónico o del segundo compuesto iónico comprenden un agente iónico de actividad superficial y el otro del primer compuesto iónico y el segundo compuesto iónico comprende un poli-electrolito iónico.

En una forma, el agente iónico de actividad superficial comprende un agente aniónico de actividad superficial

En una forma, el agente aniónico de actividad superficial comprende por lo menos un compuesto seleccionado a partir del grupo que consiste de un alquil carboxilato, un alquil éter carboxilato, un ácido N-

acilamino, un N-acil glutamato, un N-aril polipéptido, un alquil benceno sulfonato, un sulfonato parafínico, un alfa-olefina sulfonato, un lignosulfonato, un derivado de sulfosuccinato, un polinaftil metil sulfonato, un alquil sulfato, un alquil éter sulfato, un monoalquil fosfato, un polialquil fosfato, un ácido graso, una sal álcali de un ácido, una sal álcali de ácido graso, una sal alcalina de un ácido, una sal de sodio de un ácido, una sal de sodio de un ácido graso, un alquil etoxilato, un jabón, una combinación o derivado de los mismos.

En una forma, un agente iónico de actividad superficial comprende un agente catiónico de actividad superficial.

En una forma, el agente catiónico de actividad superficial comprende por lo menos un compuesto seleccionado a partir del grupo que consiste de una alquil amina, una sal alquil amina, una sal de amonio cuaternario, una sal de amonio cuaternario etoxilatado, un óxido amina, una alquil trimetil amina, una trietil amina, una alquil dimetil bencilamina, un derivado o una combinación de las mismas.

En una forma, el poli-electrolito iónico comprende un poli-electrolito aniónico.

En una forma, el poli-electrolito aniónico comprende por lo menos un compuesto seleccionado a partir del grupo que consiste de un polímero o copolímero que contiene un grupo carboxilato, un grupo sulfonato, un grupo fosfato,

un grupo fosfonato, un monómero acrílico, un monómero metacrilato, un estireno carboxilato, un vinil sulfonato, un 2-acrilamina-2-metil propil sulfonato, un 3-acrilamida-3-metil butanoato, una sal de ácido málico, un ácido poliacrílico, una poliacrilamida parcialmente hidrogenada, una carboxi metil celulosa, una celulosa modificada con un grupo funcional aniónico, un polisacárido modificado con un grupo funcional aniónico, un galactomanan modificado con un grupo funcional aniónico, un derivado y una combinación de los mismos.

En una forma, el poli-electrolito iónico comprende un poli-electrolito catiónico.

En una forma, el poli-electrolito catiónico comprende por lo menos un compuesto seleccionado a partir del grupo que consiste de: una polietileno imina, una poliamida amina, una poliamina, un cloruro de vinil bencil trimetil amonio, un cloruro de dimetil dialil amonio, un cloruro de 3-acrilamido-3-metil butil trimetil amonio, una polivinil pirrolidona, quitosan modificado con un grupo funcional catiónico, una gelatina modificada con un grupo funcional catiónico, un galactomanan modificado con un grupo funcional catiónico, una celulosa modificada con un grupo funcional catiónico, un derivado y una combinación de los mismos.

En una forma, el fluido oleaginoso comprende por lo menos un fluido seleccionado a partir del grupo que consiste de un aceite diesel, un crudo, un aceite de

parafina, un aceite mineral, un aceite mineral de baja toxicidad, una olefina, un éster, una amida, una amina, una poliolefina, un polidiorgano siloxano, un siloxano, un órgano siloxano, un éter, un acetal, un dialquil carbonato, un hidrocarburo, un derivado o una combinación de los mismos.

En una forma, el fluido que es por lo menos parcialmente inmiscible con el fluido oleaginoso comprende por lo menos un fluido seleccionado a partir del grupo que consiste de: glicerina, un glicol, una poliglicol amina, un poliol, agua potable, agua de mar, una salmuera, un derivado o una combinación de los mismos.

De acuerdo con otro aspecto de la presente invención, se proporciona un método que comprende: proporcionar una composición de emulsión estabilizada formada mediante la combinación de componentes que comprenden un fluido oleaginoso, un fluido que es por lo menos parcialmente inmiscible con el fluido oleaginoso y un agente estabilizador de emulsión, el cual comprende un primer compuesto iónico soluble en el fluido oleaginoso o el fluido que es por lo menos parcialmente inmiscible con este último; y un segundo compuesto iónico con una carga de signo opuesto del primer compuesto iónico y que es por lo menos parcialmente soluble en el fluido opuesto como el primer compuesto iónico; y colocar a la composición de emulsión estabilizada en una formación subterránea

como parte de una aplicación a la misma. La composición de emulsión estabilizada puede comprender una o más de las formas descritas anteriormente.

De acuerdo con otro aspecto de la presente invención, se proporciona un método que comprende: proporcionar una composición de emulsión estabilizada que incluye: un fluido oleaginoso; un fluido que es por lo menos parcialmente inmiscible con este último; y un agente estabilizador de emulsión, el cual comprende un primer compuesto iónico soluble en el fluido oleaginoso o el fluido que es por lo menos parcialmente inmiscible con este último; y un segundo compuesto iónico con una carga de signo opuesto a la del primer compuesto iónico y que es por lo menos parcialmente soluble en el fluido opuesto como el primer compuesto iónico; y la perforación de un orificio de pozo en una formación subterránea utilizando a la composición de emulsión estabilizada. La composición de emulsión estabilizada puede comprender una o más de las formas descritas anteriormente.

Todavía otro aspecto de la presente invención comprende un método para preparar una composición de emulsión estabilizada, el cual comprende: proporcionar un fluido oleaginoso; proporcionar un fluido que es por lo menos parcialmente inmiscible con el fluido oleaginoso; proporcionar un agente estabilizador de emulsión, el cual comprende: un primer compuesto iónico soluble en el fluido oleaginoso o el fluido que es por lo menos

parcialmente inmiscible con el fluido oleaginoso; y un segundo compuesto iónico con una carga de signo opuesto del primer compuesto iónico y que es por lo menos parcialmente soluble en el fluido opuesto como el primer compuesto iónico; y combinar al fluido oleaginoso, al fluido que es por lo menos parcialmente inmiscible con el fluido oleaginoso y el agente estabilizador de emulsión para formar una composición de emulsión estabilizada. La emulsión estabilizada puede comprender una o más de las formas descritas anteriormente.

Las características y ventajas de la presente invención serán evidentes para los expertos en el arte. Si bien estos últimos pueden realizar numerosos cambios, los mismos caen dentro de los alcances de la invención.

DESCRIPCION DE LAS FORMAS PREFERIDAS

La presente invención se refiere a emulsiones y métodos para el uso de las mismas. En forma más particular, la presente invención se refiere a agentes estabilizadores de emulsión y su uso en aplicaciones subterráneas.

Si bien existen muchas ventajas en la presente invención, se describen aquí solamente algunas de ellas. Los agentes estabilizadores de emulsión proporcionados por la presente invención pueden ser ventajosos debido a que se cree que las interacciones electrostáticas de las moléculas pueden servir para fijar a los agentes de actividad superficial a la cara de contacto entre las dos

fases presentes en las emulsiones o emulsión invertida, dando como resultado potencialmente una concentración aumentada de agente de actividad superficial o polielectrolito en la cara de contacto. Esto puede dar como resultado una estabilidad mejorada de la emulsión y permitir que se utilice una cantidad relativamente baja del agente estabilizador de emulsión a fin de obtener una emulsión estable.

La presente invención proporciona agentes estabilizadores de emulsión que contienen un par: de compuesto de agente de actividad superficial cargado y compuestos electrolito de carga opuesta. Los agentes estabilizadores de emulsión de la presente invención pueden ser utilizados en forma ventajosa para estabilizar a las composiciones de emulsión. Estas últimas que contienen a los agentes estabilizadores de emulsión de la presente invención pueden ser referidos como "composiciones de emulsión estabilizada" de esta última. Se forman las composiciones de emulsión estabilizada mediante la combinación de componentes que contienen un fluido oleaginoso, un fluido que es por lo menos parcialmente inmiscible con este último y un agente estabilizador de emulsión de la presente invención. Después de la mezcla, estos componentes pueden ser o no pueden ser identificables separadamente, dependiendo de la complejidad de la técnica utilizada. Las composiciones de emulsión estabilizada pueden ser

apropiada para uso en una variedad de aplicaciones subterráneas en las cuales son apropiadas las emulsiones aceite en agua o agua en aceite. Tales aplicaciones pueden incluir aplicaciones subterráneas que comprenden operaciones de estimulación tales como tratamiento de fracturación y control, tal como la instalación de un relleno de grava. Tales operaciones pueden incluir perforación y terminación. También pueden ser apropiadas otras aplicaciones subterráneas. Un experto en el arte, con el beneficio de esta descripción, reconocerá otros usos apropiados para estas composiciones de emulsión.

El fluido oleaginoso utilizado en las composiciones de emulsión estabilizada pueden comprender cualesquiera fluidos tradicionales con base de aceite apropiados para uso en las emulsiones. El fluido oleaginoso pueden proceder de una fuente natural o sintética. Ejemplos de fluidos oleaginosos apropiados incluyen aceites diesel, crudos, aceites de parafina, aceites minerales, aceites minerales de baja toxicidad, olefinas, ésteres, amidas, aminas, aceites sintéticos (tales como poliolefinas, polidiorgano siloxanos, siloxanos, órgano siloxanos y sus combinaciones), éteres, acetales, dialquil carbonatos, hidrocarburos y sus combinaciones. Ejemplos de fluidos oleaginosos apropiados incluyen aquellos comercialmente disponibles en Halliburton Energy Services, Inc., en Houston, Texas, U.S.A. bajo las denominaciones comerciales ("ACCOLADETM", un fluido base

de emulsión invertida de una mezcla de olefina interna y éster, "PETROFREE® un fluido base de emulsión invertida con base de éster, "PETROFREE® LV" un fluido base de emulsión invertida con base de éster y "PETROFREE® S.F.", un fluido base de emulsión invertida con base de olefina interna. Los factores que pueden determinar que el fluido oleaginoso será utilizado en una aplicación particular, incluyen pero no están limitados a características de costo y rendimiento de dicho fluido oleaginoso. Un factor adicional que puede ser considerado es la polaridad del fluido oleaginoso. Por ejemplo, los aceites diesel serán generalmente más polares que los aceites de parafina. Otros factores que pueden ser considerados son compatibilidad ambiental y prácticas de perforación regional. Por ejemplo, en aplicaciones del Mar del Norte, se puede preferir un éster u olefina interna (OI). En el Golfo de México, las aplicaciones pueden preferir el uso de "ACCOLADE™" o un aceite mineral de baja viscosidad. Un experto en el arte con la ayuda de esta descripción podrá elegir un fluido oleaginoso apropiado para una aplicación particular, en vista de estas consideraciones. En ciertas formas ejemplares de la presente invención, el fluido oleaginoso puede ser un crudo.

Las composiciones de emulsión de la presente invención pueden comprender también un fluido que es por lo menos parcialmente inmiscible en el fluido oleaginoso.

Este fluido parcialmente inmiscible puede ser un fluido no oleaginoso que es recíprocamente insoluble con el fluido oleaginoso elegido. Ejemplos apropiados de fluidos parcialmente inmiscibles incluye fluidos con base acuosa, glicerina, glicoles, poliglicol aminas, polioles, sus derivados que son parcialmente inmiscibles en el fluido oleaginoso y sus combinaciones. Se define aquí al término "derivado" para incluir cualquier compuesto preparado a partir de los compuestos enumerados, por ejemplo, mediante el reemplazo de un átomo en el compuesto base con otro átomo o grupo de átomos. Los fluidos con base acuosa pueden incluir pero no están limitados a agua potable, agua de mar, agua salada y salmueras (por ejemplo, aguas saladas saturadas). Se puede utilizar cualquier salmuera con las emulsiones de la presente invención, que no interfiera con agentes estabilizadores de emulsión. Un experto en el arte apreciará que pueden ocurrir interacciones perjudiciales entre algunos componentes de algunas salmueras y agentes cargados de actividad superficial o pares de poli-electrolito. Las salmueras apropiadas pueden incluir salmueras pesadas. Las salmueras pesadas, para propósitos de esta solicitud, incluyen salmueras que pueden ser utilizadas para aumentar el peso de un fluido, tal como un fluido de tratamiento, en vez de utilizar agentes tradicionales para impartir peso. Las salmueras pueden contener sales solubles en agua. En ciertas formas

ejemplares, las sales apropiadas solubles en agua pueden comprender cloruro de sodio, cloruro de calcio, bromuro de calcio, bromuro de zinc, carbonato de potasio, formato de sodio, formato de potasio, acetato de sodio, acetato de potasio, acetato de calcio, acetato de amonio, cloruro de amonio, bromuro de amonio, nitrato de sodio, nitrato de potasio, nitrato de amonio, nitrato de calcio, carbonato de sodio, carbonato de potasio y sus combinaciones. En otras formas ejemplares, la sal soluble en agua puede ser cualquier sal que reduce la actividad de la base acuosa de la emulsión. Los factores que determinan cuál será el fluido parcialmente inmiscible utilizado en una aplicación particular, pueden incluir costo, disponibilidad y cuál fluido oleaginoso ha sido elegido. Otro factor que puede ser considerado es la aplicación de la emulsión. Por ejemplo, si la aplicación requiere una emulsión de alto peso, se puede elegir una salmuera de bromuro de zinc o cloruro de calcio. Un experto en el arte, con la ayuda de esta descripción y en vista de las consideraciones presentadas, podrá elegir un fluido parcialmente inmiscible especialmente apropiado para una aplicación particular.

Como se indicó anteriormente, las composiciones de emulsión estabilizada de la presente invención comprenden también un agente estabilizador. Los agentes estabilizadores de emulsión comprenden por lo menos un

par de compuestos que pueden contener generalmente dos moléculas de agente de actividad superficial, moléculas de poli-electrolito o cualquier combinación de los mismos que tienen cargas opuestas, que pueden tener o no la misma magnitud. En general, los miembros del par serán catiónicos o aniónicos. La carga en uno o ambos de los compuestos puede tener se origen en uno o más grupos funcionales iónicos. Tal como se emplea aquí, el término "iónico" o "grupo funcional iónico puede referirse a cualquier compuesto capaz de llevar por lo menos una carga positiva o negativa, ya sea inherente en la estructura química o formada debido a la presencia de cualesquiera otros componentes en una mezcla. Tales compuestos pueden incluir grupos o compuestos iónicos, grupos o compuestos polares, grupos o compuestos anfóteros o cualquier otro tipo de material capaz de llevar o desarrollar una carga. En algunas formas, el miembro aniónico del par puede ser por lo menos parcialmente soluble en la fase oleaginoso, mientras que el miembro catiónico puede ser por lo menos parcialmente soluble en el fluido que es por lo menos parcialmente inmiscible en el fluido oleaginoso. En otras formas, el miembro catiónico del par puede ser por lo menos parcialmente soluble en la fase oleaginoso, mientras que el miembro aniónico puede ser por lo menos parcialmente soluble en el fluido que es por lo menos parcialmente inmiscible en el fluido oleaginoso. Si bien no se desea

limitarse a ninguna teoría, se cree que las interacciones electrostáticas pueden ocurrir en la cara de contacto entre la fase oleaginosa y el fluido que es por lo menos parcialmente inmiscible en el fluido oleaginoso. Si bien cada miembro del par de agentes estabilizadores de emulsión puede ser soluble en una de las fases, el componente combinado formado por las interacciones electrostáticas puede ser por lo menos parcialmente insoluble en ambas fases. El par resultante de agentes estabilizadores de emulsión puede permanecer en la cara de contacto entre las fases, dando como resultado una estabilidad mejorada de la emulsión.

En una forma, un miembro del par de agentes estabilizadores de emulsión puede ser un agente de actividad superficial que puede llevar una carga aniónica o catiónica. En una forma, un agente de actividad superficial útil con el agente estabilizador de emulsión descrito aquí puede comprender por lo menos un grupo funcional aniónico. Grupos funcionales ejemplares pueden incluir carboxilatos, sulfonatos, sulfatos, aminas, iminas, fosfatos y fosfonatos. Los agentes ejemplares catiónicos de actividad superficial pueden incluir pero no están limitados a alquil aminas, sales alquil amina, sal de amonio cuaternario, sales de amonio cuaternario etoxilatado, óxidos de amina, alquil trimetil amina, trietil amina, alquil dimetil bencilamina. Los agentes ejemplares aniónicos de actividad superficial pueden

incluir pero no están limitados a alquil carboxilatos, alquil éter carboxilatos, ácidos N-acilamino, N-acil glutamatos, N-acil polipéptidos, alquil benceno sulfonatos, sulfonatos parafínicos, alfa-olefina sulfonatos, lignosulfatos, derivados de sulfosuccinatos, polinaftil metil sulfonatos, alquil sulfatos, alquil éter sulfatos, monoalquil fosfatos, polialquil fosfatos, ácidos grasos, sales álcali de ácidos, sales álcali de ácidos grasos, sales alcalinas de ácidos, sales de sodio de ácidos, sales de sodio de acido graso, alquil etoxilato y jabones. Un experto en el arte podría determinar la fase a la cual se debe agregar el agente iónico de actividad superficial, el cual puede basarse en la composición de cada fase contenida en la emulsión, la solubilidad del componente en cada fase, las condiciones operativas (por ejemplo, temperatura) y cualesquiera aditivos presentes en cualquier fase (por ejemplo, sales). Por ejemplo, los agentes aniónicos de actividad superficial pueden reaccionar con cualquier calcio presente en el fluido que es por lo menos parcialmente inmiscible en el fluido oleaginoso, para formar compuestos que no pueden ser estabilizadores efectivos. De este modo, un experto en el arte puede evitar el uso de agentes aniónicos de actividad superficial en el fluido que es por lo menos parcialmente inmiscible en el fluido acuoso cuando están presentes iones de calcio.

En una forma, un miembro del par de agentes estabilizadores de emulsión puede ser un electrolito que puede llevar una carga aniónica o catiónica. Tal como se emplea aquí, un poli-electrolito puede ser un polímero cuyas unidades repetidas comprenden un grupo electrolito. Estos grupos pueden disociarse en soluciones que contienen un fluido acuoso, permitiendo que los polímeros lleven una carga formal hasta cierto grado. Por ejemplo, se puede preparar un polímero que contiene un monómero aniónico para impartir un carácter aniónico a la molécula. Los poli-electrolitos aniónicos ejemplares incluyen pero no están limitados a polímeros o copolímeros derivados a partir de monómeros aniónicos que contienen carboxilatos, sulfonatos, fosfatos, fosfonatos, monómeros acrilato, metacrilato, 2-acrilamina-2-metil-propil sulfonato, 3-acrilamida-3-metil butanoato, estireno carboxilato, vinil sulfonato, sales de ácido málico, ácido poliacrílico (PAA), poliacrilamida parcialmente hidrogenada (PHPA), carboxi metil celulosa, derivados de celulosa, polisacáridos (por ejemplo xantan, goma arábiga) y galactomananos modificados con grupos funcionales aniónicos. Los monómeros no iónicos pueden ser incluidos en estos compuestos, por ejemplo, como en un copolímero entre un monómero aniónico y un monómero neutro. Los poli-electrolitos catiónicos ejemplares incluyen pero no están limitados a polímeros o copolímeros que contienen grupos catiónicos tales como

iminas, aminas y copolímeros con monómeros neutros. Ejemplos específicos pueden incluir pero no están limitados a polietilenoimina, poliamida amina, poliaminas, cloruro de vinil bencil trimetil amonio, cloruro de dimetildialil amonio, cloruro de 3-acrilamido-3-metil butil trimetil amonio y polivinil pirrolidona. Por ejemplo, los polímeros que comprenden quitosanos, gelatinas, galactomananos y celulosa pueden ser modificados con monómeros catiónicos para formar poli-electrolitos catiónicos. Los poli-electrolitos útiles con los agentes estabilizadores descritos aquí, pueden ser preparados mediante cualquier método conocido por los expertos en el arte.

En una forma, el agente estabilizador de emulsión puede ser agregado a la composición de emulsión estabilizada en cualquier cantidad capaz de estabilizar a la emulsión hasta el grado deseado. El par de agentes estabilizadores de emulsión puede ser agregado sobre una base de carga equilibrada. Por ejemplo, si el miembro aniónico del par de agentes estabilizadores de emulsión lleva una carga formal igual a dos veces la del miembro catiónico de dicho par de agentes, entonces, el miembro aniónico de los mismos puede ser agregado en una cantidad igual a la mitad de la cantidad total del miembro catiónico del par de agentes estabilizadores de emulsión, sobre una base molar. En otras formas, los miembros del par de agentes estabilizadores de emulsión puede ser

agregado en una proporción no relacionada con la carga en los miembros de dicho par. Por ejemplo, si se espera que un miembro del par pueda interactuar con otros componentes de la emulsión estabilizada, entonces, se puede agregar más o menos de ese miembro del par a fin de compensar la interacción. En una forma, el agente estabilizador de la emulsión puede ser agregado a una composición de emulsión estabilizada en una cantidad que varía desde más o menos 0,1 libras por barril (lb/barril) hasta más o menos 12 libras por barril (aproximadamente 0,29 kg/metro³ hasta más o menos 34 kg/metro³) de la composición de emulsión estabilizada. En otra forma, el agente estabilizador de emulsión puede ser agregado a una composición de emulsión estabilizada en una cantidad que varía desde más o menos 0,25 lbs/barril hasta más o menos 4 lbs/barril (más o menos 0,71 kgs/m³ hasta mas o menos 11 kg/metro³) de la composición de emulsión estabilizada.

La composición de emulsión estabilizada de la presente invención puede contener opcionalmente una variedad de aditivos. Ejemplos de aditivos útiles en las emulsiones estabilizadas pueden incluir pero no están limitados a sólidos, agentes para impartir peso, sólidos inertes, agentes para controlar la pérdida de fluido, emulsionadores, sales, ayudas de dispersión, inhibidores de la corrosión, diluyentes de emulsión, espesadores de emulsión, agentes para impartir viscosidad y cualquier combinación de los mismos.

En algunas formas, se puede utilizar el agente para impartir peso a fin de aumentar la densidad de la emulsión estabilizada. Los agentes para impartir peso, los cuales sirven para aumentar la densidad de las emulsiones estabilizadas, pueden ser cualesquiera sólidos conocidos por los expertos en el arte como útiles para tal propósito y que no interactúan perjudicialmente con la composición de agente estabilizador de emulsión. Ejemplos de agentes para impartir peso pueden incluir pero no están limitados a barita, calcita, ilmenita, mulita, galena, óxidos de manganeso, óxidos de hierro, mezclas de los mismos, etc. Por ejemplo, como el agente para impartir peso se puede utilizar un aditivo molido de sulfato de bario que tiene la denominación comercial BAROID® y está disponible en Halliburton Energy Services, Inc., en Houston, Texas, U.S.A. El material para impartir peso puede ser agregado típicamente para alterar la densidad de la emulsión estabilizada. La densidad del fluido puede ser menos de aproximadamente 20 (más o menos 2400 kg/metro³) o menos de aproximadamente 15 (más o menos 1800 kg/metro³) o, de otro modo, menos de aproximadamente 10 libras por galón (más o menos 1200 kg/m³). Un experto en el arte podría estar en capacidad de determinar la cantidad de agente para impartir peso a ser agregada para producir una emulsión estabilizada con una densidad deseada.

En una forma, una emulsión estabilizada puede comprender aditivos de control de pérdida de fluido, emulsionadores o ambos. Se puede agregar también a la emulsión estabilizada agentes para el control de pérdida de fluido tales como lignita modificada, polímeros, asfalto oxidado y gilsonita. Generalmente, se puede emplear a tales agentes para control de pérdida de fluido en una cantidad que es por lo menos 0,1, por lo menos 1 o por lo menos 5 por ciento en peso del fluido total. Por ejemplo, se puede utilizar un aditivo que tiene la denominación comercial ADAPTA™ disponible en Halliburton Energy Services, Inc., en Houston, Texas, U.S.A. como un aditivo para controlar la pérdida de fluido. Se puede utilizar también material álcali, preferiblemente cal (hidróxido de calcio u óxido de calcio) para fijar o reaccionar con gases ácidos (por ejemplo, CO₂ y H₂S) encontrados durante la perforación en la formación, siempre y cuando dicho material álcali no interfiera con los agentes estabilizadores de emulsión descritos aquí. La cantidad de cal libre en un fluido de perforación puede variar desde más o menos 1 hasta más o menos 10 libras/barril (más o menos 2,9 kg/metro³ hasta más o menos 29 kg/metro³) o más preferiblemente más o menos 1 a más o menos 4 lbs/barril (más o menos 2,9 kg/metro³ a más o menos 11 kg/metro³, aunque se prefiere escalas más bajas tal como menos de 2 libras/barril (más o menos 5,7 kg/metro³) para ciertos ésteres que tienden a

hidrolizarse en presencia de compuestos alcalinos, tal como lo comprenden los expertos en el arte. Se puede utilizar también otros agentes apropiados como una alternativa a la cal, para ajustar y/o estabilizar a las emulsiones con respecto a los ácidos.

En las emulsiones estabilizadas se puede incorporar opcionalmente varios agentes suplementarios de actividad superficial y agentes humectantes convencionalmente utilizados en emulsiones. Tales agentes de actividad superficial pueden ser, por ejemplo, ácidos grasos, jabones de ácidos grasos, aminos amido, poliamidas, poliaminas, derivados imidazolina, aceite de sebo bruto y oxidado, ésteres de fosfato orgánico, sulfatos y sulfonatos alquil aromáticos, así como también mezclas de los anteriores. En general, se puede emplear a tales agentes de actividad superficial en una cantidad que no interfiere con el uso de emulsiones estabilizadas. Por ejemplo, los agentes de actividad superficial o agentes humectantes pueden ser utilizados en una cantidad que no interfiere con la capacidad de una emulsión estabilizada para actuar como un fluido de perforación o perforar en fluido y remover los escombros desde el orificio de pozo.

Además, se puede agregar o mezclar con la emulsión estabilizada otros fluidos o materiales. Tales materiales pueden incluir, por ejemplo, aditivos destinados a reducir o controlar la reología de temperatura o proporcionar dilución tales como, por

ejemplo, aditivos que tienen las denominaciones comerciales COLDTROL®, RHEMOD™ L, ATC® y OMC 2™, aditivos para proporcionar viscosidad aumentada temporal destinada a transporte (transporte hacia el sitio del pozo) y para uso en barridos, tales como por ejemplo un aditivo que tiene la denominación comercial TEMPERUS™ (ácido graso modificado), aditivos para formar fuente en roca porosa tales como, por ejemplo, aditivos que tienen la denominación comercial BARACARB® 50; aditivos para controlar la filtración a alta presión y alta temperatura (HTHP FILTRATE) y estabilidad de la emulsión tales como, por ejemplo, aditivos que tienen la denominación comercial FACTANT™ (derivado de aceite de sebo altamente concentrado) y aditivos suplementarios para emulsionamiento tales como, por ejemplo, aditivos que tienen las denominaciones comerciales EZ MUL™ NT o LE SUPERMUL™ (ácidos grasos poliaminados). Mezclas de diluyentes tales como OMC 2™, COLDTROL® y ATC® pueden ser también efectivas en emulsiones estabilizadas de la invención. Todos los productos con marca de fábrica mencionados anteriormente se encuentran disponibles en Halliburton Energy Services, Inc., en Houston, Texas, U.S.A.

Se puede emplear opcionalmente agentes para impartir viscosidad en las emulsiones estabilizadas de la presente invención. En general, se puede emplear agentes para impartir viscosidad tales como polímeros solubles en

aceite y agua, resinas poliamida, ácidos policarboxílicos y jabones de ácido graso. La cantidad del agente para impartir viscosidad utilizado en la composición variará necesariamente dependiendo del uso final de la misma. Generalmente, se emplea a tales agentes para impartir viscosidad en una cantidad que es por lo menos aproximadamente 0,1, por lo menos aproximadamente 2 o por lo menos aproximadamente 5 por ciento en peso del fluido total. Por ejemplo, como un agente para impartir viscosidad se puede utilizar TAU-MOD™ o BARAZAN® D PLUS, ambos disponibles en Halliburton Energy Services, Inc., en Houston, Texas, U.S.A.

Además, se puede utilizar ayudas de dispersión, inhibidores de la corrosión y/o despumadores. Estos y otros elementos auxiliares y aditivos se utilizan en cantidades conocidas por los expertos en el arte, dependiendo de las condiciones del orificio de pozo particular y de la formación subterránea.

En general, las emulsiones estabilizadas de la presente invención pueden ser obtenidas mediante el uso de cualquier técnica conocida en el arte. Por ejemplo, los componentes pueden ser mezclados en cualquier orden bajo condiciones de agitación. Un método representativo para preparar la emulsión estabilizada puede comprender la mezcla de una cantidad apropiada del fluido que es por lo menos parcialmente insoluble en el fluido oleaginoso y una cantidad apropiada del agente estabilizador de la

emulsión y cualesquiera aditivos opcionales bajo agitación continua y moderada. Luego, se puede agregar un fluido oleaginoso mientras se mezcla hasta que se forme una emulsión estabilizada. Si es necesario agregar agentes para impartir peso, tales como aquellos descritos anteriormente, entonces se agrega típicamente a los mismos una vez formada la emulsión estabilizada. De otro modo, las emulsiones estabilizadas de la presente invención pueden ser preparadas simplemente agregando el agente estabilizador de emulsión a un material existente de fluido de perforación. La efectividad de este tratamiento puede depender de los constituyentes del fluido.

Un ejemplo de un método de la presente invención es aquel destinado a tratar a una formación subterránea y que comprende las etapas de proporcionar un fluido de tratamiento que contiene una emulsión estabilizada que comprende un fluido oleaginoso, un fluido que es por lo menos parcialmente inmiscible con este último y un agente estabilizador de emulsión; y tratar a la formación subterránea. En ciertas formas ejemplares de la presente invención, un método para el tratamiento de una formación subterránea incluye una operación de terminación de pozo o una operación de perforación. En otras formas ejemplares de la presente invención, un método para el tratamiento de una formación subterránea incluye una operación de estimulación. Ejemplos de operaciones de

estimulación de la presente invención incluyen operaciones de fracturación y operaciones de estimulación con ácido, tal como acidificación de matriz y un proceso de acidificación por fracturación. En otras formas ejemplares de la presente invención, un método para el tratamiento de una formación subterránea incluye una operación de control de arena, tal como la instalación de un relleno de grava.

Otro ejemplo de un método de la presente invención es un método de perforación de un orificio de pozo en una formación subterránea mediante el uso de un fluido de perforación con emulsión estabilizada que contiene un fluido oleaginoso, un fluido que es por lo menos parcialmente inmiscible en el fluido oleaginoso y un agente estabilizador de emulsión.

Un método ejemplar de la presente invención es un método para emulsionar crudo y el cual comprende las etapas de proporcionar un crudo, un fluido que es por lo menos parcialmente inmiscible con este último y un agente estabilizador de emulsión; y la mezcla del crudo, del fluido que es por lo menos parcialmente inmiscible con este último y el agente estabilizador de emulsión para formar una emulsión estabilizada de crudo.

Para permitir una mejor comprensión de la presente invención, se ofrece los siguientes ejemplos de ciertos aspectos de algunas formas. En ninguna forma los

siguientes ejemplos limitan o definen los alcances de la invención.

EJEMPLOS

Para demostrar la estabilización de una emulsión con los agentes estabilizadores descritos aquí, se preparó varios ejemplos de emulsiones estabilizadas y se dejó envejecer durante períodos diferentes. En este ejemplo, se mezcló 1,5 lbs/barril de poli-electrolito (EZ-MUD® GOLD, disponible en Halliburton Energy Services, Inc., en Houston, Texas, U.S.A.) y 6 libras/barril de un agente para el control de la filtración (N-DRIL® HT PLUS, disponible en Halliburton Energy Services, Inc., en Houston, Texas, U.S.A.) con agua de sal KCl al 3%, utilizando un multi-mezclador, durante 5 minutos, seguido por 1,0 libras/barril de agentes hidrofóbicos de actividad superficial (octadecil amina con un grado técnico de 90%) durante otros 5 minutos. Se agregó una cantidad de diesel comprendiendo 20% del volumen de fluido total y se mezcló durante otros 30 minutos. La mezcla resultante fue laminada en caliente durante 16 horas a 230°F (110°C) para formar una muestra marcada "Muestra 1". Se preparó una segunda tanda del fluido de acuerdo con el mismo procedimiento y se marcó "Muestra 2". La segunda tanda del fluido fue tratada con el agente para impartir viscosidad (BARAZAN® D PLUS, disponible en Halliburton Energy Services, Inc., en Houston, Texas, U.S.A.) y se laminó en caliente durante 72 horas. La

Tabla 1 contiene las propiedades reológicas de las 8,0
libras/galón de los fluidos.

Tabla 1. Preparación y Propiedades de Diesel en un Fluido Acuoso			
Descripción	Unidades	Muestra 1	Muestra 2
Densidad	lb/galón (kg/metro ³)	8,0(960)	8,0(960)
Agua	barriles (metro ³)	0,789(0,094)	0,789(0,094)
BARAZAN® D PLUS	libras/kg	0	0,5(0,2)
N-DRIL™ HT PLUS	libras	6(2,7)	6(2,7)
Mezcla de emulsionador	libras	2,5(1,1)	2,5(1,1)
Diesel	barriles	0,199 (0,0316)	0,199 (0,0316)
Propiedades Reológicas			
Laminado en caliente a 120°F (49°C)	horas	0	16
Mezclado nuevamente en un multi-mezclador	minutos	3	3
Viscosidad plástica	cP (gramo/cm. segundo)	29(029)	37(0,37)
Punto de deformación	lbs/100 pies ² (kPa)	71(34)	53(25)
10 segs. gel	lbs/100 pies ² (kPa)	11(5,3)	5(2,4)
10 mins. gel	lbs/100 pies ² (kPa)	14(6,7)	4(1,9)
Lecturas Fann 35 @ 120°F (49°C)			
600 rpm		129	127
300 rpm		100	90
200 rpm		86	71
100 rpm			
6 rpm		18	6
3 rpm		13	4

Una muestra de fluido preparada de acuerdo con el procedimiento descrito anteriormente fue envejecida durante aproximadamente seis semanas. Una inspección visual de fluido confirmó que había ocurrido poca o

ninguna separación de fase. Este resultado demuestra que la emulsión puede permanecer estable durante períodos prolongados mediante el uso de los agentes estabilizadores de emulsión descritos aquí. Además, la emulsión estable ofreció la oportunidad de ajustar la viscosidad del fluido con BARAZAN® D PLUS, sin afectar perjudicialmente la estabilidad de la emulsión.

Por lo tanto, la presente invención está bien adaptada para lograr los fines y ventajas mencionados, así como también aquellas que son inherentes en este caso. Las formas particulares descritas anteriormente son ilustrativas solamente ya que la presente invención puede ser modificada y llevada a la práctica en formas diferentes pero equivalentes evidentes para los expertos en el arte, con la ayuda de los principios descritos aquí. Además, no se pretende establecer limitaciones a los detalles de construcción o diseño ilustrados aquí, que no sean los descritos en las reivindicaciones presentadas más adelante. Por lo tanto, es evidente que las formas ilustrativas particulares descritas anteriormente pueden ser alteradas o modificadas y todas esas variaciones se consideran dentro de los alcances de la presente invención. Si bien se describe a las composiciones y métodos en términos de "comprendiendo", "conteniendo" o "incluyendo" varios componentes o etapas, las composiciones y métodos pueden "consistir también esencialmente de" o "consisten" de los varios componentes

y etapas. Todos los números y escalas descritos aquí pueden variar en la misma magnitud. Siempre que se describe una escala numérica con un límite inferior y un límite superior, se describe específicamente cualquier número y cualquier escala incluida que cae dentro de la misma. En particular, cada escala de valores (en la forma de "desde más o menos a hasta más o menos b" o en forma equivalente "desde aproximadamente a hasta b" o de manera equivalente "desde aproximadamente a-b") descrita aquí se entenderá como expresando cada número y escala abarcada dentro de la escala más amplia de valores. Además, los artículos indefinidos "uno" o "una", tal como se emplean en las reivindicaciones, se definen aquí para significar uno o más de uno de los elementos que introduce. Del mismo modo, los términos en las reivindicaciones tienen su significado normal y ordinario, a menos que sea definido de otro modo en forma explícita y clara por el propietario de la patente. Si existe algún conflicto en los empleos de una palabra o términos en esta Memoria Descriptiva y una o más patentes u otros documentos que pueden ser incorporados aquí a modo de referencia, se debe adoptar las definiciones que son compatibles con esta Memoria Descriptiva.

REIVINDICACIONES

1. Una composición de emulsión estabilizada que contiene un fluido oleaginoso; un fluido que es por lo menos parcialmente inmiscible con este último y un agente estabilizador de emulsión, el cual comprende un primer compuesto iónico soluble en el fluido oleaginoso o en el fluido que es por lo menos parcialmente inmiscible con este último; y un segundo compuesto iónico con una carga de signo opuesto al del primer compuesto iónico y que es por lo menos parcialmente insoluble en el fluido opuesto como el primer compuesto iónico.
2. Una composición de emulsión estabilizada, de acuerdo con la reivindicación 1, en la cual el primer compuesto iónico, el segundo compuesto iónico o ambos contienen un agente de actividad superficial.
3. Una composición de emulsión estabilizada, de acuerdo con la reivindicación 1 o 2, en la cual el primer compuesto iónico, el segundo compuesto iónico o ambos contienen un poli-electrolito iónico.
4. Una composición de emulsión estabilizada, de acuerdo con la reivindicación 2 o 3, cuando dependen de la reivindicación 2, en la cual el agente iónico de actividad superficial comprende un agente aniónico de actividad superficial.
5. Una composición de emulsión estabilizada, de acuerdo con la reivindicación 4, en la cual el agente aniónico de

actividad superficial comprende por lo menos un compuesto seleccionado a partir del grupo que consiste de: alquil carboxilato, un alquil éter carboxilato, un ácido N-acilamino, un N-acil glutamato, un N-aril polipéptido, un alquil benceno sulfonato, un sulfonato parafínico, un alfa-olefina sulfonato, un lignosulfonato, un derivado de sulfosuccinato, un polinaftil metil sulfonato, un alquil sulfato, un alquil éter sulfato, un monoalquil fosfato, un polialquil fosfato, un ácido graso, una sal álcali de un ácido, una sal álcali de ácido graso, una sal alcalina de un ácido, una sal de sodio de un ácido, una sal de sodio de un ácido graso, un alquil etoxilato, un jabón, una combinación o derivado de los mismos.

6. Una composición de emulsión estabilizada, de acuerdo con la reivindicación 2 o cualquier reivindicación que depende de la reivindicación 2, en la cual el agente iónico de actividad superficial comprende un agente catiónico de actividad superficial.

7. Una composición de emulsión estabilizada, de acuerdo con la reivindicación 6, en la cual el agente catiónico de actividad superficial comprende por lo menos un compuesto seleccionado a partir del grupo que consiste de: una alquil amina, una sal alquil amina, una sal de amonio cuaternario, una sal de amonio cuaternario etoxilatado, un óxido amina, una alquil trimetil amina, una trietil amina, una alquil dimetil bencilamina, un derivado o una combinación de las mismas.

8. Una composición de emulsión estabilizada, de acuerdo con la reivindicación 3, en la cual el poli-electrolito iónico comprende un poli-electrolito aniónico.

9. Una composición de emulsión estabilizada, de acuerdo con la reivindicación 8, en la cual el polielectrolito aniónico comprende por lo menos un compuesto seleccionado a partir del grupo que consiste de: un polímero o copolímero que contiene un grupo carboxilato, un grupo sulfonato, un grupo fosfato, un grupo fosfonato, un monómero acrílico, un monómero metacrilato, un estireno carboxilato, un vinil sulfonato, un 2-acrilamina-2-metil propil sulfonato, un 3-acrilamida-3-metil butanoato, una sal de ácido málico, un ácido poliacrílico, una poliacrilamida parcialmente hidrogenada, una carboxi metil celulosa, una celulosa modificada con un grupo funcional aniónico, un polisacárido modificado con un grupo funcional aniónico, un galactomanan modificado con un grupo funcional aniónico, un derivado y una combinación de los mismos.

10. Una composición de emulsión estabilizada, de acuerdo con la reivindicación 3 o cualquier reivindicación que depende de la reivindicación 3, en la cual el poli-electrolito iónico comprende un polielectrolito catiónico.

11. Una composición de emulsión estabilizada, de acuerdo con la reivindicación 10, en la cual el poli-electrolito catiónico comprende por lo menos un compuesto

seleccionado a partir del grupo que consiste de: aceite diesel, un crudo, un aceite de parafina, un aceite mineral, un aceite mineral de baja toxicidad, una olefina, un éster, una amida, una amina, una poliolefina, un polidiorgano siloxano, un siloxano, un órgano siloxano, un éter, un acetal, un dialquil carbonato, un hidrocarburo, un derivado o una combinación de los mismos.

13. Una composición de emulsión estabilizada, de acuerdo con la cualesquiera reivindicaciones anteriores, en la cual el fluido que es por lo menos parcialmente inmiscible con el fluido oleaginoso comprende por lo menos un fluido seleccionado a partir del grupo que consiste de: glicerina, un glicol, una poliglicol amina, un poliol, agua potable, agua de mar, agua salada, una salmuera, un derivado o combinación de los mismos.

14. Un método que comprende: proporcionar una composición de emulsión estabilizada de acuerdo con cualesquiera reivindicaciones 1 a 13, y colocar a la misma en una formación subterránea como parte de una aplicación bajo tierra.

15. Un método que comprende: proporcionar una composición de emulsión estabilizada de acuerdo con cualesquiera reivindicaciones 1 a 13; y perforar un orificio de pozo en una formación subterránea utilizando a la composición de emulsión estabilizada.

16. Un método para preparar una composición de emulsión estabilizada, el cual comprende: proporcionar un fluido oleaginoso; proporcionar un fluido que es por lo menos parcialmente inmiscible con el fluido oleaginoso; proporcionar un agente estabilizador de emulsión que comprende un primer compuesto iónico soluble en el fluido oleaginoso o el fluido que es por lo menos parcialmente inmiscible con dicho fluido oleaginoso; y un segundo compuesto iónico con una carga de signo opuesto al del primer compuesto iónico y que es por lo menos parcialmente soluble en el fluido opuesto como el primer compuesto iónico; y combinar al fluido oleaginoso, al fluido que es por lo menos parcialmente inmiscible con este último y el agente estabilizador de emulsión para formar una composición de emulsión estabilizada.

17. Un método, de acuerdo con la reivindicación 16, el cual comprende además colocar a la composición de emulsión estabilizada en una formación subterránea como parte de una operación de perforación.

**AGENTES ESTABILIZADORES DE EMULSION PARA FLUIDOS DE
PERFORACION Y TERMINACION**

Resumen

La presente invención proporciona una composición de emulsión estabilizada que comprende: un fluido oleaginoso; un fluido que es por lo menos parcialmente inmiscible con este último y un agente estabilizador de emulsión que comprende un primer compuesto iónico soluble en el fluido oleaginoso o el fluido que es por lo menos parcialmente inmiscible con este último; y un segundo compuesto iónico con una carga de signo opuesto al primer compuesto iónico y que es por lo menos parcialmente soluble en el fluido opuesto como el primer compuesto iónico. La presente invención proporciona también métodos que implican el uso de la composición de emulsión estabilizada y métodos para preparar a esta última.

EMULSION STABILIZING AGENTS FOR DRILLING AND COMPLETION FLUIDS

BACKGROUND

[0001] The present invention relates to emulsions and methods of using such emulsions. More particularly, the present invention relates to emulsion stabilizing agents and their uses in subterranean applications.

[0002] Emulsions usually comprise two immiscible phases. The two immiscible phases may include a continuous (or external) phase and a discontinuous (or internal) phase. The discontinuous phase may comprise the secondary fluid that usually exists in droplets in the continuous phase. Two varieties of emulsions are oil-in-water and water-in-oil. Oil-in-water emulsions usually include a fluid at least partially immiscible in an oleaginous fluid (usually an aqueous-based fluid) as the continuous phase and an oleaginous fluid as the discontinuous phase. Water-in-oil emulsions are the opposite, having the oleaginous fluid as the continuous phase and a fluid at least partially immiscible in the oleaginous fluid (usually an aqueous-based fluid) as the discontinuous phase. Water-in-oil emulsions may be also referred to as invert emulsions.

[0003] Such emulsions have been used in various oil and gas applications. For instance, emulsions may be used in the oil and gas industry for subterranean treatment applications, including drilling, production, and completion operations. Invert emulsions may be used because oleaginous-based treatment fluids (also known as muds) may have desirable performance characteristics when compared with water-based muds in some situations, *e.g.*, when there is an abundance of water reactive materials in a well bore. These performance characteristics may include, *e.g.*, better lubrication of the drilling strings and downhole tools, thinner filter cake formation, and better hole stability.

[0004] A water-in-oil type emulsion, that does not have an emulsifying agent capable of stabilizing the fluid that is at least partially immiscible in the oleaginous fluid typically will undergo natural degradation processes, such as droplet coalescence and Ostwald ripening, until the two phases which are at least partially immiscible separate and the emulsion no longer exists. Having an unstable invert emulsion may be problematic because if the emulsion destabilizes, it may not have consistent, reliable properties. This problem may be exacerbated by the physical forces that the emulsion may undergo when being used in subterranean applications, such as thermal, mechanical, and chemical stresses. Emulsion stabilizing agents, sometimes referred to as emulsifiers, may be useful in emulsions as stabilizers, especially when used in subterranean applications. The term "emulsion stabilizing agent" or emulsifier as used herein may refer to any compound capable of lowering the interfacial tension between an oleaginous fluid and a fluid at least partially immiscible in the oleaginous fluid.

[0005] Some traditional emulsion stabilizing agents are surfactant-based. Surfactant-based emulsion stabilizing agents usually comprise a hydrophobic part that interacts with

the oil phase and a hydrophilic part that interacts with the non-oleaginous phase. These interactions generally decrease the surface tension of the interface between the water droplet and the oil, which may slow the natural tendency of the two immiscible phases to separate.

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SUMMARY

[0006] The present invention relates to emulsions and methods of using such emulsions. More particularly, the present invention relates to emulsion stabilizing agents and their uses in subterranean applications.

[0007] According to a first aspect of the present invention, there is provided a
 10 stabilized emulsion composition comprising: an oleaginous fluid, a fluid that is at least partially immiscible with the oleaginous fluid, and an emulsion stabilizing agent, wherein the emulsion stabilizing agent comprises a first ionic compound soluble in the oleaginous fluid or the fluid that is at least partially immiscible with the oleaginous fluid, and a second ionic compound with a charge of opposite sign of the first ionic compound and that is at least partially soluble in the opposite fluid
 15 as the first ionic compound.

[0008] In an embodiment, the first ionic compound, the second ionic compound, or both comprise an ionic surfactant.

[0009] In an embodiment, the first ionic compound, the second ionic compound, or both comprise an ionic polyelectrolyte.

20 [0010] In an embodiment, one of the first ionic compound and the second ionic compound comprises an ionic surfactant and the other of the first ionic compound and the second ionic compound comprises an ionic polyelectrolyte.

[0011] In an embodiment, the ionic surfactant comprises an anionic surfactant.

[0012] In an embodiment, the anionic surfactant comprises at least one compound
 25 selected from the group consisting of: an alkyl carboxylate, an alkylether carboxylate, a N-acylaminoacid, a N-acylglutamate, a N-acylpolypeptide, an alkylbenzenesulfonate, a paraffinic sulfonate, an α -olefinsulfonate, a lignosulfate, a derivative of a sulfosuccinate, a polynaphthylmethylsulfonate, an alkyl sulfate, an alkylethersulfate, a monoalkylphosphate, a polyalkylphosphate, a fatty acid, an alkali salt of an acid, an alkali salt of a fatty acid, an alkaline
 30 salt of an acid, a sodium salt of an acid, a sodium salt of a fatty acid, an alkyl ethoxylate, a soap, a combination thereof, and a derivative thereof.

[0013] In an embodiment, the ionic surfactant comprises a cationic surfactant.

[0014] In an embodiment, the cationic surfactant comprises at least one compound selected from the group consisting of: an alkyl amine, an alkyl amine salt, a quaternary ammonium
 35 salt, an ethoxylated quaternary ammonium salt, an amine oxide, an alkyltrimethyl amine, a triethyl amine, an alkyldimethylbenzylamine, a derivative thereof, and a combination thereof.

[0015] In an embodiment, the ionic polyelectrolyte comprises an anionic polyelectrolyte.

[0016] In an embodiment, the anionic polyelectrolyte comprises at least one compound selected from the group consisting of: a polymer or copolymer comprising a carboxylate group, a sulfonate group, a phosphate group, a phosphonate group, an acrylate monomer, a methacrylate monomer, a styrene carboxylate, a vinyl sulfonate, a 2-acrylamine-2-methyl-propyl sulfonate, a 3-acrylamide-3-methyl butanoate, a salt of malic acid, a polyacrylic acid, a partially-hydrogenated polyacrylamide, a carboxy methyl cellulose, a cellulose modified with an anionic functional group, a polysaccharide modified with an anionic functional group, a galactomannan modified with an anionic functional group, a derivative thereof, and a combination thereof.

[0017] In an embodiment, the ionic polyelectrolyte comprises a cationic polyelectrolyte.

[0018] In an embodiment, the cationic polyelectrolyte comprises at least one compound selected from the group consisting of: a polyethylene imine, a polyamide amine, a polyamine, a vinyl benzyl trimethyl ammonium chloride, a dimethyldiallyl ammonium chloride, a 3-acrylamido-3-methyl butyl trimethyl ammonium chloride, a polyvinylpyrrolidone, chitosan modified with a cationic functional group, a gelatin modified with a cationic functional group, a galactomannan modified with a cationic functional group, a cellulose modified with a cationic functional group, a derivative thereof, and a combination thereof.

[0019] In an embodiment, the oleaginous fluid comprises at least one fluid selected from the group consisting of: a diesel oil, a crude oil, a paraffin oil, a mineral oil, a low toxicity mineral oil, an olefin, an ester, an amide, an amine, a polyolefin, a polydiorganosiloxane, a siloxane, an organosiloxane, an ether, an acetal, a dialkylcarbonate, a hydrocarbon, a derivative thereof, and a combination thereof.

[0020] In an embodiment, the fluid that is at least partially immiscible with the oleaginous fluid comprises at least one fluid selected from the group consisting of: glycerin, a glycol, a polyglycol amine, a polyol, fresh water, sea water, salt water, a brine, a derivative thereof, and a combination thereof.

[0021] According to another aspect of the present invention, there is provided a method comprising: providing a stabilized emulsion composition formed by combining components that comprise: an oleaginous fluid, a fluid that is at least partially immiscible with the oleaginous fluid, and an emulsion stabilizing agent, wherein the emulsion stabilizing agent comprises a first ionic compound soluble in the oleaginous fluid or the fluid that is at least partially immiscible with the oleaginous fluid, and a second ionic compound with a charge of opposite sign of the first ionic compound and that is at least partially soluble in the opposite fluid as the first ionic compound, and placing the stabilized emulsion composition in a subterranean formation as part of a subterranean application. The stabilized emulsion composition may comprise one or more of the embodiments described above.

[0022] According to another aspect of the present invention, there is provided a method comprising: providing a stabilized emulsion composition comprising: an oleaginous fluid, a

fluid that is at least partially immiscible with the oleaginous fluid, and an emulsion stabilizing agent, wherein the emulsion stabilizing agent comprises a first ionic compound soluble in the oleaginous fluid or the fluid that is at least partially immiscible with the oleaginous fluid, and a second ionic compound with a charge of opposite sign of the first ionic compound and that is at least partially soluble in the opposite fluid as the first ionic compound, and drilling a well bore in a subterranean formation using the stabilized emulsion composition. The stabilized emulsion composition may comprise one or more of the embodiments described above.

[0023] Yet another aspect of the present invention comprises a method of preparing a stabilized emulsion composition comprising: providing an oleaginous fluid; providing a fluid that is at least partially immiscible with the oleaginous fluid; providing an emulsion stabilizing agent, wherein the emulsion stabilizing agent comprises: a first ionic compound soluble in the oleaginous fluid or the fluid that is at least partially immiscible with the oleaginous fluid, and a second ionic compound with a charge of opposite sign of the first ionic compound and that is at least partially soluble in the opposite fluid as the first ionic compound; and combining the oleaginous fluid, the fluid that is at least partially immiscible with the oleaginous fluid, and the emulsion stabilizing agent to form a stabilized emulsion composition. The stabilized emulsion composition may comprise one or more of the embodiments described above.

[0024] The features and advantages of the present invention will be apparent to those skilled in the art. While numerous changes may be made by those skilled in the art, such changes are within the scope of the invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0025] The present invention relates to emulsions and methods of using such emulsions. More particularly, the present invention relates to emulsion stabilizing agents and their use in subterranean applications.

[0026] While there are many advantages to the present invention, only some are disclosed herein. The emulsion stabilizing agents provided by the present invention may be advantageous because it is believed that the electrostatic interactions of the molecules may serve to anchor the surfactants to the interface between the two phases present in the emulsion or invert emulsion, potentially resulting in an increased surfactant or polyelectrolyte concentration at the interface. This may result in an improved stability of the emulsion and allow a relatively low amount of the emulsion stabilizing agent to be used to achieve a stable emulsion.

[0027] The present invention provides emulsion stabilizing agents that comprise a pair of charged surfactant or polyelectrolyte compounds of opposite charge. The emulsion stabilizing agents of the present invention may be used beneficially to stabilize emulsion compositions. Such emulsion compositions that comprise the emulsion stabilizing agents of the present invention may be referred to herein as the “stabilized emulsion compositions” of the present

invention. These stabilized emulsion compositions are formed by combining components that comprise an oleaginous fluid, a fluid that is at least partially immiscible with the oleaginous fluid, and an emulsion stabilizing agent of the present invention. After mixing, these components may or may not be separately identifiable, depending on the sophistication of the technique used. The stabilized emulsion compositions may be suitable for use in a variety of subterranean applications wherein oil-in-water or a water-in-oil emulsions are suitable. These may include subterranean applications comprising stimulation operations such as fracturing and sand control treatments such as installing a gravel pack. These may also include drilling and completion operations. Other subterranean applications also may be suitable. One of ordinary skill in the art, with the benefit of this disclosure, will recognize other suitable uses for these emulsion compositions.

[0028] The oleaginous fluid utilized in the stabilized emulsion compositions may comprise any traditional oil-based fluids suitable for use in emulsions. The oleaginous fluid may be from a natural or synthetic source. Examples of suitable oleaginous fluids include diesel oils, crude oils, paraffin oils, mineral oils, low toxicity mineral oils, olefins, esters, amides, amines, synthetic oils (such as polyolefins, polydiorganosiloxanes, siloxanes, organosiloxanes and combinations thereof), ethers, acetals, dialkylcarbonates, hydrocarbons and combinations thereof. Examples of suitable oleaginous fluids include those commercially available from Halliburton Energy Services, Inc., in Houston, Tex., U.S.A., under the tradenames "ACCOLADE™," an internal olefin and ester blend invert emulsion base fluid, "PETROFREE®," an ester based invert emulsion base fluid, "PETROFREE® LV" an ester based invert emulsion base fluid, and "PETROFREE® S.F.," an internal olefin based invert emulsion base fluid. Factors that may determine what oleaginous fluid will be used in a particular application, include but are not limited to, cost and performance characteristics of the oleaginous fluid. An additional factor that may be considered is the polarity of the oleaginous fluid. For example, diesel oils are generally more polar than paraffin oils. Other factors that may be considered are environmental compatibility and regional drilling practices. For example, in North Sea applications, an ester or internal olefin (IO) may be preferred. In the Gulf of Mexico, applications may prefer to utilize "ACCOLADE™" or a low toxicity mineral oil. One skilled in the art with the benefit of this disclosure will be able to choose a suitable oleaginous fluid for a particular application in view of these considerations. In certain exemplary embodiments of the present invention, the oleaginous fluid may be crude oil.

[0029] The emulsion compositions of the present invention also comprise a fluid that is at least partially immiscible in the oleaginous fluid. This partially immiscible fluid may be a non-oleaginous fluid that is mutually insoluble with the chosen oleaginous fluid. Suitable examples of partially immiscible fluids include aqueous-based fluids, glycerin, glycols, polyglycol amines, polyols, derivatives thereof that are partially immiscible in the oleaginous fluid, and combinations thereof. The term "derivative" is defined herein to include any compound that is made from one of the listed compounds, for example, by replacing one atom in the base compound with another atom or group of atoms. Aqueous-based fluids may include, but are not limited to, fresh water, sea water,

salt water, and brines (*e.g.*, saturated salt waters). Any brine may be used with the emulsions of the present invention that does not interfere with the emulsion stabilizing agents. One of ordinary skill in the art will appreciate that detrimental interactions may occur between some components of some brines and charged surfactants or polyelectrolyte pairs. Suitable brines may include heavy brines.

- 5 Heavy brines, for the purposes of this application, include brines that may be used to weight up a fluid, such as a treatment fluid, instead of using traditional weighting agents. Brines may comprise H₂O soluble salts. In certain exemplary embodiments, suitable H₂O soluble salts may comprise sodium chloride, calcium chloride, calcium bromide, zinc bromide, potassium carbonate, sodium formate, potassium formate, sodium acetate, potassium acetate, calcium acetate, ammonium acetate,
- 10 ammonium chloride, ammonium bromide, sodium nitrate, potassium nitrate, ammonium nitrate, calcium nitrate, sodium carbonate, potassium carbonate, and combinations thereof. In other exemplary embodiments, the H₂O soluble salt may be any salt which reduces the water phase activity of the emulsion. Factors that determine what partially immiscible fluid will be used in a particular application may include cost, availability, and which oleaginous fluid has been chosen.
- 15 Another factor that may be considered is the application of the emulsion. For example, if the application needs an emulsion with a heavy weight, a zinc bromide or calcium chloride brine may be chosen. One skilled in the art with the benefit of this disclosure in view of the considerations will be able to choose a particularly suitable partially immiscible fluid for a particular application.

- [0030] As noted above, the stabilized emulsion compositions of the present
- 20 invention also comprise an emulsion stabilizing agent of the present invention. The emulsion stabilizing agents comprise at least a pair of compounds that may generally comprise two surfactant molecules, polyelectrolyte molecules, or any combination thereof that have opposite charges, which may or may not be of the same magnitude. In general, the members of the pair will be either cationic or anionic. The charge on one or both of the compounds may result from one or more ionic
- 25 functional groups. As used herein, the term “ionic” or “ionic functional group” may refer to any compound capable of carrying at least a partial positive or negative charge, whether inherent in the chemical structure or formed due to the presence of any other components in a mixture. Such compounds may include ionic groups or compounds, polar groups or compounds, amphoteric groups or compounds, or any other type of material capable of carrying or developing a charge. In
- 30 some embodiments, the anionic member of the pair may be at least partially soluble in the oleaginous phase while the cationic member may be at least partially soluble in the fluid that is at least partially immiscible in the oleaginous fluid. In other embodiments, the cationic member of the pair may be at least partially soluble in the oleaginous phase while the anionic member may be at least partially soluble in the fluid that is at least partially immiscible in the oleaginous fluid. While
- 35 not wishing to be limited by theory, it is believed that the electrostatic interactions may occur at the interface between the oleaginous phase and the fluid that is at least partially immiscible in the oleaginous fluid. While each member of the emulsion stabilizing agent pair may be soluble in one of the phases, the combined component formed by the electrostatic interactions may be at least

partially insoluble in both phases. The resulting emulsion stabilizing agent pair may remain at the interface between the phases, resulting in an improved stability of the emulsion.

[0031] In an embodiment, a member of the emulsion stabilizing agent pair may be a surfactant that may carry an anionic or cationic charge. In an embodiment, a surfactant useful with the emulsion stabilizing agent disclosed herein may comprise at least one ionic functional group. Exemplary functional groups may include carboxylates, sulfonates, sulfates, amines, imines, phosphates, and phosphonates. Exemplary cationic surfactants may include, but are not limited to, alkyl amines, alkyl amine salts, quaternary ammonium salt, ethoxylated quaternary ammonium salts, amine oxides, alkyltrimethyl amine, triethyl amine, alkyldimethylbenzylamine. Exemplary anionic surfactants may include, but are not limited to, alkyl carboxylates, alkylether carboxylates, N-acylaminoacids, N-acylglutamates, N-acylpolypeptides, alkylbenzenesulfonates, paraffinic sulfonates, α -olefinsulfonates, lignosulfates, derivatives of sulfosuccinates, polynaphthylmethylsulfonates, alkyl sulfates, alkylethersulfates, monoalkylphosphates, polyalkylphosphates, fatty acids, alkali salts of acids, alkali salts of fatty acids, alkaline salts of acids, sodium salts of acids, sodium salts of fatty acid, alkyl ethoxylate, and soaps. One of ordinary skill in the art would be able to determine the phase to which the ionic surfactant should be added, which may be based on the composition of each phase in the emulsion, the solubility of the component in each phase, the operating conditions (*e.g.*, temperature), and any additives present in either phase (*e.g.*, salts). For example, anionic surfactants may react with any calcium present in the fluid that is at least partially immiscible in the oleaginous fluid to form compounds that may not be effective stabilizers. As such, one of ordinary skill in the art may avoid the use of anionic surfactants in the fluid that is at least partially immiscible in the oleaginous fluid when calcium ions are present.

[0032] In an embodiment, a member of the emulsion stabilizing agent pair may be a polyelectrolyte that may carry an anionic or cationic charge. As used herein, a polyelectrolyte may be a polymer whose repeating units comprise an electrolyte group. These groups may dissociate in solutions comprising an aqueous fluid, allowing the polymers to carry a formal charge to some degree. For example, a polymer may be prepared that contains an anionic monomer to impart an anionic character to the molecule. Exemplary anionic polyelectrolytes include, but are not limited to, polymers or copolymers derived from anionic monomers containing carboxylates, sulfonates, phosphates, phosphonates, acrylate monomers, methacrylate, 2-acrylamine-2-methyl-propyl sulfonate, 3-acrylamide-3-methyl butanoate, styrene carboxylate, vinyl sulfonate, salts of malic acid, polyacrylic acid (PAA), partially-hydrogenated polyacrylamide (PHPA), carboxy methyl cellulose, derivatives of cellulose, polysaccharides (*e.g.*, xanthan, arabic gum), and galactomannans modified with anionic functional groups. Non-ionic monomers may be included in these compounds, *e.g.*, as in a copolymer between an anionic monomer and a neutral monomer. Exemplary cationic polyelectrolytes include, but are not limited to, polymers or copolymers comprising cationic groups such as imines, amines, and copolymers with neutral monomers.

Specific examples may include, but are not limited to, polyethylene imine, polyamide amine, polyamines, vinyl benzyl trimethyl ammonium chloride, dimethyldiallyl ammonium chloride, 3-acrylamido-3-methyl butyl trimethyl ammonium chloride, and polyvinylpyrrolidone. For example, polymers comprising chitosanes, gelatins, galactomannans and cellulose may be modified with cationic monomers to form cationic polyelectrolytes. The polyelectrolytes useful with the emulsion stabilizing agents disclosed herein may be prepared by any method known to one of ordinary skill in the art.

[0033] In an embodiment, the emulsion stabilizing agent may be added to the stabilized emulsion composition in any amount capable of stabilizing the emulsion to a desired degree. The emulsion stabilizing agent pair may be added on a charge balanced basis. For example, if the anionic member of the emulsion stabilizing agent pair carried a formal charge equal to twice that of the cationic member of the emulsion stabilizing agent pair, then the anionic member of the emulsion stabilizing agent pair may be added in an amount equal to half of the total amount of the cationic member of the emulsion stabilizing agent pair on a mole basis. In other embodiments, the members of the emulsion stabilizing agent pair may be added in a ratio not related to the charge on the emulsion stabilizing agent pair members. For example, if it is expected that one member of the pair may interact with other components of the stabilized emulsion, then more or less of that member of the pair may be added to compensate for the interaction. In an embodiment, the emulsion stabilizing agent may be added to a stabilized emulsion composition in an amount ranging from about 0.1 pounds per barrel (lb/bbl) to about 12 lb/bbl (about 0.29 kg/metre³ to about 34 kg/metre³) of the stabilized emulsion composition. In another embodiment, the emulsion stabilizing agent may be added to a stabilized emulsion composition in an amount ranging from about 0.25 lb/bbl to about 4 lb/bbl (about 0.71 kg/metre³ to about 11 kg/metre³) of the stabilized emulsion composition.

[0034] The stabilized emulsion compositions of the present invention may optionally contain a variety of additives. Examples of additives useful in the stabilized emulsions may include, but are not limited to, solids, weighting agents, inert solids, fluid loss control agents, emulsifiers, salts, dispersion aids, corrosion inhibitors, emulsion thinners, emulsion thickeners, viscosifiers, and any combination thereof.

[0035] In some embodiments, a weighting agent may be used to increase the density of the stabilized emulsion. The weighting agents, which serve to increase the density of the stabilized emulsions, may be any solids known to those skilled in the art as useful for such purpose that do not adversely interact with the emulsion stabilizing agent composition. Examples of weighting agents may include, but are not limited to, barite, calcite, ilmenite, mullite, gallena, manganese oxides, iron oxides, mixtures of these and the like. For example, a ground barium sulfate additive having the tradename BAROID® available from Halliburton Energy Services, Inc. in Houston, Tex., U.S.A. may be used as a weighting agent. The weighting material may typically be added in order to alter the density of the stabilized emulsion. The density of the fluid may be

less than about 20 (about 2400 kg/metre³), or less than about 15 (about 1800 kg/metre³), or alternatively less than about 10 pounds per gallon (about 1200 kg/metre³). One of ordinary skill in the art would be able to determine the amount of weighting agent to add to produce a stabilized emulsion with a desired density.

5 [0036] In an embodiment, the stabilized emulsion may comprise fluid-loss control additives, emulsifiers, or both. Fluid loss control agents such as modified lignite, polymers, oxidized asphalt and gilsonite may also be added to the stabilized emulsion. Usually such fluid loss control agents may be employed in an amount which is at least about 0.1, at least about 1, or at least about 5 percent by weight of the total fluid. For example, an additive having the trade name
 10 ADAPTA™ available from Halliburton Energy Services, Inc. in Houston, Tex., U.S.A. may be used as a fluid loss control additive. Alkali may also be used, preferably lime (calcium hydroxide or calcium oxide), to bind or react with acidic gases (*e.g.*, CO₂ and H₂S) encountered during drilling in the formation so long as the alkali does not interfere with the emulsion stabilizing agents disclosed herein. The quantity of free lime in a drilling fluid may range from about 1 to about 10
 15 lbs/bbl (about 2.9 kg/metre³ to about 29 kg/metre³), or more preferably about 1 to about 4 lbs/bbl (about 2.9 kg/metre³ to about 11 kg/metre³), although lower ranges such as less than about 2 lbs/bbl (about 5.7 kg/metre³) are preferred for certain esters that tend to hydrolyze in the presence of alkaline compounds as will be known to those skilled in the art. Other suitable agents as an alternative to lime may also be used to adjust and/or stabilize the emulsions with respect to acids.

20 [0037] Various supplemental surfactants and wetting agents conventionally used in emulsions may optionally be incorporated in the stabilized emulsions. Such surfactants may be, for example, fatty acids, soaps of fatty acids, amido amines, polyamides, polyamines, imidazoline derivatives, oxidized crude tall oil, organic phosphate esters, alkyl aromatic sulfates and sulfonates, as well as, mixtures of the above. Generally, such surfactants may be employed in an amount
 25 which does not interfere with the use of the stabilized emulsions. For example, the surfactants or wetting agents may be used in an amount that does not interfere with the ability of an a stabilized emulsion to act as a drilling fluid or drill in fluid and remove cuttings from the well bore.

[0038] Further, the stabilized emulsion may have added to it or mixed with the stabilized emulsion, other fluids or materials. Such materials may include for example additives to
 30 reduce or control temperature rheology or to provide thinning, such as, for example, additives having the tradenames COLDTROL®, RHEMOD™ L, ATC®, and OMC 2™; additives for providing temporary increased viscosity for shipping (transport to the well site) and for use in sweeps, such as, for example an additive having the tradename TEMPERUS™ (modified fatty acid); additives for bridging porous rock, such as, for example additives having the tradename
 35 BARACARB® 50; additives for high temperature high pressure filtration control (HTHP FILTRATE) and emulsion stability, such as, for example, additives having the tradename FACTANT™ (highly concentrated tall oil derivative); and supplemental additives for emulsification, such as, for example additives having the tradenames EZ MUL™ NT or LE

SUPERMUL™ (polyaminated fatty acids). Blends of thinners such as the OMC 2™, COLDTROL®, and ATC® may also be effective in stabilized emulsions of the invention. All of the aforementioned trademarked products are available from Halliburton Energy Services, Inc. in Houston, Tex., U.S.A.

5 [0039] Viscosifying agents may optionally be employed in the stabilized emulsions of the present invention. Usually, viscosifying agents such as oil and water soluble polymers, polyamide resins, polycarboxylic acids and fatty acid soaps may be employed. The amount of viscosifying agent used in the composition will necessarily vary depending upon the end use of the composition. Usually such viscosifying agents are employed in an amount which is at least about
10 0.1, at least about 2, or at least about 5 percent by weight of the total fluid. For example, TAU-MOD™ or BARAZAN® D PLUS, both available from Halliburton Energy Services, Inc. in Houston, Tex., U.S.A., may be used as a viscosifying agent.

[0040] Still further, dispersion aids, corrosion inhibitors and/or defoamers may be used. These and other suitable auxiliaries and additives are used in amounts known to those skilled
15 in the art depending on the conditions of the particular well bore and subterranean formation.

[0041] Generally, the stabilized emulsions of the present invention may be formed using any technique known in the art. For example, the components may be mixed together in any order under agitation condition. A representative method of preparing the stabilized emulsion may comprises mixing an appropriate quantity of the fluid that is at least partially insoluble in the
20 oleaginous fluid and an appropriate quantity of the emulsion stabilizing agent and any optional additives during continuous, mild agitation. An oleaginous fluid may then be added while mixing until a stabilized emulsion is formed. If weighting agents, such as those described above, are to be added, then the weighting agents are typically added after the stabilized emulsion is formed. Alternatively, the stabilized emulsions of the present invention may be prepared by simply adding
25 the emulsion stabilizing agent to an existing stock of drilling fluid. The effectiveness of this treatment may depend on the constituents of the fluid.

[0042] An example of a method of the present invention is a method of treating a subterranean formation comprising the steps of providing a treatment fluid comprising a stabilized emulsion comprising an oleaginous fluid, a fluid that is at least partially immiscible with the
30 oleaginous fluid, and an emulsion stabilizing agent; and treating the subterranean formation. In certain exemplary embodiments of the present invention, a method of treating a subterranean formation includes a well completion operation or a drilling operation. In other exemplary embodiments of the present invention, a method of treating a subterranean formation includes a stimulation operation. Examples of stimulation operations of the present invention include
35 fracturing operations and acid stimulation operations, like matrix acidizing and a fracturing acidizing processes. In other exemplary embodiments of the present invention, a method of treating a subterranean formation includes a sand control operation such as installing a gravel pack.

[0043] Another example of a method of the present invention is a method of drilling a well bore in a subterranean formation using a stabilized emulsion drilling fluid comprising an oleaginous fluid, a fluid that is at least partially immiscible with the oleaginous fluid, and an emulsion stabilizing agent.

[0044] An exemplary method of the present invention is a method of emulsifying crude oil comprising the steps of providing crude oil, a fluid that is at least partially immiscible with the crude oil and an emulsion stabilizing agent; and mixing the crude oil, the fluid that is at least partially immiscible with the crude oil and the emulsion stabilizing agent so as to form a stabilized crude oil emulsion.

[0045] To facilitate a better understanding of the present invention, the following examples of certain aspects of some embodiments are given. In no way should the following examples be read to limit, or define, the scope of the invention.

EXAMPLES

[0046] In order to demonstrate the stabilization of an emulsion with the emulsion stabilizing agents disclosed herein, several samples of stabilized emulsions were prepared and allowed to age different time periods. In this example, 1.5 lb/bbl of polyelectrolyte (EZ-MUD® GOLD, available from Halliburton Energy Services of Houston, Texas) and 6 lb/bbl of a filtration control agent (N-DRIL® HT PLUS, available from Halliburton Energy Services of Houston, Texas) were mixed with 3% KCl salt water using a multi-mixer for 5 minutes followed with 1.0 lb/bbl of hydrophobic surfactants (Octadecylamine with a technical grade of 90%) for another 5 minutes. An amount of diesel comprising 20% of the overall fluid volume was added and mixed for another 30 minutes. The resulting mixture was hot-rolled for 16 hours at 230°F (110°C) to form a sample labeled "Sample 1." A second batch of the fluid was prepared according to the same procedure and labeled "Sample 2." The second batch of fluid was viscosified with a viscosifier (BARAZAN® D PLUS, available from Halliburton Energy Services, of Houston, Texas) and hot-rolled for 16 hours. The fluid appearance showed little to no phase separation after 24 hours and 72 hours. The rheological properties of the 8.0 lb/gal fluids are shown Table 1.

Table 1. Formulation and Properties of Diesel in an Aqueous Fluid			
Description	Units	Sample 1	Sample 2
Density	lb/gal (kg/metre ³)	8.0 (960)	8.0 (960)
Water	bbl (metre ³)	0.789 (0.094)	0.789 (0.094)
BARAZAN® D PLUS	lb (kg)	0	0.5 (0.2)
N-DRIL™ HT PLUS	lb	6 (2.7)	6 (2.7)
Emulsifier Blend	lb	2.5 (1.1)	2.5 (1.1)
Diesel	bbl	0.199 (0.0316)	0.199 (0.0316)

Table 1. Formulation and Properties of Diesel in an Aqueous Fluid			
Description	Units	Sample 1	Sample 2
Rheological Properties			
Hot-rolled at 120°F (49°C)	hr	0	16
Remixed on a Multi-mixer	min	3	3
Plastic viscosity	cP (gram/cm.second)	29 (0.29)	37 (0.37)
Yield Point	lb/100ft2 (kPa)	71 (34)	53 (25)
10 Sec gel	lb/100ft2 (kPa)	11 (5.3)	5 (2.4)
10 Min gel	lb/100ft2 (kPa)	14 (6.7)	4 (1.9)
Fann 35 Readings @120°F (49°C)			
600 rpm		129	127
300 rpm		100	90
200 rpm		86	71
100 rpm		66	46
6 rpm		18	6
3 rpm		13	4

[0047] A fluid sample prepared according to the procedure described above was prepared and allowed to age for approximately six weeks. A visual inspection of the fluid confirmed that little to no phase separation had occurred. This result demonstrates that the emulsion is capable of remaining stable for extended periods of time using the emulsion stabilizing agents disclosed herein. Further, the stable emulsion offered the opportunity to adjust the viscosity of the fluid with BARAZAN® D PLUS without adversely affecting the stability of the emulsion.

[0048] Therefore, the present invention is well adapted to attain the ends and advantages mentioned as well as those that are inherent therein. The particular embodiments disclosed above are illustrative only, as the present invention may be modified and practiced in different but equivalent manners apparent to those skilled in the art having the benefit of the teachings herein. Furthermore, no limitations are intended to the details of construction or design herein shown, other than as described in the claims below. It is therefore evident that the particular illustrative embodiments disclosed above may be altered or modified and all such variations are considered within the scope of the present invention. While compositions and methods are described in terms of “comprising,” “containing,” or “including” various components or steps, the compositions and methods can also “consist essentially of” or “consist of” the various components and steps. All numbers and ranges disclosed above may vary by some amount. Whenever a numerical range with a lower limit and an upper limit is disclosed, any number and any included range falling within the range is specifically disclosed. In particular, every range of values (of the form, “from about a to about b,” or, equivalently, “from approximately a to b,” or, equivalently, “from approximately a-b”) disclosed herein is to be understood to set forth every number and range

encompassed within the broader range of values. Moreover, the indefinite articles “a” or “an”, as used in the claims, are defined herein to mean one or more than one of the element that it introduces. Also, the terms in the claims have their plain, ordinary meaning unless otherwise explicitly and clearly defined by the patentee. If there is any conflict in the usages of a word or
5 term in this specification and one or more patent or other documents that may be incorporated herein by reference, the definitions that are consistent with this specification should be adopted.

CLAIMS

1. A stabilized emulsion composition comprising: an oleaginous fluid, a fluid that is at least partially immiscible with the oleaginous fluid, and an emulsion stabilizing agent, wherein the emulsion stabilizing agent comprises a first ionic compound soluble in the oleaginous fluid or the fluid that is at least partially immiscible with the oleaginous fluid, and a second ionic compound with a charge of opposite sign of the first ionic compound and that is at least partially soluble in the opposite fluid as the first ionic compound.
2. A stabilized emulsion composition according to claim 1, wherein the first ionic compound, the second ionic compound, or both comprise an ionic surfactant.
3. A stabilized emulsion composition according to claim 1 or 2, wherein the first ionic compound, the second ionic compound, or both comprise an ionic polyelectrolyte.
4. A stabilized emulsion composition according to claim 2 or claim 3 when dependent on claim 2, wherein the ionic surfactant comprises an anionic surfactant.
5. A stabilized emulsion composition according to claim 4, wherein the anionic surfactant comprises at least one compound selected from the group consisting of: an alkyl carboxylate, an alkylether carboxylate, a N-acylaminoacid, a N-acylglutamate, a N-acylpolypeptide, an alkylbenzenesulfonate, a paraffinic sulfonate, an α -olefinsulfonate, a lignosulfate, a derivative of a sulfosuccinate, a polynaphthylmethylsulfonate, an alkyl sulfate, an alkylethersulfate, a monoalkylphosphate, a polyalkylphosphate, a fatty acid, an alkali salt of an acid, an alkali salt of a fatty acid, an alkaline salt of an acid, a sodium salt of an acid, a sodium salt of a fatty acid, an alkyl ethoxylate, a soap, a combination thereof, and a derivative thereof.
6. A stabilized emulsion composition according to claim 2 or any claim dependent on claim 2, wherein the ionic surfactant comprises a cationic surfactant.
7. A stabilized emulsion composition according to claim 6, wherein the cationic surfactant comprises at least one compound selected from the group consisting of: an alkyl amine, an alkyl amine salt, a quaternary ammonium salt, an ethoxylated quaternary ammonium salt, an amine oxide, an alkyltrimethyl amine, a triethyl amine, an alkyl dimethylbenzylamine, a derivative thereof, and a combination thereof.
8. A stabilized emulsion composition according to claim 3 or any claim dependent on claim 3, wherein the ionic polyelectrolyte comprises an anionic polyelectrolyte.

9. A stablized emulsion composition according to claim 8, wherein the anionic polyelectrolyte comprises at least one compound selected from the group consisting of: a polymer or copolymer comprising a carboxylate group, a sulfonate group, a phosphate group, a phosphonate group, an acrylate monomer, a methacrylate monomer, a styrene carboxylate, a vinyl sulfonate, a 2-acrylamine-2-methyl-propyl sulfonate, a 3-acrylamide-3-methyl butanoate, a salt of malic acid, a polyacrylic acid, a partially-hydrogenated polyacrylamide, a carboxy methyl cellulose, a cellulose modified with an anionic functional group, a polysaccharide modified with an anionic functional group, a galactomannan modified with an anionic functional group, a derivative thereof, and a combination thereof.

10. A stablized emulsioncomposition according to claim 3 or any claim dependent on claim 3, wherein the ionic polyelectrolyte comprises a cationic polyelectrolyte.

11. A stablized emulsion composition according to claim 10, wherein the cationic polyelectrolyte comprises at least one compound selected from the group consisting of: a polyethylene imine, a polyamide amine, a polyamine, a vinyl benzyl trimethyl ammonium chloride, a dimethyldiallyl ammonium chloride, a 3-acrylamido-3-methyl butyl trimethyl ammonium chloride, a polyvinylpyrrolidone, chitosan modified with a cationic functional group, a gelatin modified with a cationic functional group, a galactomannan modified with a cationic functional group, a cellulose modified with a cationic functional group, a derivative thereof, and a combination thereof.

12. A stablized emulsion composition according to any preceding claim, wherein the oleaginous fluid comprises at least one fluid selected from the group consisting of: a diesel oil, a crude oil, a paraffin oil, a mineral oil, a low toxicity mineral oil, an olefin, an ester, an amide, an amine, a polyolefin, a polydiorganosiloxane, a siloxane, an organosiloxane, an ether, an acetal, a dialkylcarbonate, a hydrocarbon, a derivative thereof, and a combination thereof.

13. A stablized emulsion composition according to any preceding claim, wherein the fluid that is at least partially immiscible with the oleaginous fluid comprises at least one fluid selected from the group consisting of: glycerin, a glycol, a polyglycol amine, a polyol, fresh water, sea water, salt water, a brine, a derivative thereof, and a combination thereof.

14. A method comprising: providing a stabilized emulsion composition according to any one of claims 1 to 13; and placing the stabilized emulsion composition in a subterranean formation as part of a subterranean application.

15. A method comprising: providing a stabilized emulsion composition according to any one of claims 1 to 13; and drilling a well bore in a subterranean formation using the stabilized emulsion composition.

5 16. A method of preparing a stabilized emulsion composition, the method comprising: providing an oleaginous fluid; providing a fluid that is at least partially immiscible with the oleaginous fluid; providing an emulsion stabilizing agent, wherein the emulsion stabilizing agent comprises: a first ionic compound soluble in the oleaginous fluid or the fluid that is at least partially immiscible with the oleaginous fluid, and a second ionic compound with a charge of opposite sign
10 of the first ionic compound and that is at least partially soluble in the opposite fluid as the first ionic compound; and combining the oleaginous fluid, the fluid that is at least partially immiscible with the oleaginous fluid, and the emulsion stabilizing agent to form a stabilized emulsion composition.

17. A method according to claim 16, further comprising placing the stabilized emulsion
15 composition in a subterranean formation as part of a drilling operation.

ABSTRACT

The present invention provides a stabilized emulsion composition comprising: an oleaginous fluid, a fluid that is at least partially immiscible with the oleaginous fluid, and an emulsion stabilizing agent, wherein the emulsion stabilizing agent comprises a first ionic compound soluble in the
5 oleaginous fluid or the fluid that is at least partially immiscible with the oleaginous fluid, and a second ionic compound with a charge of opposite sign of the first ionic compound and that is at least partially soluble in the opposite fluid as the first ionic compound. The present invention also provides methods involving the use of the stabilized emulsion composition and methods of preparing the stabilized emulsion composition.

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) EC/N/27997 WO

Box No. I TITLE OF INVENTION	
EMULSION STABILIZING AGENTS FOR DRILLING AND COMPLETION FLUIDS	
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.)	
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☐ 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)*If none of the following sub-boxes is used, this sheet should not be included in the request.*

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.)

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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:

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☐ applicant and inventor
☐ inventor only (If this check-box is marked, do not fill in below.)

Applicant's registration No. with the Office

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State (that is, country) of residence:

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- ☐ applicant only
☐ applicant and inventor
☐ inventor only (If this check-box is marked, do not fill in below.)

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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:

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☐ 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 (v) 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:*

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(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 agent(s) 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 4.11(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 4.11(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,
CURTIS, Philip Anthony,
GILL, Ian Stephen,
HEDGES, Martin Nicholas,
TURNER, Craig Robert,
BENNETT, Adrian Robert James,
SOUTH, Nicholas Geoffrey,
JENNINGS, Michael John,
AMERY, Marcus James
PATEL, Nikesh Prakash.

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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
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(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) 10/07/2009 (10 July 2009)	12/501,267	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

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Incorporation by reference: where an element of the international application referred to in Article 11(1)(iii)(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)(iii) 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

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

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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):*

Number of
declarations

- | | | |
|---|--|---|
| ☐ 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 | : |
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| ☐ Box No. VIII (v) | Declaration as to non-prejudicial disclosures or exceptions to lack of novelty | : |

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) : 15 claims : 3 abstract : 1 drawings : _____ Sub-total number of sheets : 24 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 : 24 (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 document(s) identified in Box No. VI as item(s): (1) : 1 7. ☐ translation of international application into (language): _____ : _____ 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)(i) 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)(ii) 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	Number of items
Figure of the drawings which should accompany the abstract: _____	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> COTTRILL, Emily Elizabeth Helen 9 July 2010		
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1. Date of actual receipt of the purported international application: _____ 3. Corrected date of actual receipt due to later but timely received papers or drawings completing the purported international application: _____ 4. Date of timely receipt of the required corrections under PCT Article 11(2): _____ 5. International Searching Authority (if two or more are competent): ISA /	2. Drawings: ☐ received: ☐ not received: 6. ☐ Transmittal of search copy delayed until search fee is paid	
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Published:

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

(54) Title: EMULSION STABILIZING AGENTS FOR DRILLING AND COMPLETION FLUIDS

(57) Abstract: The present invention provides a stabilized emulsion composition comprising: an oleaginous fluid, a fluid that is at least partially immiscible with the oleaginous fluid, and an emulsion stabilizing agent, wherein the emulsion stabilizing agent comprises a first ionic compound soluble in the oleaginous fluid or the fluid that is at least partially immiscible with the oleaginous fluid, and a second ionic compound with a charge of opposite sign of the first ionic compound and that is at least partially soluble in the opposite fluid as the first ionic compound. The present invention also provides methods involving the use of the stabilized emulsion composition and methods of preparing the stabilized emulsion composition.

WO 2011/004163 A1

EMULSION STABILIZING AGENTS FOR DRILLING AND COMPLETION FLUIDS**BACKGROUND**

[0001] The present invention relates to emulsions and methods of using such emulsions. More particularly, the present invention relates to emulsion stabilizing agents and their uses in subterranean applications.

[0002] Emulsions usually comprise two immiscible phases. The two immiscible phases may include a continuous (or external) phase and a discontinuous (or internal) phase. The discontinuous phase may comprise the secondary fluid that usually exists in droplets in the continuous phase. Two varieties of emulsions are oil-in-water and water-in-oil. Oil-in-water emulsions usually include a fluid at least partially immiscible in an oleaginous fluid (usually an aqueous-based fluid) as the continuous phase and an oleaginous fluid as the discontinuous phase. Water-in-oil emulsions are the opposite, having the oleaginous fluid as the continuous phase and a fluid at least partially immiscible in the oleaginous fluid (usually an aqueous-based fluid) as the discontinuous phase. Water-in-oil emulsions may be also referred to as invert emulsions.

[0003] Such emulsions have been used in various oil and gas applications. For instance, emulsions may be used in the oil and gas industry for subterranean treatment applications, including drilling, production, and completion operations. Invert emulsions may be used because oleaginous-based treatment fluids (also known as muds) may have desirable performance characteristics when compared with water-based muds in some situations, e.g., when there is an abundance of water reactive materials in a well bore. These performance characteristics may include, e.g., better lubrication of the drilling strings and downhole tools, thinner filter cake formation, and better hole stability.

[0004] A water-in-oil type emulsion, that does not have an emulsifying agent capable of stabilizing the fluid that is at least partially immiscible in the oleaginous fluid typically will undergo natural degradation processes, such as droplet coalescence and Ostwald ripening, until the two phases which are at least partially immiscible separate and the emulsion no longer exists. Having an unstable invert emulsion may be problematic because if the emulsion destabilizes, it may not have consistent, reliable properties. This problem may be exacerbated by the physical forces that the emulsion may undergo when being used in subterranean applications, such as thermal, mechanical, and chemical stresses. Emulsion

stabilizing agents, sometimes referred to as emulsifiers, may be useful in emulsions as stabilizers, especially when used in subterranean applications. The term "emulsion stabilizing agent" or emulsifier as used herein may refer to any compound capable of lowering the interfacial tension between an oleaginous fluid and a fluid at least partially immiscible in the
5 oleaginous fluid.

[0005] Some traditional emulsion stabilizing agents are surfactant-based. Surfactant-based emulsion stabilizing agents usually comprise a hydrophobic part that interacts with the oil phase and a hydrophilic part that interacts with the non-oleaginous phase. These interactions generally decrease the surface tension of the interface between the water droplet and
10 the oil, which may slow the natural tendency of the two immiscible phases to separate.

SUMMARY

[0006] The present invention relates to emulsions and methods of using such emulsions. More particularly, the present invention relates to emulsion stabilizing agents and
15 their uses in subterranean applications.

[0007] According to a first aspect of the present invention, there is provided a stabilized emulsion composition comprising: an oleaginous fluid, a fluid that is at least partially immiscible with the oleaginous fluid, and an emulsion stabilizing agent, wherein the emulsion stabilizing agent comprises a first ionic compound soluble in the oleaginous fluid or the fluid
20 that is at least partially immiscible with the oleaginous fluid, and a second ionic compound with a charge of opposite sign of the first ionic compound and that is at least partially soluble in the opposite fluid as the first ionic compound.

[0008] In an embodiment, the first ionic compound, the second ionic compound, or both comprise an ionic surfactant.

25 [0009] In an embodiment, the first ionic compound, the second ionic compound, or both comprise an ionic polyelectrolyte.

[0010] In an embodiment, one of the first ionic compound and the second ionic compound comprises an ionic surfactant and the other of the first ionic compound and the second ionic compound comprises an ionic polyelectrolyte.

30 [0011] In an embodiment, the ionic surfactant comprises an anionic surfactant.

[0012] In an embodiment, the anionic surfactant comprises at least one compound selected from the group consisting of: an alkyl carboxylate, an alkylether carboxylate, a N-acylaminoacid, a N-acylglutamate, a N-acylpolypeptide, an

alkylbenzenesulfonate, a paraffinic sulfonate, an α -olefinsulfonate, a lignosulfate, a derivative of a sulfosuccinate, a polynaphthylmethylsulfonate, an alkyl sulfate, an alkylethersulfate, a monoalkylphosphate, a polyalkylphosphate, a fatty acid, an alkali salt of an acid, an alkali salt of a fatty acid, an alkaline salt of an acid, a sodium salt of an acid, a sodium salt of a fatty acid, an alkyl ethoxylate, a soap, a combination thereof, and a derivative thereof.

[0013] In an embodiment, the ionic surfactant comprises a cationic surfactant.

[0014] In an embodiment, the cationic surfactant comprises at least one compound selected from the group consisting of: an alkyl amine, an alkyl amine salt, a quaternary ammonium salt, an ethoxylated quaternary ammonium salt, an amine oxide, an alkyltrimethyl amine, a triethyl amine, an alkyldimethylbenzylamine, a derivative thereof, and a combination thereof.

[0015] In an embodiment, the ionic polyelectrolyte comprises an anionic polyelectrolyte.

[0016] In an embodiment, the anionic polyelectrolyte comprises at least one compound selected from the group consisting of: ~~a polymer or copolymer comprising~~ a carboxylate group, a sulfonate group, a phosphate group, a phosphonate group, an acrylate monomer, a methacrylate monomer, a styrene carboxylate, a vinyl sulfonate, a 2-acrylamine-2-methyl-propyl sulfonate, a 3-acrylamide-3-methyl butanoate, a salt of malic acid, a polyacrylic acid, a partially-hydrogenated polyacrylamide, a carboxy methyl cellulose, a cellulose modified with an anionic functional group, a polysaccharide modified with an anionic functional group, a galactomannan modified with an anionic functional group, a derivative thereof, and a combination thereof.

[0017] In an embodiment, the ionic polyelectrolyte comprises a cationic polyelectrolyte.

[0018] In an embodiment, the cationic polyelectrolyte comprises at least one compound selected from the group consisting of: a polyethylene imine, a polyamide amine, a polyamine, a vinyl benzyl trimethyl ammonium chloride, a dimethyldiallyl ammonium chloride, a 3-acrylamido-3-methyl butyl trimethyl ammonium chloride, a polyvinylpyrrolidone, chitosan modified with a cationic functional group, a gelatin modified with a cationic functional group, a galactomannan modified with a cationic functional group, a cellulose modified with a cationic functional group, a derivative thereof, and a combination thereof.

[0019] In an embodiment, the oleaginous fluid comprises at least one fluid selected from the group consisting of: a diesel oil, a crude oil, a paraffin oil, a mineral oil, a low

toxicity mineral oil, an olefin, an ester, an amide, an amine, a polyolefin, a polydiorganosiloxane, a siloxane, an organosiloxane, an ether, an acetal, a dialkylcarbonate, a hydrocarbon, a derivative thereof, and a combination thereof.

[0020] In an embodiment, the fluid that is at least partially immiscible with the
5 oleaginous fluid comprises at least one fluid selected from the group consisting of: glycerin, a glycol, a polyglycol amine, a polyol, fresh water, sea water, salt water, a brine, a derivative thereof, and a combination thereof.

[0021] According to another aspect of the present invention, there is provided a method comprising: providing a stabilized emulsion composition formed by combining
10 components that comprise: an oleaginous fluid, a fluid that is at least partially immiscible with the oleaginous fluid, and an emulsion stabilizing agent, wherein the emulsion stabilizing agent comprises a first ionic compound soluble in the oleaginous fluid or the fluid that is at least partially immiscible with the oleaginous fluid, and a second ionic compound with a charge of opposite sign of the first ionic compound and that is at least partially soluble in the opposite
15 fluid as the first ionic compound, and placing the stabilized emulsion composition in a subterranean formation as part of a subterranean application. The stabilized emulsion composition may comprise one or more of the embodiments described above.

[0022] According to another aspect of the present invention, there is provided a method comprising: providing a stabilized emulsion composition comprising: an oleaginous
20 fluid, a fluid that is at least partially immiscible with the oleaginous fluid, and an emulsion stabilizing agent, wherein the emulsion stabilizing agent comprises a first ionic compound soluble in the oleaginous fluid or the fluid that is at least partially immiscible with the oleaginous fluid, and a second ionic compound with a charge of opposite sign of the first ionic compound and that is at least partially soluble in the opposite fluid as the first ionic compound,
25 and drilling a well bore in a subterranean formation using the stabilized emulsion composition. The stabilized emulsion composition may comprise one or more of the embodiments described above.

[0023] Yet another aspect of the present invention comprises a method of preparing a stabilized emulsion composition comprising: providing an oleaginous fluid;
30 providing a fluid that is at least partially immiscible with the oleaginous fluid; providing an emulsion stabilizing agent, wherein the emulsion stabilizing agent comprises: a first ionic compound soluble in the oleaginous fluid or the fluid that is at least partially immiscible with the oleaginous fluid, and a second ionic compound with a charge of opposite sign of the first

ionic compound and that is at least partially soluble in the opposite fluid as the first ionic compound; and combining the oleaginous fluid, the fluid that is at least partially immiscible with the oleaginous fluid, and the emulsion stabilizing agent to form a stabilized emulsion composition. The stabilized emulsion composition may comprise one or more of the
5 embodiments described above.

[0024] The features and advantages of the present invention will be apparent to those skilled in the art. While numerous changes may be made by those skilled in the art, such changes are within the scope of the invention.

10 DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0025] The present invention relates to emulsions and methods of using such emulsions. More particularly, the present invention relates to emulsion stabilizing agents and their use in subterranean applications.

~~[0026] While there are many advantages to the present invention, only some are~~
15 disclosed herein. The emulsion stabilizing agents provided by the present invention may be advantageous because it is believed that the electrostatic interactions of the molecules may serve to anchor the surfactants to the interface between the two phases present in the emulsion or invert emulsion, potentially resulting in an increased surfactant or polyelectrolyte concentration at the interface. This may result in an improved stability of the emulsion and allow a relatively
20 low amount of the emulsion stabilizing agent to be used to achieve a stable emulsion.

[0027] The present invention provides emulsion stabilizing agents that comprise a pair of charged surfactant or polyelectrolyte compounds of opposite charge. The emulsion stabilizing agents of the present invention may be used beneficially to stabilize emulsion compositions. Such emulsion compositions that comprise the emulsion stabilizing agents of the
25 present invention may be referred to herein as the "stabilized emulsion compositions" of the present invention. These stabilized emulsion compositions are formed by combining components that comprise an oleaginous fluid, a fluid that is at least partially immiscible with the oleaginous fluid, and an emulsion stabilizing agent of the present invention. After mixing, these components may or may not be separately identifiable, depending on the sophistication of
30 the technique used. The stabilized emulsion compositions may be suitable for use in a variety of subterranean applications wherein oil-in-water or a water-in-oil emulsions are suitable. These may include subterranean applications comprising stimulation operations such as fracturing and

sand control treatments such as installing a gravel pack. These may also include drilling and completion operations. Other subterranean applications also may be suitable. One of ordinary skill in the art, with the benefit of this disclosure, will recognize other suitable uses for these emulsion compositions.

5 [0028] The oleaginous fluid utilized in the stabilized emulsion compositions may comprise any traditional oil-based fluids suitable for use in emulsions. The oleaginous fluid may be from a natural or synthetic source. Examples of suitable oleaginous fluids include diesel oils, crude oils, paraffin oils, mineral oils, low toxicity mineral oils, olefins, esters, amides, amines, synthetic oils (such as polyolefins, polydiorganosiloxanes, siloxanes, organosiloxanes
10 and combinations thereof), ethers, acetals, dialkylcarbonates, hydrocarbons and combinations thereof. Examples of suitable oleaginous fluids include those commercially available from Halliburton Energy Services, Inc., in Houston, Tex., U.S.A., under the tradenames "ACCOLADE™," an internal olefin and ester blend invert emulsion base fluid, "PETROFREE®," an ester based invert emulsion base fluid, "PETROFREE® LV" an ester based
15 invert emulsion base fluid, and "PETROFREE® S.F.," an internal olefin-based invert emulsion base fluid. Factors that may determine what oleaginous fluid will be used in a particular application, include but are not limited to, cost and performance characteristics of the oleaginous fluid. An additional factor that may be considered is the polarity of the oleaginous fluid. For example, diesel oils are generally more polar than paraffin oils. Other factors that may be
20 considered are environmental compatibility and regional drilling practices. For example, in North Sea applications, an ester or internal olefin (IO) may be preferred. In the Gulf of Mexico, applications may prefer to utilize "ACCOLADE™" or a low toxicity mineral oil. One skilled in the art with the benefit of this disclosure will be able to choose a suitable oleaginous fluid for a particular application in view of these considerations. In certain exemplary embodiments of the
25 present invention, the oleaginous fluid may be crude oil.

 [0029] The emulsion compositions of the present invention also comprise a fluid that is at least partially immiscible in the oleaginous fluid. This partially immiscible fluid may be a non-oleaginous fluid that is mutually insoluble with the chosen oleaginous fluid. Suitable examples of partially immiscible fluids include aqueous-based fluids, glycerin, glycols,
30 polyglycol amines, polyols, derivatives thereof that are partially immiscible in the oleaginous fluid, and combinations thereof. The term "derivative" is defined herein to include any compound that is made from one of the listed compounds, for example, by replacing one atom in the base compound with another atom or group of atoms. Aqueous-based fluids may include,

but are not limited to, fresh water, sea water, salt water, and brines (e.g., saturated salt waters). Any brine may be used with the emulsions of the present invention that does not interfere with the emulsion stabilizing agents. One of ordinary skill in the art will appreciate that detrimental interactions may occur between some components of some brines and charged surfactants or polyelectrolyte pairs. Suitable brines may include heavy brines. Heavy brines, for the purposes of this application, include brines that may be used to weight up a fluid, such as a treatment fluid, instead of using traditional weighting agents. Brines may comprise H₂O soluble salts. In certain exemplary embodiments, suitable H₂O soluble salts may comprise sodium chloride, calcium chloride, calcium bromide, zinc bromide, potassium carbonate, sodium formate, potassium formate, sodium acetate, potassium acetate, calcium acetate, ammonium acetate, ammonium chloride, ammonium bromide, sodium nitrate, potassium nitrate, ammonium nitrate, calcium nitrate, sodium carbonate, potassium carbonate, and combinations thereof. In other exemplary embodiments, the H₂O soluble salt may be any salt which reduces the water phase activity of the emulsion. Factors that determine what partially immiscible fluid will be used in a particular application may include cost, availability, and which oleaginous fluid has been chosen. Another factor that may be considered is the application of the emulsion. For example, if the application needs an emulsion with a heavy weight, a zinc bromide or calcium chloride brine may be chosen. One skilled in the art with the benefit of this disclosure in view of the considerations will be able to choose a particularly suitable partially immiscible fluid for a particular application.

[0030] As noted above, the stabilized emulsion compositions of the present invention also comprise an emulsion stabilizing agent of the present invention. The emulsion stabilizing agents comprise at least a pair of compounds that may generally comprise two surfactant molecules, polyelectrolyte molecules, or any combination thereof that have opposite charges, which may or may not be of the same magnitude. In general, the members of the pair will be either cationic or anionic. The charge on one or both of the compounds may result from one or more ionic functional groups. As used herein, the term "ionic" or "ionic functional group" may refer to any compound capable of carrying at least a partial positive or negative charge, whether inherent in the chemical structure or formed due to the presence of any other components in a mixture. Such compounds may include ionic groups or compounds, polar groups or compounds, amphoteric groups or compounds, or any other type of material capable of carrying or developing a charge. In some embodiments, the anionic member of the pair may be at least partially soluble in the oleaginous phase while the cationic member may be at least

partially soluble in the fluid that is at least partially immiscible in the oleaginous fluid. In other embodiments, the cationic member of the pair may be at least partially soluble in the oleaginous phase while the anionic member may be at least partially soluble in the fluid that is at least partially immiscible in the oleaginous fluid. While not wishing to be limited by theory, it is
5 believed that the electrostatic interactions may occur at the interface between the oleaginous phase and the fluid that is at least partially immiscible in the oleaginous fluid. While each member of the emulsion stabilizing agent pair may be soluble in one of the phases, the combined component formed by the electrostatic interactions may be at least partially insoluble in both phases. The resulting emulsion stabilizing agent pair may remain at the interface
10 between the phases, resulting in an improved stability of the emulsion.

[0031] In an embodiment, a member of the emulsion stabilizing agent pair may be a surfactant that may carry an anionic or cationic charge. In an embodiment, a surfactant useful with the emulsion stabilizing agent disclosed herein may comprise at least one ionic functional group. Exemplary functional groups may include carboxylates, sulfonates, sulfates,
15 ~~amines, imines, phosphates, and phosphonates.~~ Exemplary cationic surfactants may include, but are not limited to, alkyl amines, alkyl amine salts, quaternary ammonium salt, ethoxylated quaternary ammonium salts, amine oxides, alkyltrimethyl amine, triethyl amine, alkyl dimethylbenzylamine. Exemplary anionic surfactants may include, but are not limited to, alkyl carboxylates, alkylether carboxylates, N-acylaminoacids, N-acylglutamates, N-
20 acylpolypeptides, alkylbenzenesulfonates, paraffinic sulfonates, α -olefinsulfonates, lignosulfates, derivatives of sulfosuccinates, polynaphthylmethylsulfonates, alkyl sulfates, alkylethersulfates, monoalkylphosphates, polyalkylphosphates, fatty acids, alkali salts of acids, alkali salts of fatty acids, alkaline salts of acids, sodium salts of acids, sodium salts of fatty acid, alkyl ethoxylate, and soaps. One of ordinary skill in the art would be able to determine the
25 phase to which the ionic surfactant should be added, which may be based on the composition of each phase in the emulsion, the solubility of the component in each phase, the operating conditions (e.g., temperature), and any additives present in either phase (e.g., salts). For example, anionic surfactants may react with any calcium present in the fluid that is at least partially immiscible in the oleaginous fluid to form compounds that may not be effective
30 stabilizers. As such, one of ordinary skill in the art may avoid the use of anionic surfactants in the fluid that is at least partially immiscible in the oleaginous fluid when calcium ions are present.

[0032] In an embodiment, a member of the emulsion stabilizing agent pair may be a polyelectrolyte that may carry an anionic or cationic charge. As used herein, a polyelectrolyte may be a polymer whose repeating units comprise an electrolyte group. These groups may dissociate in solutions comprising an aqueous fluid, allowing the polymers to carry
5 a formal charge to some degree. For example, a polymer may be prepared that contains an anionic monomer to impart an anionic character to the molecule. Exemplary anionic polyelectrolytes include, but are not limited to, polymers or copolymers derived from anionic monomers containing carboxylates, sulfonates, phosphates, phosphonates, acrylate monomers, methacrylate, 2-acrylamine-2-methyl-propyl sulfonate, 3-acrylamide-3-methyl butanoate,
10 styrene carboxylate, vinyl sulfonate, salts of malic acid, polyacrylic acid (PAA), partially-hydrogenated polyacrylamide (PHPA), carboxy methyl cellulose, derivatives of cellulose, polysaccharides (*e.g.*, xanthan, arabic gum), and galactomannans modified with anionic functional groups. Non-ionic monomers may be included in these compounds, *e.g.*, as in a copolymer between an anionic monomer and a neutral monomer. Exemplary cationic
15 ~~polyelectrolytes include, but are not limited to, polymers or copolymers comprising cationic~~ groups such as imines, amines, and copolymers with neutral monomers. Specific examples may include, but are not limited to, polyethylene imine, polyamide amine, polyamines, vinyl benzyl trimethyl ammonium chloride, dimethyldiallyl ammonium chloride, 3-acrylamido-3-methyl butyl trimethyl ammonium chloride, and polyvinylpyrrolidone. For example, polymers
20 comprising chitosanes, gelatins, galactomannans and cellulose may be modified with cationic monomers to form cationic polyelectrolytes. The polyelectrolytes useful with the emulsion stabilizing agents disclosed herein may be prepared by any method known to one of ordinary skill in the art.

[0033] In an embodiment, the emulsion stabilizing agent may be added to the
25 stabilized emulsion composition in any amount capable of stabilizing the emulsion to a desired degree. The emulsion stabilizing agent pair may be added on a charge balanced basis. For example, if the anionic member of the emulsion stabilizing agent pair carried a formal charge equal to twice that of the cationic member of the emulsion stabilizing agent pair, then the anionic member of the emulsion stabilizing agent pair may be added in an amount equal to half
30 of the total amount of the cationic member of the emulsion stabilizing agent pair on a mole basis. In other embodiments, the members of the emulsion stabilizing agent pair may be added in a ratio not related to the charge on the emulsion stabilizing agent pair members. For example, if it is expected that one member of the pair may interact with other components of the stabilized

emulsion, then more or less of that member of the pair may be added to compensate for the interaction. In an embodiment, the emulsion stabilizing agent may be added to a stabilized emulsion composition in an amount ranging from about 0.1 pounds per barrel (lb/bbl) to about 12 lb/bbl (about 0.29 kg/metre³ to about 34 kg/metre³) of the stabilized emulsion composition.

5 In another embodiment, the emulsion stabilizing agent may be added to a stabilized emulsion composition in an amount ranging from about 0.25 lb/bbl to about 4 lb/bbl (about 0.71 kg/metre³ to about 11 kg/metre³) of the stabilized emulsion composition.

[0034] The stabilized emulsion compositions of the present invention may optionally contain a variety of additives. Examples of additives useful in the stabilized
10 emulsions may include, but are not limited to, solids, weighting agents, inert solids, fluid loss control agents, emulsifiers, salts, dispersion aids, corrosion inhibitors, emulsion thinners, emulsion thickeners, viscosifiers, and any combination thereof.

[0035] In some embodiments, a weighting agent may be used to increase the density of the stabilized emulsion. The weighting agents, which serve to increase the density of
15 ~~the stabilized emulsions, may be any solids known to those skilled in the art as useful for such~~ purpose that do not adversely interact with the emulsion stabilizing agent composition. Examples of weighting agents may include, but are not limited to, barite, calcite, ilmenite, mullite, gallena, manganese oxides, iron oxides, mixtures of these and the like. For example, a ground barium sulfate additive having the tradename BAROID® available from Halliburton
20 Energy Services, Inc. in Houston, Tex., U.S.A. may be used as a weighting agent. The weighting material may typically be added in order to alter the density of the stabilized emulsion. The density of the fluid may be less than about 20 (about 2400 kg/metre³), or less than about 15 (about 1800 kg/metre³), or alternatively less than about 10 pounds per gallon (about 1200 kg/metre³). One of ordinary skill in the art would be able to determine the amount
25 of weighting agent to add to produce a stabilized emulsion with a desired density.

[0036] In an embodiment, the stabilized emulsion may comprise fluid-loss control additives, emulsifiers, or both. Fluid loss control agents such as modified lignite, polymers, oxidized asphalt and gilsonite may also be added to the stabilized emulsion. Usually such fluid loss control agents may be employed in an amount which is at least about 0.1, at least
30 about 1, or at least about 5 percent by weight of the total fluid. For example, an additive having the trade name ADAPTA™ available from Halliburton Energy Services, Inc. in Houston, Tex., U.S.A. may be used as a fluid loss control additive. Alkali may also be used, preferably lime (calcium hydroxide or calcium oxide), to bind or react with acidic gases (e.g., CO₂ and H₂S)

encountered during drilling in the formation so long as the alkali does not interfere with the emulsion stabilizing agents disclosed herein. The quantity of free lime in a drilling fluid may range from about 1 to about 10 lbs/bbl (about 2.9 kg/metre³ to about 29 kg/metre³), or more preferably about 1 to about 4 lbs/bbl (about 2.9 kg/metre³ to about 11 kg/metre³), although lower
5 ranges such as less than about 2 lbs/bbl (about 5.7 kg/metre³) are preferred for certain esters that tend to hydrolyze in the presence of alkaline compounds as will be known to those skilled in the art. Other suitable agents as an alternative to lime may also be used to adjust and/or stabilize the emulsions with respect to acids.

[0037] Various supplemental surfactants and wetting agents conventionally used
10 in emulsions may optionally be incorporated in the stabilized emulsions. Such surfactants may be, for example, fatty acids, soaps of fatty acids, amido amines, polyamides, polyamines, imidazoline derivatives, oxidized crude tall oil, organic phosphate esters, alkyl aromatic sulfates and sulfonates, as well as, mixtures of the above. Generally, such surfactants may be employed in an amount which does not interfere with the use of the stabilized emulsions. For example, the
15—surfactants or wetting agents may be used in an amount that does not interfere with the ability of—
an a stabilized emulsion to act as a drilling fluid or drill in fluid and remove cuttings from the well bore.

[0038] Further, the stabilized emulsion may have added to it or mixed with the stabilized emulsion, other fluids or materials. Such materials may include for example additives
20 to reduce or control temperature rheology or to provide thinning, such as, for example, additives having the tradenames COLDTROL[®], RHEMOD[™] L, ATC[®], and OMC 2[™]; additives for providing temporary increased viscosity for shipping (transport to the well site) and for use in sweeps, such as, for example an additive having the tradename TEMPERUS[™] (modified fatty acid); additives for bridging porous rock, such as, for example additives having the tradename
25 BARACARB[®] 50; additives for high temperature high pressure filtration control (HTHP FILTRATE) and emulsion stability, such as, for example, additives having the tradename FACTANT[™] (highly concentrated tall oil derivative); and supplemental additives for emulsification, such as, for example additives having the tradenames EZ MUL[™] NT or LE SUPERMUL[™] (polyaminated fatty acids). Blends of thinners such as the OMC 2[™],
30 COLDTROL[®], and ATC[®] may also be effective in stabilized emulsions of the invention. All of the aforementioned trademarked products are available from Halliburton Energy Services, Inc. in Houston, Tex., U.S.A.

[0039] Viscosifying agents may optionally be employed in the stabilized emulsions of the present invention. Usually, viscosifying agents such as oil and water soluble polymers, polyamide resins, polycarboxylic acids and fatty acid soaps may be employed. The amount of viscosifying agent used in the composition will necessarily vary depending upon the end use of the composition. Usually such viscosifying agents are employed in an amount which is at least about 0.1, at least about 2, or at least about 5 percent by weight of the total fluid. For example, TAU-MOD™ or BARAZAN® D PLUS, both available from Halliburton Energy Services, Inc. in Houston, Tex., U.S.A., may be used as a viscosifying agent.

[0040] Still further, dispersion aids, corrosion inhibitors and/or defoamers may be used. These and other suitable auxiliaries and additives are used in amounts known to those skilled in the art depending on the conditions of the particular well bore and subterranean formation.

[0041] Generally, the stabilized emulsions of the present invention may be formed using any technique known in the art. For example, the components may be mixed together in any order under agitation condition. A representative method of preparing the stabilized emulsion may comprises mixing an appropriate quantity of the fluid that is at least partially insoluble in the oleaginous fluid and an appropriate quantity of the emulsion stabilizing agent and any optional additives during continuous, mild agitation. An oleaginous fluid may then be added while mixing until a stabilized emulsion is formed. If weighting agents, such as those described above, are to be added, then the weighting agents are typically added after the stabilized emulsion is formed. Alternatively, the stabilized emulsions of the present invention may be prepared by simply adding the emulsion stabilizing agent to an existing stock of drilling fluid. The effectiveness of this treatment may depend on the constituents of the fluid.

[0042] An example of a method of the present invention is a method of treating a subterranean formation comprising the steps of providing a treatment fluid comprising a stabilized emulsion comprising an oleaginous fluid, a fluid that is at least partially immiscible with the oleaginous fluid, and an emulsion stabilizing agent; and treating the subterranean formation. In certain exemplary embodiments of the present invention, a method of treating a subterranean formation includes a well completion operation or a drilling operation. In other exemplary embodiments of the present invention, a method of treating a subterranean formation includes a stimulation operation. Examples of stimulation operations of the present invention include fracturing operations and acid stimulation operations, like matrix acidizing and a fracturing acidizing processes. In other exemplary embodiments of the present invention, a

method of treating a subterranean formation includes a sand control operation such as installing a gravel pack.

[0043] Another example of a method of the present invention is a method of drilling a well bore in a subterranean formation using a stabilized emulsion drilling fluid comprising an oleaginous fluid, a fluid that is at least partially immiscible with the oleaginous fluid, and an emulsion stabilizing agent.

[0044] An exemplary method of the present invention is a method of emulsifying crude oil comprising the steps of providing crude oil, a fluid that is at least partially immiscible with the crude oil and an emulsion stabilizing agent; and mixing the crude oil, the fluid that is at least partially immiscible with the crude oil and the emulsion stabilizing agent so as to form a stabilized crude oil emulsion.

[0045] To facilitate a better understanding of the present invention, the following examples of certain aspects of some embodiments are given. In no way should the following examples be read to limit, or define, the scope of the invention.

15

EXAMPLES

[0046] In order to demonstrate the stabilization of an emulsion with the emulsion stabilizing agents disclosed herein, several samples of stabilized emulsions were prepared and allowed to age different time periods. In this example, 1.5 lb/bbl of polyelectrolyte (EZ-MUD[®] GOLD, available from Halliburton Energy Services of Houston, Texas) and 6 lb/bbl of a filtration control agent (N-DRIL[®] HT PLUS, available from Halliburton Energy Services of Houston, Texas) were mixed with 3% KCl salt water using a multi-mixer for 5 minutes followed with 1.0 lb/bbl of hydrophobic surfactants (Octadecylamine with a technical grade of 90%) for another 5 minutes. An amount of diesel comprising 20% of the overall fluid volume was added and mixed for another 30 minutes. The resulting mixture was hot-rolled for 16 hours at 230°F (110°C) to form a sample labeled "Sample 1." A second batch of the fluid was prepared according to the same procedure and labeled "Sample 2." The second batch of fluid was viscosified with a viscosifier (BARAZAN[®] D PLUS, available from Halliburton Energy Services, of Houston, Texas) and hot-rolled for 16 hours. The fluid appearance showed little to no phase separation after 24 hours and 72 hours. The rheological properties of the 8.0 lb/gal fluids are shown Table 1.

Table 1. Formulation and Properties of Diesel in an Aqueous Fluid			
Description	Units	Sample 1	Sample 2
Density	lb/gal (kg/metre ³)	8.0 (960)	8.0 (960)
Water	bbl (metre ³)	0.789 (0.094)	0.789 (0.094)
BARAZAN [®] D PLUS	lb (kg)	0	0.5 (0.2)
N-DRIL [™] HT PLUS	lb	6 (2.7)	6 (2.7)
Emulsifier Blend	lb	2.5 (1.1)	2.5 (1.1)
Diesel	bbl	0.199 (0.0316)	0.199 (0.0316)
Rheological Properties			
Hot-rolled at 120°F (49°C)	hr	0	16
Remixed on a Multi-mixer	min	3	3
Plastic viscosity	cP (gram/cm.second)	29 (0.29)	37 (0.37)
Yield Point	lb/100ft ² (kPa)	71 (34)	53 (25)
10 Sec gel	lb/100ft ² (kPa)	11 (5.3)	5 (2.4)
10-Min-gel	lb/100ft ² (kPa)	14 (6.7)	4 (1.9)
Fann 35 Readings @120°F (49°C)			
600 rpm		129	127
300 rpm		100	90
200 rpm		86	71
100 rpm		66	46
6 rpm		18	6
3 rpm		13	4

[0047] A fluid sample prepared according to the procedure described above was prepared and allowed to age for approximately six weeks. A visual inspection of the fluid confirmed that little to no phase separation had occurred. This result demonstrates that the emulsion is capable of remaining stable for extended periods of time using the emulsion stabilizing agents disclosed herein. Further, the stable emulsion offered the opportunity to adjust the viscosity of the fluid with BARAZAN[®] D PLUS without adversely affecting the stability of the emulsion.

[0048] Therefore, the present invention is well adapted to attain the ends and advantages mentioned as well as those that are inherent therein. The particular embodiments disclosed above are illustrative only, as the present invention may be modified and practiced in different but equivalent manners apparent to those skilled in the art having the benefit of the

5 teachings herein. Furthermore, no limitations are intended to the details of construction or design herein shown, other than as described in the claims below. It is therefore evident that the particular illustrative embodiments disclosed above may be altered or modified and all such variations are considered within the scope of the present invention. While compositions and methods are described in terms of "comprising," "containing," or "including" various components or steps, the compositions and methods can also "consist essentially of" or "consist of" the various components and steps. All numbers and ranges disclosed above may vary by some amount. Whenever a numerical range with a lower limit and an upper limit is disclosed, any number and any included range falling within the range is specifically disclosed. In particular, every range of values (of the form, "from about a to about b," or, equivalently, "from approximately a to b," or, equivalently, "from approximately a-b") disclosed herein is to be understood to set forth every number and range encompassed within the broader range of values. Moreover, the indefinite articles "a" or "an", as used in the claims, are defined herein to mean one or more than one of the element that it introduces. Also, the terms in the claims have their ~~15 plain, ordinary meaning unless otherwise explicitly and clearly defined by the patentee. If there~~ is any conflict in the usages of a word or term in this specification and one or more patent or other documents that may be incorporated herein by reference, the definitions that are consistent with this specification should be adopted.

CLAIMS

1. A stabilized emulsion composition comprising: an oleaginous fluid, a fluid that is at least partially immiscible with the oleaginous fluid, and an emulsion stabilizing agent, wherein the
5 emulsion stabilizing agent comprises a first ionic compound soluble in the oleaginous fluid or the fluid that is at least partially immiscible with the oleaginous fluid, and a second ionic compound with a charge of opposite sign of the first ionic compound and that is at least partially soluble in the opposite fluid as the first ionic compound.
- 10 2. A stabilized emulsion composition according to claim 1, wherein the first ionic compound, the second ionic compound, or both comprise an ionic surfactant.
3. A stabilized emulsion composition according to claim 1 or 2, wherein the first ionic compound, the second ionic compound, or both comprise an ionic polyelectrolyte.
- 15 4. A stabilized emulsion composition according to claim 2 or claim 3 when dependent on claim 2, wherein the ionic surfactant comprises an anionic surfactant.
5. A stabilized emulsion composition according to claim 4, wherein the anionic surfactant
20 comprises at least one compound selected from the group consisting of: an alkyl carboxylate, an alkylether carboxylate, a N-acylaminoacid, a N-acylglutamate, a N-acylpolypeptide, an alkylbenzenesulfonate, a paraffinic sulfonate, an α -olefinsulfonate, a lignosulfate, a derivative of a sulfosuccinate, a polynaphthylmethylsulfonate, an alkyl sulfate, an alkylethersulfate, a monoalkylphosphate, a polyalkylphosphate, a fatty acid, an alkali salt of an acid, an alkali salt of
25 a fatty acid, an alkaline salt of an acid, a sodium salt of an acid, a sodium salt of a fatty acid, an alkyl ethoxylate, a soap, a combination thereof, and a derivative thereof.
6. A stabilized emulsion composition according to claim 2 or any claim dependent on claim 2, wherein the ionic surfactant comprises a cationic surfactant.
- 30 7. A stabilized emulsion composition according to claim 6, wherein the cationic surfactant comprises at least one compound selected from the group consisting of: an alkyl amine, an alkyl amine salt, a quaternary ammonium salt, an ethoxylated quaternary ammonium salt, an amine

oxide, an alkyltrimethyl amine, a triethyl amine, an alkyldimethylbenzylamine, a derivative thereof, and a combination thereof.

8. A stablized emulsion composition according to claim 3 or any claim dependent on claim 3, wherein the ionic polyelectrolyte comprises an anionic polyelectrolyte.

9. A stablized emulsion composition according to claim 8, wherein the anionic polyelectrolyte comprises at least one compound selected from the group consisting of: a polymer or copolymer comprising a carboxylate group, a sulfonate group, a phosphate group, a phosphonate group, an acrylate monomer, a methacrylate monomer, a styrene carboxylate, a vinyl sulfonate, a 2-acrylamine-2-methyl-propyl sulfonate, a 3-acrylamide-3-methyl butanoate, a salt of malic acid, a polyacrylic acid, a partially-hydrogenated polyacrylamide, a carboxy methyl cellulose, a cellulose modified with an anionic functional group, a polysaccharide modified with an anionic functional group, a galactomannan modified with an anionic functional group, a derivative thereof, and a combination thereof.

10. A stablized emulsion composition according to claim 3 or any claim dependent on claim 3, wherein the ionic polyelectrolyte comprises a cationic polyelectrolyte.

11. A stablized emulsion composition according to claim 10, wherein the cationic polyelectrolyte comprises at least one compound selected from the group consisting of: a polyethylene imine, a polyamide amine, a polyamine, a vinyl benzyl trimethyl ammonium chloride, a dimethyldiallyl ammonium chloride, a 3-acrylamido-3-methyl butyl trimethyl ammonium chloride, a polyvinylpyrrolidone, chitosan modified with a cationic functional group, a gelatin modified with a cationic functional group, a galactomannan modified with a cationic functional group, a cellulose modified with a cationic functional group, a derivative thereof, and a combination thereof.

12. A stablized emulsion composition according to any preceding claim, wherein the oleaginous fluid comprises at least one fluid selected from the group consisting of: a diesel oil, a crude oil, a paraffin oil, a mineral oil, a low toxicity mineral oil, an olefin, an ester, an amide, an amine, a polyolefin, a polydiorganosiloxane, a siloxane, an organosiloxane, an ether, an acetal, a dialkylcarbonate, a hydrocarbon, a derivative thereof, and a combination thereof.

13. A stablized emulsion composition according to any preceding claim, wherein the fluid that is at least partially immiscible with the oleaginous fluid comprises at least one fluid selected from the group consisting of: glycerin, a glycol, a polyglycol amine, a polyol, fresh water, sea
5 water, salt water, a brine, a derivative thereof, and a combination thereof.

14. A method comprising: providing a stabilized emulsion composition according to any one of claims 1 to 13; and placing the stabilized emulsion composition in a subterranean formation as part of a subterranean application.

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15. A method comprising: providing a stabilized emulsion composition according to any one of claims 1 to 13; and drilling a well bore in a subterranean formation using the stabilized emulsion composition.

15 16. A method of preparing a stabilized emulsion composition, the method comprising: providing an oleaginous fluid; providing a fluid that is at least partially immiscible with the oleaginous fluid; providing an emulsion stabilizing agent, wherein the emulsion stabilizing agent comprises: a first ionic compound soluble in the oleaginous fluid or the fluid that is at least partially immiscible with the oleaginous fluid, and a second ionic compound with a charge
20 of opposite sign of the first ionic compound and that is at least partially soluble in the opposite fluid as the first ionic compound; and combining the oleaginous fluid, the fluid that is at least partially immiscible with the oleaginous fluid, and the emulsion stabilizing agent to form a stabilized emulsion composition.

25 17. A method according to claim 16, further comprising placing the stabilized emulsion composition in a subterranean formation as part of a drilling operation.

INTERNATIONAL SEARCH REPORT

International application No

PCT/GB2010/001317

A. CLASSIFICATION OF SUBJECT MATTER
 INV. C09K8/28 C09K8/36
 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

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 6 613 720 B1 (FERAUD JEAN PIERRE [FR] ET AL) 2 September 2003 (2003-09-02) column 13, lines 25 - 60 column 16, lines 12-22; example 1 the whole document	1-17
X	EP 0 037 699 A2 (EXXON RESEARCH ENGINEERING CO [US]) 14 October 1981 (1981-10-14) claims 1,7-9,14 the whole document	1,2,4-7, 12-17
X	US 4 542 791 A (DRAKE EVELYN N [US] ET AL) 24 September 1985 (1985-09-24) column 3, line 65 - column 4, line 17 column 8, line 43 - column 9, line 3; claim 1; example 1 the whole document	1-4,6, 8-14,16



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.

"Z" document member of the same patent family

Date of the actual completion of the international search

8 October 2010

Date of mailing of the international search report

18/10/2010

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/GB2010/001317

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 6613720	B1	02-09-2003	NONE	
EP 0037699	A2	14-10-1981	CA 1142742 A1 DE 3170092 D1	15-03-1983 30-05-1985
US 4542791	A	24-09-1985	NONE	



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Industria y Comercio
 SUPERINTENDENCIA

PATENTE DE INVENCION ☐MODELO DE UTILIDAD ☐

Art 33 Decisión 486/00

☐	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 ☐