

No. 11-142080- -00000-0000

Fecha: 2011-10-24 09:14:16 Dep. 2020 DIR.NUEVASCR
Tra. 11 PATENTEIYII Eve: 378 FASENACIONALI
Act. 411 PRESENTACION Folios: 129

Industria y Comercio

SUPERINTENDENCIA

DELEGATURA PROPIEDAD INDUSTRIAL

SOLICITUD DE PATENTE DE INVENCION
PCT

EXPEDIENTE No _____

TITULO MÉTODO PARA MEJORAR LA
ESTABILIDAD DE FLUIDOS DE PERFORACIÓN
CON BASE DE ACEITE A ALTAS TEMPERATURAS

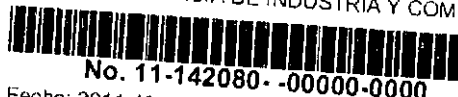
CLASIFICACION INTERNACIONAL _____

SOLICITANTE HALLIBURTON ENERGY SERVICES,
INC

DOMICILIO Duncan, Oklahoma, Estados Unidos de
América

APODERADO LUZ HELENA ADARVE GOMEZ

BOGOTA D.C. _____



No. 11-142080- -00000-0000

Fecha: 2011-10-24 09:14:16 Dep. 2020 DIR.NUEVASCR
Tra. 11 PATENTEIYII Eve. 378 FASENACIONALI
Act. 411 PRESENTACION Folios: 129

**FORMULARIO UNICO DE SOLICITUD DE PATENTE
PCT
ENTRADA EN FASE NACIONAL**

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SOLICITUD DE:

☒

Patente de Invención

☐

Patente de Modelo de Utilidad

☒

Capítulo I

☐

Capítulo II

②

SOLICITANTE

Nombre: **HALLIBURTON ENERGY SERVICES, INC**

Dirección: **IPO Box 1431, Duncan, Oklahoma 73536**

Nacionalidad o Domicilio: **Duncan, Oklahoma, Estados Unidos de América**

Lugar de Constitución: **Estados Unidos de América**

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IDENTIFICACION

☐ NIT

☐ NIT

☐ Otro

☒ Otro

Cuál
Número

③

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IDENTIFICACION

☒ NIT

☐ NIT

☐ Otro

☐ Otro

Cual
Número **41575435** TP **14884**
BTA **C.S.J.**

④

**INVENTOR(ES)
(72)**

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Nacionalidad o Domicilio: **Londres, Gran Bretaña**

⑤ **PCT (86)**

Solicitud Internacional No. **WO 2010/122302 A1** Fecha **28.10.2010**

Publicación Internacional No. **PCT/GB2010/000804** Fecha **22.04.2010**

⑥

**Título(54): METODO PARA MEJORAR LA ESTABILIDAD DE FLUIDOS DE
PERFORACIÓN CON BASE DE ACEITE A ALTAS TEMPERATURAS**

⑦

Clasificación Internacional (51):

⑧

Prioridad

SI ☒ NO ☐

(33) País de Origen

US

(32) Fecha

24.04.2009

(31) N° de Solicitud

12/386,944

⑨

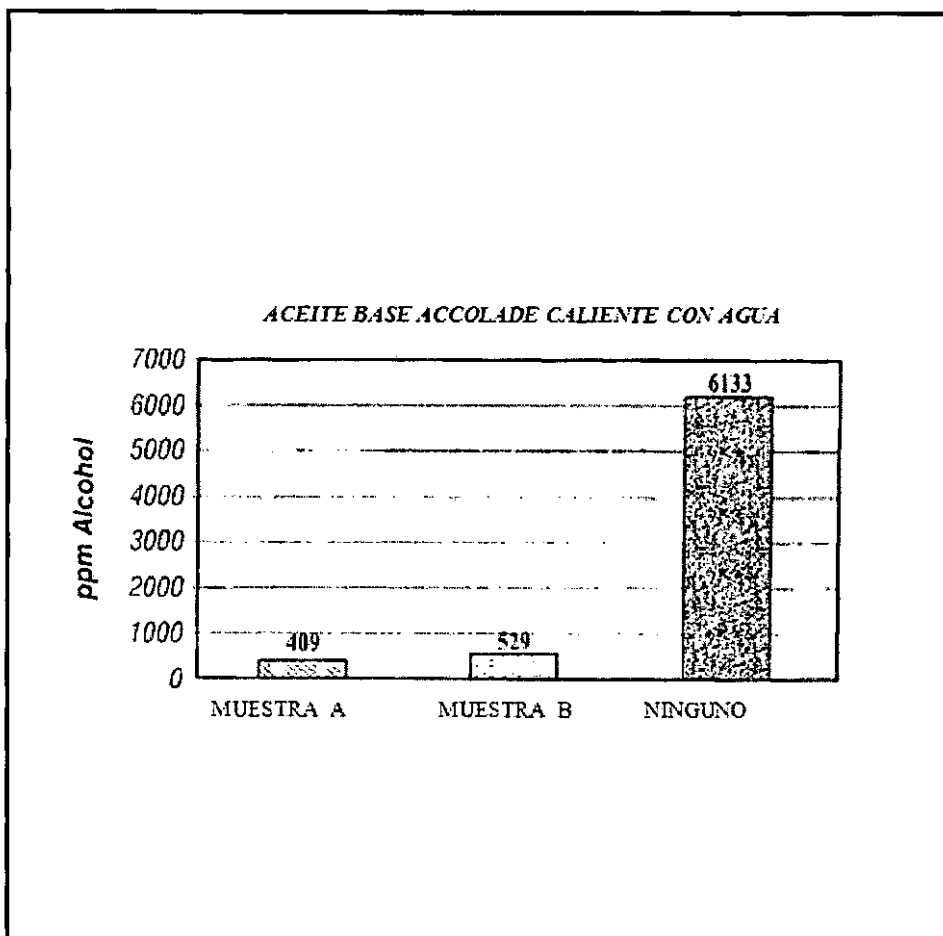
Comprobante de Pago No.: 11-102764

Fecha 20.10.2011

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, Resumen, descripción, reivindicaciones, dibujos)
- ☐ Copia del examen preliminar internacional efectuado por la Autoridad Internacional de Examen Preliminar (IPEA)
- ☐ Traducción del examen preliminar internacional efectuado por la IPEA.
- ☐ De ser el caso, copia del contrato de acceso.
- ☐ De ser el caso, documento que acredite la licencia o autorización de uso de conocimientos tradicionales de las comunidades indígenas.
- ☐ De ser el caso, certificado de depósito del material biológico.
- ☒ Arte final 12x12.
- ☐ De ser el caso, información sobre otras solicitudes de patente o títulos obtenidos en el extranjero por el mismo titular o su causante, relacionadas parcial o totalmente con la invención de esta solicitud.
- ☐ Recibo Reivindicaciones adicionales No 11-102777
- ☒ Prioridad
<http://www.wipo.int/patentscope/search/en/detail.jsf;jsessionid=1E9CB2CD25DBF388E3B2846E18B10F28.wap2?docId=WO2010122302&recNum=1&tab=PCTDocuments&maxRec=&office=&prevFilter=&sortOption=&queryString=>

11 FIGURA CARACTERISTICA



12

Solicito la Concesión de la patente

NOMBRE: LUZ HELENA ADARVE GOMEZ

FIRMA:

[Handwritten Signature]

Ug. C.C. 41575435 BTA TP. 14884 CSJ

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



RECIBO DE CAJA

No. 11 - 102764

Bogotá D.C., Octubre 20 de 2011 - 15:29:01

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	427474460	20/10/2011	9.764.000.00

*** Conceptos Pagados ***

CANT. RENTISTICO	CONCEPTO	Vr. UNIDITARIO	Vr. CONCEPTO
1 50005-01-01 SOLICITUDES	1 TRAMITES DE SOL. DE PATENTE DE INVENCIÓN	571.000.00	571.000.00
			\$571.000.00

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

Responsable: _____

Recibo de Caja Aplicado al Expediente No. _____

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO

No. 11-142080- -00000-0000
Fecha: 2011-10-24 09:14:16 Dep. 2020 DIR.NUEVASCR
Tra. 11 PATENTEIYII Eve: 378 FASENACIONALI
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ABOGADOS

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

 Industria y Comercio SUPERINTENDENCIA	RECIBO DE CAJA	No. 11 - 102777
		Bogotá D.C., Octubre 20 de 2011 - 15:29:01

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	427474460	20/10/2011	9.764.000.00

*** Conceptos Pagados ***				
CANT.	RENTISTICO	CONCEPTO	Vr.UNDITARIO	Vr.CONCEPTO
10	50005-01-01 SOLICITUDES	1607 REIVINDICACION UNITARIA ADICIONAL A LAS 10 INICIALES	27.000.00	270.000.00
				\$270.000.00

SON: **DOSCIENTOS SETENTA MIL PESOS MONEDA CORRIENTE***

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

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO

No. 11-142080-00000-0000
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Tra. 11 PATENTEIYII Eve: 378 FASENACIONALI
Act. 411 PRESENTACION Folios: 129

RECIBIDO



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) Anthony Curtis Philip

(74) Apoderado: LUZ HELENA ADARVE GOMEZ

(30) Prioridad	(31) No. Prioridad	32) Fecha	(33) País
	12/386,944	24.04.2009	US

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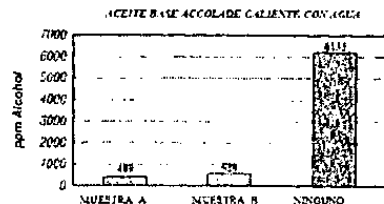
(86) Datos relativos a la presentación de la solicitud PCT

Fecha de presentación de la solicitud: 22.04.2010

No. de solicitud PCT/GB2010/000804

(54) Título MÉTODO PARA MEJORAR LA ESTABILIDAD DE FLUIDOS DE PERFORACIÓN CON BASE DE ACEITE A ALTAS TEMPERATURAS

(21) N° de solicitud:		(22) Fecha de solicitud:	
(51) Clasificación Internacional :			
(71) Solicitante(s) HALLIBURTON ENERGY SERVICES, INC			
(72) Inventor(es) Anthony Curtis Philip			
(74) Apoderado: LUZ HELENA ADARVE GOMEZ			
(30) Prioridad	(31) No. Prioridad	(32) Fecha	(33) País
	12/386,944	24.04.2009	US
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(86) Datos relativos a la presentación de la solíc. PCT		Fecha: 28.10.2010	
Fecha de presentación de la solicitud: 22.04.2010		No. Publicación WO2010/122302 A1	
No. de solicitud PCT/GB2010/000804			



(54) Título: **METODO PARA MEJORAR LA ESTABILIDAD DE FLUIDOS DE PERFORACIÓN CON BASE DE ACEITE A ALTAS TEMPERATURAS**

(57) Resumen:

Se describen métodos para mejorar la estabilidad de fluidos de perforación con base de éster, introducir entubado y/o cementar un orificio de pozo en una formación subterránea, así como también fluidos mejorados de perforación con base de éster para uso a altas temperaturas. Se logran las ventajas de la invención mediante la inhibición de la hidrólisis de los ésteres contenidos en el fluido de perforación, mediante la adición de un inhibidor de hidrólisis carbodiimida monomérica o polimérica al fluido de perforación.



Industria y Comercio

SUPERINTENDENCIA

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO

DIVISION DE NUEVAS CREACIONES

EXTRACTO PARA PUBLICACIÓN

SOLICITUD DE PATENTE DE INVENCION

(21) N° de solicitud:		(51) Int Cl:	
22) Fecha de solicitud:		(71) Solicitante(s) HALLIBURTON ENERGY SERVICES, INC	
(30) Prioridad	(31) No. Prioridad	32) Fecha	(33) País
	12/386,944	24.04.2009	US
		(72) Inventor(es) Anthony Curtis Philip	
		(74) Apoderado: LUZ HELENA ADARVE GOMEZ	
(54) Título: MÉTODO PARA MEJORAR LA ESTABILIDAD DE FLUIDOS DE PERFORACIÓN CON BASE DE ACEITE A ALTAS TEMPERATURAS			

Resumen:

Se describen métodos para mejorar la estabilidad de fluidos de perforación con base de éster, introducir entubado y/o cementar un orificio de pozo en una formación subterránea, así como también fluidos mejorados de perforación con base de éster para uso a altas temperaturas. Se logran las ventajas de la invención mediante la inhibición de la hidrólisis de los ésteres contenidos en el fluido de perforación, mediante la adición de un inhibidor de hidrólisis carbodiimida monomérica o polimérica al fluido de perforación.

ESPAÑOL
DESCRIPCION

METODO PARA MEJORAR LA ESTABILIDAD DE FLUIDOS DE PERFORACION CON BASE DE ACEITE A ALTAS TEMPERATURAS

ANTECEDENTES DE LA INVENCION

1. Campo de la Invención

La presente invención se refiere a composiciones y métodos para perforar, cementar y entubar orificios de pozo en formaciones subterráneas, particularmente formaciones que contienen hidrocarburo. En forma más particular, la presente invención se refiere a fluidos de perforación con base de aceite o fluido sintético que comprenden emulsiones invertidas, tales como fluidos que utilizan por ejemplo ésteres, los cuales combinan alta compatibilidad ecológica con buenas propiedades de estabilidad y rendimiento.

2. Descripción del Arte Pertinente

Un fluido o lodo de perforación es un fluido especialmente diseñado que circula a través de un orificio de pozo conforme está siendo perforado, para facilitar la operación de perforación. Las varias funciones de un fluido de perforación incluyen retirar todos los escombros de la perforación desde el orificio de pozo, enfriar y lubricar a la broca de perforación, ayudar a sostener al tubo y a la broca de perforación; y proporcionar una presión hidrostática para conservar la integridad de las paredes del orificio de pozo y evitar explosiones en el mismo. Los sistemas de fluido específico de perforación están seleccionados para mejorar una operación de perforación de acuerdo con las características de una formación geológica particular.

Se utiliza normalmente lodos basados en aceite o fluido sintético para perforar esquistos que se esponjan o derrumban, sal, yeso, anhidrita u otras formaciones de evaporación, formaciones que contienen sulfuro de hidrógeno y orificios calientes o de alta temperatura (más de 300 grados Fahrenheit ("°F")), pero pueden ser utilizados en otros orificios que penetran a la formación subterránea. A menos que se indique de otro modo, se comprenderá que los términos "lodo de aceite" o "lodo con base de aceite" o "fluido de perforación" incluyen aceites sintéticos u otros fluidos sintéticos así como también aceites naturales o tradicionales; se entenderá que tales aceites pueden comprender soluciones invertidas.

Los lodos con base de aceite utilizados en la perforación, comprenden típicamente: un aceite base (o fluido sintético) que contiene a la fase externa de una emulsión invertida; una solución salina acuosa (típicamente una solución que contiene más o menos 30% de cloruro de calcio) que incluye a la fase interna de la emulsión invertida; emulsionadores en la cara de contacto de las fases interna y externa; y otros agentes o aditivos para control de la suspensión, peso o densidad, humectación con aceite, pérdida de fluido humectante con aceite o filtración, así como control de la reología.

Un fluido de perforación con base de aceite o emulsión invertida puede contener comúnmente entre más o menos 50:50 hasta más o menos 95:5 por volumen de fase aceite a fase agua. Un lodo constituido totalmente por aceite contiene simplemente 100% de aceite en fase líquida por volumen, o sea, no existe fase acuosa interna.

Los lodos o fluidos de perforación basados en emulsión invertida (llamados también lodos de perforación invertida o lodos o fluidos invertidos) constituyen un segmento clave de la industria de fluidos de perforación. Sin embargo, los cada vez más numerosos fluidos de perforación basados en emulsión invertida han estado sometidos a mayores restricciones ambientales y exigencias de rendimiento y costo. Si bien los fluidos de perforación con emulsión invertida basados en éster satisfacen muchas preocupaciones ambientales, tienden a perder efectividad o utilidad a las altas temperaturas del campo petrolero. En consecuencia, existe una necesidad creciente e interés a nivel industrial por nuevos fluidos y métodos de perforación que proporcionan rendimiento mejorado, ofreciendo al mismo tiempo aceptación ambiental y económica.

RESUMEN DE LA INVENCION

La presente invención proporciona métodos mejorados para perforar orificios de pozo en formaciones subterráneas, empleando lodos o fluidos de perforación con base de aceite. Tal como se emplea aquí, se entenderá a los términos "perforación" o "perforación de orificios de pozo" en el sentido más amplio de las operaciones de perforación, las cuales incluyen introducción del entubado y cementación así como también perforación, a menos que se indique específicamente de otro modo. En forma más particular, la presente invención proporciona un método para mejorar la estabilidad de los fluidos de perforación con base de aceite, más particularmente a altas temperaturas. La presente invención proporciona

también fluidos de perforación con base de aceite que tienen estabilidad mejorada a esas temperaturas altas.

Cualquier fluido de perforación que lleve un componente hidrolizable puede beneficiarse con la presente invención. Los ésteres y amidas son particularmente susceptibles a hidrólisis y, así, la invención es particularmente ventajosa con fluidos de perforación de emulsión invertida que contienen ésteres y/o amidas, particularmente como el aceite base para los fluidos de perforación, pero también como aditivos o componentes en los fluidos de perforación, tales como por ejemplo emulsionadores y aditivos para el control de pérdida de fluido. Se logra los beneficios de la invención mediante la inhibición de la hidrólisis de ésteres y/o amidas que constituyen al fluido de perforación. Se logra particularmente tales beneficios a temperaturas más altas, o sea, a temperaturas de 275°F (135°C) o más altas y llegan hasta temperaturas tan altas como 450°F (232°C) o más, tales como las que pueden encontrar en la perforación de orificios de sondeo en formaciones subterráneas para recuperar hidrocarburos.

De acuerdo con el método de la invención, se agrega una carbodiimida y preferiblemente una polycarbodiimida al fluido de perforación como un inhibidor de la hidrólisis. Una cantidad de carga de 5 libras/barril (16,7 kg/m³) será efectiva típicamente para los propósitos de la invención, aunque se puede utilizar otras cantidades en forma satisfactoria con experimentación. Los fluidos de perforación de la invención comprenden una base de aceite éster o emulsión invertida y/o aditivos éster o amida tales como, por ejemplo, emulsionado-

res y aditivos para el control de pérdida de fluido, así como una carbodiimida o preferiblemente una polycarbodiimida.

BREVE DESCRIPCION DE LOS DIBUJOS

La figura 1 es un gráfico que compara la cantidad de alcohol producido, indicando hidrólisis, en muestras que contienen base éster y agua con aditivos polycarbodiimida o sin ellos, después de calentamiento a 370°F (188°C) durante 16 horas.

La figura 2 es un gráfico que compara la cantidad de alcohol producido, indicando hidrólisis, en muestras que contienen base éster y agua con aditivos polycarbodiimida y sin ellos, después de calentamiento a 370°F (188°C) durante períodos de 16 horas, 40 horas, 64 horas y 88 horas.

La figura 3 es un gráfico que compara la cantidad de alcohol producido, indicando hidrólisis, en muestras que contienen base éster, agua y cal, con aditivos polycarbodiimida y sin ellos después de calentamiento a 370°F (188°C) durante 16 horas.

La figura 4 es un gráfico que compara la cantidad de alcohol producido, indicando hidrólisis, en muestras de un fluido de perforación con emulsión invertida basada en éster, con aditivos polycarbodiimida y sin ellos, después de laminado en caliente a 150°F (66°C) durante 16 horas y luego a 370°F (188°C) durante 16 horas.

DESCRIPCION DETALLADA DE LAS FORMAS PREFERIDAS

Los fluidos de perforación con emulsión invertida basados en éster son preferidos como lodos de perforación basados en aceite, para aceptabilidad ambiental y cumplimiento de los reglamentos. Sin embargo, en los fluidos del arte anterior,

el éster puede ser vulnerable a la hidrólisis particularmente a las altas temperaturas que se pueden encontrar en la perforación de formaciones subterráneas para la recuperación de hidrocarburos. Tal hidrólisis puede dar como resultado la descomposición del fluido el cual, final o eventualmente, se vuelve inútil como fluido de perforación. En consecuencia, el uso de fluidos de perforación con base de éster es menos común a altas temperaturas, las cuales aumentan típicamente la velocidad de hidrólisis del éster.

La adición de cal a un fluido de perforación, tal como ha sido práctica común en campos petroleros, puede tener el efecto secundario negativo de aumentar la magnitud de la hidrólisis en fluidos de perforación del arte anterior. La cal proporciona una mayor concentración de ion de hidróxido nucleofílico en el fluido, lo cual puede aumentar la hidrólisis. En consecuencia, generalmente se evita el uso de la cal en fluidos de perforación con base de éster.

La presente invención proporciona un método para mejorar la estabilidad de fluidos de perforación con base de éster y aditivos para fluidos de perforación, inclusive a altas temperaturas e inclusive en presencia de cal u otras fuentes de ion hidróxido. Se logra esta mejora reduciendo la magnitud de hidrólisis que tiene lugar en los sistemas de fluido de perforación con base de aceite. La inhibición de la hidrólisis de acuerdo con la presente invención, permite una mayor aplicación de fluidos de perforación con base de éster en ambientes de alta temperatura, con mayor conservación de las propiedades deseables del fluido.

En el método de la presente invención, se logra la estabilidad mejorada de los fluidos de perforación con emulsión invertida basada en éster, mediante la adición o incorporación en el fluido de perforación de una carbodiimida, preferiblemente una polycarbodiimida. Se cree que el carbono carbodiimida es más reactivo que el carbono carbonilo de un éster y por lo tanto se espera que la reacción de la carbodiimida con agua o hidróxido (hidrólisis) sea más fácil que la hidrólisis del éster del fluido de perforación. En consecuencia, la reacción de la carbodiimida con agua o hidróxido previene o inhibe que el carbono carbonilo del éster reaccione con agua o hidróxido, que de otro modo podría hidrolizar al éster dando como resultado que este último no quede hidrolizado. Esto es particularmente importante y sorprendente en fluidos de perforación y especialmente en fluidos de perforación con emulsión invertida, debido a que tales fluidos contienen ya agua como parte de su composición. Sin embargo, la carbodiimida puede mantener la efectividad para mejorar la estabilidad del fluido con el paso del tiempo, por ejemplo durante un tiempo suficiente para perforar uno o más pozos u orificios de sondeo subterráneos. En otras palabras, la carbodiimida no es inmediatamente "utilizada" o diluida hasta que se vuelva ineficaz después de su incorporación en el fluido.

Se demuestra la efectividad de la invención en los siguientes experimentos.

Experimento 1:

Ya que la hidrólisis de un éster causa que se pierda parte de la molécula del éster como un alcohol, se puede me-

dir la efectividad de los inhibidores de hidrólisis vigilando a producción de alcohol que se forma en la hidrólisis del éster. En el caso de un fluido con emulsión invertida basada en éster, vendido por Halliburton Energy Services, Inc., en Houston, Texas y Duncan, Oklahoma, bajo la marca denominación comercial fluido de perforación ACCOLADE®, se puede vigilar la cantidad de alcohol producido mediante cromatografía gaseosa/espectrometría de masa. Así, se prepararon las muestras que contienen fluido base ACCOLADE®, salmuera de cloruro de calcio y un emulsionador, con una carga de 5 libras/barril (16,7 kg/m³) y sin ella, de una de dos polycarbodiimidas comerciales: el líquido viscoso polycarbodiimida STABAXOL® P200 (Muestra A) y la polycarbodiimida P en polvo STABAXOL® (Muestra b), ambas disponibles en Rhein Chemie Rheinau GmbH, Mannheim, Alemania. Las muestras fueron envejecidas estáticamente a 370°F (188°C) durante 16 horas y luego fueron probadas con respecto al contenido de alcohol, tal como se indica en la siguiente Tabla 1.

Aditivo	% en peso de alcohol	ppm de alcohol
Polycarbodiimida Muestra A	0,041	409
Polycarbodiimida Muestra B	0,053	529
Ninguno (Control)	0,61	6133

En la Figura 1 se ofrece los datos en forma de gráfico. Los datos indican que se observó más de 90% de reducción en la cantidad de alcohol producido en presencia de polycarbodiimidas. Esta reducción indica una reducción en la magnitud de hidrólisis del éster en el fluido base ACCOLADE®.

Experimento 2:

Las muestras de las mismas composiciones del Experimento 1 fueron envejecidas estáticamente a 370°F (188°C) durante 16 horas, 40 horas, 64 horas y 88 horas y se probaron con respecto al contenido de alcohol después de cada período transcurrido de envejecimiento, tal como se muestra en la siguiente Tabla 2.

TABLA 2

Aditivo	% en peso de alcohol	ppm de alcohol
Policarbodiimida Muestra A - Envejecida Estáticamente durante 16 horas	0,06	570
Policarbodiimida Muestra B - Envejecida Estáticamente durante 16 horas	0,16	1588
Ninguno (Control) Envejecido Estáticamente durante 16 horas	0,59	5876
Policarbodiimida Muestra A - Envejecida Estáticamente durante 40 horas	0,13	1333
Policarbodiimida Muestra B - Envejecida Estáticamente durante 40 horas	0,33	3309
Ninguno (Control) Envejecido Estáticamente durante 40 horas	1,00	10005
Policarbodiimida Muestra A - Envejecida Estáticamente durante 64 horas	0,34	3365
Policarbodiimida Muestra B - Envejecida Estáticamente durante 64 horas	0,74	7373
Ninguno (Control) Envejecido Estáticamente durante 88 horas	1,25	12470

ticamente durante 64 horas		
Policarbodiimida Muestra A - Envejecida Estáticamente durante 88 horas	0,74	7398
Policarbodiimida Muestra B - Envejecida Estáticamente durante 88 horas	1,34	13427
Ninguno (Control) Envejecido Estáticamente durante 88 horas	1,37	13749

En la Figura 2 se presentan los datos en forma de gráfico. Los datos indican que después de 64 horas, ambos aditivos policarbodiimida redujeron todavía la concentración de alcohol y, después de 88 horas, el Aditivo A presentó todavía la capacidad de reducir la magnitud de hidrólisis del éster que tuvo lugar. No está clara la razón por la cual el Aditivo A mostró un rendimiento superior frente al Aditivo B, aunque la naturaleza líquida del material pudo haber permitido su disolución completa en los fluidos libres de sólidos probados en este experimento, dando lugar a una mayor eficacia.

Experimento 3:

Las muestras que contienen base ACCOLADE®, salmuera de cloruro de calcio y un emulsionador, fueron preparadas con la carga de 5 libras/barril y sin ella, de una de dos policarbodiimidas comerciales o sea las policarbodiimidas STABAXOL® P200 y STABAXOL® P, disponibles en Rhein Chemie Rheinau GmbH, Mannheim, Alemania, como en los experimentos 1 y 2, excepto que a cada una de las muestras para este Experimento 3 se agregó cal (3 libras/barril [10 kg/m³]). Las muestras fueron envejecidas estáticamente a 370°F (180°C) durante 16 horas y

se probaron con respecto al contenido de alcohol, tal como se ilustra en la Tabla 3.

TABLA 3

Aditivo	% en peso de alcohol	ppm de alcohol
Policarbodiimida Muestra A	0,64	6434
Policarbodiimida Muestra B	0,56	5556
Ninguno (Control)	0,98	9804

La Figura 3 contiene los datos en forma de gráfico. Tales datos indican que se logra una reducción importante de la hidrólisis con los aditivos policarbodiimida inclusive en presencia de cal y aún cuando la adición de cal al fluido de perforación incrementa la magnitud de la hidrólisis debido a la presencia de mayores concentraciones del ion hidróxido más nucleofílico. El porcentaje de reducción de la hidrólisis en las muestras, logrado con los aditivos policarbodiimida, en comparación con el control fue de 34,4% en el caso de la Muestra A con policarbodiimida y de 43,3% en el caso de la Muestra B con policarbodiimida.

Experimento 4:

Se preparó muestras conteniendo al fluido de perforación con emulsión invertida ACCOLADE® con una carga de 5 libras/barril (16,7 kg/m³) y sin ella de una de dos policarbodiimidas comerciales, STABAXOL® P200 y STABAXOL® P policarbodiimidas disponibles en Rhein Chemie Rheinau GmbH, Mannheim, Alemania, tal como se indica en la Tabla 4.

TABLA 4

Muestra de Policarbodi-imida	A	B	Ninguna (Control)
Base ACCOLADE®, barriles	0,519	0,519	0,519
250.000 ppm de salmuera CaCl_2 , barriles	0,0676	0,0676	0,0676
LESUPERMUL® ácido graso poliaminatado, libras	10	10	10
FACTANT® derivado de aceite de sebo altamente concentrado, libras	1	1	1
ADAPTA® copolímero metilestireno/ acrilato para controlar la filtración HPHT, libras	3	3	3
Rev Dust, libras	20	20	20
Barita, libras	497	497	497
Policarbodiimida Muestra A, lbs	5	0	0
Policarbodiimida Muestra B, lbs	0	5	0

Todos los productos con marca comercial se encuentran disponible en Halliburton Energy Services, Inc., en Houston, Texas y Duncan Oklahoma.

Las muestras fueron laminadas en caliente a 150°F (66°C) durante 16 horas y luego fueron probadas con respecto a la concentración de alcohol. Las muestras fueron laminadas en caliente a 350°F (188°C) durante 16 horas adicionales y probadas con respecto al alcohol, tal como se ilustra en la Tabla 5.

TABLA 5

Aditivo	% en peso de alcohol	ppm de alcohol
Policarbodiimida Muestra A - laminada en caliente a 150°F	0,04	416
Policarbodiimida Muestra B - laminada en caliente a 150°F	0,03	277
Ninguno (Control) laminado en caliente a 150°F	0,06	626
Policarbodiimida Muestra A - laminada en caliente a 370°F	0,71	7129
Policarbodiimida Muestra B - laminada en caliente a 370°F	0,09	871
Ninguno (Control) laminado en caliente a 370°F	0,78	7761

Estos datos se presentan en forma de gráfico en la Figura 4. Los datos demuestran que el porcentaje de reducción de la hidrólisis con el aditivo policarbodiimida Muestra B, cuando se compara con el control, fue de 89% sobre este último después de envejecimiento a 370°F (188°C). La Muestra A no tuvo un rendimiento tan bueno en el lodo completo, debido posiblemente a que el material estaba humedecido sobre los sólidos que se encontraban presentes en el fluido.

Aunque se realizaron los experimentos con la base éster ACCOLADE® y un lodo de perforación con emulsión invertida ACCOLADE®, se puede apreciar los beneficios de la invención con otros lodos de perforación que tiene base éster. Algunos otros ejemplos de lodos de perforación que llevan emulsión invertida con base éster incluyen, sin limitación, PETROFREE®, PETROFREE® LV y PETROFREE® SF disponibles en Hallibur-

ton Energy Services, Inc. en Houston, Texas. Otros ejemplos adicionales se describen en la Patente Norteamericana No. 7.485.602 emitida el 3 de febrero de 2009 a nombre de Jeff Kirsner y otros; y en la Patente Norteamericana No. 7.456.135 emitida el 25 de noviembre de 2008 a nombre de Jeff Kirsner y otros, entre muchos otros ejemplos. Del mismo modo, los fluidos de perforación que tienen una base amida u otra base vulnerable a la hidrólisis, pueden beneficiarse con la adición de una carbodiimida o polycarbodiimida con un inhibidor de la hidrólisis.

Además, los lodos de perforación con emulsión invertida de la invención o para uso en la presente invención, han sido mezclados con su base de emulsión invertida, otros fluidos o materiales necesarios para constituir a los lodos completos de perforación. Tales materiales pueden incluir, por ejemplo: aditivos destinados a reducir o controlar la reología de la temperatura o para ofrece dilución, por ejemplo, aditivos que tienen las denominaciones comerciales COLDTROL®, ATC® y OMC2™; aditivos para mejorar la viscosidad, por ejemplo, un aditivo que tiene la denominación comercial RHEMOD L™; aditivos para proporcionar viscosidad aumentada temporal para propósitos de transporte (hasta el sitio del pozo) y para uso en barridos, por ejemplo, un aditivo que lleva la denominación comercial TEMPERUS™ (ácido graso modificado); aditivos para control de la filtración, por ejemplo, un aditivo que lleva la denominación comercial ADAPTA® (copolímero metil estireno/acrilato); aditivos para control de presión a alta temperatura (HTHP) y estabilidad de la emulsión, por ejemplo, un aditivo que lleva la denominación comercial FACTANT™ (de-

rivado de aceite de sebo altamente concentrado); aditivos para emulsiónamiento, por ejemplo, un aditivo que lleva la denominación comercial LE SUPERMUL™ (ácido graso poliaminado); y aditivos para dilución, por ejemplo aditivos que llevan las denominaciones comerciales COLDTROL® (derivado de alcohol), OMC2™ (ácido graso oligomérico) y ATC® (éster de ácido graso modificado) y los ejemplos de aditivos descritos en la Patente Norteamericana No. 7.435.706 emitida el 14 de octubre de 2008 a nombre de Heinz Mueller y otros y en la Solicitud de Patente Norteamericana No. 10/432.786 presentada el 10 de diciembre de 2003 de Heinz Mueller y otros, tituladas ambas "Diluyentes para Emulsiones Invertidas". Todos los productos con marca de fábrica mencionados anteriormente se encuentran disponibles en Halliburton Energy Services, Inc. en Houston, Texas, U.S.A. Además, los fluidos pueden comprender una solución acuosa que contiene un compuesto, composición o material para disminuir la actividad del agua, que comprende a la fase interna de la emulsión invertida. Tal solución puede ser una solución salina que contiene cloruro de calcio (típicamente más o menos 25% a más o menos 30%, dependiendo de la salinidad o actividad del agua de la formación subterránea), aunque se puede utilizar en forma alternativa o adicional otras sales o materiales para disminuir la actividad del agua, conocidos en el arte.

Muchos otros ejemplos de componentes de lodo de perforación serán fácilmente conocidos por los expertos en el arte. Se sabe también que tales componentes pueden incluir un éster o amida, conocidos como vulnerables a la hidrólisis a alta temperatura. Por ejemplo, los aditivos LE SUPERMUL®, EZ®

MUL, EZ MUL® NT, EZ MUL® NS, DRILTREAT® INVERMUL®, INVERMUL® NT y ADAPTA® son emulsionadores y aditivos para el control de la pérdida de fluido que contienen ésteres y amidas. La adición de carbodiimida, preferiblemente una polycarbodiimida, al lodo de perforación de acuerdo con la presente invención, mejora la estabilidad de tales aditivos y por lo tanto mejora la estabilidad del lodo de perforación en forma completa. En otras palabras, la carbodiimida inhibe la hidrólisis del éster o amida en tales aditivos. Así, se puede lograr ventajas mediante la adición de una carbodiimida o polycarbodiimida a un lodo de perforación que contiene aditivos éster o amida cuando el aceite base del lodo de perforación no puede contener un éster o amida.

Las preparaciones exactas de los fluidos de perforación utilizados en la perforación de orificios de sondeo varían con los requerimientos particulares de la formación subterránea. Sin embargo, los aditivos enumerados anteriormente proporcionan algunos ejemplos. Un ejemplo preferido de lodo de perforación de la presente invención puede tener la preparación utilizada en el Experimento 4 estudiado anteriormente. Un par de otros ejemplos preferidos de lodos de perforación de la presente invención tienen las preparaciones indicadas en la siguiente Tabla 6.

TABLA 6

Preparaciones Ejemplares

Fluidos y Compuestos	Fluido de Perforación con Emulsión Inverti- da ACCOLADE®	Fluido de Perforación con Emulsión Inverti- da PETROFREE® SF
Base ACCOLADE® (ba- rriles)	0,590	-----
PETROFREE® SF BASE (barriles)	-----	0,568
LE MUL ^{TM 1} (libras)	-----	4
LE SUPERMUL ^{TM 1} (li- bras)	10	6
Cal (libras)	1	4
DURATONE® HT ³ (li- bras)	-----	4
Agua potable (barri- les)	0,263	0,254
ADAPTA® ⁴ (libras)	2	-----
RHEMOD L ^{TM 5} (libras)	1	-----
GELTONE® II ⁶ (libras)	-----	5
VIS-PLUS® ⁷ (libras)	-----	1,5
BAROID® ⁸ (libras)	138	138
Cloruro de calcio (libras)	32	31
DEEP-TREAT® ⁹ (li- bras)	-----	2
Policarbodiimida (li- bras)	5	5

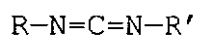
- ¹ Mezcla de aceite de sebo oxidado y estabilizador de emulsión de ácido graso poliaminatado
- ² Emulsionador de ácido graso poliaminatado
- ³ Agente Leonardita organofílica para control de la filtración
- ⁴ Agente para el control de la filtración Copolímero HTHP
- ⁵ Agente para suspensión de ácido graso modificado/
agente para impartir viscosidad

- ⁶ Agente para impartir viscosidad con arcilla organofílica
- ⁷ Agente de suspensión de ácido carboxílico
- ⁸ Agente para aumentar la densidad de sulfato de bario molido
- ⁹ Agente para aumentar la densidad de sal sulfato de sodio/diluyente

Todos los productos con marca de fábrica indicados en la Tabla 6 se encuentran disponibles en Halliburton Energy Services, Inc., en Houston, Texas, incluyendo: estabilizador de emulsión LE MULTM (una mezcla de aceite de sebo oxidado y ácido graso poliaminatado); LE SUPERMULTM (ácido graso poliaminatado); agente para el control de la filtración DURATONE® HT (leonardita organofílica); ADAPTA® agente para el control de la filtración (copolímero metilestireno/acrilato particularmente apropiado para proporcionar control de filtración HPHT en sistemas de fluido no acuoso); RHEMOD® LTM agente de suspensión/agente para impartir viscosidad (ácido graso modificado); agente para impartir viscosidad GELTONE® II (arcilla organofílica); agente de suspensión VIS-PLUS® ácido carboxílico); BAROID® agente para aumentar la densidad (sulfato de bario molido); y DEEP-TREAT® agente humectante/diluyente (sal sulfonato de sodio).

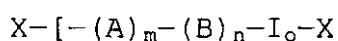
Ejemplos de policarboxiimidas preferidas comercialmente disponibles útiles en la preparación indicada en la Tabla 6 incluyen, sin limitación, policarbodiimidas STABAXOL® I, STABAXOL® P y STABAXOL® P200, todas disponibles en Rhein Chemi Rheinau GmbH, Mannheim, Alemania.

La fórmula preferida para las carbodiimidas que pueden ser utilizadas en la presente invención es la siguiente:



en la cual R y R' son iguales o diferentes y están seleccionados a partir del grupo que consiste en grupos aromáticos y grupos alquilo grupos alquenoilo y grupos alquinoilo de cadena recta y ramificada. Los grupos alquilo y aromáticos son más preferidos que los grupos alquinoilo o alquenoilo. Se prefiere las polycarbodiimidas aromáticas sobre las polycarbodiimidas de cadena recta, ramificada o cíclica, aunque se puede utilizar en la invención polycarbodiimidas de cadena recta, ramificada o cíclica. Se prefiere a las carbodiimidas poliméricas sobre las carbodiimidas. Preferiblemente, R tiene átomos de carbono C₁ a C₃₀ y en general se preferirán las polycarbodiimidas que tienen un peso molecular en la escala de más o menos 500 a más o menos 10.000 gramos/mol, para uso en la presente invención. El grupo aromático puede estar conectado al grupo N a través de un grupo hidrocarburo, tal como un grupo alquilo, por ejemplo un grupo alquilo C₁.

Carbodiimidas adicionales que se creen tienen utilidad en la presente invención se describen en la Patente Norteamericana No. 6.498.225 y en la Patente Norteamericana No. 5.360.888 a modo de ejemplo, la Patente Norteamericana No. 6.498.225 describe específicamente copolímeros con base de polycarbodiimida que tienen la fórmula general:



en la cual:

X es idéntico o diferente y está seleccionado a partir del grupo que consiste de -NHCO-R''', -NHCONH-R''', -NHCOO-R''', -NHCOS-R''', -COO-R''', -O-R''', -NR₂, -S-R''', -OH, -S-H, -NH₂, -NHR''' y -NCO y en la cual el grupo R''' denota

un radical alquilo, cicloalquilo, aralquilo o arilo que contiene 1 a 30 átomos de carbono:

m, n son independientes entre si y son cada uno un entero de 1 a 1000;

o es un entero de 1 a 500;

A está seleccionado a partir del grupo que consiste de las carbodiimidas o polycarbodiimidas de la fórmula:

$-(-N=C=N-Y)-$ en la cual Y está seleccionado a partir del grupo que consiste de compuestos aromáticos orto o biorto sustituidos, aralquilenos en los cuales el átomo de carbono enlazado al grupo carbodiimida está sustituido por grupos alquilo C_1 a C_4 ; y cicloalquilenos en los cuales el átomo de carbono enlazado al grupo carbodiimida está sustituido por grupos alquilo C_1 a C_{14} ; y

B está seleccionado a partir del grupo que consiste de (poli)dioles, (poli)diaminas, (poli)dimercaptanos, (poli)aminoalcoholes, (poli)aminomercaptanos y (poli)mercaptoalcoholes. La Patente Norteamericana No. 5.360.888 describe polycarbodiimidas que son los productos de reacción de isocianatos aromáticos sustituidos tales como: 2,6-diisopropilfenil isocianato; 1,3,5-triisopropil-2,4-diisocianatobenceno; naftaleno-1,5-diisocianato; 2,4-diisocianato-3,5-dimetiltolueno; 4,4'-metileno bis(2,6-diethylfenil isocianato); 4,4'-metileno bis(2-etil-6-metilfenil isocianato); 4,4'-metileno bis(2-isopropil-6-metil fenil isocianato); 4,4'-metileno bis(2,6-diisopropil fenil isocianato); y 4,4'-metileno bis(2-etil-6-metilciclohexil isocianato).

Como se indicó anteriormente, se puede lograr las ventajas de la invención empleando un lodo de perforación de la

invención, el cual comprende o contiene un éster o amida, en operaciones de perforación en las cuales se ha agregado a dicho lodo de perforación una carbodiimida, preferiblemente una polycarbodiimida. Las operaciones de perforación -ya sea perforación de un orificio de sondeo vertical, direccional u horizontal, realizando un barrido, introducción de entubado y cementación- pueden ser realizadas por los expertos en el arte con otros fluidos de perforación. O sea, se prepara u obtiene un lodo de perforación de la invención y se lo hace circular a través de un orificio de pozo conforme está siendo perforado (o barrido o cementado y entubado) para facilitar la operación de perforación. El fluido de perforación retira los escombros desde el orificio de pozo, enfría y lubrica a la broca de perforación, ayuda a sostener al tubo y a la broca de perforación, y proporciona una presión hidrostática para conservar la integridad de las paredes del orificio de pozo y evitar explosiones en el mismo. Se mejora la preparación específica del lodo de perforación de acuerdo con la presente invención, para la operación de perforación particular y para las características y condiciones de la formación subterránea particular (tales como temperaturas). Por ejemplo, se aumenta la densidad del fluido según sea apropiado para las presiones de la formación y se lo diluye según sea apropiado para las temperaturas de la formación. Además, los fluidos de la invención pueden ser reciclados durante una operación de perforación, de modo que los fluidos que circulan en un orificio de pozo puedan ser recirculados en este último después de retornar hacia la superficie para extraer a los escombros de la perforación, a modo de ejemplo. El lodo

de perforación de la invención puede estar seleccionado para uso en una operación de sondeo a fin de cumplir con los reglamentos ambientales que rigen las operaciones de perforación en una formación subterránea particular.

La descripción anterior de la invención se refiere a formas preferidas. Se puede realizar varios cambios en los detalles de los fluidos y métodos de uso descritos, sin apartarse de los alcances propuestos de esta invención tal como se define en las reivindicaciones finales.

REIVINDICACIONES

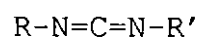
1. Un método para perforar un orificio de sondeo en una formación subterránea para la recuperación de hidrocarburos, el cual comprende las etapas de proporcionar o usar un fluido de perforación con base de aceite que contiene una carbodiimida; y perforar el orificio de sondeo en la formación subterránea.
2. Un método, de acuerdo con la reivindicación 1, en el cual la perforación en la formación subterránea incluye temperaturas en la escala desde más o menos 275°F (135°F) hasta más o menos 450°F (232°C).
3. Un método, de acuerdo con la reivindicación 1 o 2, en el cual el lodo de perforación comprende una emulsión invertida basada en éster.
4. Un método, de acuerdo con la reivindicación 1, 2 o 3, en la cual la carbodiimida tiene la fórmula:
$$R-N=C=N-R'$$
en la cual R y R' son iguales o diferentes y están seleccionados a partir del grupo que consiste en grupos aromáticos y grupos alquilo, grupos alquenilo y grupos alquinilo de cadena recta o ramificada.
5. Un método, de acuerdo con la reivindicación 4, en el cual R tiene átomos de carbono C₁ a C₃₀.
6. Un método, de acuerdo con la reivindicación 4, en el cual R' tiene átomos de carbono C₁ a C₃₀.
7. Un método, de acuerdo con la reivindicación 1 anterior, en el cual la carbodiimida es un polímero.

8. Un método, de acuerdo con cualesquiera reivindicaciones anteriores, en el cual la carbodiimida es monomérica.
9. Un método, de acuerdo con cualesquiera reivindicaciones anteriores, en el cual la carbodiimida es un inhibidor de la hidrólisis.
10. Un método, de acuerdo con cualesquiera reivindicaciones anteriores, en el cual la carbodiimida tiene un peso molecular en la escala de más o menos 500-10.000 gramos/mol.
11. Un método, de acuerdo con cualesquiera reivindicaciones anteriores, en el cual el fluido de perforación comprende un aditivo que contiene un éster.
12. Un método, de acuerdo con la reivindicación 11, en el cual el aditivo es un emulsionador.
13. Un método, de acuerdo con cualesquiera reivindicaciones anteriores, en el cual el lodo de perforación comprende un aditivo que contiene una amida.
14. Un método, de acuerdo con la reivindicación 1, en el cual el lodo de perforación contiene agua.
15. Un fluido de perforación para perforar un orificio de sondeo en una formación subterránea, el cual comprende: una base continua; una fase interna; un emulsionador; un agente para el control de la filtración; u agente para aumentar la densidad; y una carbodiimida.
16. Un fluido de perforación, de acuerdo con la reivindicación 15, en el cual la fase continua comprende una emulsión invertida con base éster.
17. Un fluido de perforación, de acuerdo con la reivindicación 15 o 16, en el cual el emulsionador comprende un éster o una amida.

18. Un fluido de perforación, de acuerdo con la reivindicación 15, 16 o 17, en el cual el agente para controlar la filtración comprende un éster o una amida.

19. Un fluido de perforación, de acuerdo con la reivindicación 15, 16, 17 o 18, en el cual la carbodiimida es una polycarbodiimida que tiene un peso molecular en la escala de 500 a más o menos 10.000.

20. Un fluido de perforación, de acuerdo con cualesquiera reivindicaciones 15 a 19, en el cual la carbodiimida tiene la fórmula:



en la cual R y R' son iguales o diferentes y están seleccionados a partir del grupo que consiste en grupos aromáticos y grupos alquilo, grupos alquenilo y grupos alquini-
lo de cadena recta o ramificada, y grupos alquilo cicli-
cos.

**METODO PARA MEJORAR LA ESTABILIDAD FLUIDOS DE PERFORACION
CON BASE DE ACEITE A ALTAS TEMPERATURAS**

Resumen

Se describen métodos para mejorar la estabilidad de fluidos de perforación con base de éster, introducir entubado y/o cementar un orificio de pozo en una formación subterránea, así como también fluidos mejorados de perforación con base de éster para uso a altas temperaturas. Se logran las ventajas de la invención mediante la inhibición de la hidrólisis de los ésteres contenidos en el fluido de perforación, mediante la adición de un inhibidor de hidrólisis carbodiimida monomérica o polimérica al fluido de perforación.

ESPAÑOL
DIBUJOS

La figura 1 es un gráfico que compara la cantidad de alcohol producido, indicando hidrólisis, en muestras que contienen base éster y agua con aditivos policarbodiimida o sin ellos, después de calentamiento a 370°F (188°C) durante 16 horas

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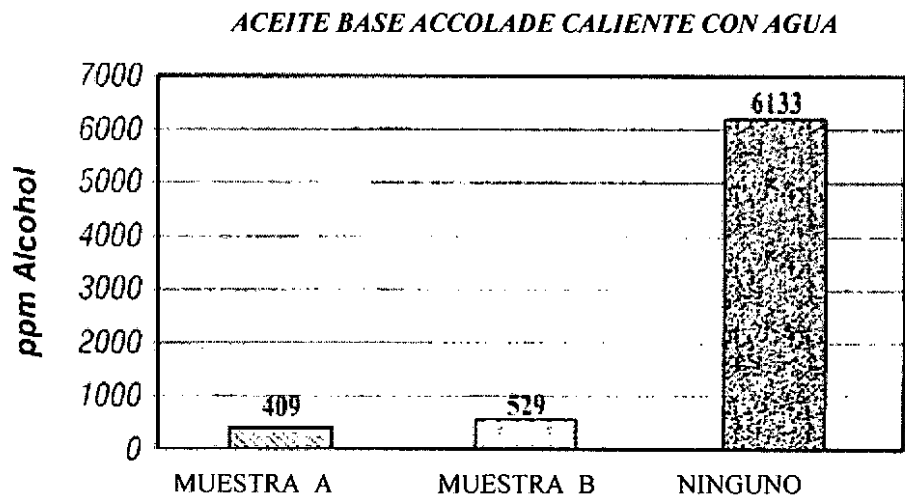


FIG. 1

ENVEJECIMIENTO PROLONGADO DE ACEITE BASE ACCOLADE CON AGUA

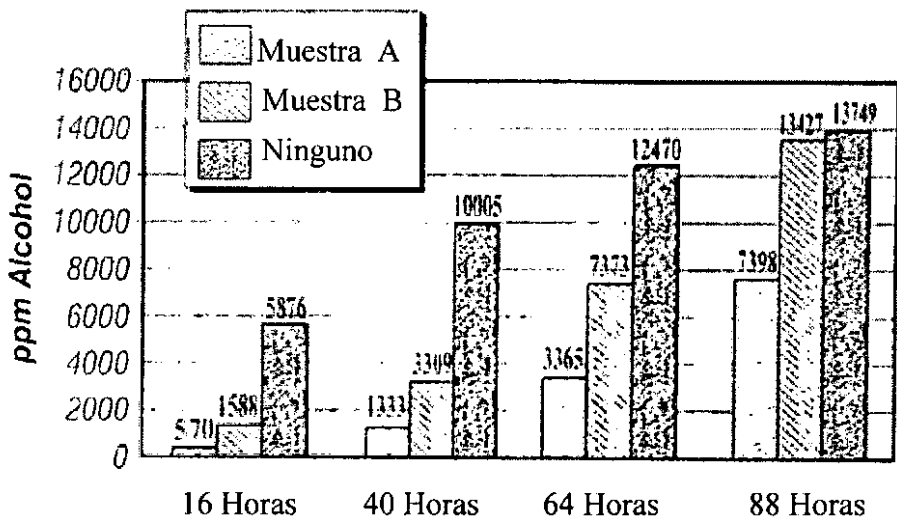


FIG. 2

La figura 2 es un gráfico que compara la cantidad de alcohol producido, indicando hidrólisis, en muestras que contienen base éster y agua con aditivos policarbodiimida y sin ellos, después de calentamiento a 370°F (188°C) durante períodos de 16 horas, 40 horas, 64 horas y 88 horas

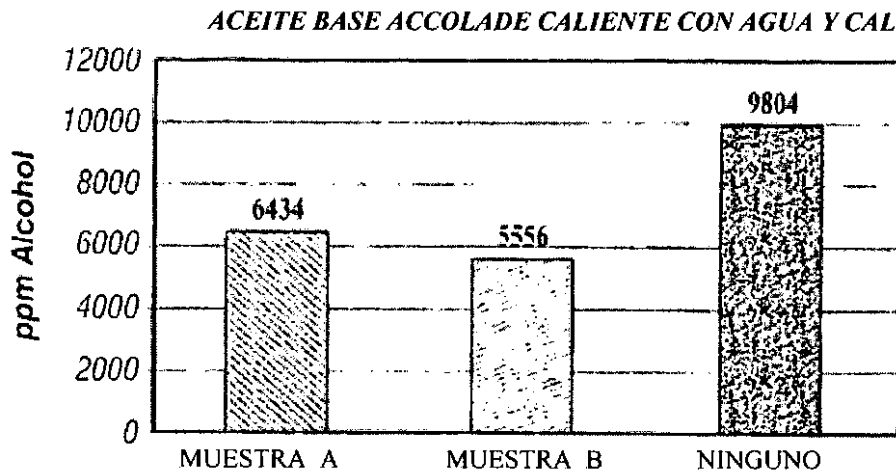


FIG. 3

La figura 3 es un gráfico que compara la cantidad de alcohol producido, indicando hidrólisis, en muestras que contienen base éster, agua y cal, con aditivos policarbodiimida y sin ellos después de calentamiento a 370°F (188°C) durante 16 horas

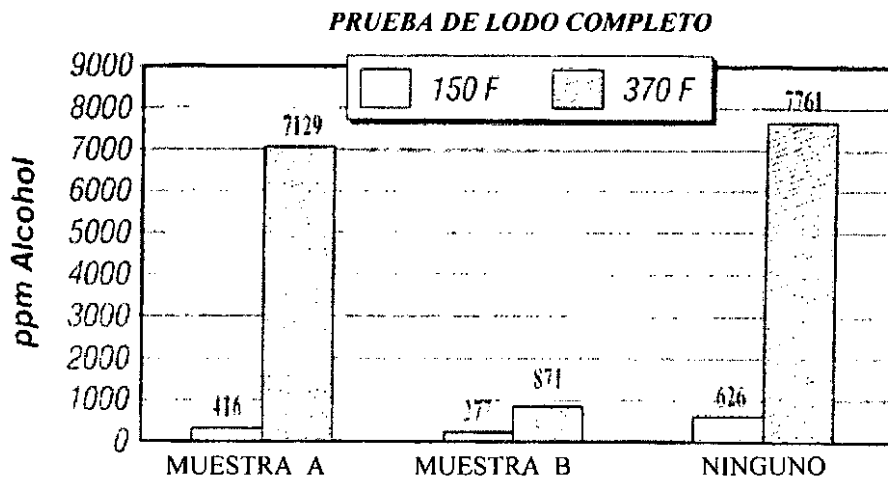


FIG. 4

La figura 4 es un gráfico que compara la cantidad de alcohol producido, indicando hidrólisis, en muestras de un fluido de perforación con emulsión invertida basada en éster, con aditivos policarbodiimida y sin ellos, después de laminado en caliente a 150°F (66°C) durante 16 horas y luego a 370°F (188°C) durante 16 horas

**METHOD FOR ENHANCING STABILITY OF
OIL BASED DRILLING FLUIDS AT HIGH TEMPERATURES**

BACKGROUND OF THE INVENTION

1. Field of the Invention

[0001] The present invention relates to compositions and methods for drilling, cementing and casing boreholes in subterranean formations, particularly hydrocarbon bearing formations. More particularly, the present invention relates to oil or synthetic fluid based drilling fluids and fluids comprising invert emulsions, such as fluids using esters for example, which combine high ecological compatibility with good stability and performance properties.

2. Description of Relevant Art

[0002] A drilling fluid or mud is a specially designed fluid that is circulated through a wellbore as the wellbore is being drilled to facilitate the drilling operation. The various functions of a drilling fluid include removing drill cuttings from the wellbore, cooling and lubricating the drill bit, aiding in support of the drill pipe and drill bit, and providing a hydrostatic head to maintain the integrity of the wellbore walls and prevent well blowouts. Specific drilling fluid systems are selected to optimize a drilling operation in accordance with the characteristics of a particular geological formation.

[0003] Oil or synthetic fluid-based muds are normally used to drill swelling or sloughing shales, salt, gypsum, anhydrite or other evaporate formations, hydrogen sulfide-containing formations, and hot or high temperature (greater than about 300 degrees Fahrenheit ("° F")) holes, but may be used in other holes penetrating a subterranean formation as well. Unless indicated otherwise, the terms "oil mud" or "oil-based mud" or "drilling fluid" shall be understood to include synthetic oils or other synthetic fluids as well as natural or traditional oils, and such oils shall be understood to comprise invert emulsions.

[0004] Oil-based muds used in drilling typically comprise: a base oil (or synthetic fluid) comprising the external phase of an invert emulsion; a saline, aqueous solution (typically a solution comprising about 30% calcium chloride) comprising the internal phase of the invert emulsion; emulsifiers at the interface of the internal and external phases; and other agents or additives for suspension, weight or density, oil-wetting, fluid loss or filtration control, and rheology control.

[0005] An oil-based or invert emulsion-based drilling fluid may commonly comprise between about 50:50 to about 95:5 by volume oil phase to water phase. An all oil mud simply comprises 100% liquid phase oil by volume; that is, there is no aqueous internal phase.

[0006] Invert emulsion-based muds or drilling fluids (also called invert drilling muds or invert muds or fluids) comprise a key segment of the drilling fluids industry. However, increasingly invert emulsion-based drilling fluids have been subjected to greater environmental restrictions and performance and cost demands. While ester based invert emulsion drilling fluids satisfy many environmental concerns, they tend to lose effectiveness or utility at high oilfield temperatures. There is consequently an increasing need and industry-wide interest in new drilling fluids and methods that provide improved performance while still affording environmental and economical acceptance.

SUMMARY OF THE INVENTION

[0007] The present invention provides improved methods of drilling wellbores in subterranean formations employing oil-based muds or drilling fluids. As used herein, the term "drilling" or "drilling wellbores" shall be understood in the broader sense of drilling operations, which include running casing and cementing as well as drilling, unless specifically indicated otherwise. More particularly, the present invention provides a method for improving the stability of oil-based drilling fluids, most particularly at high temperatures. The present invention also provides oil based drilling fluids having improved stability at such high temperatures.

[0008] Any drilling fluid comprising a hydrolysable component may benefit from the present invention. Esters and amides are particularly susceptible to hydrolysis and thus the invention is particularly advantageous with invert emulsion drilling fluids comprising esters and/or amides, particularly as the base oil for the drilling fluids but also as additives or components in the drilling fluids, such as for example, emulsifiers and fluid loss control additives. The benefits of the invention are obtained by inhibiting hydrolysis of esters and/or amides in or comprising the drilling fluid. Such benefits are particularly realized at higher temperatures, that is, at temperatures of 275°F (135°C) or higher and extending to temperatures as high as about 450°F (232°C) or more, as may be encountered in drilling boreholes in subterranean formations for recovery of hydrocarbons.

[0009] According to the method of the invention, a carbodiimide, preferably a polycarbodiimide, is added to the drilling fluid as a hydrolysis inhibitor. A 5 lb/bbl (16.7 kg/m³) loading amount will typically be effective for purposes of the invention, although other amounts may be successfully used with experimentation. Drilling fluids of the invention comprise an ester oil or invert emulsion base and/or ester or amide additives, such as, for example, emulsifiers and fluid loss control additives, and a carbodiimide, or preferably a polycarbodiimide.

BRIEF DESCRIPTION OF THE DRAWINGS

[0010] Figure 1 is a graph comparing the amount of alcohol produced, indicating hydrolysis, in samples containing ester base and water, with and without polycarbodiimide additives, after heating at 370° F (188°C) for 16 hours.

[0011] Figure 2 is a graph comparing the amount of alcohol produced, indicating hydrolysis, in samples containing ester base and water, with and without polycarbodiimide additives, after heating at 370° F (188°C) for periods of 16 hours, 40 hours, 64 hours and 88 hours.

[0012] Figure 3 is a graph comparing the amount of alcohol produced, indicating hydrolysis, in samples containing ester base, water, and lime, with and without polycarbodiimide additives, after heating at 370° F (188°C) for 16 hours.

[0013] Figure 4 is a graph comparing the amount of alcohol produced, indicating hydrolysis, in samples of an ester based invert emulsion drilling fluid, with and without polycarbodiimide additives, after hot rolling at 150°F (66°C) for 16 hours and then at 370° F (188°C) for 16 hours.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

[0014] Ester based invert emulsion drilling fluids are favored as oil based drilling fluids for environmental acceptability and regulatory compliance. However, in prior art fluids, the ester can be vulnerable to hydrolysis, particularly at high temperatures that can be encountered in drilling subterranean formations for the recovery of hydrocarbons. Such hydrolysis can result in breakdown of the fluid, which ultimately or eventually renders the fluid unusable as a drilling fluid. Consequently, the use of ester based drilling fluids is less common at high temperatures, which typically increase the rate of ester hydrolysis.

[0015] The addition of lime to a drilling fluid, as has been common practice in the oilfield, can have the negative side-effect of increasing the amount of hydrolysis of esters in prior art drilling fluids. Lime provides a greater concentration of nucleophilic hydroxide ion to the fluid, which can escalate hydrolysis. Consequently, lime is usually avoided in ester based drilling fluids.

[0016] The present invention provides a method for enhancing the stability of ester-based drilling fluids and drilling fluid additives, even at high temperatures, and even in the presence of lime or other sources of hydroxide ion. This enhancement is accomplished by reducing the amount of hydrolysis that occurs in oil-based drilling fluid systems. Hydrolysis inhibition according to the present invention allows for greater application of ester based drilling fluids in higher temperature environments with greater retention of desirable fluid properties.

[0017] In the method of the present invention, enhanced stability of ester based invert emulsion drilling fluids is obtained by adding to or including in the drilling fluid a carbodiimide, preferably a polycarbodiimide. The carbodiimide carbon is believed to be more reactive than the carbonyl carbon of an ester and hence the reaction of the carbodiimide with water or hydroxide (hydrolysis) is expected to be more facile than hydrolysis of the ester of the drilling fluid. Consequently, the reaction of the carbodiimide with the water or hydroxide prevents or inhibits the carbonyl carbon of the ester from reacting with the water or hydroxide that might otherwise hydrolyze the ester, resulting in the ester not becoming hydrolyzed. This is particularly significant, and surprising, in drilling fluids, and especially invert emulsion drilling fluids, because such fluids already contain water as part of their composition. The carbodiimide is nevertheless able to maintain effectiveness in enhancing the stability of the fluid over time, as for example for a time sufficient to drill one or more wells or subterranean boreholes. That is, the carbodiimide is not immediately "used up" or diluted to ineffectiveness upon placement into the fluid.

[0018] The effectiveness of the invention is demonstrated in the following experiments.

Experiment 1:

[0019] Since hydrolyzation of an ester causes part of the ester molecule to be lost as an alcohol, the effectiveness of hydrolysis inhibitors can be measured by monitoring the production of alcohol that is formed in ester hydrolysis. In the case of a state-of-the-art, ester-based, invert emulsion fluid sold by Halliburton Energy Services, Inc., in Houston, Texas and Duncan, Oklahoma under the tradename ACCOLADE® drilling fluid, the amount of alcohol produced can be monitored by gas chromatography/mass spectrometry. Thus, samples containing ACCOLADE® base fluid, calcium chloride brine, and an emulsifier, were formulated with and without 5 lb/bbl (16.7 kg/m³) loading of one of two commercial polycarbodiimides: the viscous liquid STABAXOL® P200 polycarbodiimide (Sample A) and the powder STABAXOL® P polycarbodiimide (Sample B), both available from Rhein Chemie Rheinau GmbH, Mannheim, Deutschland (Germany). The samples were static aged at 370°F (188°C) for 16 hours and then tested for alcohol content, as indicated in Table 1 below.

TABLE 1

Additive	wt. % alcohol	ppm alcohol
Polycarbodiimide Sample A	0.041	409
Polycarbodiimide Sample B	0.053	529
None (Control)	0.61	6133

[0020] The data is also graphed in Figure 1. The data indicates that a greater than 90% reduction in the amount of alcohol produced was observed in the presence of the polycarbodiimides. This reduction indicates a reduction in the amount of hydrolysis of the ester in the ACCOLADE® base fluid.

Experiment 2:

[0021] Samples of the same compositions of Experiment 1 were static aged at 370°F (188°C) for 16 hours, 40 hours, 64, hours and 88 hours, and tested for alcohol content after each elapsed aging period, as shown in Table 2 below.

TABLE 2

Additive	wt. % alcohol	ppm alcohol
Polycarbodiimide Sample A Static Aged 16 hours	0.06	570
Polycarbodiimide Sample B Static Aged 16 hours	0.16	1588
None (Control) Static Aged 16 hours	0.59	5876
Polycarbodiimide Sample A Static Aged 40 hours	0.13	1333
Polycarbodiimide Sample B Static Aged 40 hours	0.33	3309
None (Control) Static Aged 40 hours	1.00	10005
Polycarbodiimide Sample A Static Aged 64 hours	0.34	3365
Polycarbodiimide Sample B Static Aged 64 hours	0.74	7373
None (Control) Static Aged 64 hours	1.25	12470
Polycarbodiimide Sample A Static Aged 88 hours	0.74	7398

Polycarbodiimide Sample B Static Aged 88 hours	1.34	13427
None (Control) Static Aged 88 hours	1.37	13749

[0022] The data is also graphed in Figure 2. The data indicates that after 64 hours, both polycarbodiimide additives still reduced the alcohol concentration, and after 88 hours, Additive A still showed the ability to reduce the amount of ester hydrolysis that occurred. The reason Additive A showed superior performance to Additive B is unclear, although the liquid nature of the material may have allowed the material to be more fully solubilized in the solids-free fluids tested in this experiment leading to greater efficacy.

Experiment 3:

[0023] Samples containing ACCOLADE® base, calcium chloride brine, and an emulsifier, were formulated with and without 5 lb/bbl loading of one of two commercial polycarbodiimides, STABAXOL® P200 and STABAXOL® P polycarbodiimides, available from Rhein Chemie Rheinau GmbH, Mannheim, Deutschlands, as in Experiments 1 and 2, except to each of the samples for this Experiment 3 was added lime (3 lb/bbl [10 kg/m³]). The samples were static aged at 370°F (188°C) for 16 hours and tested for alcohol content, as shown in Table 3.

TABLE 3

Additive	wt. % alcohol	ppm alcohol
Polycarbodiimide Sample A	0.64	6434
Polycarbodiimide Sample B	0.56	5556
None (Control)	0.98	9804

[0024] The data is also graphed in Figure 3. This data shows that a significant reduction in hydrolysis is obtained with the polycarbodiimide additives, even in the presence of lime, and even though the addition of lime to a drilling fluid typically increases the amount

of hydrolysis due to the presence of greater concentrations of the more nucleophilic hydroxide ion. The percent reductions in hydrolysis in the samples with the polycarbodiimide additives when compared to the control were 34.4% in the case of polycarbodiimide Sample A and 43.3% in the case of polycarbodiimide Sample B.

Experiment 4:

[0025] Samples containing ACCOLADE® invert emulsion drilling fluid were formulated with and without 5 lb/bbl (16.7 kg/m³) loading of one of two commercial polycarbodiimides, STABAXOL® P200 and STABAXOL® P polycarbodiimides, available from Rhein Chemie Rheinau GmbH, Mannheim, Deutschland, as indicated in Table 4.

TABLE 4

Polycarbodiimide Sample	A	B	None (Control)
ACCOLADE® base, bbl	0.519	0.519	0.519
250,000 ppm CaCl ₂ brine, bbl	0.0676	0.0676	0.0676
LE SUPERMUL® polyaminated fatty acid, lb	10	10	10
FACTANT® highly concentrated tall oil derivative, lb	1	1	1
ADAPTA® methylstyrene/acrylate copolymer for HPHT filtration control, lb	3	3	3
Rev Dust, lb	20	20	20

Barite, lb	497	497	497
Polycarbodiimide Sample A, lb	5	0	0
Polycarbodiimide Sample B, lb	0	5	0

All trademarked products are available from Halliburton Energy Services, Inc. in Houston, Texas and Duncan, Oklahoma.

[0026] The samples were hot rolled at 150°F (66°C) for 16 hours and then were tested for alcohol concentration. The samples were hot rolled further at 370°F (188°C) for 16 additional hours and tested for alcohol, as shown in Table 5.

TABLE 5

Additive	wt. % alcohol	ppm alcohol
Polycarbodiimide Sample A hot rolled at 150°F	0.04	416
Polycarbodiimide Sample B hot rolled at 150°F	0.03	277
None (Control) hot rolled at 150°F	0.06	626
Polycarbodiimide Sample A hot rolled at 370°F	0.71	7129
Polycarbodiimide Sample B hot rolled at 370°F	0.09	871
None (Control) hot rolled at 370°F	0.78	7761

[0027] This data is also graphed in Figure 4. The data shows that the percent reduction in hydrolysis with the polycarbodiimide additive Sample B, when compared to the control, was 89% over the control after aging at 370°F (188°C). Sample A did not perform as well in the whole mud, possibly because the material was wetted onto solids that were present in the fluid.

[0028] Although the experiments were conducted with an ACCOLADE® ester base and an ACCOLADE® invert emulsion drilling fluid, benefits of the invention may be seen with other ester based drilling fluids. Some other examples of commercial ester based invert emulsion drilling fluids include, without limitation, PETROFREE®, PETROFREE® LV, and PETROFREE® SF drilling fluids available from Halliburton Energy Services, Inc. in Houston, Texas. Still further examples are taught in United States Patent No. 7,485,602, issued February 3, 2009, to Jeff Kirsner, et al, and in U.S. Patent No. 7,456,135, issued November 25, 2008 to Jeff Kirsner, et al., among many other examples. Also, drilling fluids having an amide base or other base vulnerable to hydrolysis may benefit from addition of a carbodiimide or polycarbodiimide as a hydrolysis inhibitor.

[0029] Further, the invert emulsion drilling fluids of the invention or for use in the present invention have added to them or mixed with their invert emulsion base, other fluids or materials needed to comprise complete drilling fluids. Such materials may include, for example: additives to reduce or control temperature rheology or to provide thinning, for example, additives having the tradenames COLDTROL®, ATC®, and OMC2™; additives for enhancing viscosity, for example, an additive having the tradename RHEMOD L™; additives for providing temporary increased viscosity for shipping (transport to the well site) and for use in sweeps, for example, an additive having the tradename TEMPERUS™ (modified fatty acid); additives for filtration control, for example, an additive having the tradename ADAPTA® (methylstyrene/acrylate copolymer); additives for high temperature high pressure control (HTHP) and emulsion stability, for example, an additive having the tradename FACTANT™ (highly concentrated tall oil derivative); additives for emulsification, for example, an additive having the tradename LE SUPERMUL™ (polyaminated fatty acid); and additives for thinning, for example additives having the tradenames COLDTROL® (alcohol derivative), OMC2™ (oligomeric fatty acid), and ATC® (modified fatty acid ester) and example additives taught in U.S. Patent No. 7,435,706, issued October 14, 2008 to Heinz

Mueller, et al. and in U.S. Patent Application No. 10/432,786, filed December 10, 2003 of Heinz Mueller, et al., both entitled "Thinners for Invert Emulsions." All of the aforementioned trademarked products are available from Halliburton Energy Services, Inc. in Houston, Texas, U.S.A. Additionally, the fluids may comprise an aqueous solution containing a water activity lowering compound, composition or material, comprising the internal phase of the invert emulsion. Such solution may be a saline solution comprising calcium chloride (typically about 25% to about 30%, depending on the subterranean formation water salinity or activity), although other salts or water activity lowering materials known in the art may alternatively or additionally be used.

[0030] Many other examples of drilling fluid components will be readily known to those of skill in the art. Also known is that such components may include an ester or an amide, known to be vulnerable at least at high temperatures to hydrolysis. For example, LE SUPERMUL®, EZ® MUL, EZ MUL® NT, EZ MUL® NS, DRILTREAT®, INVERMUL®, INVERMUL® NT and ADAPTA® additives are emulsifiers and fluid loss control additives that contain esters or amides. Adding a carbodiimide, preferably a polycarbodiimide, to the drilling fluid according to the present invention enhances the stability of such additives, and consequently enhances the stability of the drilling fluid overall. That is, the carbodiimide inhibits hydrolysis of the ester or amide in such additives. Thus advantages may be realized by adding a carbodiimide or polycarbodiimide to a drilling fluid containing ester or amide additives even when the base oil of the drilling fluid may not comprise an ester or amide.

[0031] The exact formulations of drilling fluids used in drilling boreholes vary with the particular requirements of the subterranean formation. The above listed additives, however, provide some examples. A preferred example drilling fluid of the present invention may have the formulation used in Experiment 4 discussed above. A couple of other preferred example drilling fluids of the present invention have the following example formulations set forth in Table 6 below.

TABLE 6
Example Formulations

Fluids and Compounds	ACCOLADE® Invert Emulsion Drilling Fluid	PETROFREE® SF Invert Emulsion Drilling Fluid
ACCOLADE® Base (bbl)	0.590	-----

PETROFREE® SF BASE (bbl)	-----	0.568
LE MUL™ ¹ (lb.)	-----	4
LE SUPERMUL™ ² (lb.)	10	6
Lime (lb.)	1	4
DURATONE® HT ³ (lb.)	-----	4
Freshwater (bbl)	0.263	0.254
ADAPTA® ⁴ (lb.)	2	-----
RHEMOD L™ ⁵ (lb.)	1	-----
GELTONE® II ⁶ (lb.)	-----	5
VIS-PLUS® ⁷ (lb.)	-----	1.5
BAROID® ⁸ (lb.)	138	138
Calcium chloride (lb.)	32	31
DEEP-TREAT® ⁹ (lb.)	-----	2
Polycarbodiimide (lb.)	5	5

¹ Blend of oxidized tall oil and polyaminated fatty acid emulsion stabilizer.

² Polyaminated fatty acid emulsifier.

³ Organophilic leonardite filtration control agent.

⁴ Copolymer HTHP filtration control agent for non-aqueous systems.

⁵ Modified fatty acid suspension agent/viscosifier.

⁶ Organophilic clay viscosifier.

⁷ Carboxylic acid suspension agent.

⁸ Ground barium sulfate weighting agent.

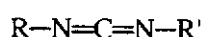
⁹ Sulfonate sodium salt wetting agent/thinner.

[0032] All trademarked products in Table 6 are available from Halliburton Energy Services, Inc. in Houston, Texas, including: LE MUL™ emulsion stabilizer (a blend of oxidized tall oil and polyaminated fatty acid); LE SUPERMUL™ emulsifier (polyaminated fatty acid); DURATONE® HT filtration control agent (organophilic leonardite); ADAPTA® filtration control agent (methylstyrene/acrylate copolymer particularly suited for providing HPHT filtration control in non-aqueous fluid systems); RHEMOD L™ suspension agent/viscosifier (modified fatty acid); GELTONE® II viscosifier (organophilic clay); VIS-

PLUS® suspension agent (carboxylic acid); BAROID® weighting agent (ground barium sulfate); and DEEP-TREAT® wetting agent/thinner (sulfonate sodium salt).

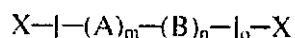
[0033] Examples of preferred commercially available polycarbodiimides useful in the formulations set forth in Table 6 include, without limitation, STABAXOL® I, STABAXOL® P, and STABAXOL® P200 polycarbodiimides, all available from Rhein Chemie Rheinau GmbH, Mannheim, Deutschland (Germany).

[0034] The preferred formula for carbodiimides for use in the present invention is as follows:



where R and R' are the same or different and are selected from the group consisting of aromatic groups, and straight chain, branched, and cyclic alkyl groups, alkenyl groups, and alkynyl groups. Alkyl and aromatic groups are more preferred than alkynyl or alkenyl groups. Aromatic polycarbodiimides are preferred over straight chain, branched, or cyclic polycarbodiimides, although straight chain, branched, or cyclic polycarbodiimides can be used in the invention. Polymeric carbodiimides are preferred over carbodiimides. Preferably R has C₁ to C₃₀ carbon atoms, and generally polycarbodiimides having a molecular weight in the range of about 500 to about 10,000 g/mol will be preferred for use in the present invention. The aromatic group may be connected to the N group via a hydrocarbon group, such as an alkyl group, eg a C₁ alkyl group.

[0035] Further carbodiimides believed to have utility in the present invention are described in United States Patent No. 6,498,225 and in United States Patent No. 5,360,888, for example. United States Patent No. 6,498,225 specifically teaches polycarbodiimide-based copolymers having the general formula:



where:

X is identical or different and is selected from the group consisting of -NHCO-R''', -NHCONH-R''', -NHCOO-R''', -NHCOS-R''', -COO-R''', -O-R''', -NR₂, -S-R''', -OH, -S-H, -NH₂, -NHR''', and -NCO, and wherein the group R''' denotes an alkyl, cycloalkyl, aralkyl or aryl radical containing 1 to 30 carbon atoms;

m, n are independent of one another and are each an integer from 1 to 1000;

o is an integer from 1 to 500;

A is selected from the group consisting of the carbodiimides or polycarbodiimides of the formula: $-(N=C=N-Y)-$ where Y is selected from the group consisting of ortho-or bisortho-substituted aromatics, aralkylenes in which the carbon atom linked to the carbodiimide group is substituted by C₁ to C₁₄-alkyl groups, and cycloalkylenes in which the carbon atom linked to the carbodiimide group is substituted by C₁ to C₁₄-alkyl groups; and

B is selected from the group consisting of (poly)diols, (poly)diamines, (poly)dimercaptans, (poly)aminoalcohols, (poly)aminomercaptans and (poly)mercaptoalcohols. United States Patent No. 5,360,888 teaches polycarbodiimides that are reaction products of substituted aromatic isocyanates, such as: 2,6-diisopropylphenyl isocyanate; 1,3,5-triisopropyl-2,4-diisocyanatobenzene; naphthalene-1,5-diisocyanate; 2,4-diisocyanato-3,5-dimethyltoluene; 4,4'-methylenebis(2,6-diethylphenyl isocyanate); 4,4'-methylenebis(2-ethyl-6-methylphenyl isocyanate); 4,4'-methylenebis(2-isopropyl-6-methylphenyl isocyanate); 4,4'-methylenebis(2,6-diisopropylphenyl isocyanate); and 4,4'-methylenebis(2-ethyl-6-methylcyclohexyl isocyanate).

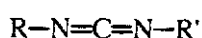
[0036] As indicated above, the advantages of the invention may be obtained by employing a drilling fluid of the invention, comprising or containing an ester or amide, in drilling operations, wherein the drilling fluid has added thereto a carbodiimide, preferably a polycarbodiimide. The drilling operations—whether drilling a vertical or directional or horizontal borehole, conducting a sweep, or running casing and cementing—may be conducted as known to those skilled in the art with other drilling fluids. That is, a drilling fluid of the invention is prepared or obtained and circulated through a wellbore as the wellbore is being drilled (or swept or cemented and cased) to facilitate the drilling operation. The drilling fluid removes drill cuttings from the wellbore, cools and lubricates the drill bit, aids in support of the drill pipe and drill bit, and provides a hydrostatic head to maintain the integrity of the wellbore walls and prevent well blowouts. The specific formulation of the drilling fluid in accordance with the present invention is optimized for the particular drilling operation and for the particular subterranean formation characteristics and conditions (such as temperatures). For example, the fluid is weighted as appropriate for the formation pressures and thinned as appropriate for the formation temperatures. Further, the fluids of the invention may be recycled during a drilling operation such that fluids circulated in a wellbore may be recirculated in the wellbore after returning to the surface for removal of drill cuttings for

example. The drilling fluid of the invention may even be selected for use in a drilling operation to comply with environmental regulations governing drilling operations in a particular subterranean formation.

[0037] The foregoing description of the invention is intended to be a description of preferred embodiments. Various changes in the details of the described fluids and methods of use can be made without departing from the intended scope of this invention as defined by the appended claims.

CLAIMS

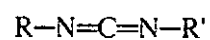
1. A method for drilling a borehole in a subterranean formation for the recovery of hydrocarbons, comprising the steps of: providing or using an oil-based drilling fluid comprising a carbodiimide; and drilling the borehole in the subterranean formation.
2. A method according to claim 1, wherein the drilling in the subterranean formation includes temperatures in the range of about 275°F (135°C) to about 450°F (232°C).
3. A method according to claim 1 or 2, wherein the drilling fluid comprises an ester based invert emulsion.
4. A method according to claim 1, 2 or 3, wherein the carbodiimide has the formula:



where R and R' are the same or different and are selected from the group consisting of aromatic groups and straight chain, branched, and cyclic alkyl groups, alkenyl groups, and alkynyl groups.

5. A method according to claim 4, wherein R has C₁ to C₃₀ carbon atoms.
6. A method according to claim 4, wherein R' has C₁ to C₃₀ carbon atoms.
7. A method according to any preceding claim 1 wherein the carbodiimide is a polymer.
8. A method according to any preceding claim, wherein the carbodiimide is monomeric.
9. A method according to any preceding claim, wherein the carbodiimide is a hydrolysis inhibitor.

10. A method according to any preceding claim, wherein the carbodiimide has a molecular weight in the range of about 500-10,000 g/mol.
11. A method according to any preceding claim, wherein the drilling fluid comprises an additive comprising an ester.
12. A method according to claim 11 wherein the additive is an emulsifier.
13. A method according to any preceding claim, wherein the drilling fluid comprises an additive comprising an amide.
14. A method according to any preceding claim 1 wherein the drilling fluid comprises water.
15. A drilling fluid for drilling a borehole in a subterranean formation comprising: a continuous phase; an internal phase; an emulsifier; a filtration control agent; a weighting agent; and a carbodiimide.
16. A drilling fluid according to claim 15, wherein the continuous phase comprises an ester based invert emulsion.
17. A drilling fluid according to claim 15 or 16, wherein the emulsifier comprises an ester or an amide.
18. A drilling fluid according to claim 15, 16 or 17, wherein the filtration control agent comprises an ester or an amide.
19. A drilling fluid according to claim 15, 16, 17 or 18, wherein the carbodiimide is a polycarbodiimide, having a molecular weight in the range of 500 to about 10,000.
20. A drilling fluid according to any one of claims 15 to 19 wherein the wherein the carbodiimide has the formula:



where R and R' are the same or different and are selected from the group consisting of aromatic groups and straight chain, branched, and cyclic alkyl groups, alkenyl groups, and alkynyl groups.

ABSTRACT

Methods for enhancing the stability of ester based drilling fluids for drilling, running casing in, and/or cementing a borehole in a subterranean formation are disclosed, as well as improved ester based drilling fluids for use at high temperatures. The advantages of the invention are realized by inhibiting hydrolysis of the esters in the drilling fluid by adding a monomeric or polymeric carbodiimide hydrolysis inhibitor to the drilling fluid.

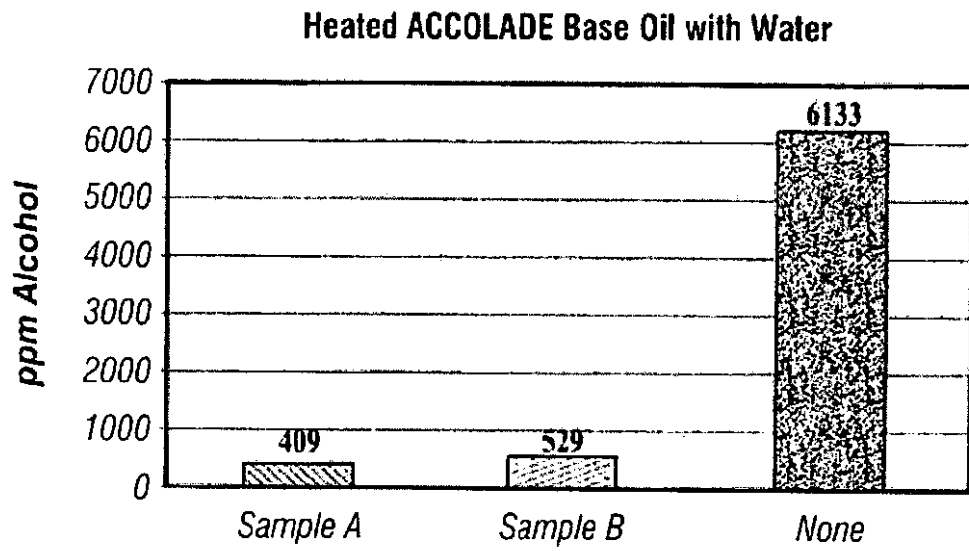


FIG. 1

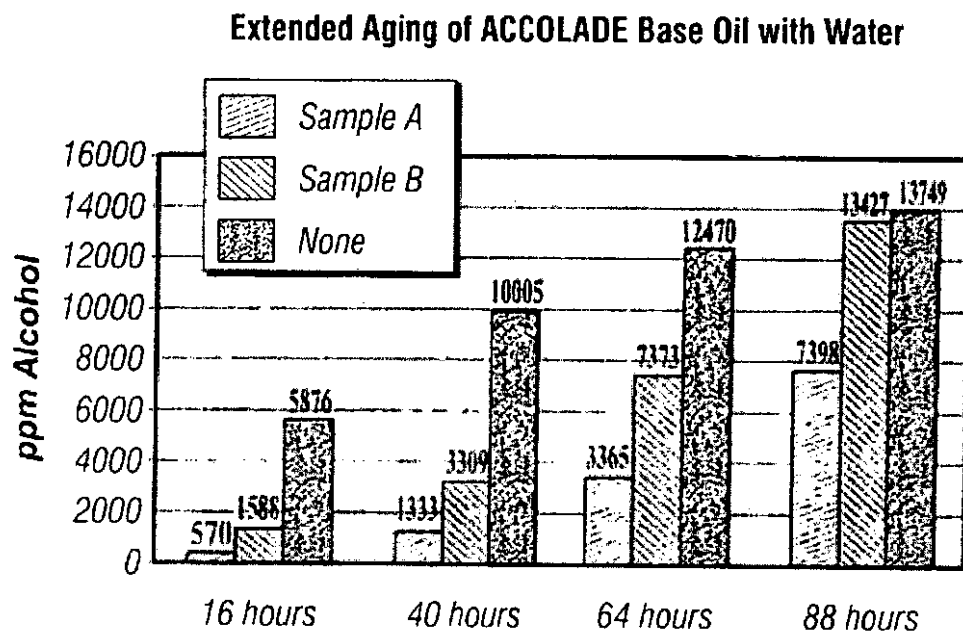


FIG. 2

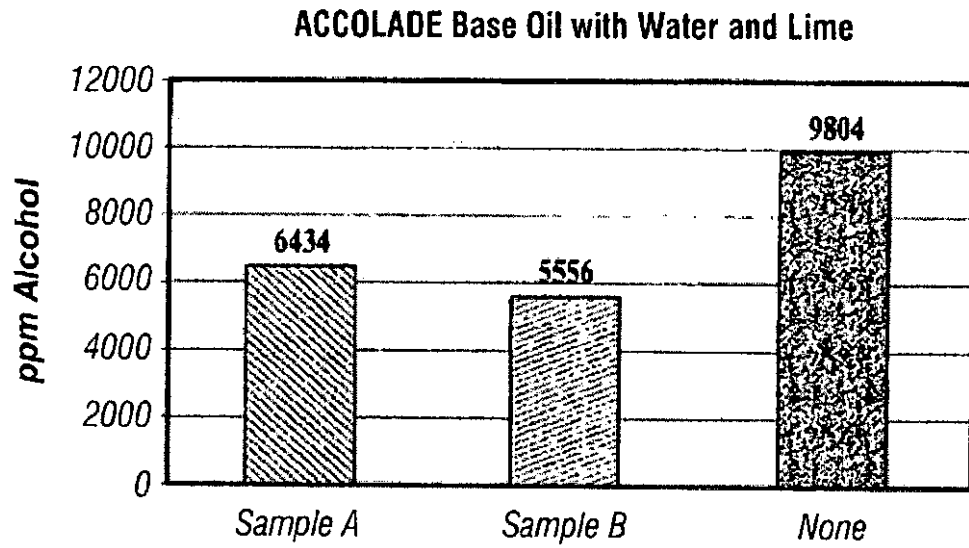


FIG. 3

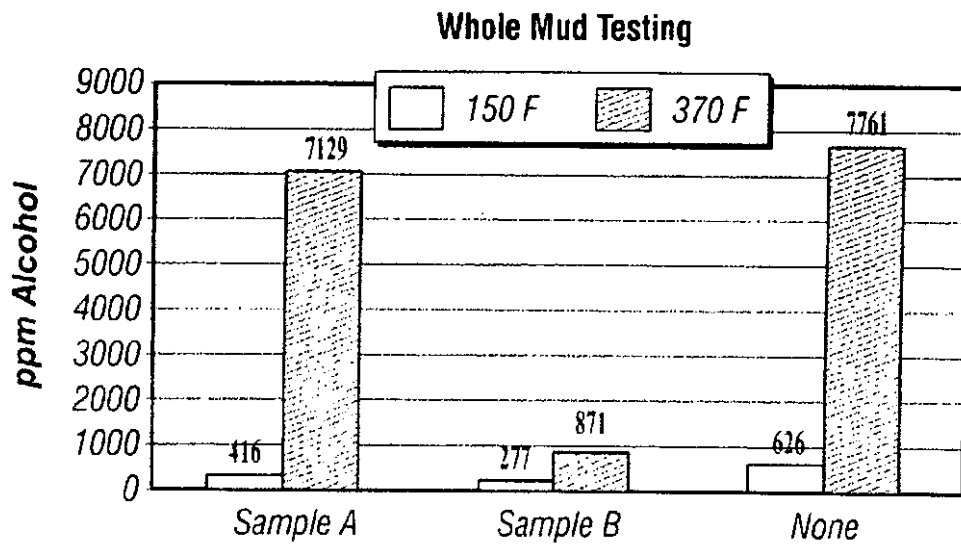


FIG. 4

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

(19) World Intellectual Property Organization
International Bureau

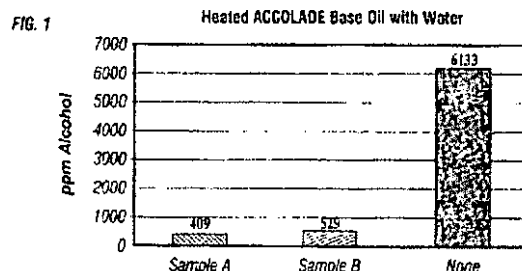


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(54) Title: METHOD FOR ENHANCING STABILITY OF OIL BASED DRILLING FLUIDS AT HIGH TEMPERATURES



(57) Abstract: Methods for enhancing the stability of ester based drilling fluids for drilling, running casing in, and/or cementing a borehole in a subterranean formation are disclosed, as well as improved ester based drilling fluids for use at high temperatures. The advantages of the invention are realized by inhibiting hydrolysis of the esters in the drilling fluid by adding a monomeric or polymeric carbodiimide hydrolysis inhibitor to the drilling fluid.

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**METHOD FOR ENHANCING STABILITY OF
OIL BASED DRILLING FLUIDS AT HIGH TEMPERATURES**

BACKGROUND OF THE INVENTION

1. Field of the Invention

[0001] The present invention relates to compositions and methods for drilling, cementing and casing boreholes in subterranean formations, particularly hydrocarbon bearing formations. More particularly, the present invention relates to oil or synthetic fluid based drilling fluids and fluids comprising invert emulsions, such as fluids using esters for example, which combine high ecological compatibility with good stability and performance properties.

2. Description of Relevant Art

[0002] A drilling fluid or mud is a specially designed fluid that is circulated through a wellbore as the wellbore is being drilled to facilitate the drilling operation. The various functions of a drilling fluid include removing drill cuttings from the wellbore, cooling and lubricating the drill bit, aiding in support of the drill pipe and drill bit, and providing a hydrostatic head to maintain the integrity of the wellbore walls and prevent well blowouts. Specific drilling fluid systems are selected to optimize a drilling operation in accordance with the characteristics of a particular geological formation.

[0003] Oil or synthetic fluid-based muds are normally used to drill swelling or sloughing shales, salt, gypsum, anhydrite or other evaporate formations, hydrogen sulfide-containing formations, and hot or high temperature (greater than about 300 degrees Fahrenheit ("° F")) holes, but may be used in other holes penetrating a subterranean formation as well. Unless indicated otherwise, the terms "oil mud" or "oil-based mud" or "drilling fluid" shall be understood to include synthetic oils or other synthetic fluids as well as natural or traditional oils, and such oils shall be understood to comprise invert emulsions.

[0004] Oil-based muds used in drilling typically comprise: a base oil (or synthetic fluid) comprising the external phase of an invert emulsion; a saline, aqueous solution (typically a solution comprising about 30% calcium chloride) comprising the internal phase of the invert emulsion; emulsifiers at the interface of the internal and external phases; and other agents or additives for suspension, weight or density, oil-wetting, fluid loss or filtration control, and rheology control.

[0005] An oil-based or invert emulsion-based drilling fluid may commonly comprise between about 50:50 to about 95:5 by volume oil phase to water phase. An all oil mud simply comprises 100% liquid phase oil by volume; that is, there is no aqueous internal phase.

[0006] Invert emulsion-based muds or drilling fluids (also called invert drilling muds or invert muds or fluids) comprise a key segment of the drilling fluids industry. However, increasingly invert emulsion-based drilling fluids have been subjected to greater environmental restrictions and performance and cost demands. While ester based invert emulsion drilling fluids satisfy many environmental concerns, they tend to lose effectiveness or utility at high oilfield temperatures. There is consequently an increasing need and industry-wide interest in new drilling fluids and methods that provide improved performance while still affording environmental and economical acceptance.

SUMMARY OF THE INVENTION

[0007] The present invention provides improved methods of drilling wellbores in subterranean formations employing oil-based muds or drilling fluids. As used herein, the term "drilling" or "drilling wellbores" shall be understood in the broader sense of drilling operations, which include running casing and cementing as well as drilling, unless specifically indicated otherwise. More particularly, the present invention provides a method for improving the stability of oil-based drilling fluids, most particularly at high temperatures. The present invention also provides oil based drilling fluids having improved stability at such high temperatures.

[0008] Any drilling fluid comprising a hydrolysable component may benefit from the present invention. Esters and amides are particularly susceptible to hydrolysis and thus the invention is particularly advantageous with invert emulsion drilling fluids comprising esters and/or amides, particularly as the base oil for the drilling fluids but also as additives or components in the drilling fluids, such as for example, emulsifiers and fluid loss control additives. The benefits of the invention are obtained by inhibiting hydrolysis of esters and/or amides in or comprising the drilling fluid. Such benefits are particularly realized at higher temperatures, that is, at temperatures of 275°F (135°C) or higher and extending to temperatures as high as about 450°F (232°C) or more, as may be encountered in drilling boreholes in subterranean formations for recovery of hydrocarbons.

[0009] According to the method of the invention, a carbodiimide, preferably a polycarbodiimide, is added to the drilling fluid as a hydrolysis inhibitor. A 5 lb/bbl (16.7 kg/m³) loading amount will typically be effective for purposes of the invention, although other amounts may be successfully used with experimentation. Drilling fluids of the invention comprise an ester oil or invert emulsion base and/or ester or amide additives, such as, for example, emulsifiers and fluid loss control additives, and a carbodiimide, or preferably a polycarbodiimide.

BRIEF DESCRIPTION OF THE DRAWINGS

[0010] Figure 1 is a graph comparing the amount of alcohol produced, indicating hydrolysis, in samples containing ester base and water, with and without polycarbodiimide additives, after heating at 370° F (188°C) for 16 hours.

[0011] Figure 2 is a graph comparing the amount of alcohol produced, indicating hydrolysis, in samples containing ester base and water, with and without polycarbodiimide additives, after heating at 370° F (188°C) for periods of 16 hours, 40 hours, 64 hours and 88 hours.

[0012] Figure 3 is a graph comparing the amount of alcohol produced, indicating hydrolysis, in samples containing ester base, water, and lime, with and without polycarbodiimide additives, after heating at 370° F (188°C) for 16 hours.

[0013] Figure 4 is a graph comparing the amount of alcohol produced, indicating hydrolysis, in samples of an ester based invert emulsion drilling fluid, with and without polycarbodiimide additives, after hot rolling at 150°F (66°C) for 16 hours and then at 370° F (188°C) for 16 hours.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

[0014] Ester based invert emulsion drilling fluids are favored as oil based drilling fluids for environmental acceptability and regulatory compliance. However, in prior art fluids, the ester can be vulnerable to hydrolysis, particularly at high temperatures that can be encountered in drilling subterranean formations for the recovery of hydrocarbons. Such hydrolysis can result in breakdown of the fluid, which ultimately or eventually renders the fluid unusable as a drilling fluid. Consequently, the use of ester based drilling fluids is less common at high temperatures, which typically increase the rate of ester hydrolysis.

[0015] The addition of lime to a drilling fluid, as has been common practice in the oilfield, can have the negative side-effect of increasing the amount of hydrolysis of esters in prior art drilling fluids. Lime provides a greater concentration of nucleophilic hydroxide ion to the fluid, which can escalate hydrolysis. Consequently, lime is usually avoided in ester based drilling fluids.

[0016] The present invention provides a method for enhancing the stability of ester-based drilling fluids and drilling fluid additives, even at high temperatures, and even in the presence of lime or other sources of hydroxide ion. This enhancement is accomplished by reducing the amount of hydrolysis that occurs in oil-based drilling fluid systems. Hydrolysis inhibition according to the present invention allows for greater application of ester based drilling fluids in higher temperature environments with greater retention of desirable fluid properties.

[0017] In the method of the present invention, enhanced stability of ester based invert emulsion drilling fluids is obtained by adding to or including in the drilling fluid a carbodiimide, preferably a polycarbodiimide. The carbodiimide carbon is believed to be more reactive than the carbonyl carbon of an ester and hence the reaction of the carbodiimide with water or hydroxide (hydrolysis) is expected to be more facile than hydrolysis of the ester of the drilling fluid. Consequently, the reaction of the carbodiimide with the water or hydroxide prevents or inhibits the carbonyl carbon of the ester from reacting with the water or hydroxide that might otherwise hydrolyze the ester, resulting in the ester not becoming hydrolyzed. This is particularly significant, and surprising, in drilling fluids, and especially invert emulsion drilling fluids, because such fluids already contain water as part of their composition. The carbodiimide is nevertheless able to maintain effectiveness in enhancing the stability of the fluid over time, as for example for a time sufficient to drill one or more wells or subterranean boreholes. That is, the carbodiimide is not immediately "used up" or diluted to ineffectiveness upon placement into the fluid.

[0018] The effectiveness of the invention is demonstrated in the following experiments.

Experiment 1:

[0019] Since hydrolyzation of an ester causes part of the ester molecule to be lost as an alcohol, the effectiveness of hydrolysis inhibitors can be measured by monitoring the production of alcohol that is formed in ester hydrolysis. In the case of a state-of-the-art, ester-based, invert emulsion fluid sold by Halliburton Energy Services, Inc., in Houston, Texas and Duncan, Oklahoma under the tradename ACCOLADE® drilling fluid, the amount of alcohol produced can be monitored by gas chromatography/mass spectrometry. Thus, samples containing ACCOLADE® base fluid, calcium chloride brine, and an emulsifier, were formulated with and without 5 lb/bbl (16.7 kg/m³) loading of one of two commercial polycarbodiimides: the viscous liquid STABAXOL® P200 polycarbodiimide (Sample A) and the powder STABAXOL® P polycarbodiimide (Sample B), both available from Rhein Chemie Rheinau GmbH, Mannheim, Deutschland (Germany). The samples were static aged at 370°F (188°C) for 16 hours and then tested for alcohol content, as indicated in Table 1 below.

TABLE 1

Additive	wt. % alcohol	ppm alcohol
Polycarbodiimide Sample A	0.041	409
Polycarbodiimide Sample B	0.053	529
None (Control)	0.61	6133

[0020] The data is also graphed in Figure 1. The data indicates that a greater than 90% reduction in the amount of alcohol produced was observed in the presence of the polycarbodiimides. This reduction indicates a reduction in the amount of hydrolysis of the ester in the ACCOLADE® base fluid.

Experiment 2:

[0021] Samples of the same compositions of Experiment 1 were static aged at 370°F (188°C) for 16 hours, 40 hours, 64, hours and 88 hours, and tested for alcohol content after each elapsed aging period, as shown in Table 2 below.

TABLE 2

Additive	wt. % alcohol	ppm alcohol
Polycarbodiimide Sample A Static Aged 16 hours	0.06	570
Polycarbodiimide Sample B Static Aged 16 hours	0.16	1588
None (Control) Static Aged 16 hours	0.59	5876
Polycarbodiimide Sample A Static Aged 40 hours	0.13	1333
Polycarbodiimide Sample B Static Aged 40 hours	0.33	3309
None (Control) Static Aged 40 hours	1.00	10005
Polycarbodiimide Sample A Static Aged 64 hours	0.34	3365
Polycarbodiimide Sample B Static Aged 64 hours	0.74	7373
None (Control) Static Aged 64 hours	1.25	12470
Polycarbodiimide Sample A Static Aged 88 hours	0.74	7398

Polycarbodiimide Sample B Static Aged 88 hours	1.34	13427
None (Control) Static Aged 88 hours	1.37	13749

[0022] The data is also graphed in Figure 2. The data indicates that after 64 hours, both polycarbodiimide additives still reduced the alcohol concentration, and after 88 hours, Additive A still showed the ability to reduce the amount of ester hydrolysis that occurred. The reason Additive A showed superior performance to Additive B is unclear, although the liquid nature of the material may have allowed the material to be more fully solubilized in the solids-free fluids tested in this experiment leading to greater efficacy.

Experiment 3:

[0023] Samples containing ACCOLADE® base, calcium chloride brine, and an emulsifier, were formulated with and without 5 lb/bbl loading of one of two commercial polycarbodiimides, STABAXOL® P200 and STABAXOL® P polycarbodiimides, available from Rhein Chemie Rheinau GmbH, Mannheim, Deutschlandas, as in Experiments 1 and 2, except to each of the samples for this Experiment 3 was added lime (3 lb/bbl [10 kg/m³]). The samples were static aged at 370°F (188°C)for 16 hours and tested for alcohol content, as shown in Table 3.

TABLE 3

Additive	wt. % alcohol	ppm alcohol
Polycarbodiimide Sample A	0.64	6434
Polycarbodiimide Sample B	0.56	5556
None (Control)	0.98	9804

[0024] The data is also graphed in Figure 3. This data shows that a significant reduction in hydrolysis is obtained with the polycarbodiimide additives, even in the presence of lime, and even though the addition of lime to a drilling fluid typically increases the amount

of hydrolysis due to the presence of greater concentrations of the more nucleophilic hydroxide ion. The percent reductions in hydrolysis in the samples with the polycarbodiimide additives when compared to the control were 34.4% in the case of polycarbodiimide Sample A and 43.3% in the case of polycarbodiimide Sample B.

Experiment 4:

[0025] Samples containing ACCOLADE® invert emulsion drilling fluid were formulated with and without 5 lb/bbl (16.7 kg/m³) loading of one of two commercial polycarbodiimides, STABAXOL® P200 and STABAXOL® P polycarbodiimides, available from Rhein Chemie Rheinau GmbH, Mannheim, Deutschland, as indicated in Table 4.

TABLE 4

Polycarbodiimide Sample	A	B	None (Control)
ACCOLADE® base, bbl	0.519	0.519	0.519
250,000 ppm CaCl ₂ brine, bbl	0.0676	0.0676	0.0676
LE SUPERMUL® polyaminated fatty acid, lb	10	10	10
FACTANT® highly concentrated tall oil derivative, lb	1	1	1
ADAPTA® methylstyrene/acrylate copolymer for HPHT filtration control, lb	3	3	3
Rev Dust, lb	20	20	20

Barite, lb	497	497	497
Polycarbodiimide Sample A, lb	5	0	0
Polycarbodiimide Sample B, lb	0	5	0

All trademarked products are available from Halliburton Energy Services, Inc. in Houston, Texas and Duncan, Oklahoma.

[0026] The samples were hot rolled at 150°F (66°C) for 16 hours and then were tested for alcohol concentration. The samples were hot rolled further at 370°F (188°C) for 16 additional hours and tested for alcohol, as shown in Table 5.

TABLE 5

Additive	wt. % alcohol	ppm alcohol
Polycarbodiimide Sample A hot rolled at 150°F	0.04	416
Polycarbodiimide Sample B hot rolled at 150°F	0.03	277
None (Control) hot rolled at 150°F	0.06	626
Polycarbodiimide Sample A hot rolled at 370°F	0.71	7129
Polycarbodiimide Sample B hot rolled at 370°F	0.09	871
None (Control) hot rolled at 370°F	0.78	7761

[0027] This data is also graphed in Figure 4. The data shows that the percent reduction in hydrolysis with the polycarbodiimide additive Sample B, when compared to the control, was 89% over the control after aging at 370°F (188°C). Sample A did not perform as well in the whole mud, possibly because the material was wetted onto solids that were present in the fluid.

[0028] Although the experiments were conducted with an ACCOLADE® ester base and an ACCOLADE® invert emulsion drilling fluid, benefits of the invention may be seen with other ester based drilling fluids. Some other examples of commercial ester based invert emulsion drilling fluids include, without limitation, PETROFREE®, PETROFREE® LV, and PETROFREE® SF drilling fluids available from Halliburton Energy Services, Inc. in Houston, Texas. Still further examples are taught in United States Patent No. 7,485,602, issued February 3, 2009, to Jeff Kirsner, et al, and in U.S. Patent No. 7,456,135, issued November 25, 2008 to Jeff Kirsner, et al., among many other examples. Also, drilling fluids having an amide base or other base vulnerable to hydrolysis may benefit from addition of a carbodiimide or polycarbodiimide as a hydrolysis inhibitor.

[0029] Further, the invert emulsion drilling fluids of the invention or for use in the present invention have added to them or mixed with their invert emulsion base, other fluids or materials needed to comprise complete drilling fluids. Such materials may include, for example: additives to reduce or control temperature rheology or to provide thinning, for example, additives having the tradenames COLDTROL®, ATC®, and OMC2™; additives for enhancing viscosity, for example, an additive having the tradename RHEMOD L™; additives for providing temporary increased viscosity for shipping (transport to the well site) and for use in sweeps, for example, an additive having the tradename TEMPERUS™ (modified fatty acid); additives for filtration control, for example, an additive having the tradename ADAPTA® (methylstyrene/acrylate copolymer); additives for high temperature high pressure control (HTHP) and emulsion stability, for example, an additive having the tradename FACTANT™ (highly concentrated tall oil derivative); additives for emulsification, for example, an additive having the tradename LE SUPERMUL™ (polyaminated fatty acid); and additives for thinning, for example additives having the tradenames COLDTROL® (alcohol derivative), OMC2™ (oligomeric fatty acid), and ATC® (modified fatty acid ester) and example additives taught in U.S. Patent No. 7,435,706, issued October 14, 2008 to Heinz

Mueller, et al. and in U.S. Patent Application No. 10/432,786, filed December 10, 2003 of Heinz Mueller, et al., both entitled "Thinners for Invert Emulsions." All of the aforementioned trademarked products are available from Halliburton Energy Services, Inc. in Houston, Texas, U.S.A. Additionally, the fluids may comprise an aqueous solution containing a water activity lowering compound, composition or material, comprising the internal phase of the invert emulsion. Such solution may be a saline solution comprising calcium chloride (typically about 25% to about 30%, depending on the subterranean formation water salinity or activity), although other salts or water activity lowering materials known in the art may alternatively or additionally be used.

[0030] Many other examples of drilling fluid components will be readily known to those of skill in the art. Also known is that such components may include an ester or an amide, known to be vulnerable at least at high temperatures to hydrolysis. For example, LE SUPERMUL®, EZ® MUL, EZ MUL® NT, EZ MUL® NS, DRILTREAT®, INVERMUL®, INVERMUL® NT and ADAPTA® additives are emulsifiers and fluid loss control additives that contain esters or amides. Adding a carbodiimide, preferably a polycarbodiimide, to the drilling fluid according to the present invention enhances the stability of such additives, and consequently enhances the stability of the drilling fluid overall. That is, the carbodiimide inhibits hydrolysis of the ester or amide in such additives. Thus advantages may be realized by adding a carbodiimide or polycarbodiimide to a drilling fluid containing ester or amide additives even when the base oil of the drilling fluid may not comprise an ester or amide.

[0031] The exact formulations of drilling fluids used in drilling boreholes vary with the particular requirements of the subterranean formation. The above listed additives, however, provide some examples. A preferred example drilling fluid of the present invention may have the formulation used in Experiment 4 discussed above. A couple of other preferred example drilling fluids of the present invention have the following example formulations set forth in Table 6 below.

TABLE 6
Example Formulations

Fluids and Compounds	ACCOLADE® Invert Emulsion Drilling Fluid	PETROFREE® SF Invert Emulsion Drilling Fluid
ACCOLADE® Base (bbl)	0.590	-----

PETROFREE® SF BASE (bbl)	-----	0.568
LE MUL™ ¹ (lb.)	-----	4
LE SUPERMUL™ ² (lb.)	10	6
Lime (lb.)	1	4
DURATONE® HT ³ (lb.)	-----	4
Freshwater (bbl)	0.263	0.254
ADAPTA® ⁴ (lb.)	2	-----
RHEMOD L™ ⁵ (lb.)	1	-----
GELTONE® II ⁶ (lb.)	-----	5
VIS-PLUS® ⁷ (lb.)	-----	1.5
BAROID® ⁸ (lb.)	138	138
Calcium chloride (lb.)	32	31
DEEP-TREAT® ⁹ (lb.)	-----	2
Polycarbodiimide (lb.)	5	5

¹ Blend of oxidized tall oil and polyaminated fatty acid emulsion stabilizer.

² Polyaminated fatty acid emulsifier.

³ Organophilic leonardite filtration control agent.

⁴ Copolymer HTHP filtration control agent for non-aqueous systems.

⁵ Modified fatty acid suspension agent/viscosifier.

⁶ Organophilic clay viscosifier.

⁷ Carboxylic acid suspension agent.

⁸ Ground barium sulfate weighting agent.

⁹ Sulfonate sodium salt wetting agent/thinner.

[0032] All trademarked products in Table 6 are available from Halliburton Energy Services, Inc. in Houston, Texas, including: LE MUL™ emulsion stabilizer (a blend of oxidized tall oil and polyaminated fatty acid); LE SUPERMUL™ emulsifier (polyaminated fatty acid); DURATONE® HT filtration control agent (organophilic leonardite); ADAPTA® filtration control agent (methylstyrene/acrylate copolymer particularly suited for providing HPHT filtration control in non-aqueous fluid systems); RHEMOD L™ suspension agent/viscosifier (modified fatty acid); GELTONE® II viscosifier (organophilic clay); VIS-

PLUS® suspension agent (carboxylic acid); BAROID® weighting agent (ground barium sulfate); and DEEP-TREAT® wetting agent/thinner (sulfonate sodium salt).

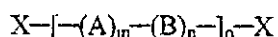
[0033] Examples of preferred commercially available polycarbodiimides useful in the formulations set forth in Table 6 include, without limitation, STABAXOL® I, STABAXOL® P, and STABAXOL® P200 polycarbodiimides, all available from Rhein Chemie Rheinau GmbH, Mannheim, Deutschland (Germany).

[0034] The preferred formula for carbodiimides for use in the present invention is as follows:



where R and R' are the same or different and are selected from the group consisting of aromatic groups, and straight chain, branched, and cyclic alkyl groups, alkenyl groups, and alkynyl groups. Alkyl and aromatic groups are more preferred than alkynyl or alkenyl groups. Aromatic polycarbodiimides are preferred over straight chain, branched, or cyclic polycarbodiimides, although straight chain, branched, or cyclic polycarbodiimides can be used in the invention. Polymeric carbodiimides are preferred over carbodiimides. Preferably R has C₁ to C₃₀ carbon atoms, and generally polycarbodiimides having a molecular weight in the range of about 500 to about 10,000 g/mol will be preferred for use in the present invention. The aromatic group may be connected to the N group via a hydrocarbon group, such as an alkyl group, eg a C₁ alkyl group.

[0035] Further carbodiimides believed to have utility in the present invention are described in United States Patent No. 6,498,225 and in United States Patent No. 5,360,888, for example. United States Patent No. 6,498,225 specifically teaches polycarbodiimide-based copolymers having the general formula:



where:

X is identical or different and is selected from the group consisting of -NHCO-R^{'''}, -NHCONH-R^{'''}, -NHCOO-R^{'''}, -NHCOS-R^{'''}, -COO-R^{'''}, -O-R^{'''}, -NR₂, -S-R^{'''}, -OH, -S-H, -NH₂, -NHR^{'''}, and -NCO, and wherein the group R^{'''} denotes an alkyl, cycloalkyl, aralkyl or aryl radical containing 1 to 30 carbon atoms;

m, n are independent of one another and are each an integer from 1 to 1000;

o is an integer from 1 to 500;

A is selected from the group consisting of the carbodiimides or polycarbodiimides of the formula: $-(N=C=N-Y)-$ where Y is selected from the group consisting of ortho-or bisortho-substituted aromatics, aralkylenes in which the carbon atom linked to the carbodiimide group is substituted by C₁ to C₁₄-alkyl groups, and cycloalkylenes in which the carbon atom linked to the carbodiimide group is substituted by C₁ to C₁₄-alkyl groups; and

B is selected from the group consisting of (poly)diols, (poly)diamines, (poly)dimercaptans, (poly)aminoalcohols, (poly)aminomercaptans and (poly)mercaptoalcohols. United States Patent No. 5,360,888 teaches polycarbodiimides that are reaction products of substituted aromatic isocyanates, such as: 2,6-diisopropylphenyl isocyanate; 1,3,5-triisopropyl-2,4-diisocyanatobenzene; naphthalene-1,5-diisocyanate; 2,4-diisocyanato-3,5-dimethyltoluene; 4,4'-methylenebis(2,6-diethylphenyl isocyanate); 4,4'-methylenebis(2-ethyl-6-methylphenyl isocyanate); 4,4'-methylenebis(2-isopropyl-6-methylphenyl isocyanate); 4,4'-methylenebis(2,6-diisopropylphenyl isocyanate); and 4,4'-methylenebis(2-ethyl-6-methylcyclohexyl isocyanate).

[0036] As indicated above, the advantages of the invention may be obtained by employing a drilling fluid of the invention, comprising or containing an ester or amide, in drilling operations, wherein the drilling fluid has added thereto a carbodiimide, preferably a polycarbodiimide. The drilling operations—whether drilling a vertical or directional or horizontal borehole, conducting a sweep, or running casing and cementing—may be conducted as known to those skilled in the art with other drilling fluids. That is, a drilling fluid of the invention is prepared or obtained and circulated through a wellbore as the wellbore is being drilled (or swept or cemented and cased) to facilitate the drilling operation. The drilling fluid removes drill cuttings from the wellbore, cools and lubricates the drill bit, aids in support of the drill pipe and drill bit, and provides a hydrostatic head to maintain the integrity of the wellbore walls and prevent well blowouts. The specific formulation of the drilling fluid in accordance with the present invention is optimized for the particular drilling operation and for the particular subterranean formation characteristics and conditions (such as temperatures). For example, the fluid is weighted as appropriate for the formation pressures and thinned as appropriate for the formation temperatures. Further, the fluids of the invention may be recycled during a drilling operation such that fluids circulated in a wellbore may be recirculated in the wellbore after returning to the surface for removal of drill cuttings for

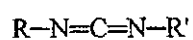
example. The drilling fluid of the invention may even be selected for use in a drilling operation to comply with environmental regulations governing drilling operations in a particular subterranean formation.

[0037] The foregoing description of the invention is intended to be a description of preferred embodiments. Various changes in the details of the described fluids and methods of use can be made without departing from the intended scope of this invention as defined by the appended claims.

CLAIMS

1. A method for drilling a borehole in a subterranean formation for the recovery of hydrocarbons, comprising the steps of: providing or using an oil-based drilling fluid comprising a carbodiimide; and drilling the borehole in the subterranean formation.
2. A method according to claim 1, wherein the drilling in the subterranean formation includes temperatures in the range of about 275°F (135°C) to about 450°F (232°C).
3. A method according to claim 1 or 2, wherein the drilling fluid comprises an ester based invert emulsion.
4. A method according to claim 1, 2 or 3, wherein the carbodiimide has the formula:
$$R-N=C=N-R'$$
where R and R' are the same or different and are selected from the group consisting of aromatic groups and straight chain, branched, and cyclic alkyl groups, alkenyl groups, and alkynyl groups.
5. A method according to claim 4, wherein R has C₁ to C₃₀ carbon atoms.
6. A method according to claim 4, wherein R' has C₁ to C₃₀ carbon atoms.
7. A method according to any preceding claim 1 wherein the carbodiimide is a polymer.
8. A method according to any preceding claim, wherein the carbodiimide is monomeric.
9. A method according to any preceding claim, wherein the carbodiimide is a hydrolysis inhibitor.

10. A method according to any preceding claim, wherein the carbodiimide has a molecular weight in the range of about 500-10,000 g/mol.
11. A method according to any preceding claim, wherein the drilling fluid comprises an additive comprising an ester.
12. A method according to claim 11 wherein the additive is an emulsifier.
13. A method according to any preceding claim, wherein the drilling fluid comprises an additive comprising an amide.
14. A method according to any preceding claim 1 wherein the drilling fluid comprises water.
15. A drilling fluid for drilling a borehole in a subterranean formation comprising: a continuous phase; an internal phase; an emulsifier; a filtration control agent; a weighting agent; and a carbodiimide.
16. A drilling fluid according to claim 15, wherein the continuous phase comprises an ester based invert emulsion.
17. A drilling fluid according to claim 15 or 16, wherein the emulsifier comprises an ester or an amide.
18. A drilling fluid according to claim 15, 16 or 17, wherein the filtration control agent comprises an ester or an amide.
19. A drilling fluid according to claim 15, 16, 17 or 18, wherein the carbodiimide is a polycarbodiimide, having a molecular weight in the range of 500 to about 10,000.
20. A drilling fluid according to any one of claims 15 to 19 wherein the wherein the carbodiimide has the formula:



where R and R' are the same or different and are selected from the group consisting of aromatic groups and straight chain, branched, and cyclic alkyl groups, alkenyl groups, and alkynyl groups.

1/2

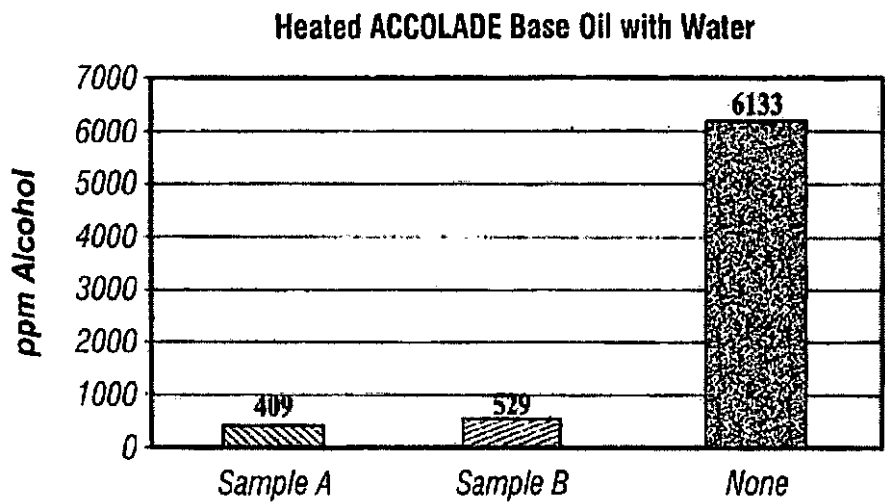


FIG. 1

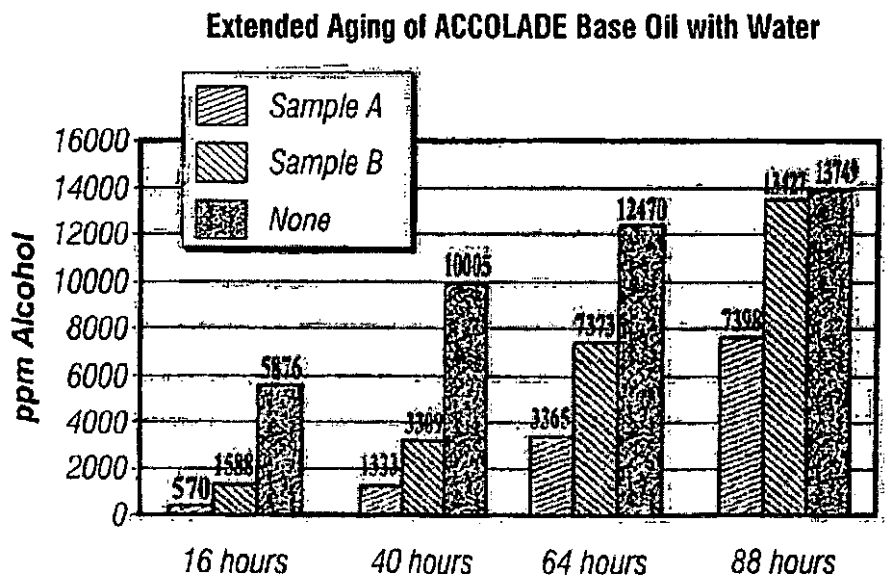


FIG. 2

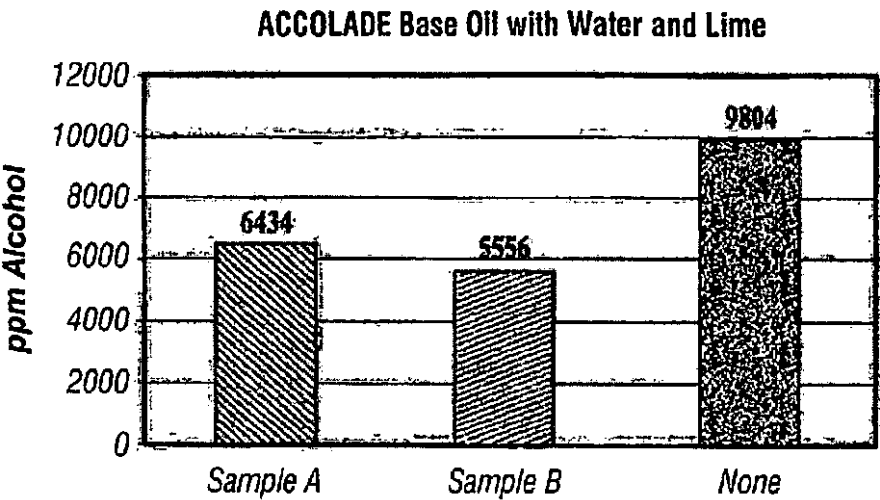


FIG. 3

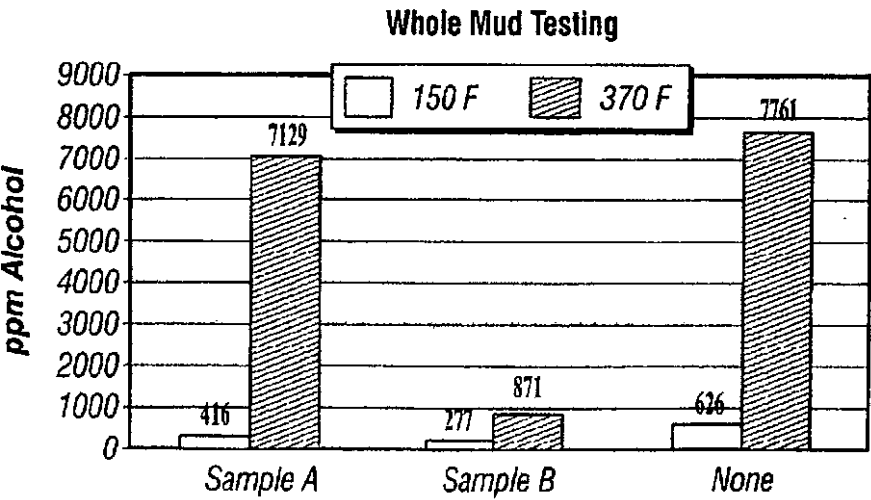


FIG. 4

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2010/000804

A. CLASSIFICATION OF SUBJECT MATTER

INV. C09K8/34 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 C08G

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No
Y	US 2001/009890 A1 (PATEL ARVIND D [US] ET AL) 26 July 2001 (2001-07-26) example 4 claims 1-13	1-20
Y	EP 1 138 706 A1 (RHEIN CHEMIE RHEINAU GMBH [DE]) 4 October 2001 (2001-10-04) claims 6, 1 paragraph [0027]	1-20
Y	US 2004/072696 A1 (PATEL ARVIND D [US]) 15 April 2004 (2004-04-15) claims 1-21 examples 1-14	1-20
A,P	WO 2009/106987 A1 (M I DRILLING FLUIDS UK LTD [GB]; BALLARD DAVID ANTONY [GB]) 3 September 2009 (2009-09-03) claims 1-20	1-20

☐ 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

- *I* 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
- *A* document member of the same patent family

Date of the actual completion of the international search

21 June 2010

Date of mailing of the international search report

21/07/2010

Name and mailing address of the ISA/

European Patent Office, P.O. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel: (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer

Zimpfer, Emmanuel

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/GB2010/000804

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2001009890	A1	26-07-2001	NONE
EP 1138706	A1	04-10-2001	CA 2342048 A1 29-09-2001 DE 10015658 A1 04-10-2001 JP 2001278944 A 10-10-2001 US 2001037010 A1 01-11-2001
US 2004072696	A1	15-04-2004	NONE
WO 2009106987	A1	03-09-2009	AR 070476 A1 07-04-2010

DIC.
PRESENTACION
SOLICITUD
INTERNACIONAL

PATENT COOPERATION TREATY

RECEIVED
29 APR 2010

From the RECEIVING OFFICE

To:
A A Thornton & Co
235 High Holborn
London
WC1V 7LE

RECEIVED
27 APR 2010
PAC

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

(PCT Rule 20.2(c))

Date of mailing
(day/month/year)

26 APR 2010

Applicant's or agent's file reference PAC/N/27868 WO		IMPORTANT NOTIFICATION	
International application No. PCT/GB2010/000804	International filing date (day/month/year) 22/04/2010	Priority date (day/month/year) 24/04/2009	
Applicant Halliburton Energy Services Inc et al			
Title of the invention Method for enhancing stability of oil based drilling fluids at high temperatures			

1. The applicant is hereby notified that the international application has been accorded the international application number and the international filing date indicated above.

2. The applicant is further notified that the record copy of the international application:

☒ was transmitted to the International Bureau on 26 APR 2010

☐ has not yet been transmitted to the International Bureau for the reason indicated below and a copy of this notification has been sent to the International Bureau*:

☐ because the necessary national security clearance has not yet been obtained.

☐ because (reason to be specified):

* The International Bureau monitors the transmittal of the record copy by the receiving Office and will notify the applicant (with Form PCT/IB/301) of its receipt. Should the record copy not have been received by the expiration of 14 months from the priority date, the International Bureau will notify the applicant (Rule 22.1(c)).

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

Form PCT/RO/105 (July 2008)

Intellectual Property Office is an operating name of the Patent Office

PCT

REQUEST

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

For receiving Office use only

International Application No.

International Filing Date

Name of receiving Office and "PCT International Application"

Applicant's or agent's file reference
(if desired) (12 characters maximum) PAC/N/27868 WO

Box No. I	TITLE OF INVENTION	
METHOD FOR ENHANCING STABILITY OF OIL BASED DRILLING FLUIDS AT HIGH TEMPERATURES		
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.)		Telephone No.
HALLIBURTON ENERGY SERVICES, INC. P O Box 1431 Duncan Oklahoma 73536 US		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.)		Telephone No.
CURTIS, Philip, Anthony, A A Thornton & Co 235 High Holborn London WC1V 7LE GB		+44 20 7405 4044
		Facsimile No.
		+44 20 7405 3580
		Agent's registration No. with the Office
☐ Address for correspondence: Mark this check-box where no agent or common representative is has been appointed and the space above is used instead to indicate a special address to which correspondence should be sent.		

Box No. III FURTHER APPLICANT(S) AND/OR (FURTHER) INVENTOR(S)	
<i>If none of the following sub-boxes is used, this sheet should not be included in the request.</i>	
Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.) DEVILLE, Jay, Paul, 2623 Woodsboro Drive Spring Texas 77388 US	This person is: ☐ applicant only ☒ applicant and inventor ☐ inventor only (If this check-box is marked, do not fill in below.) Applicant's registration No. with the Office
State (that is, country) of nationality: US	State (that is, country) of residence: US
This person is applicant for the purposes of: ☐ all designated States ☐ all designated States except the United States of America ☒ the United States of America only ☐ the States indicated in the Supplemental Box	
Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.) CURTIS, Philip, Anthony, A A Thornton & Co 235 High Holborn London WC1V 7LE GB	This person is: ☒ applicant only ☐ applicant and inventor ☐ inventor only (If this check-box is marked, do not fill in below.) Applicant's registration No. with the Office
State (that is, country) of nationality: GB	State (that is, country) of residence: GB
This person is applicant for the purposes of: ☐ all designated States ☐ all designated States except the United States of America ☐ the United States of America only ☒ the States indicated in the Supplemental Box	
Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)	This person is: ☐ applicant only ☐ applicant and inventor ☐ inventor only (If this check-box is marked, do not fill in below.) Applicant's registration No. with the Office
State (that is, country) of nationality:	State (that is, country) of residence:
This person is applicant for the purposes of: ☐ all designated States ☐ all designated States except the United States of America ☐ the United States of America only ☐ the States indicated in the Supplemental Box	
Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)	This person is: ☐ applicant only ☐ applicant and inventor ☐ inventor only (If this check-box is marked, do not fill in below.) Applicant's registration No. with the Office
State (that is, country) of nationality:	State (that is, country) of residence:
This person is applicant for the purposes of: ☐ all designated States ☐ all designated States except the United States of America ☐ the United States of America only ☐ the States indicated in the Supplemental Box	
☐ Further applicants and/or (further) inventors are indicated on another continuation sheet.	

Supplemental Box

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

1. If, in any of the Boxes, except Boxes Nos. VIII(i) to (vi) 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.

CONTINUATION OF BOX III

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

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

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:

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

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

(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. II, there are further agents: in such case, write "Continuation of Box No. II" 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 4.11a(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 4.11a(iv) and 49bis.1(d)).

Box No. V DESIGNATIONS

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

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

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

Box No. VI PRIORITY CLAIM

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

Filing date of earlier application (day/month/year)	Number of earlier application	Where earlier application is:		
		national application: country or Member of WTO	regional application: regional Office	international application: receiving Office
item (1) 24/04/2009 (24 April 2009)	12/386,944	US		
item (2)				
item (3)				

☐ Further priority claims are indicated in the Supplemental Box.

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

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

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

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

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

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

Box No. VIII DECLARATIONS

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

		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	:
☐ Box No. VIII (iv)	Declaration of inventorship (only for the purposes of the designation of the United States of America)	:
☐ Box No. VIII (v)	Declaration as to non-prejudicial disclosures or exceptions to lack of novelty	:

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 2 Sub-total number of sheets 26 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 26 (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 items) (mark the applicable check-boxes below and indicate in right column the number of each item): 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): : 7. ☐ translation of international application into (language): : 8. ☐ separate indications concerning deposited microorganism or other biological material : 9. ☐ sequence listing in electronic form (indicate type and number of carriers) (i) ☐ copy submitted for the purposes of international search under Rule 13ter only (and not as part of the international application) : (ii) ☐ (only where check-box (b)(i) or (c)(i) is marked in left column) 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 (indicate type and number of carriers) (i) ☐ copy submitted for the purposes of international search under Section 802(b-quater) only (and not as part of the international application) : (ii) ☐ (only where check-box (b)(ii) or (c)(ii) is marked in left column) 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 (specify): Letter : 1
Figure of the drawings which should accompany the abstract: Fig 1	Language of filing of the international application: English
Box No. X SIGNATURE OF APPLICANT, AGENT OR COMMON REPRESENTATIVE <i>Next to each signature, indicate the name of the person signing and the capacity in which the person signs (if such capacity is not obvious from reading the request).</i> CURTIS Philip Anthony 22 April 2010	

For receiving Office use only	
1. Date of actual receipt of the purported international application:	2. Drawings: ☐ received: ☐ not received:
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 /	6. ☐ Transmittal of search copy delayed until search fee is paid
For International Bureau use only Date of receipt of the record copy by the International Bureau:	

PATENT COOPERATION TREATY

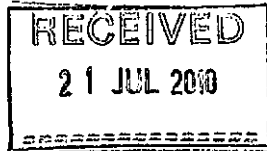
RECEIVED

23 JUL 2010

From the INTERNATIONAL SEARCHING AUTHORITY

PCT

To:
Curtis, Philip Anthony
A.A. Thornton & Co.
235 High Holborn
London
WC1V 7LE
GRANDE BRETAGNE



NOTIFICATION OF TRANSMITTAL OF
THE INTERNATIONAL SEARCH REPORT AND
THE WRITTEN OPINION OF THE INTERNATIONAL
SEARCHING AUTHORITY, OR THE DECLARATION

(PCT Rule 44.1)

Date of mailing (day/month/year)		21 July 2010 (21-07-2010)
Applicant's or agent's file reference PAC/N/27858 WO		FOR FURTHER ACTION See paragraphs 1 and 4 below
International application No. PCT/GB2010/000804		International filing date (day/month/year) 22 April 2010 (22-04-2010)
Applicant HALLIBURTON ENERGY SERVICES, INC.		

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

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

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

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

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

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

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

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

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

4. **Reminders**

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

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

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

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

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

RECORDS NOTED	
Name and mailing address of the International Searching Authority	Date: Authorized officer
 European Patent Office NL-2280 HV Rijswijk Tel. (+31-70) 340-2040 Fax: (+31-70) 340-3016	P.E. 5818 Patentlaan 2 Action: Article 19 amendments due 21 Sept 10

Form PCT/ISA/220 (July 2009)

(See notes on accompanying sheet)

NOTES TO FORM PCT/ISA/220

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

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

INSTRUCTIONS CONCERNING AMENDMENTS UNDER ARTICLE 19

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

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

What parts of the international application may be amended?

Under Article 19, only the claims may be amended.

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

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

When?

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

Where not to file the amendments?

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

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

How?

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

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

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

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

What documents must/may accompany the amendments?

Letter (Section 205(b)):

The amendments must be submitted with a letter.

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

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

NOTES TO FORM PCT/ISA/220 (continued)

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

PATENT COOPERATION TREATY

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference PAC/N/27868 WO	FOR FURTHER ACTION see Form PCT/ISA/220 as well as, where applicable, Item 5 below.	
International application No. PCT/GB2010/000804	International filing date (day/month/year) 22/04/2010	(Earliest) Priority Date (day/month/year) 24/04/2009
Applicant HALLIBURTON ENERGY SERVICES, INC.		

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

This international search report consists of a total of 3 sheets.

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

1. Basis of the report

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

☒ the international application in the language in which it was filed

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

b. ☐ This international search report has been established taking into account the **rectification of an obvious mistake** authorized by or notified to this Authority under Rule 91 (Rule 43.6b/s(e)).

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

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

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

4. With regard to the title,

☒ the text is approved as submitted by the applicant

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

5. With regard to the abstract,

☒ the text is approved as submitted by the applicant

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

6. With regard to the drawings,

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

☒ as suggested by the applicant

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

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

b. ☐ none of the figures is to be published with the abstract

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2010/000804A. CLASSIFICATION OF SUBJECT MATTER
INV. C09K8/34 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 C08G

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2001/009890 A1 (PATEL ARVIND D [US] ET AL) 26 July 2001 (2001-07-26) example 4 claims 1-13 -----	1-20
Y	EP 1 138 706 A1 (RHEIN CHEMIE RHEINAU GMBH [DE]) 4 October 2001 (2001-10-04) claims 6, 1 paragraph [0027] -----	1-20
Y	US 2004/072696 A1 (PATEL ARVIND D [US]) 15 April 2004 (2004-04-15) claims 1-21 examples 1-14 -----	1-20
A,P	WO 2009/106987 A1 (M I DRILLING FLUIDS UK LTD [GB]; BALLARD DAVID ANTONY [GB]) 3 September 2009 (2009-09-03) claims 1-20 -----	1-20

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

* Special categories of cited documents:

A document defining the general state of the art which is not considered to be of particular relevance

E earlier document but published on or after the international filing date

L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

O document referring to an oral disclosure, use, exhibition or other means

P document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

& document member of the same patent family

Date of the actual completion of the international search

21 June 2010

Date of mailing of the international search report

21/07/2010

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentplan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040
Fax: (+31-70) 340-3016

Authorized officer

Zimpfer, Emmanuel

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/GB2010/000804

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2001009890 A1	26-07-2001	NONE	
EP 1138706 A1	04-10-2001	CA 2342048 A1 DE 10015658 A1 JP 2001278944 A US 2001037010 A1	29-09-2001 04-10-2001 10-10-2001 01-11-2001
US 2004072696 A1	15-04-2004	NONE	
WO 2009106987 A1	03-09-2009	AR 070476 A1	07-04-2010

PATENT COOPERATION TREATY

From the
INTERNATIONAL SEARCHING AUTHORITY

To:

see form PCT/ISA/220

PCT

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

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

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

FOR FURTHER ACTION
See paragraph 2 below

International application No. PCT/GB2010/000804	International filing date (day/month/year) 22.04.2010	Priority date (day/month/year) 24.04.2009
--	--	--

International Patent Classification (IPC) or both national classification and IPC
INV. C09K8/34 C09K8/36

Applicant
HALLIBURTON ENERGY SERVICES, INC.

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

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

2. FURTHER ACTION

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

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

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

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

Name and mailing address of the ISA:  European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Fax: +49 89 2399 - 4465	Date of completion of this opinion see form PCT/ISA/210	Authorized Officer Zimpfer, Emmanuel Telephone No. +49 89 2399-7881 
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**WRITTEN OPINION OF THE
INTERNATIONAL SEARCHING AUTHORITY**

International application No.
PCT/GB2010/000804

Box No. I Basis of the opinion

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

Box No. II Priority

1. ☒ The validity of the priority claim has not been considered because the International Searching Authority does not have in its possession a copy of the earlier application whose priority has been claimed or, where required, a translation of that earlier application. This opinion has nevertheless been established on the assumption that the relevant date (Rules 43bis.1 and 64.1) is the claimed priority date.
2. ☐ This opinion has been established as if no priority had been claimed due to the fact that the priority claim has been found invalid (Rules 43bis.1 and 64.1). Thus for the purposes of this opinion, the international filing date indicated above is considered to be the relevant date.
3. Additional observations, if necessary:

**WRITTEN OPINION OF THE
INTERNATIONAL SEARCHING AUTHORITY**

International application No.
PCT/GB2010/000804

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

1. Statement

Novelty (N)	Yes: Claims	<u>1-20</u>
	No: Claims	
Inventive step (IS)	Yes: Claims	
	No: Claims	<u>1-20</u>
Industrial applicability (IA)	Yes: Claims	<u>1-20</u>
	No: Claims	

2. Citations and explanations

see separate sheet

Box No. VIII Certain observations on the international application

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

see separate sheet

Re Item V

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

Reference is made to the following documents:

- D1 US 2001/009890 A1 (PATEL ARVIND D [US] ET AL) 26 July 2001 (2001-07-26)
- D2 EP 1 138 706 A1 (RHEIN CHEMIE RHEINAU GMBH [DE]) 4 October 2001 (2001-10-04)
- D3 US 2004/072696 A1 (PATEL ARVIND D [US]) 15 April 2004 (2004-04-15)

1 Novelty :

- 1.1 Since none of the documents cited in the search report disclose all the features of independent **claim 1**, it is considered that said claim as well as dependent **claims 2-9** are novel over said prior art documents.
- 1.2 Since none of the documents cited in the search report disclose all the features of independent **claim 15**, it is considered that said claim as well as dependent **claims 16-20** are novel over said prior art documents.

2 Inventive step :

- 2.1 **Claim 1** relates to a method for drilling a borehole in a subterranean formation for the recovery of hydrocarbons, comprising the steps of: providing or using an oil-based drilling fluid comprising a carbodiimide; and drilling the borehole in the subterranean formation.
- 2.2 None of the cited document discloses an oil-based fluid, or an ester based invert emulsion, comprising a carbodiimide.
The technical problem solved by this differentiating feature is to improve the effectiveness of ester based invert emulsion (which satisfy many environmental concerns) at high oilfield temperature, by acting as a hydolysis inhibitor.

- 2.3 Hence, it has to be noted that the alledged technical problem is only solved if the oil-based drilling fluid is an ester based invert emulsion.

Therefore, it appears clearly here that the technical effect is not present for the whole claimed area, but only for ester based invert emulsions (dependent claim 3). Furthermore, the examples are only considering ester based invert emulsion, confirming that the technical effect is only shown for this kind of base fluid.

Therefore, if a positive contribution to inventive can be granted, this can only be done is the scope of claim 1 is limited to ester based invert emulsions.

- 2.4 **Document D1** discloses ester based invert emulsions, used as drilling fluids (see claims). In the example, it is shown that the properties are measured up to 250 °F, and are satisfying.

Document D3, disclosing a similar method and drilling fluids, states even (see examples) that this kind of ester based invert emulsions are stable up to 300 °F.

This seems to indicate that a temperature limitation (such as done in present dependent claim 2) is also mandatory in present independent claim 1, in order to have the technical effect present over the whole claimed area.

- 2.5 On the other hand, **document EP 1 138 706 (D2)** discloses a process for the preparation of polycarbodiimide, as well as the use as ester hydrolysis inhibitors.

Hence, the skilled person, starting from D1, and wanting to use such ester based invert emulsion at higher temperature, knows that he will have to inhibit the hydrolysis of said ester (which is highly influenced by the temperature). Since the use of polycarbodiimide as ester hydrolysis inhibitors is known from other chemical field, the skilled person would consider that solution, to improve the method of document D1.

Therefore, the subject-matter of independent **claims 1 or 15** is not considered as being inventive over a combination D1 and D2.

- 2.6 Dependent **claims 2-14 and 16-20** do not appear to contain any additional features which, in combination with the features of any claim to which they refer, meet the requirements of the PCT with respect to inventive step.

Re Item VIII

Certain observations on the international application

- 1 The term "about" used in **claims 2, 10, 19** is vague and unclear and leaves the reader in doubt as to the meaning of the technical features to which it refers, thereby rendering the definition of the subject-matter of said claims unclear.
- 2 **Claim 16** is unclear under Art. 6 PCT. Indeed, said "continuous phase" is continuous, and cannot be an "invert emulsion", as it is stated in said claim.
- 3 In **claim 20**, the wording "wherein the wherein the carbodiimide..." should be corrected, since it is unclear (Art. 6 PC).

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

General information	For all international applications filed on or after 01/01/2004 the competent ISA will establish an ISR. It is accompanied by the WO-ISA. Unlike the former written opinion of the IPEA (Rule 66.2 PCT), the WO-ISA is not meant to be responded to, but to be taken into consideration for further procedural steps. This document explains about the possibilities.
Amending claims under Art. 19 PCT	Within 2 months after the date of mailing of the ISR and the WO-ISA the applicant may file amended claims under Art. 19 PCT directly with the International Bureau of WIPO. The PCT reform of 2004 did not change this procedure. For further information please see Rule 46 PCT as well as form PCT/ISA/220 and the corresponding Notes to form PCT/ISA/220.
Filing a demand for international preliminary examination	In principle, the WO-ISA will be considered as the written opinion of the IPEA. This should, in many cases, make it unnecessary to file a demand for international preliminary examination. If the applicant nevertheless wishes to file a demand this must be done before expiry of 3 months after the date of mailing of the ISR/ WO-ISA or 22 months after priority date, whichever expires later (Rule 54bis PCT). Amendments under Art. 34 PCT can be filed with the IPEA as before, normally at the same time as filing the demand (Rule 66.1 (b) PCT). If a demand for international preliminary examination is filed and no comments/amendments have been received the WO-ISA will be transformed by the IPEA into an IPRP (International Preliminary Report on Patentability) which would merely reflect the content of the WO-ISA. The demand can still be withdrawn (Art. 37 PCT).
Filing informal comments	After receipt of the ISR/WO-ISA the applicant may file informal comments on the WO-ISA directly with the International Bureau of WIPO. These will be communicated to the designated Offices together with the IPRP (International Preliminary Report on Patentability) at 30 months from the priority date. Please also refer to the next box.
End of the international phase	At the end of the international phase the International Bureau of WIPO will transform the WO-ISA or, if a demand was filed, the written opinion of the IPEA into the IPRP, which will then be transmitted together with possible informal comments to the designated Offices. The IPRP replaces the former IPER (international preliminary examination report).
Relevant PCT Rules and more information	Rule 43 PCT, Rule 43bis PCT, Rule 44 PCT, Rule 44bis PCT, PCT Newsletter 12/2003, OJ 11/2003, OJ 12/2003

PATENT COOPERATION TREATY

WO 2010/122302
PCT/GB2010/000804

From the INTERNATIONAL BUREAU

PCTNOTIFICATION CONCERNING
AVAILABILITY OF THE PUBLICATION
OF THE INTERNATIONAL APPLICATION

To:

CURTIS, Philip, Anthony
A A Thornton & Co
235 High Holborn
London WC1V 7LE
ROYAUME-UNI**RECEIVED**

02 NOV 2010

Date of mailing (day/month/year)
28 October 2010 (28.10.2010)Applicant's or agent's file reference
PAC/N/27868 WO

IMPORTANT NOTICE

International application No.
PCT/GB2010/000804International filing date (day/month/year)
22 April 2010 (22.04.2010)Priority date (day/month/year)
24 April 2009 (24.04.2009)

Applicant

HALLIBURTON ENERGY SERVICES, INC. et al

The applicant is hereby notified that the International Bureau:

☒ has published the above-indicated international application on 28 October 2010 (28.10.2010) under
No. WO 2010/122302☐ has republished the above-indicated international application on under
No. WOFor an explanation as to the reason for this republication of the international application, reference is made to INID codes
(15), (48) or (88) (as the case may be) on the front page of the published international application.A copy of the international application is available for viewing and downloading on WIPO's website at the following address:
www.wipo.int/pctdb (in the appropriate field of the structured search, enter the PCT or WO number).The applicant may also obtain a paper copy of the published international application from the International Bureau by sending an e-mail
to patentscope@wipo.int or by submitting a written request to the contact details provided below.**RECORDS
NOTED**The International Bureau of WIPO
54, chemin des Colonibettes
1211 Geneva 20, Switzerland

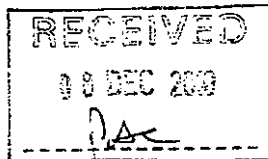
Authorized officer

Dorothee Mülhausen

Facsimile No. +41 22 338 82 70

e-mail: pt01.pct@wipo.int

Form PCT/IB/311 (January 2009)



PATENT COOPERATION TREATY

PCT/GB2010/000804

PCTCOMMUNICATION IN CASES FOR WHICH
NO OTHER FORM IS APPLICABLE**RECEIVED**

From the INTERNATIONAL BUREAU

To:

CURTIS, Philip, Anthony
A A Thomson & Co
235 High Holborn
London WC1V 7LE
ROYAUME-UNI

Date of mailing (day/month/year) 08 December 2010 (08.12.2010)	
Applicant's or agent's file reference PAC/N/27868 WO	REPLY DUE see paragraph 1 below
International application No. PCT/GB2010/000804	International filing date (day/month/year) 22 April 2010 (22.04.2010)
Applicant HALLIBURTON ENERGY SERVICES, INC. et al	

1. ☐ REPLY DUE within months/days from the above date of mailing
☐ NO REPLY DUE, however, see below
☐ IMPORTANT COMMUNICATION
☐ INFORMATION ONLY

2. COMMUNICATION:

It has been brought to the attention of the International Bureau that in respect of the above-identified international application, the inventor's name was wrongly indicated on the publication dated 28 October 2010.

The International Bureau will publish a corrected version of the front page reflecting the correct inventor's name DEVILLE, Jay, Paul on 20 January 2011.

Please be also informed that the correct bibliographic data will be available within 24 hours on the WIPO's Internet site, at
<http://www.wipo.int/patentscope/search/en/search.jsf>

A copy of this Notification is being sent to the receiving Office (RO/GB) and to the designated Offices concerned.

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland	Authorized officer Carrié Christine e-mail pt01.pct@wipo.int Telephone No. +41 22 338 74 01
---	---

Facsimile No. +41 22 338 87 40

Form PCT/IB/345 (July 1992; reprint January 2004)

1/EOTZOYTT10

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

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
3 September 2009 (03.09.2009)

(10) International Publication Number
WO 2009/106987 A1

PCT

(51) International Patent Classification:
C09K 8/035 (2006.01) C09K 8/588 (2006.01)
C09K 8/575 (2006.01) C09K 17/18 (2006.01)

(21) International Application Number:
PCT/IB2009/005037

(22) International Filing Date:
5 February 2009 (05.02.2009)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
61/031,577 26 February 2008 (26.02.2008) US

(71) Applicant (for all designated States except US): M-I
DRILLING FLUIDS UK LIMITED [GB/GB]; John-
stone House, 52-54 Rose Street, Aberdeen, Scotland
AB10 1UD (GB).

(72) Inventor: and

(75) Inventor/Applicant (for US only): BALLARD, David,
Antony [GB/GB]; 6 William Mackie Avenue, Stone-
haven, Kincardineshire, Aberdeenshire, Scotland AB39
2PQ (GB).

(74) Agent: OSHA LIANG; 32 avenue de l' Opéra, 75002
Paris (FR).

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

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

Published:

- with international search report (Art. 21(3))
- before the expiration of the time limit for amending the
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(54) Title: CROSSLINKING AGENTS FOR PRODUCING GELS FOR OILFIELD APPLICATIONS

(57) Abstract: A process for treating an earth formation that includes injecting a gelling agent having at least one active hydrogen into the earthen formation; injecting a polycarbodiimide crosslinking agent into the earthen formation; and allowing the gelling agent and the polycarbodiimide crosslinking agent to form a gel is disclosed.

CROSSLINKING AGENTS FOR PRODUCING GELS FOR OILFIELD APPLICATIONS

BACKGROUND OF INVENTION

Field of the Invention

[0001] Embodiments disclosed herein relate generally to gels for use in downhole oilfield applications. More particularly, embodiments disclosed herein relate to gels and methods for treating a wellbore such as methods of strengthening a wellbore.

Background Art

[0002] It is well known in the petroleum industry that some hydrocarbon-bearing formations are weakly consolidated or, in fact, may be unconsolidated formations. While such formations are known to contain substantial quantities of oil and gas, the production of oil and gas from these formations is difficult because of the movement of particulates such as sand particles and other finely divided particulate solids from the unconsolidated or weakly consolidated formation into the wellbore. This movement is a result of the movement of fluids and may be a result of the differential pressure between the formation and the wellbore created by pumping or by the production of fluids upwardly through the wellbore.

[0003] Some formations are weakly consolidated or unconsolidated initially and others become weakly consolidated as a result of the production of fluids from the formation, especially when water is present in the produced fluid. Formations of this type are formations which are, at least in part, consolidated by the presence of clays in the formation. Such clays can become dispersed and expanded by the production of aqueous fluids from the formation, thereby weakening the overall formation to the point where it becomes unconsolidated or weakly consolidated with the resulting production of particulates into the wellbore. As a result, uncemented, weakly consolidated or unconsolidated formations impose limits on the draw-down pressure which can be used to produce fluids from the formation. This limits the rate at which fluids can be produced from the subterranean formation.

[0004] Further, during drilling of such wells, lost circulation of the drilling fluid is a recurring drilling problem, characterized by loss of drilling mud into downhole formations that are fractured, highly permeable, porous, cavernous, or vugular. These

earth formations can include shale, sands, gravel, shell beds, reef deposits, limestone, dolomite, and chalk, among others. Other problems encountered while drilling and producing oil and gas include stuck pipe, hole collapse, loss of well control, and loss of or decreased production. Induced mud losses may also occur when the mud weight, required for well control and to maintain a stable wellbore, exceeds the fracture resistance of the formations. A particularly challenging situation arises in depleted reservoirs, in which the drop in pore pressure weakens hydrocarbon-bearing rocks, but neighboring or inter-bedded low permeability rocks, such as shales, maintain their pore pressure. This can make the drilling of certain depleted zones impossible because the mud weight required to support the shale exceeds the fracture resistance of the sands and silts.

[0005] In attempting to cure these and other problems, crosslinkable or absorbing polymers, loss control material (LCM) pills, and cement squeezes have been employed. Gels, in particular, have found utility in preventing mud loss, stabilizing and strengthening the wellbore, zone isolation, and water shutoff treatments.

[0006] For example, with respect to zonal isolation, situations may arise during which isolation of certain zones within a formation may be beneficial. Specifically, one method to increase the production of a well is to perforate the well in a number of different locations, either in the same hydrocarbon bearing zone or in different hydrocarbon bearing zones, and thereby increase the flow of hydrocarbons into the well. The problem associated with producing from a well in this manner relates to the control of the flow of fluids from the well and to the management of the reservoir. For example, in a well producing from a number of separate zones (or from laterals in a multilateral well) in which one zone has a higher pressure than another zone, the higher pressure zone may disemboque into the lower pressure zone rather than to the surface. Similarly, in a horizontal well that extends through a single zone, perforations near the "heel" of the well, i.e., nearer the surface, may begin to produce water before those perforations near the "toe" of the well. The production of water near the heel reduces the overall production from the well. Thus, it may be advantageous to also use a cement or gel to isolate one zone from another in managing a hydrocarbon reservoir.

[0007] Further, with respect to water shut-off treatments, some wells generate much more water than anticipated, or in other cases, the rate of water production suddenly increases. One of the primary techniques used to restrict water from entering the well bore includes the injection of gels into the formation that shut off water-bearing channels or fractures within the formation, and prevent water from making its way to the well.

[0008] Thus, there is a continuing need for the development of gels for various downhole applications.

SUMMARY OF INVENTION

[0009] In one aspect, embodiments disclosed herein relate to a process for treating an earth formation that includes injecting a gelling agent having at least one active hydrogen into the earthen formation; injecting a polycarbodiimide crosslinking agent into the earthen formation; and allowing the gelling agent and the polycarbodiimide crosslinking agent to form a gel.

[0010] In another aspect, embodiments disclosed herein relate to a gel that includes the reaction product of a gelling agent and a polycarbodiimide crosslinking agent; wherein the gelling agent comprises at least one of a lignin, a lignosulfonate, a tannin, a tannic acid, a modified lignin, a modified lignosulfonate, a modified tannin, a modified tannic acid, biopolymers, starches, carboxy methyl cellulose, polyacrylates, polyacrylamides, polyamines, alloxylated amines, poly vinyl amines, polyethylene imines, and combinations thereof.

[0011] Other aspects and advantages of the invention will be apparent from the following description and the appended claims.

DETAILED DESCRIPTION

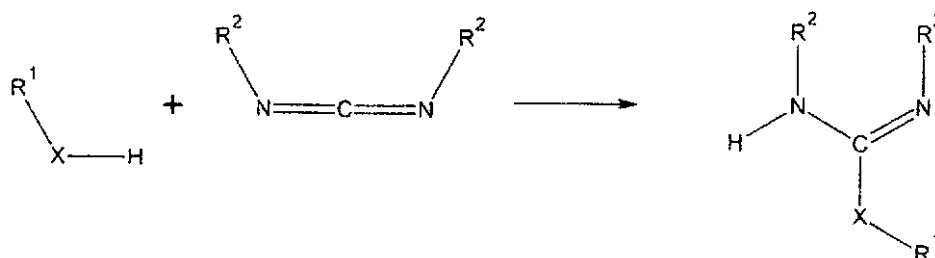
[0012] In one aspect, embodiments disclosed herein relate to gels formed from carbodiimide crosslinking agents. In other aspects, embodiments disclosed herein relate to processes for making such gels, and applications in which the gels disclosed herein may be useful.

[0013] A gel is a colloidal system in which an extended porous network of interconnected molecules spans the volume of a liquid medium. Although gels appear

to be solid, jelly-like materials, by weight, gels are mostly liquid. The gels of the present disclosure may be used in downhole applications as a component of drilling mud and may be preformed and pumped downhole. Alternatively, reactants or components may be introduced simultaneously or sequentially downhole forming the gel *in situ*. For example, the components may be pumped into a wellbore which traverses a loosely consolidated formation, and allowed to cure, thereby forming a polymeric network which stabilizes the formation and the wellbore as a whole.

[0014] The polycarbodiimide crosslinking agent and a gelling agent (the material to be crosslinked) having an active hydrogen functional group may be reacted to form a gel. In some embodiments, the gelling agent may be dissolved in water to form a solution, and a crosslinking agent may be added to the solution, reacting with the gelling agent to form a gel. In other embodiments, the pH of the solution may be adjusted to effect or enhance gel formation.

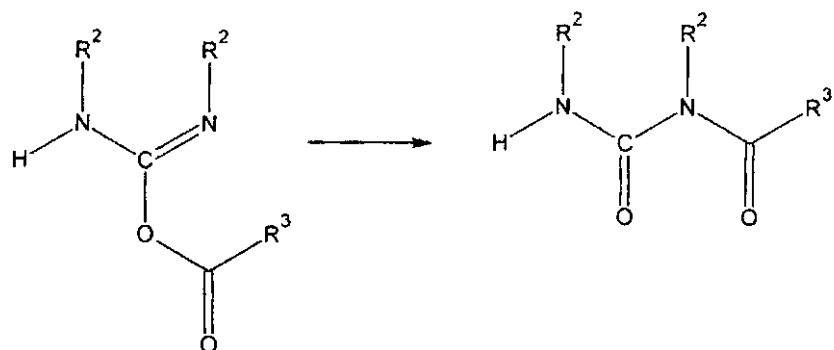
[0015] Thus, the desired gel may be achieved by exposing a gelling agent having at least one active hydrogen functional group and a polycarbodiimide crosslinking agent. A polycarbodiimide crosslinking agent is a molecule containing two or more carbodiimide functional groups, $-N=C=N-$. As known in the art, the term active hydrogen compound refers to a compound that will give up or transfer a hydrogen atom to another substance, such as amine, carboxylic acid, sulfonic acid, phosphoric acid, or hydroxyl groups. The reaction between a carbodiimide and an active hydrogen compound proceeds by the addition of the active hydrogen bond to one of the carbon-nitrogen double bonds as shown below in Eq. 1:



Eq. 1

[0016] However, the type of active hydrogen compound may have some bearing on whether any further reaction occurs. Specifically, for a carboxylic acid reacting with a carbodiimide, upon the addition reaction between the carbodiimide and the

carboxylic acid, the following the addition reaction may result in a less stable O-isoacylurea, which may then rearrange to form a more stable N-acylurea, as shown in Eq. 2 below:



Eq.

2

[0017] Further, one skilled in the art would appreciate that due to the formation of the less stable intermediate, O-isoacylurea, it is possible that such intermediate may react with any available amines or carboxylic acids, for example, to form amides or acid anhydrides, respectively, with urea by products.

[0018] **Polycarbodiimide**

[0019] Thus, as described above, a polycarbodiimide compound is a carbodiimide compound containing at least two carbodiimide groups, i.e. $-\text{N}=\text{C}=\text{N}-$ within the molecule. Such polycarbodiimide compounds may be used alone or two or more of them may be used in combination. Such polycarbodiimide compounds containing two or more carbodiimide groups may be formed by subjecting a polyisocyanate compound (containing at least two isocyanate groups) to decarboxylation in an organic solvent in the presence of a carbodiimide formation catalyst.

[0020] Examples of such polyisocyanates which may be used include aliphatic, alicyclic, aromatic or araliphatic diisocyanate compounds. Aliphatic polyisocyanates may include hexamethylene diisocyanate, trimethylhexamethylene diisocyanate, dimeric acid diisocyanate, lysine diisocyanate and the like, and biuret-type adducts and isocyanurate ring adducts of these polyisocyanates. Alicyclic diisocyanates may include isophorone diisocyanate, 4,4'-methylenebis(cyclohexylisocyanate), methylcyclohexane-2,4- or -2,6-diisocyanate, 1,3- or 1,4-di(isocyanatomethyl)cyclohexane, 1,4-cyclohexane diisocyanate, 1,3-cyclopentane

diisocyanate, 1,2-cyclohexane diisocyanate, and the like, and biuret-type adducts and isocyanurate ring adducts of these polyisocyanate. Aromatic diisocyanate compounds may include xylylene diisocyanate, metaxylylene diisocyanate, tetramethylxylylene diisocyanate, tolylene diisocyanate, 4,4'-diphenylmethane diisocyanate, 1,5-naphthalene diisocyanate, 1,4-naphthalene diisocyanate, 4,4'-toluidine diisocyanate, 4,4'-diphenyl ether diisocyanate, m- or p-phenylene diisocyanate, 4,4'-biphenylene diisocyanate, 3,3'-dimethyl-4,4'-biphenylene diisocyanate, bis(4-isocyanatophenyl)-sulfone, isopropylidenebis (4-phenylisocyanate), and the like, and biuret type adducts and isocyanurate ring adducts of these polyisocyanates. Polyisocyanates having three or more isocyanate groups per molecule may include, for example, triphenylmethane-4,4',4''-triisocyanate, 1,3,5-triisocyanato-benzene, 2,4,6-triisocyanatotoluene, 4,4'-dimethyldiphenylmethane-2,2',5,5'-tetraisocyanate, and the like, biuret type adducts and isocyanurate ring adducts of these polyisocyanates. Additionally, isocyanate compounds used herein may include urethanation adducts formed by reacting hydroxyl groups of polyols such as ethylene glycol, propylene glycol, 1,4-butylene glycol, dimethylolpropionic acid, polyalkylene glycol, trimethylolpropane, hexanetriol, and the like with the polyisocyanate compounds, and biuret type adducts and isocyanurate ring adducts of these polyisocyanates.

[0021] Other isocyanate compounds may include tetramethylene diisocyanate, toluene diisocyanate, hydrogenated diphenylmethane diisocyanate, hydrogenated xylylene diisocyanate, and trimers of these isocyanate compounds; terminal isocyanate group-containing compounds obtained by reacting the above isocyanate compound in an excess amount and a low molecular weight active hydrogen compounds (*e.g.*, ethylene glycol, propylene glycol, trimethylolpropane, glycerol, sorbitol, ethylenediamine, monoethanolamine, diethanolamine, triethanolamine etc.) or high molecular weight active hydrogen compounds such as polyesterpolyols, polyetherpolyols, polyamides and the like may be used in embodiments disclosed herein.

[0022] Other useful polyisocyanates include, but are not limited to 1,2-ethylenediisocyanate, 2,2,4- and 2,4,4-trimethyl-1,6-hexamethylenediisocyanate, 1,12-dodecandiisocyanate, omega, omega-diisocyanatodipropylether, cyclobutan-1,3-diisocyanate, cyclohexan-1,3- and 1,4-diisocyanate, 2,4- and 2,6-diisocyanato-1-

methylcyclohexane, 3-isocyanatomethyl-3,5,5-trimethylcyclohexylisocyanate ("isophoronediiisocyanate"), 2,5- and 3,5-bis-(isocyanatomethyl)-8-methyl-1,4-methano, decahydronaphthathalin, 1,5-, 2,5-, 1,6- and 2,6-bis-(isocyanatomethyl)-4,7-methanohexahydroindan, 1,5-, 2,5-, 1,6- and 2,6-bis-(isocyanato)-4,7-methanohexahydroindan, dicyclohexyl-2,4'- and -4,4'-diisocyanate, omega, omega-diisocyanato-1,4-diethylbenzene, 1,3- and 1,4-phenylenediisocyanate, 4,4'-diisocyanatodiphenyl, 4,4'-diisocyanato-3,3'-dichlorodiphenyl, 4,4'-diisocyanato-3,3'-methoxy-diphenyl, 4,4'-diisocyanato-3,3'-diphenyl-diphenyl, naphthalene-1,5-diisocyanate, N-N'-(4,4'-dimethyl-3,3'-diisocyanatodiphenyl)-uretdion, 2,4,4'-triisocyanatano-diphenylether, 4,4',4''-triisocyanatotriphenylmethant, and tris(4-isocyanatophenyl)-thiophosphate.

[0023] Other suitable polyisocyanates may include: 1,8-octamethylenediisocyanate; 1,11-undecane-methylenediisocyanate; 1,12-dodecamethylenediisocyanate; 1-isocyanato-3-isocyanatomethyl-3,5,5-trimethylcyclohexane; 1-isocyanato-1-methyl-4(3)-isocyanatomethylcyclohexane; 1-isocyanato-2-isocyanatomethylcyclopentane; (4,4'- and/or 2,4'-) diisocyanato-dicyclohexylmethane; bis-(4-isocyanato-3-methylcyclohexyl)-methane; a,a,a',a'-tetramethyl-1,3- and/or -1,4-xylylenediisocyanate; 1,3- and/or 1,4-hexahydroxylylene-diisocyanate; 2,4- and/or 2,6-hexahydroxytoluene-diisocyanate; 2,4- and/or 2,6-toluene-diisocyanate; 4,4'- and/or 2,4'-diphenylmethane-diisocyanate; n-isopropenyl-dimethylbenzyl-isocyanate; any double bond containing isocyanate; and any of their derivatives having urethane-, isocyanurate-, allophanate-, biuret-, uretdione-, and/or iminooxadiazindione groups.

[0024] Polyisocyanates may also include aliphatic compounds such as trimethylene, pentamethylene, 1,2-propylene, 1,2-butylene, 2,3-butylene, 1,3-butylene, ethylidene and butylidene diisocyanates, and substituted aromatic compounds such as dianisidine diisocyanate, 4,4'-diphenylether diisocyanate and chlorodiphenylene diisocyanate.

[0025] Other isocyanate compounds are described in, for example, U.S. Patent Nos. 6,288,176, 5,559,064, 4,637,956, 4,870,141, 4,767,829, 5,108,458, 4,976,833, and 7,157,527, U.S. Patent Application Publication Nos. 20050187314, 20070023288, 20070009750, 20060281854, 20060148391, 20060122357, 20040236021, 20020028932, 20030194635, and 20030004282, each of which is hereby incorporated by reference. Isocyanates formed from polycarbamates are described in, for example,

U.S. Patent No. 5,453,536, hereby incorporated by reference herein. Carbonate isocyanates are described in, for example, U.S. Patent No. 4,746,754, hereby incorporated by reference herein.

[0026] Further, no limitation on the type of polyisocyanate compound from which a polycarbodiimide may be derived is intended to be placed on the gels of the present disclosure. It is also appreciated that one or more polyisocyanates may be used in accordance with some embodiments of the present disclosure.

[0027] Additionally, in the decarboxylation condensation reaction between the one or more polycarbodiimides, it may also be desirable to include a monofunctional water-soluble or dispersible organic compound or component to impart solubility or dispersibility in water to the polycarbodiimide compound being formed, depending on the type of gel desired to be formed (aqueous gel or non-aqueous gel). The compound should be one which has monofunctionality and can react with the terminal isocyanate groups of the polycarbodiimide compound derived from the isocyanate as discussed above to block the terminal groups. Such water-soluble or water-dispersible organic compounds may be any compounds which have one group capable of reacting with an isocyanate group, *e.g.*, a hydroxyl group, carboxylic acid group, amine group or sulfonyl group, and which are soluble or dispersible in water. Thus, for example, such compounds may include monoalkyl esters and monoalkyl ethers of bifunctional, water-soluble or water-dispersible organic compounds having preferably OH groups at terminal ends thereof, *e.g.*, polyethylene glycol, polypropylene glycol and the like, and monofunctional organic compounds having a cationic functional group (*e.g.*, a group containing nitrogen) or an anionic functional group (*e.g.*, a group containing a sulfonyl group). Specific examples may include polyethylene glycol monomethyl ether, polypropylene glycol monomethyl ether, and the like. Alternatively, where hydrophilicity is not desired, one skilled in the art would appreciate that a monoisocyanate may be used at the terminal ends of the carbodiimide, and that such ends may also be blocked with blocking agents, as known in the art.

[0028] Organic solvents which may be used to form such carbodiimides are ones having a high boiling point and having no active hydrogen atom reactive with the isocyanate compound or the carbodiimide group-containing compound formed. Specifically, such solvents may include aromatic hydrocarbons such as toluene,

xylene and diethylbenzene; glycol ether esters such as diethylene glycol diacetate, dipropylene glycol dibutyrate, hexylene glycol diacetate, glycol diacetate, methylglycol acetate, ethylglycol acetate, butylglycol acetate, ethyldiglycol acetate and butyldiglycol acetate; ketones such as ethyl butyl ketone, acetophenone, propiophenone, diisobutyl ketone and cyclohexanone; and aliphatic esters such as amyl acetate, propyl propionate, ethyl butyrate, and the like may be used alone or in combination. Further, examples of carbodiimide formation catalyst may include any known in the art, including phospholenes, phospholene oxides and so forth. U.S. Patent Nos. 5,958,516, 6,124,398, 5,688,875, and 5,360,933 disclose the synthesis and use of various carbodiimides, which are herein incorporated by reference in their entirety. Further, examples of commercially available polycarbodiimides that may be used as crosslinking agents include those sold under the tradename Carbodilite V-Series from Nisshinbo Industries, Inc. (Chiba, Japan).

[0029] Gelling Agents / Materials to be Crosslinked

[0030] For reaction between a gelling agent and a polycarbodiimide crosslinking agent to occur, the gelling agent must contain at least one functional group reactive with a carbodiimide. As discussed above, carbodiimides are reactive with functional groups having an active hydrogen, *i.e.*, a hydrogen available to be given up or transferred to another substance (the carbodiimide), such as amine, carboxylic acid, sulfonic acid, phosphoric acid, or hydroxyl groups. Thus, there is no limit on the type of materials that may be crosslinked with the carbodiimides, so long as they (or a modified version thereof) contain(s) an active hydrogen group reactive with a carbodiimide. It is envisioned that the gelling agents that may be crosslinked with the polycarbodiimide crosslinking agents of the present disclosure may include a wide variety of compounds, including conventional gelling agents, as well as compounds not typically used as gelling agents in downhole application.

[0031] For example, in some embodiments, gelling agents, or the materials to be crosslinked, may include lignins, lignosulfonates, tannins, tannic acids, modified versions thereon (such as to include higher phenol content or active hydrogen content, *e.g.*, amine functional groups, etc.) and combinations thereof. Such types of gelling agents are frequently used in downhole applications; however, they have been conventionally crosslinked with crosslinking agents such as bichromate,

epichlorohydrin, and aldehydes, etc., which are not considered to be environmentally acceptable due to the relatively high toxicity of the crosslinking agents, while more environmentally acceptable crosslinking agent may not provide the desired gel strength.

[0032] In addition to conventional lignitic or tannic based gelling agent, other gelling agents suitable for use in the present disclosure may include biopolymers including starches, celluloses, chitin, alginates or other gums, etc., and synthetic polymers such as polyacrylates, polyacrylamides, polyols, polyamines, polyesters, polyurethanes, polyvinylalcohols, combinations thereof, and copolymers thereof, etc.

[0033] Suitable starches may include natural starches, chemically modified starches, and mixtures of one or more natural and/or chemically modified starches. Natural starches may include those of potato, wheat, tapioca, rice, corn, and roots having a high starch content, among others. Chemically modified starches may include carboxymethyl starch, hydroxyethyl starch, hydroxypropyl starch, acetate starch, sulfamate starch, phosphate-modified starch, nitrogen-modified starch, and dextrin, among others. Suitable cellulosic materials may include cellulose or derivatives thereof including hydroxyethyl cellulose, carboxymethyl cellulose, hydroxypropyl methyl cellulose, etc.

[0034] Further, suitable synthetic polymers include, for example, polyacrylates, polyacrylamides, polyols, polyamines, polyesters, polyurethanes, polyvinylalcohols, etc.

[0035] Aliphatic polyols useful in preparing polyurethane gels may have a molecular weight of 62 up to 2000 and include, for example, monomeric and polymeric polyols having two or more hydroxyl groups. Examples of the monomeric polyols include ethylene glycol, propylene glycol, butylene glycol, hexamethylene glycol, cyclohexamethylenediol, 1,1,1-trimethylolpropane, pentaerythritol, and the like. Examples of polymeric polyols include the polyoxyalkylene polyols (i.e., the diols, triols, and tetrols), the polyester diols, triols, and tetrols of organic dicarboxylic acids and polyhydric alcohols, and the polylactone diols, triols, and tetrols having a molecular weight of 106 to about 2000. Other examples of suitable polyols include: glycerine monoalkanoates (e.g., glycerine monostearates); dimer fatty alcohols; diethylene glycol; triethylene glycol; tetraethylene glycol; 1,4-

dimethylolcyclohexane; dodecanediol; bisphenol-A; hydrogenated bisphenol A; 1,3-hexanediol; 1,3-octanediol; 1,3-decanediol; 3-methyl-1,5-pentanediol; 3,3-dimethyl-1,2-butanediol; 2-methyl-1,3-pentanediol; 2-methyl-2,4-pentanediol; 3-hydroxymethyl-4-heptanol; 2-hydroxymethyl-2,3-dimethyl-1-pentanol; glycerine; trimethylol ethane; trimethylol propane; trimerized fatty alcohols; isomeric hexanetriols; sorbitol; pentaerythritol; di- and/or tri-methylolpropane; di-pentaerythritol; diglycerine; 2,3-butanediol; trimethylol propane monoallylether; fumaric and/or maleinic acid containing polyesters; 4,8-bis-(hydroxymethyl)-tricyclo[5,2,0(2,6)]-decane long chain alcohols. Suitable hydroxy-functional esters may be prepared by the addition of the above-mentioned polyols with epsilon-caprolactone or reacted in a condensation reaction with an aromatic or aliphatic diacid. These polyols may be reacted with any of the isocyanates described above. Further, in addition to such polyols, one skill in the art would appreciate that polyurethane prepolymers formed from isocyanates and polyols may also be reacted with the polycarbodiimide crosslinking agents to form a gel in accordance with the present disclosure.

[0036] Aliphatic polyamines useful in preparing polyureas may have a molecular weight of 60 to 2000 and include monomeric and polymeric primary and secondary aliphatic amines having at least two amino groups. Examples include alkylene diamines such as ethylene diamine; 1,2-diaminopropane; 1,3-diaminopropane; 2,5-diamino-2,5-dimethylhexane; 1,11-diaminoundecane; 1,12-diaminododecane; piperazine, as well as other aliphatic polyamines such as polyethylenimines (PEI), which are ethylenediamine polymers and are commercially available under the trade name Lupasol® from BASF (Germany). PEIs may vary in degree of branching and therefore may vary in degree of crosslinking. LUPASOL® PEIs may be small molecular weight constructs such as LUPASOL® FG with an average molecular weight of 800 or large molecular weight constructs such as LUPASOL® SK with average molecular weight of 2,000,000. Cycloaliphatic diamines suitable for use may include those such as isophoronediamine; ethylenediamine; 1,2-propylenediamine; 1,3-propylenediamine; N-methyl-propylene-1,3-diamine; 1,6-hexamethylenediamine; 1,4-diaminocyclohexane; 1,3-diaminocyclohexane; N,N'-dimethylethylenediamine; and 4,4'-dicyclohexyl-methanediamine for example, in addition to aromatic diamines,

such as 2,4-diaminotoluene; 2,6-diaminotoluene; 3,5-diethyl-2,4-diaminotoluene; and 3,5-diethyl-2,6-diaminotoluene for example; and primary, mono-, di-, tri- or tetraalkyl-substituted 4,4'-diamino-diphenylmethanes. Additionally, while many diamines are listed above, one of ordinary skill in the art would appreciate that tri- and tetraamines may also be used in other embodiments of the present disclosure.

[0037] In yet another embodiment the aliphatic amine may be a polyetheramine such as those commercially available under the trade name JEFFAMINE® Huntsman Performance Products (Woodlands, TX). For example, useful JEFFAMINE® products may include triamines JEFFAMINE® T-5000 and JEFFAMINE® T-3000 or diamines such as JEFFAMINE® D-400 and JEFFAMINE® D-2000. Useful polyetheramines may possess a repeating polyether backbone and may vary in molecular weight from about 200 to about 5000 g/mol. In addition, hydrazino compounds such as adipic dihydrazide or ethylene dihydrazine may be used, as may also, alkanolamines such as ethanolamine, diethanolamine, and tris(hydroxyethyl)ethylenediamine. Further, in another embodiment, the polyamine may be a polyethylenimine (PEI), which are ethylenediamine polymers and are commercially available under the trade name Lupasol® from BASF (Germany). PEIs may vary in degree of branching and therefore may vary in degree of crosslinking.

[0038] Further, various carboxylate containing polymers may include such as polymers as polyacrylates (formed from monomers such as acrylic acid, itaconic acid, maleic acid, fumaric acid, and crotonic acid or an anhydride thereof with an acrylic ester such as methyl acrylate, ethyl acrylate, butyl acrylate, 2-ethylhexyl acrylate, and 2-hydroxyethyl acrylate, methyl methacrylate, and TMPTA with a non-acrylic acid comonomer such as acrylamide and acrylonitrile, and optionally α -methylstyrene, vinyl acetate or the like), polyesters (formed by a monoesterification reaction between glycol or polyester glycol terminated with a hydroxyl group and tetracarboxylic acid dianhydride to thereby extend the chain), polyaspartates (which also contain amides), and polyacetates, amide containing polymers such as polyacrylamide, in addition to other polymers containing suitable functional groups, such as hydroxyl, amine, sulfonic acid, carboxylic acid groups, etc.

[0039] Additionally, such list is not intended to be exhaustive. Rather, any variation on the type of gelling agent may be expected depending on the type of gel desired.

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One skilled in the art would appreciate that depending on the type of gel desired, suitable monomers may be selected to have impart the desired hydrophobicity or hydrophilicity to the polymer. Thus, where an aliphatic base fluid is used, one may select a longer chain compound such as a long chain ester of acrylic or methacrylic acid, a vinyl ester of a long chain acid, a vinyl alkyl ether, ethylene, propylene, butadiene or isoprene, a hydroxyl group-containing long chain fatty acid, poly-t-butyl styrene terminated with amine, hydroxyl, carboxyl or unsaturated groups, or polyisobutylene, polybutadiene or polyisoprene terminated with amine, hydroxyl or carboxyl groups. Where the base fluid includes aromatic hydrocarbons, somewhat shorter chain analogs of these polymers may be employed, such as polymers of methyl or ethoxyethyl methacrylate, ethyl acrylate, styrene or vinyl toluene. Where the base fluid is weakly polar, *e.g.*, a higher alcohol, ketone or ester, suitable solvatable components include aliphatic polyethers, polycesters from short-chain difunctional acids and alcohols, short-chain alcohol esters of acrylic or methacrylic acids, and polymers of short-chain hydroxy-acids. If a strongly polar base fluid is used, such as methanol, ethanol, glycols, the polymer may include polymers of acrylic or methacrylic acids, ethylene oxide or vinyl pyrrolidone, polyvinyl alcohol or polymers of glycerol or glycol monomethacrylates. Further, if an aqueous base fluid is used, a synthetic polymer may be formed from comonomers possessing functional groups such as hydroxyl, cishydroxyl, carboxyl, sulfate, sulfonate, amino or amide. Further, one skilled in the art would appreciate that such monomers may be combined with comonomers including, for example, vinyl phosphonic acid, vinyl phosphoric acid, vinyl sulfonic acid, vinyl sulfuric acid, vinyl arsonic acid, vinyl arsenic acid, vinyl selenonic acid, vinyl selenic acid, vinyl benzoic acid, acrylic acid, or derivatives thereof, including salts and esters (mono or bis) derivatives thereof and styrene derivatives thereof, so that desired crosslinking with carbodiimides may occur.

[0040] In yet other embodiments, combinations of any of the above listed materials to be crosslinked may be used. Further, one skilled in the art would appreciate that depending the gelling agent selected, it may be necessary to adjust the pH so that the crosslinking reaction between the gelling agent and the crosslinking agent may be enabled or enhanced by effecting the active hydrogen functional groups. Adjustment of pH may be achieved using typical agents known in the art.

[0041] Crosslinking Conditions

[0042] When combining the gelling agents with the polycarbodiimide crosslinking agents, the crosslinking agent may be present in an amount effective to crosslink the gelling agent. In some embodiments, the crosslinking agent may be used in an amount ranging from about 0.05 to about 50 weight percent based on the total weight of the gelling agent(s). In other embodiments, the crosslinking agent may be used in an amount ranging from about 5 to about 40 weight percent based on the total weight of the gelling agent(s); from about 10 to about 35 weight percent in yet other embodiments. In other embodiments, a weight ratio of the crosslinking agent to the gelling agent may be from 1:2000 to 1:1; from 1:20 to 1:2 in other embodiments, and from 1:10 to about 1:3 in yet other embodiments.

[0043] The amount of crosslinking agent may affect the hardness of the resulting gel. For example, in some embodiments, for a constant weight of gelling agent, increasing the amount of crosslinking agent may result in a higher crosslinking density, and therefore a harder gel. Using the guidelines provided herein, those skilled in the art will be capable of determining a suitable amount of cross-linking agent to employ to achieve a gel of the desired hardness.

[0044] Aging Temperature

[0045] In some embodiments, the gelling agent and the crosslinking agent may be reacted at a temperature from -50 to 300°C. In other embodiments, the gelling agent and the crosslinking agent may be reacted at a temperature from 25 to 250°C; from 50 to 150°C in other embodiments; and from 60 to 100°C in yet other embodiments. In certain embodiments, the reaction temperature determines the amount of time required for gel formation.

[0046] Time Required for Gel Formation

[0047] Embodiments of the gels disclosed herein may be formed by mixing a gelling agent with a crosslinking agent. In some embodiments, a gel may form immediately upon mixing the gelling agent and the crosslinking agent. In other embodiments, a gel may form within 1 minute of mixing; within 5 minutes of mixing in other embodiments; within 30 minutes of mixing in other embodiments. In some embodiments, a gel may form within 1 hour of mixing; within 8 hours in other embodiments; within 16 hours in other embodiments; within 80 hours in other embodiments; within 120 hours in yet other embodiments.

[0048] pH

[0049] In some embodiments, the gelling agent and the crosslinking agent may be reacted in a medium having a pH greater than 4. In other embodiments, the gelling agent and the crosslinking agent may be reacted in a medium having a pH greater than 6; a pH greater than 7 in other embodiments; a pH greater than 8 in other embodiments; a pH greater than 9 in yet other embodiments.

[0050] Reagents which may be used to adjust the pH may include alkali metal hydroxides, such as sodium hydroxide, potassium hydroxide, calcium hydroxide, and rubidium hydroxide, lithium hydroxides, benzyltrimethylammonium hydroxides, and the partially neutralized salts of organic acids, such as tri-sodium ethylenediaminetetraacetic acid. In some embodiments, the alkali metal hydroxide, pH adjusting agent, or buffer, may act as a catalyst, effecting or enhancing the crosslinking reaction between the gelling agent and the crosslinking agent.

[0051] Water Concentration

[0052] In some embodiments, a solution of gelling agent(s) and crosslinking agent(s) in water may initially have a viscosity similar to that of water. A water-like viscosity may allow the solution to effectively penetrate voids, small pores, and crevices, such as encountered in fine sands, coarse silts, and other formations. In other embodiments, the viscosity may be varied to obtain a desired degree of flow sufficient for decreasing the flow of water through or increasing the load-bearing capacity of a formation. The viscosity of the solution may be varied by increasing or decreasing the amount of water relative to the crosslinking and gelling agents, by employing viscosifying agents, or by other techniques common in the art.

[0053] In some embodiments, the combined amount of gelling agents and crosslinking agents may range from 0.5 to 100 weight percent, based upon the total weight of water in the solution. In other embodiments, the combined amount of gelling agents and crosslinking agents may range from 5 to 100 weight percent, based upon the total weight of water in the solution; from 20 to 70 weight percent in other embodiments; from 25 to 65 weight percent in yet other embodiments. As used herein, total weight of water is exclusive of any additional water added with pH adjusting reagents.

[0054] The gelling agent and the crosslinking agent may react to form gel beads. For example, in some embodiments, bead formation may be effected by agitation of the

solution. In other embodiments, bead formation may be effected by forming an emulsion or suspension of the reactants in water. In certain embodiments, an emulsion or suspension may be formed using an organic solvent, emulsifying agents, or combinations thereof.

[0055] Hardness

[0056] The reaction of the gelling agent and the crosslinking agent may produce gels having a consistency ranging from a viscous sludge to a hard gel. In some embodiments, the reaction of the gelling agent and the crosslinking agent may result in a soft elastic gel. In other embodiments, the reaction may result in a good gel; in a hard gel in yet other embodiments. The hardness of the gel is the force necessary to break the gel structure, which may be quantified by measuring the force required for a needle to penetrate the crosslinked structure. Hardness is a measure of the ability of the gel to resist to an established degree the penetration of a weighted test needle.

[0057] Hardness may be measured by using a Brookfield QTS-25 Texture Analysis Instrument. This instrument consists of a probe of changeable design that is connected to a load cell. The probe may be driven into a test sample at specific speeds or loads to measure the following parameters or properties of a sample: springiness, adhesiveness, curing, breaking strength, fracturability, peel strength, hardness, cohesiveness, relaxation, recovery, tensile strength burst point, and spreadability. The hardness may be measured by driving a 2.5mm diameter, cylindrical, flat faced probe into the gel sample at a constant speed of 30 mm per minute. When the probe is in contact with the gel, a force is applied to the probe due to the resistance of the gel structure until it fails, which is recorded via the load cell and computer software. As the probe travels through the sample, the force on the probe and the depth of penetration are measured. The force on the probe may be recorded at various depths of penetration, such as 20, 25, and 30mm, providing an indication of the gel's overall hardness.

[0058] In some embodiments, the resulting gel may have a hardness value from 10 to 100000 gram-force. In other embodiments, the resulting gel may be a soft elastic gel having a hardness value in the range from 10 to 100 gram-force. In other embodiments, the resulting gel may be a firm gel having a hardness value from 100 to 500 gram-force. In other embodiments, the resulting gel may range from hard to tough, having a hardness value from 500 to 100000 gram-force; from 1500 to 75000

gram-force in other embodiments; from 2500 to 50000 gram-force in yet other embodiments; from 5000 to 30000 gram-force in yet other embodiments.

[0059] In other embodiments, the hardness of the gel may vary with the depth of penetration. For example, the gel may have a hardness of 1500 gram-force or greater at a penetration depth of 20 mm in some embodiments. In other embodiments, the gel may have a hardness of 5000 gram-force or greater at a penetration depth of 20 mm; 15,000 gram-force or greater at a penetration depth of 20 mm in other embodiments; and 25000 gram-force or greater at a penetration depth of 25 mm in yet other embodiments.

[0060] With respect to the variables listed above (i.e. temperature, time, etc.), those having ordinary skill in light of the disclosure will appreciate that, by using the present disclosure as a guide, properties may be tailored as desired.

[0061] Applications

[0062] Some embodiments of the gels disclosed herein may be formed in a one-solution single component system, where the crosslinking agent(s) are premixed with the gelling agent (material to be crosslinked). The gel may then be placed or injected prior to cure. The gel times may be adjusted by changing the quantity of water (or other solvent) in the solution. Other embodiments of the gels disclosed herein may also be formed in a two-component system, where the crosslinking and gelling agents may be mixed separately and combined immediately prior to injection. Alternatively, one reagent, the crosslinking or gelling agent, may be placed in the wellbore or the near-wellbore region where it may then be contacted by the other reagent, either the crosslinking or gelling agent as required.

[0063] Embodiments of the gels disclosed herein may be used in applications including: as an additive in drilling muds; as an additive for enhancing oil recovery (EOR); as one additive in loss circulation material (LCM) pills; wellbore (WB) strengthening treatments; soil stabilization; as a dust suppressant; as a water retainer or a soil conditioner; as hydrotreating (HT) fluid loss additives, and others.

[0064] Use in Drilling Muds

[0065] Drilling fluids or muds typically include a base fluid (for example water, diesel or mineral oil, or a synthetic compound), weighting agents (for example, barium sulfate or barite may be used), bentonite clay, and various additives that

serve specific functions, such as polymers, corrosion inhibitors, emulsifiers, and lubricants. Those having ordinary skill in the art will recognize that a number of different muds exist, and limitations on the present invention is not intended by reference to particular types. During drilling, the mud is injected through the center of the drill string to the drill bit and exits in the annulus between the drill string and the wellbore, fulfilling, in this manner, the cooling and lubrication of the bit, casing of the well, and transporting the drill cuttings to the surface.

[0066] The gels disclosed herein may be used as an additive in drilling mud. In some embodiments, the gels may form a filter cake or one component of a filter cake that forms along the wellbore as drilling progresses. The gels contained in the drilling fluid may be deposited along the wellbore throughout the drilling process, potentially strengthening the wellbore by stabilizing shale formations and other sections encountered while drilling. Improved wellbore stability may reduce the occurrence of stuck pipe, hole collapse, hole enlargement, lost circulation, and may improve well control.

[0067] Wellbore stability may also be enhanced by the injection of a low viscosity mixture of a gelling agent and a crosslinking agent into formations along the wellbore. The mixture may then continue to react, strengthening the formation along the wellbore upon gelation of the mixture.

[0068] In other embodiments, the gels disclosed herein may aid in lifting solid debris from tubing walls and through the tubing annulus. Hard gels circulating through the drill pipe during drilling may scrape and clean the drill pipe, removing any pipe scale, mud, clay, or other agglomerations that may have adhered to the drill pipe or drill tubing. In this manner, the drill pipe may be maintained free of obstructions that could otherwise hinder removal of drilled solids from the drill pipe during drilling.

[0069] Enhanced Oil Recovery

[0070] Embodiments of the gels disclosed herein may be used to enhance secondary oil recovery efforts. In secondary oil recovery, it is common to use an injection well to inject a treatment fluid, such as water or brine, downhole into an oil-producing formation to force oil toward a production well. Thief zones and other permeable strata may allow a high percentage of the injected fluid to pass through only a small percentage of the volume of the reservoir, for example, and may thus require an

excessive amount of treatment fluid to displace a high percentage of crude oil from a reservoir.

[0071] To combat the thief zones or high permeability zones of a formation, embodiments of the gels disclosed herein may be injected into the formation. Gels injected into the formation may partially or wholly restrict flow through the highly conductive zones. In this manner, the gels may effectively reduce channeling routes through the formation, forcing the treating fluid through less porous zones, and potentially decreasing the quantity of treating fluid required and increasing the oil recovery from the reservoir.

[0072] In other embodiments, gels may also be formed in situ within the formation to combat the thief zones. Gelling agents may be injected into the formation, allowing the gelling agents to penetrate further into the formation than if a gel was injected. The crosslinking agents may then be injected, causing the previously injected gelling agents to crosslink within the formation. By forming the gels in situ in the formation, it may be possible to avert channeling that may have otherwise occurred further into the formation, such as where the treatment fluid traverses back to the thief zone soon after bypassing the injected gels as described above.

[0073] LCM Pills

[0074] As mentioned above, gels disclosed herein may be used as one component in a drilling fluid. The gels may form part of a filter cake, minimizing seepage of drilling fluids to underground formations and lining the wellbore. As another example, embodiments of the gels disclosed herein may be used as one component in loss circulation material (LCM) pills that are used when excessive seepage or circulation loss problems are encountered, requiring a higher concentration of loss circulation additives. LCM pills are used to prevent or decrease loss of drilling fluids to porous underground formations encountered while drilling.

[0075] In some embodiments, the crosslinking agent and gelling agent / material may be mixed prior to injection of the pill into the drilled formation. The mixture may be injected while maintaining a low viscosity, prior to gel formation, such that the gel may be formed downhole. In other embodiments, the gelling material and crosslinking agent may be injected into the formation in separate shots, mixing and reacting to form a gel in situ (in the formation following injection of the LCM pill shots). In this manner, premature gel formation may be avoided.

- [0076] For example, a first mixture containing a gelling agent may be injected into the wellbore and into the lost circulation zone. A second mixture containing a crosslinking agent and/or pH modifier may be injected, causing the gelling agent to crosslink in situ to the point that the gel expands in size. The expanded and hardened gel may plug fissures and thief zones, closing off the lost circulation zone.
- [0077] Soil Stabilization
- [0078] Gels described herein may be used as one component of a soil stabilizer. For example, lignosulfonates may be used for stabilizing road base courses and the like. Pulverized soil may be mixed and worked with the stabilizing composition in a single or multiple layer, compacting each layer as it is laid down. The compaction may be by any suitable method such as rubber-tired rollers or sheepfoot rollers. The amount of stabilizing composition used depends on the type of soil, moisture content and other factors. The exact amount of stabilizing composition and the amount of water dilution vary with soil type, moisture content and other factors.
- [0079] Dust Suppressant
- [0080] Gels described herein may also be utilized for dust control, dust suppression, dust palliative treatment, road stabilization and many other dust binding applications. The lignin molecule functions by adsorbing on the substrate and the binding effect results from intermolecular forces between the lignin molecule and the substrate. The lignin molecule is unique as it has several different polar groups and aromatic systems. This increases the affinity of the molecule which results in improved adhesion, and makes it suitable for a wide range of substrates.
- [0081] The binding property of lignin-based products may be utilized in many types of dust control and dust prevention, such as dust-suppression in roads, parking lots, racing tracks, quarries, paddocks, and construction sites, dust-palliative or dust prevention treatment of public and private roads, road and soil-stabilization of secondary roads and areas, sand dune and earth stabilization on areas to be kept free from dust and wind erosion, and others.
- [0082] For example, to prevent the loss of road surface fines and prolong the useful driving life of unpaved roads, dust control measures are usually employed before maintenance is required. The primary dust suppressants in use are: water (fresh and sea), chloride compounds, lignin derivatives, and resinous adhesives. When used as dust suppressant, the lignin polymers act as glue binding the soil particles together.

[0083] Gels disclosed herein may be used in other processes, including the aforementioned applications such as water retainers, soil conditioners, and hydrotreating (HT) fluid loss additives. It is further contemplated that gels described herein may be useful in other processes and applications known to those skilled in the art.

[0084] Advantageously, embodiments disclosed herein provide for the formation of a gel formed using low or non-toxic crosslinking agents. These gels have the benefit of being formed from materials that provide a better health, safety, and environmental profile as compared dichromates, aldehydes, and epichlorohydrins. The crosslinking agents disclosed herein may also provide a low-cost alternative for the formation of desired gels. Embodiments of the gels disclosed herein may form a soft elastic gel. Other embodiments of the gels disclosed herein may form a hard gel.

[0085] While the invention has been described with respect to a limited number of embodiments, those skilled in the art, having benefit of this disclosure, will appreciate that other embodiments can be devised which do not depart from the scope of the invention as disclosed herein. Accordingly, the scope of the invention should be limited only by the attached claims.

CLAIMS

What is claimed:

1. A process for treating an earth formation, comprising:
injecting a gelling agent having at least one active hydrogen into the earthen formation;
injecting a polycarbodiimide crosslinking agent into the earthen formation; and
allowing the gelling agent and the polycarbodiimide crosslinking agent to form a gel.
2. The process of claim 1, wherein the gelling agent and the crosslinking agent are injected simultaneously.
3. The process of claim 1, wherein the gelling agent and the crosslinking agent are injected sequentially.
4. The process of claim 1, wherein the polycarbodiimide is formed from the decarbonation of at least one diisocyanate.
5. The process of claim 1, wherein the gelling agent comprises at least one of a lignin, lignosulfonate, tannin, modified versions thereof, or combinations thereof.
6. The process of claim 1, wherein the gelling agent comprises at least one biopolymer selected from a starch, a cellulosic material, modified versions thereof, and combinations thereof.
7. The process of claim 1, wherein the gelling agent comprises at least one synthetic polymer selected from polyacrylates, polyacrylamides, polyols, polyamines, polyesters, polyurethanes, polyvinylalcohols, combinations thereof, and copolymers thereof.
8. The process of claim 1, wherein a weight ratio of the crosslinking agent to the gelling agent ranges from about 1:20 to about 1:2.
9. A gel comprising:
the reaction product of a gelling agent and a polycarbodiimide crosslinking agent;

- wherein the gelling agent comprises at least one of a lignin, a lignosulfonate, a tannin, a tannic acid, a modified lignin, a modified lignosulfonate, a modified tannin, a modified tannic acid, biopolymers, starches, carboxy methyl cellulose, polyacrylates, polyacrylamides, polyamines, alloxylated amines, poly vinyl amines, polyethylene imines, and combinations thereof.
10. The gel of claim 9, wherein the polycarbodiimide is formed from the decarbonation of at least one diisocyanate.
 11. The gel of claim 9, wherein the gelling agent comprises at least one of a lignin, lignosulfonate, tannin, modified versions thereof, or combinations thereof.
 12. The gel of claim 9, wherein the gelling agent comprises at least one biopolymer selected from a starch, a cellulosic material, modified versions thereof, and combinations thereof.
 13. The gel of claim 9, wherein the gelling agent comprises at least one synthetic polymer selected from polyacrylates, polyacrylamides, polyols, polyamines, polyesters, polyurethanes, polyvinylalcohols, combinations thereof, and copolymers thereof.
 14. The gel of claim 9, wherein a weight ratio of the crosslinking agent to the gelling agent ranges from about 1:20 to about 1:2.
 15. The gel of claim 9, wherein the reaction product is formed at a temperature between 25°C and 350°C.
 16. The gel of claim 9, wherein the gel has a hardness of 1500 gram-force or greater at a penetration depth of 20 mm.
 17. The gel of claim 9, wherein the gel has a hardness of 5000 gram-force or greater at a penetration depth of 20 mm.
 18. The gel of claim 9, wherein the gel has a hardness of 15,000 gram-force or greater at a penetration depth of 20 mm.
 19. The gel of claim 9, wherein the gel has a hardness of 25,000 gram-force or greater at a penetration depth of 25 mm.

20. Use of the gel of claim 9 in a drilling fluid, in a loss circulation material pill, in wellbore strengthening, in zonal isolation, as a soil stabilizing agent, as a dust suppressant, or as a heat transfer fluid loss additive.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/IB2009/005037

A. CLASSIFICATION OF SUBJECT MATTER

INV. C09K8/035 C09K8/575 C09K8/588 C09K17/18

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C09K E21B

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 2007/039732 A1 (DAWSON JEFFREY C [US] ET AL) 22 February 2007 (2007-02-22) paragraphs [0001], [0053], [0058]; claims 1,26,36,38	1-13, 15-20
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☒ 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

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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.

G document member of the same patent family

Date of the actual completion of the international search

1 July 2009

Date of mailing of the international search report

20/07/2009

Name and mailing address of the ISA/

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Authorized officer

Redecker, Michael

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2009/005037

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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INTERNATIONAL SEARCH REPORT

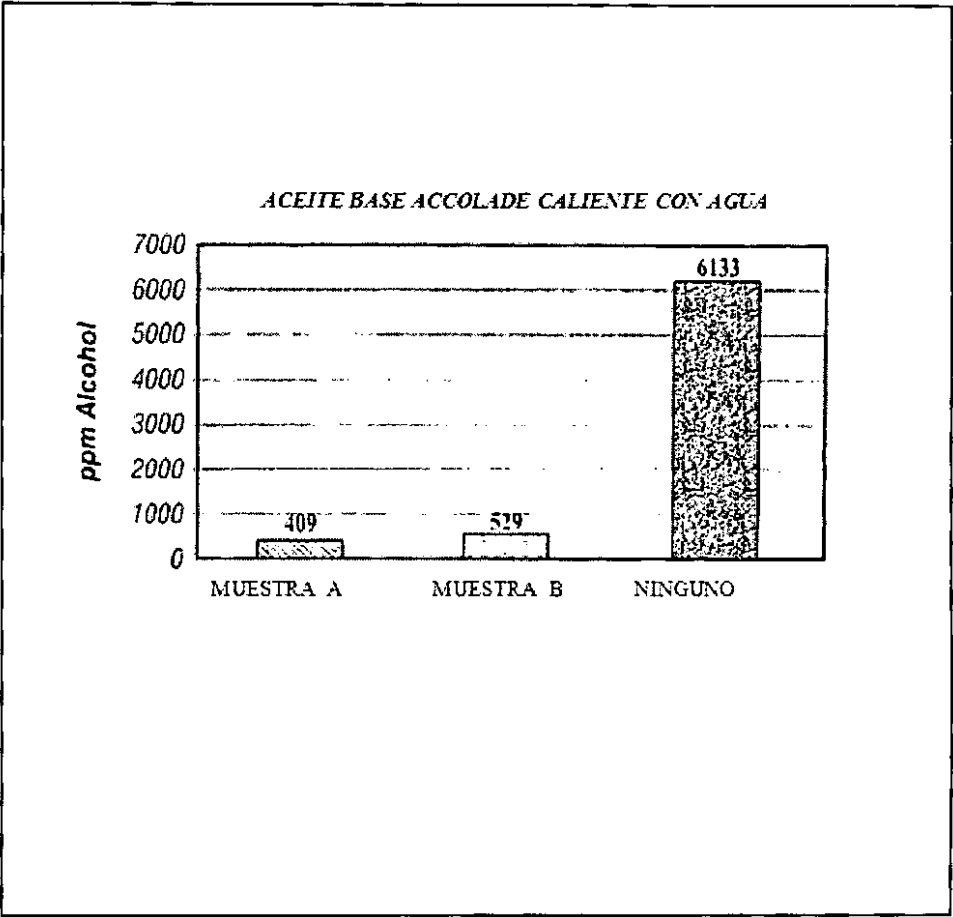
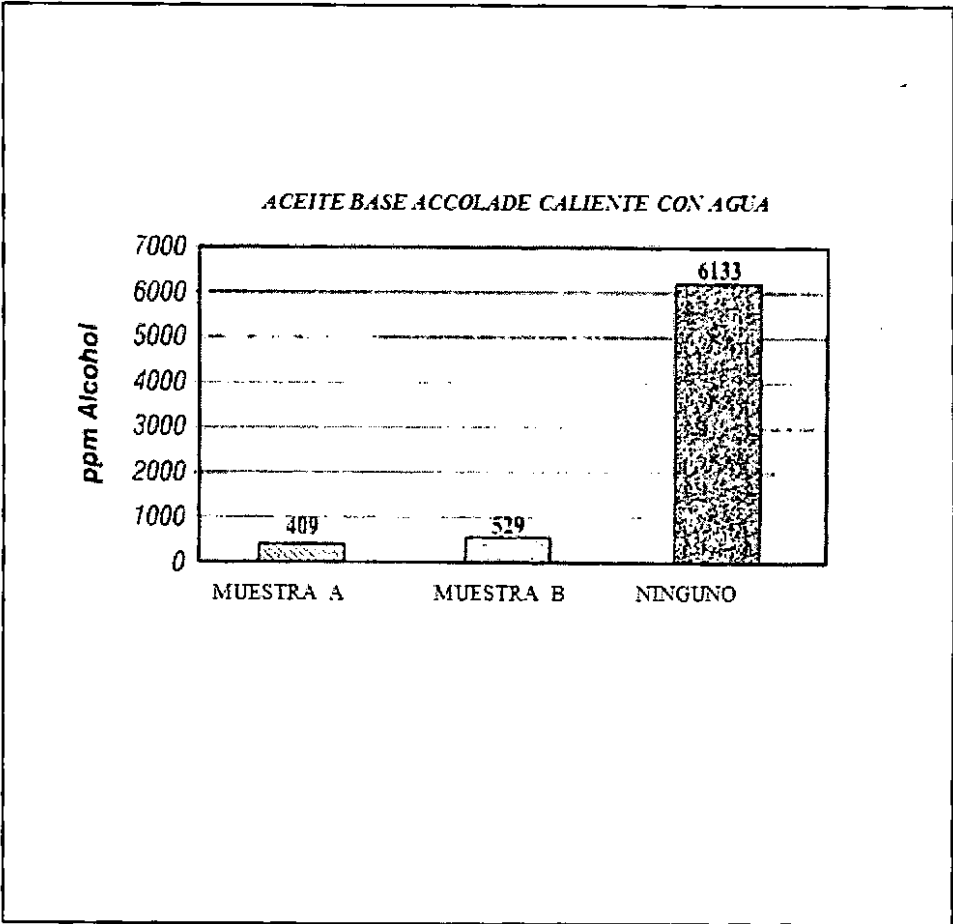
Information on patent family members

International application No

PCT/182009/005037

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ARTES 12 X 12





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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)
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DISEÑO INDUSTRIAL ☐

(Art. 119 Decisión 486/00)

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☐	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
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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 ☐