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Trámite : DE PATENTES B

Dependencia: 2020 División de Nuevas Creaciones

SUPERINTENDENCIA Y COMERCIO

Folios: 2

Señor

**SUPERINTENDENTE DE INDUSTRIA Y COMERCIO
DIVISION DE NUEVAS CREACIONES**

E. S. D.

REF: Expediente No.: 01-062.411

Patente de invención: "PERFORACIÓN DE POZOS Y FLUIDOS DE SERVICIO; Y MÉTODOS DE REMOCIÓN DE AGLUTINANTES EN FILTROS DEPOSITADOS EN ESTOS"

Titular: HALLIBURTON ENERGY SERVICES, INC.

Publicada en la Gaceta de la Propiedad Industrial No. 521 de 30 de Octubre de 2002

SOLICITUD DE EXAMEN DE PATENTABILIDAD

HUMBERTO RUBIO CAMACHO, mayor de edad, domiciliado en Bogotá, D.C., identificado con la cédula de ciudadanía número 17.192.062 de Bogotá, abogado Titulado con Tarjeta Profesional No. 50.007 del Consejo Superior de la Judicatura, actuando en carácter de APODERADO de la Sociedad HALLIBURTON ENERGY SERVICES, INC.; domiciliada en Duncan, Oklahoma, Estados Unidos de América; respetuosamente solicito a esa Dependencia:

- 1.- De conformidad con lo establecido en el Artículo 44 de la Decisión 486 de la Comisión de la Comunidad Andina y estando dentro del término legal de seis meses contados desde la fecha de publicación en la Gaceta No. 521 de 30 de Octubre de 2002, de la solicitud de la patente de la referencia, solicito se sirvan proceder a efectuar el examen de patentabilidad de la invención.
- 2.- Para que la presente petición sea viable, estoy anexando el siguiente documento:
 - 2.1. Recibo de pago No. 03 - 16,988 de 10 de Marzo de 2003 por la suma de \$ 335.000.00, de acuerdo con la Resolución No. 41687 de 24 de Diciembre de 2002
- 3.- Por lo anterior solicito se continúe con el trámite correspondiente.

Del Señor Superintendente,

HUMBERTO RUBIO CAMACHO
C.C. 17.192.062 de Bogotá
T.P. 50.007 Consejo Superior
de la Judicatura.
COD. 4134

01/448-05/PI

SUPERINTENDENCIA Y COMERCIO

Radicación : 01-042411 006-0005
Fecha (min): 2003-04-22 11:23:22
Procede : 002 PATENTES Y 1 REGISTRAR: 550 PETICIA
Dependencia: 2020 DIVISION DE ALENGS OPERACIONES
SUPERINTENDENCIA

PARA USO EXCLUSIVO DE
HUMBERTO RUBIO & CIA. LTDA

Examen de Patentabilidad
Expediente No.: 01-042.411
Patente de invención: "PERFORACIÓN DE
POZOS Y FLUIDOS DE SERVICIO; Y MÉTODOS DE
REMOCIÓN DE AGLUTINANTES EN FILTROS
DEPOSITADOS EN ESTOS"
NIT : 800176089-2
Titular: HALLIBURTON ENERGY SERVICES, INC.

RECIBO OFICIAL DE CAJA : 03 - 16,988
FECHA : MARZO 10 DE 2003

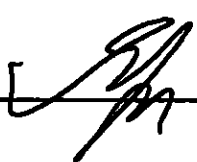
***** CONSIGNACION *****

DEPOSITANTE	TIPO PAGO	BANCO	CUENTA	Nº. PAGO	FECHA PAGO	Vr. PAGO
HUMBERTO RUBIO CANACHO	CONSIGNACION	BANCO POPULAR	050-00110-6	3121545	10/03/2003	10,047,000.00

***** CONCEPTO *****

CANT. CONTABILISTICO	CONCEPTO	TOTAL CONCEPTO
1 50005-01-01 SOLICITUDES	85 EXAMEN DE PATENTABILIDAD DE INVEN	335,000.00
	TOTAL :	\$ 335,000.00

SOM: TRESCIENTOS TREINTA Y CINCO MIL PESOS

RESPONSABLE : 

RECIBO DE CAJA APLICADO AL EXPEDIENTE No. _____

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**SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO
DIVISION DE NUEVAS CREACIONES**

2020
Bogotá, D.C., 19 de enero de 2006

Doctor
HUMBERTO RUBIO CAMACHO
Apoderado

Oficio No. **723**

ASUNTO	Radicación	01-62411
	Trámite	002
	Evento	001
	Actuación	430
	Folios	016

Como resultado del examen de fondo, realizado con fundamento en el artículo 45 de la Decisión 486 de la Comisión de la Comunidad Andina, se le comunica:

1. Documentos estudiados

- Para el presente estudio se tuvo en cuenta el capítulo descriptivo que se encuentra en los folios 5 a 17 y el capítulo reivindicatorio que se encuentra en los folios 18 a 24 que comprende cuarenta (40) reivindicaciones.
- De acuerdo con el folio 105 de la solicitud en estudio, se considerará la prioridad reivindicada sobre la solicitud de Estados Unidos No. 09/629,959 del 1 de agosto de 2000.

2. Objeto de la Invención

- La invención propuesta se relaciona con la perforación de pozos y los fluidos de servicio utilizados en la producción de formaciones y en la remoción de aglutinantes del filtro depositados por los fluidos en las formaciones.

En la reivindicación Independiente 1 se define un fluido de perforación o de servicio de pozos para uso en la producción de formaciones y que deposita aglutinantes de filtros que contienen agua, una sal soluble en agua de densidad creciente, un agente de control de pérdidas de fluidos, un agente de suspensión de sólidos de polímeros hidratable y un agente puente de partículas sólidas, la mejora en donde dicho agente puente de partículas sólidas comprende un compuesto Inorgánico que es soluble en una solución de limpieza compuesta por agua y una sal de amonio.

En la reivindicación Independiente 16 se define un método de remoción del aglutinante del filtro de las paredes de la perforación de un pozo que penetra una producción de formaciones depositadas en éste por medio de un fluido de perforación o de servicio compuesto por agua, una sal soluble en agua que incrementa la densidad, un agente de control de pérdida de fluido, un agente de suspensión de sólidos de polímeros hidratables y un agente puente de partículas sólidas que comprende la siguientes etapas:

- a) Utilización como agente puente de partículas sólidas en dicho servicio de perforación o de servicio un compuesto inorgánico que es soluble en una solución de limpieza comprendida por agua y sal de amonio y
- b) Contacto del aglutinante del filtro con una solución de limpieza comprendida por agua y una sal de amonio durante un período de tiempo tal que dicho agente puente del óxido metálico se disuelva por medio de éste.

En la reivindicación Independiente 30 se define un método para remover el aglutinante del filtro de las paredes de una perforación de un pozo que penetra una producción de formaciones depositado en éste por un fluido de perforación o de servicio que comprende las siguientes etapas:

- a) Utilización como fluido de perforación o de servicio, un fluido compuesto por agua, una sal soluble en agua que aumenta la densidad seleccionada del grupo compuesto por cloruro de sodio, bromuro de sodio, cloruro de potasio, cloruro de calcio, bromuro de calcio y mezclas de éste, un agente de control de pérdida de fluidos compuesto de almidón, un agente en suspensión de sólidos de polímero hidratable compuesto por Xantan y un agente puente de óxido de metal de partículas sólidas que es soluble en una solución de sal de amonio acuoso; y
 - b) Del contacto de dicho aglutinante del filtro con una solución de limpieza compuesta por agua y una sal de amonio por un periodo de tiempo tal que dicho agente puente de óxido de metal se disuelva por medio de ésta.
- Los procesos de remoción de aglutinante de filtro formado en pozos de perforación a causa del fluido de perforación se realizan convencionalmente mediante diferentes métodos. Uno de ellos consiste en incluir un agente puente de partículas sólidas soluble en ácido, en el fluido de perforación o de servicio para hacer un llenado sobre los orificios de la formación. El aglutinante se pone en contacto con solución fuertemente ácida y al permanecer en contacto con el aglutinante del filtro también corroe las superficies metálicas y el equipo de terminación, como las pantallas de arena, que producen fallas. La solución ácida también puede ser incompatible con la producción de formaciones y puede causar daños a esta.

De otro lado, el agente puente de partículas sólidas también ha sido utilizado en fluidos de perforación o de servicio y el aglutinante del filtro ha sido puesto en contacto con soluciones de sal acuosa saturadas. Sin embargo, estas soluciones acuosas subsaturadas requieren un período de tiempo largo para disolver las partículas. Así mismo, otros tratamientos son largos, costosos y sigue habiendo riesgo de corrosión.

Por ello, se afirma que existe la continua necesidad de tener mejores fluidos de perforación y de servicio, y de métodos para remover el aglutinante del filtro depositado por los fluidos de producción de formaciones.

- El objeto de la invención definido se catalogó como E21B 7/18 y E21B 43/114, según la Clasificación Internacional de Patentes (IPC).

3. Claridad de la solicitud

El artículo 28 de la Decisión 486 de la Comisión de la Comunidad Andina establece "La descripción deberá divulgar la invención de manera suficientemente clara y completa para su comprensión y para que una persona capacitada en la materia técnica correspondiente pueda ejecutarla".

- El capítulo descriptivo adolece de problemas de traducción que desmejoran la comprensión. Por lo tanto, se recomienda revisar y rectificar.
- En conclusión, el capítulo descriptivo no cumpliría con el requisito de claridad de acuerdo con el artículo 28 de la Decisión 486.

El artículo 30 de la Decisión 486 de la Comisión de la Comunidad Andina establece que: "Las reivindicaciones definirán la materia que se desea proteger mediante la patente. Deben ser claras y concisas y estar enteramente sustentadas por la descripción.

Las reivindicaciones podrán ser independientes o dependientes. Una reivindicación será independiente cuando defina la materia que se desea proteger sin referencia a otra reivindicación anterior. Una reivindicación será dependiente cuando defina la materia que se desea proteger refiriéndose a una reivindicación anterior. Una reivindicación que se refiera a dos o más reivindicaciones anteriores se considerará una reivindicación dependiente múltiple".

- El capítulo reivindicatorio completo presenta problemas de redacción que posiblemente se deban a una traducción deficiente. Dado lo anterior, se recomienda revisar la copia original y anexar un nuevo capítulo reivindicatorio corregido de tal manera que la traducción y redacción sean comprensibles.
- Se recomienda que las reivindicaciones del capítulo se presenten en la forma de preámbulo y parte caracterizante donde en el preámbulo se sitúe el campo de la invención y contenga las características que ya forman parte del estado de la técnica. La parte caracterizante diferenciada del preámbulo por la expresión "caracterizado por" debería contener las características técnicas novedosas, es decir, el aporte del inventor.
- La reivindicación independiente 1 resulta ser definida de una manera demasiado amplia pues se entiende que lo importante es la mejora de incluir en el fluido de perforación un compuesto inorgánico con particularidades de disolución.

Dado que el estado de la técnica está formado por un gran número de fluidos de perforación con diversas opciones de composición química susceptible de remoción por lavado, la solicitud en estudio podría abarcar lo conocido y ser afectada en el estudio de la patentabilidad. Se recomienda por tanto que la reivindicación Independiente 1 comprenda la composición química del fluido de perforación mencionando la naturaleza química de los componentes en ella misma.

- En las reivindicaciones 1 y 11 a 15 se incluyen características técnicas de la solución de limpieza empleada para disolver el agente puente de partículas sólidas que contiene el fluido de perforación.

En primer lugar, es necesario resaltar que las características técnicas de la solución de limpieza no están relacionadas con el fluido de perforación ni éste puede ser definido por la solución de limpieza. Las características técnicas de la solución de limpieza están mejor relacionadas con especificaciones del lavado que tiene el método de remoción de aglutinante como bien se realiza en las reivindicaciones 25 a 29. Por lo tanto se recomienda eliminar las reivindicaciones 11 a 15 dependientes del fluido de perforación de la reivindicación 1.

- En la reivindicación independiente 16 se define un método de remoción del aglutinante del filtro de las paredes de la perforación de un pozo mediante dos etapas a) y b). La etapa a) es la utilización de un compuesto inorgánico y la etapa b) es el contacto del aglutinante con una solución de limpieza. No obstante, la forma de redacción de la reivindicación es confusa no permitiendo identificar claramente las características técnicas novedosas de la propuesta pues es convencional que se utilice un compuesto inorgánico y se ponga en contacto la torta con un flujo de limpieza. Es importante que se modifique el planteamiento de la reivindicación citada de tal manera que las etapas técnicas sean muy claras y permitan comprender el método de remoción y el aporte realizado. Esto se puede lograr identificando muy bien la secuencia de etapas del método y también empleando la formalidad de preámbulo y parte caracterizante, además de revisar la copia original y la traducción e incluir el aporte novedoso.
- En las reivindicaciones 17 a 24 y 31 a 35 se intenta especificar el método a partir de las características técnicas del fluido de perforación.

Esta forma de especificación no es apropiada ya que así como un producto se define por la estructura, composición o elementos, un método debe definirse por las etapas, secuencia y condiciones de operación del método. No es posible definir un producto por un método y un método mediante las características de un producto. De hecho la información de las reivindicaciones arriba citadas resulta innecesaria por ser repetitiva al ya estar formulada en las reivindicaciones 1 a 10. Por ello se recomienda eliminar dichas reivindicaciones.

- En conclusión el capítulo reivindicatorio no cumpliría con el requisito de claridad de acuerdo con el artículo 30 de la Decisión 486. Por lo tanto, se recomienda realizar las modificaciones pertinentes según las observaciones incluidas y allegar un nuevo capítulo reivindicatorio con tales modificaciones.

4. Determinación del estado de la técnica

El artículo 16 de la Decisión 486 de la Comisión establece: "El estado de la técnica comprenderá todo lo que haya sido accesible al público por una descripción escrita u oral, utilización, comercialización o cualquier otro medio antes de la fecha de presentación de la solicitud de patente o, en su caso, de la prioridad reconocida.

Sólo para el efecto de la determinación de la novedad, también se considerará dentro del estado de la técnica, el contenido de una solicitud de patente en trámite ante la oficina nacional competente, cuya fecha de presentación o de prioridad fuese anterior a la fecha de presentación o de prioridad de la solicitud de patente que se estuviese examinando, siempre que dicho contenido esté incluido en la solicitud de fecha anterior cuando ella se publique o hubiese transcurrido el plazo previsto en el artículo 40."

- A pesar de los defectos de claridad detallados en el numeral 3 de la presente comunicación, se consultaron las bases de datos con que cuenta y tiene acceso la entidad y se consideró el 1 de agosto de 2000 como fecha para investigar el estado de la técnica.

- De acuerdo con lo establecido en el artículo 16 se determinó el estado de la técnica y se encontraron los siguientes antecedentes:

No.	Documento No.	Título	Fecha de Publicación
1	US6131661	"METHOD FOR REMOVING FILTERCAKE"	17 de octubre de 2000
2	US5607905	"WELL DRILLING AND SERVICING FLUIDS WHICH DEPOSIT AN EASILY REMOVABLE FILTER CAKE"	4 de marzo de 1997

Respecto al estado de la técnica:

- En el documento **US6131661** (llamado D1 de aquí en adelante) se divulga un método para remover torta de filtro desde un pozo subterráneo lo cual comprende perforar el pozo con un fluido que incluye aditivos para formar una torta de filtro que tiene un componente degradable a la oxidación, preferiblemente un polímero. La torta de filtro es contactada con un precursor que forma un agente oxidizante a temperaturas del pozo para degradar los polímeros dentro de la torta de filtro. Alternativamente uno o más catalizadores para activar el precursor de un agente oxidizante es incorporado dentro de la torta. El catalizador activa el precursor como el precursor es fluido sobre la torta de filtro y permanece en contacto con esta para formar un agente oxidizante para degradar el agente que se degrada con oxidación y descomponer la torta de filtro. Las partículas remanentes de la torta de filtro descompuesta son entonces evacuadas fuera del pozo.

En el método de D1, el fluido de perforación preferido es una salmuera, más preferiblemente, una salmuera de bromuro de calcio con un almidón catiónico un reticulante, un almidón no catiónico, tiosulfato de sodio, óxido de magnesio y biopolímero de xantano.

El agente de puente dentro del fluido de perforación puede incluir materiales solubles en agua o solubles en ácido como por ejemplo sales sólidas en soluciones saturadas, carbonatos, entre otros.

Los polímeros del fluido pueden ser almidones y xantanos. Alternativamente, el polímero puede ser seleccionado desde derivados de almidón, derivados de celulosa y biopolímeros tales como hidroxipropil almidón, hidroxietil almidón, carboximetil almidón y sus correspondientes derivados reticulantes; carboximetil celulosa, hidroxietil celulosa, entre otros.

- En el documento **US5607905** (llamado D2 de aquí en adelante) se divulga un fluido de perforación y de servicio basado en agua alcalina el cual deposita una torta de filtro fácilmente removible y degradable sobre los lados del hoyo de perforación. Los fluidos contienen uno o más polímeros polisacáridos, partículas de puente, y un peróxido seleccionado del grupo que consiste de peróxidos de metales de tierras alcalinas, peróxido de zinc, y mezclas de estos. Los fluidos depositan una torta que contiene el peróxido. La invención además provee procesos para mejorar la remoción de la torta de filtro los cuales comprenden depositar una torta de filtro que comprende un peróxido y hacer esto sobre los lados del hoyo, luego contactar dicha torta con una solución ácida para activar el peróxido el cual degrada después de esto al polisacárido de la torta. Preferiblemente, la torta de filtro que contiene el polímero degradado es lavada con un fluido en el cual las partículas puente son solubles para remover la torta entera desde los lados del hoyo perforado.

5. Evaluación de los requisitos de patentabilidad

El artículo 14 de la Decisión 486 de la Comisión de la Comunidad Andina establece: "Los Países Miembros otorgarán patentes para las invenciones, sean de producto o de procedimiento, en todos los campos de la tecnología, siempre que sean nuevas, tengan nivel inventivo y sean susceptibles de aplicación industrial."

En cumplimiento con este artículo, se procedió a evaluar los requisitos de novedad, nivel inventivo y aplicación industrial con el fin de establecer la patentabilidad de la invención reivindicada en la solicitud en estudio.

Evaluación de la Novedad

El artículo 16 de la Decisión 486 de la Comisión de la Comunidad Andina establece: "Una invención se considerará nueva cuando no está comprendida en el estado de la técnica." "El estado de la técnica comprenderá todo lo que haya sido accesible al público por una descripción escrita u oral, utilización, comercialización o cualquier otro medio antes de la fecha de presentación de la solicitud de patente o, en su caso, de la prioridad reconocida."

Sólo para el efecto de la determinación de la novedad, también se considerará dentro del estado de la técnica, el contenido de una solicitud de patente en trámite ante la oficina nacional competente, cuya fecha de presentación o de prioridad fuese anterior a la fecha de presentación o de prioridad de la solicitud de patente que se estuviese examinando, siempre que dicho contenido esté incluido en la solicitud de fecha anterior cuando ella se publique o hubiese transcurrido el plazo previsto en el artículo 40."

- En la reivindicación independiente 1 se plantea que la composición del fluido de perforación presenta la mejora en la naturaleza química del agente puente de partículas sólidas pues comprende un compuesto inorgánico soluble en una solución de limpieza compuesta por agua y una sal de amonio. No obstante, en D1 se mencionan modalidades de la invención y una de ellas también revela una formulación de un fluido de perforación que presenta una sal soluble en agua de densidad creciente, un agente de control de pérdidas de fluidos como almidón o hidroxietilcelulosa, un agente de suspensión de sólidos tal como el xantano, un agente de puente de partículas como son los carbonatos además de mencionarse el óxido de magnesio como componente del fluido de perforación.

Aún cuando D1 no menciona explícitamente que el agente puente de partículas es soluble en una solución de limpieza compuesta por agua y una sal de amonio, se deduce que también se cumple dicha característica porque la naturaleza química y física del agente puente de partículas es el mismo que el de la solicitud y por ende tendrá el mismo comportamiento de disolverse en una solución de agua y sal de amonio aún cuando no sea manifiesta.

- Es importante mencionar que la forma de redacción de la reivindicación independiente resulta tan amplia que básicamente se entiende que la mejora se centra en que el agente puente de partículas sólidas comprende un compuesto inorgánico soluble en una solución de limpieza específica. Sin embargo, teniendo en cuenta que las características técnicas de la solución de limpieza no pueden definir ni delimitar un fluido de perforación porque cada uno tiene naturaleza independiente, se comprende que lo esencial es que el agente puente de partículas sólidas sea un compuesto inorgánico, que según la reivindicación dependiente 2 puede ser seleccionado del grupo compuesto por óxidos de metales, hidróxidos de metales, carbonatos de metal, sulfatos de metales, peróxidos de metal entre otros.

Teniendo en cuenta lo anterior, otro documento que se denominó D2 también revela que los agentes puente de partículas sólidas que puede contener un fluido de perforación formador de torta de filtro puede ser un **peróxido de metal alcalino**, lo cual demuestra que realizar una mejora como esta no es novedosa.

- En cuanto al método de remoción, sigue siendo recomendable realizar las correcciones de claridad expresadas en el numeral 3 de la presente comunicación particularmente definiendo claramente (además de las otras etapas) la etapa de lavado con una solución de limpieza compuesta por agua y una sal de amonio.
- En conclusión, el fluido de perforación definido en las reivindicaciones 1 a 10 se encontraría afectado en el requisito de novedad de acuerdo con el artículo 16 de la Decisión 486.

6. Conclusiones

- Los requisitos de patentabilidad de la presente solicitud se encuentran afectados así:

No.	Documento	Reivindicaciones Afectadas	Requisito que afecta
1.	US6131661	1 – 10	Novedad
2.	US5607905	1, 2, 5 – 10	Novedad

Se anexan los apartes principales de las anterioridades en el documento adjunto.

En cumplimiento del artículo 45 de la Decisión 486 de la Comisión de la Comunidad Andina, se le indica que debe dar respuesta dentro del término de sesenta días contados a partir de la fecha de notificación de la presente comunicación. En caso de no dar respuesta al presente requerimiento, o si a pesar de la respuesta subsistieran los impedimentos para la concesión, se denegará la patente.

Notifíquese el presente oficio conforme a lo dispuesto en el numeral 5.2, literal e), del capítulo quinto del título primero de la circular única No. 10 de 2001.



ALIX CARMENZA CESPEDES DE VERGEL
Jefe de División de Nuevas Creaciones

26 ENE. 2006

El anterior requerimiento fue notificado por fijación en lista, de fecha _____

CONCEPTO TECNICO No. 023	EXAMINADOR TECNICO Código No. 202042
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US006131661A

United States Patent [19]
Conner et al.

[11] **Patent Number:** **6,131,661**
[45] **Date of Patent:** **Oct. 17, 2000**

[54] **METHOD FOR REMOVING FILTERCAKE**
[75] **Inventors:** **Richard Paul Conner; Joseph Robert Murphy, both of Spring, Tex.**
[73] **Assignee:** **Tetra Technologies Inc., The Woodlands, Tex.**
[21] **Appl. No.:** **09/127,842**
[22] **Filed:** **Aug. 3, 1998**
[51] **Int. Cl.⁷** **E21B 37/00**
[52] **U.S. Cl.** **166/300; 166/307; 166/312**
[58] **Field of Search** **166/300, 305.1, 166/307, 312**

4,941,537	7/1990	Langemeter et al.	166/308
4,969,526	11/1990	Cawicord	166/300
5,054,552	10/1991	Tall et al.	166/278
5,055,209	10/1991	Bridges et al.	252/8.51
5,143,157	9/1992	Flarna	166/300
5,238,065	8/1993	Mondakine et al.	166/300
5,247,995	9/1993	Tjoo-Joe-Pin et al.	166/312
5,253,711	10/1993	Mondakine	166/300
5,386,874	2/1995	Larmany et al.	166/300
5,447,199	9/1995	Dawson et al.	166/300
5,501,276	3/1996	Weaver et al.	166/291
5,607,905	3/1997	Dolson, Jr. et al.	507/211
5,783,527	7/1998	Dolson, Jr. et al.	166/300

Primary Examiner—William Neuder
Attorney, Agent, or Firm—Jo Katherine D'Ambrosio

[57] **ABSTRACT**

A method for removing filtercake from a subterranean borehole comprising drilling the borehole with a drilling fluid that includes additives to form a filtercake having an oxidation-degradable component, preferably a polymer. The filtercake is contacted with a precursor that forms an oxidizing agent at downhole temperatures to degrade the polymers within the filtercake. Alternatively one or more catalysts for activating the precursor of an oxidizing agent is embedded within the filtercake. The catalyst activates the precursor as the precursor is flushed over the filtercake and remains in contact with the filtercake to form an oxidizing agent to degrade the oxidation-degradable agent and decompose the filtercake. The remaining particles of decomposed filtercake are then flushed away.

25 Claims, No Drawings

[56] **References Cited**

U.S. PATENT DOCUMENTS

1,984,668	12/1934	Wier et al.	166/21
2,221,353	11/1940	Limerick et al.	166/21
3,167,510	1/1965	Alter	252/8.55
3,816,151	6/1974	Podlas	106/194
3,818,991	6/1974	Nimerick	166/283
3,922,173	11/1975	Misak	106/194
4,144,179	3/1979	Chatterji	252/8.55
4,259,205	3/1981	Murphy	252/326
4,552,674	11/1985	Brown et al.	252/8.55
4,560,486	12/1985	Hinkel	252/8.55
4,591,443	5/1986	Brown et al.	210/747
4,594,170	6/1986	Brown et al.	252/8.55
4,609,475	9/1986	Hansen et al.	252/8.55
4,610,795	9/1986	Norris et al.	252/8.551
4,853,478	8/1989	Colvin et al.	560/32

METHOD FOR REMOVING FILTERCAKE

FIELD OF THE INVENTION

The present invention relates to a method for removing filtercake from a subterranean borehole, particularly to a method for filtercake removal by contacting the filtercake with a precursor to an oxidizing agent and more particularly to a method of filtercake removal in which a catalyst is included in the formation of the filtercake forming fluid to accelerate the conversion of the precursor to the oxidizing agent.

BACKGROUND OF THE INVENTION

The walls of oil and gas formations are exposed during the process of drilling a borehole. The successful completion of a wellbore requires the deposit of a low-permeable filtercake on the walls of the wellbore to seal the permeable formation exposed by the drilling bit. A filtercake can limit drilling fluid losses from the wellbore and protect the natural formation from possible damage by the fluids permeating into the wellbore. Solids in the drilling fluid may also damage the formation, particularly drilling fines. The suspension of fine particles that enters the formation while the cake is being established is known as "mud spurt" and the liquid that enters subsequently is known as "filtrate". Both filtration rate and mud spurt must be minimized when penetrating potentially productive formations because productivity may be reduced by any one of the following: the swelling of clays in the formation when they come in contact with the filtrate; particles transported into the pores of the formation that plug flow channels and greatly reduce the permeability of the rock; and the pressure of some reservoirs that is not great enough to drive all of the aqueous filtrate out of the pores of the rock when the well is brought into production.

Contamination of the formation with drill solids in the fluids can be avoided by formulating the drilling fluid with other soluble solids that can be incorporated in the filtercake and dissolved at a later time, thereby diluting the effect of the insoluble solids. Sized salt solids, in salt saturated solutions, and finely ground calcium carbonate are examples of solids purposely added to the drilling, workover, or completion fluids to form a filtercake that can later be partially dissolved by aqueous or acid flushes.

For a filtercake to form, the drilling fluid must contain some particles of a size only slightly smaller than the pore openings of the formation. These particles are known as bridging particles and are trapped in surface pores, thereby forming a bridge over the formation pores. Filtercake building fluids can also contain polymers for suspension of solids and for reducing liquid loss through the filtercake by encapsulating the bridging particles. These can be either natural or synthetic polymers. The polymers can include one polymer such as xanthan selected for its rheological properties and a second polymer, a starch for example, selected for reduction of fluid loss.

At completion of the drilling or other well servicing, the filtercake must be removed to allow production of the formation fluids or bonding of cement to the formation at the completion stage. Removal of the deposited filtercake should be as complete as possible to recover permeability within the formation.

Previous chemical treatments for filtercake removal have employed an acid to dissolve carbonates and/or hydrolyze polysaccharide polymers. Dobson, Jr. et al., U.S. Pat. No. 5,607,905, reveal a process for enhancing the removal of filtercake by the use of inorganic peroxides as oxidizing

agents. The process disclosed in the '905 patent incorporates alkaline earth metal peroxides, zinc peroxides or a mixture thereof within the filtercake as an integral component thereof and then contacts the filtercake with an acidic solution. Weir et al., U.S. Pat. No. 1,984,668, discloses a method of cleaning the walls of mudded boreholes. A first reagent is included in the mud-coating of the borehole. Subsequently, the mud-coating is impregnated with a second reagent that reacts with the first reagent. The first reagent is generally a carbonate. The second reagent is generally an acid that reacts with the carbonate to form carbon dioxide gas.

Tjon-Joe-Pin et al., U.S. Pat. No. 5,247,995, disclose a method for removing a polysaccharide-containing filtercake formed on surfaces during fracturing with a viscosified fluid. The '995 method discloses removal of the filtercake by pumping downhole an aqueous fluid containing enzymes that degrade polysaccharide. The use of non-metallic persulfates as an oxidant in filtercake removal systems is also disclosed.

A composition and method of removing polymeric material from a formation is found in Hanlon, U.S. Pat. No. 4,609,475. The method disclosed comprises contacting the formation with an oxidizing agent and carboxylic acid. A source said to be effective in promoting the decomposition of the oxidizing agent is added to the aqueous solution containing the oxidizing agent.

The addition of an alkali metal or alkaline earth metal salt of hypochlorous acid, or a chlorinated isocyanurate is disclosed in Langensier et al., U.S. Pat. No. 4,941,537, for the reduction of viscosity of aqueous fluids thickened with a tertiary amino polygalactomannan.

Methods of filtercake removal that incorporate a solid oxidizing agent precursor in the filtercake are not totally insoluble at the temperatures of application so that some oxidizing materials are released with premature degrading of the polymer. Also, the materials are only applicable in high pH fluids, thereby limiting their use. Finally, these compositions cannot be used in formulations with significant amounts of reducing agents, such as iron control agents, oxygen scavengers, or bromide or formate brines.

A problem associated with the use of acid to activate a precursor in field use is that sufficient acid does not always contact all parts of the filtercake. Sometimes the acid must be "weighted up" (formulated with high weight brines to increase fluid density). Thus the actual acid content is low. As the acid is reacting with the carbonates in the filtercake, a stoichiometric amount of acid is required, and this volume can be greater than the actual exposed wellbore volume; the acid must be continuously replaced. In some cases, the acid initially dissolves a small region of the filtercake, because of the vastly increased fluid loss of this region, the remaining acid flows to this small region and out into the formation. What is needed is a method that attacks the filtercake in a manner which does not completely remove the filtercake in a small region and does not require large stoichiometric amounts of agent.

In the drilling and completion of a well, several operations after the drilling process are often required before production can begin. These operations require the displacement of the drilling fluid without degradation or removal of the filtercake. What is needed, therefore, is a method for removal of filtercake that does not depend on the presence of a drilling fluid.

In the case of horizontal open hole drilling of unconsolidated formations, it is desirable to gravel pack the wellbore

after drilling the zone but before the filtercake is completely removed. The problem is that the act of gravel packing the wellbore annulus further limits acid contact with the filtercake, as it both reduces the physical volume of acid in the zone and blocks its flow.

Consequently, there remains the need for a filtercake removal technology that does not depend solely on acid hydrolysis for removal of the filtercake. And there is an additional need to provide a method for oxidizing filtercake materials in which the oxidizing agent is not activated prematurely, i.e. at ambient temperatures, so that the oxidizing agent works in concert with drilling fluid formulations that have easily oxidized materials.

SUMMARY OF THE INVENTION

In the method of this invention, the removal of a filtercake from a subterranean borehole comprises the steps of drilling the borehole with a drilling fluid to form a filtercake comprising an oxidation degradable component, contacting the filtercake with an organic hydroperoxide, allowing the organic hydroperoxide to remain at the downhole temperature for a period of time effective to form an oxidizing agent to degrade the oxidation-degradable agent and decompose the filtercake and flushing away the decomposed filtercake. The oxidation-degradable component can be a polymer.

Preferably, the polymer comprises starch, cellulose or xanthan. In one aspect, organic hydroperoxide is thermally activatable at the downhole temperature of the filtercake. In a preferred embodiment, the organic hydroperoxide is t-butylhydroperoxide and the borehole temperature is at least about 80° C. Alternatively, the organic hydroperoxide is selected from the group consisting of cumene hydroperoxide, t-butyl dihydroperoxide, and amylhydroperoxide, and the borehole temperature is at least about 80° C.

In one embodiment, an activating agent for the organic hydroperoxide is flushed over the filtercake prior to the organic hydroperoxide flush. In an alternative embodiment, the filtercake comprises an activating agent for activating the organic hydroperoxide. Preferably, the activating agent comprises an ascorbic acid. Alternatively, the activating agent comprises a tertiary amine. In another embodiment, activating agent is diethylaminoisopropanol. Alternatively, the tertiary amine comprises triethanolamine. In one aspect, the activating agent is a polymer comprising pendant tertiary amine moieties. The oxidation-degradable polymer is functionalized with the amine moieties. An additional activating agent selected from the group consisting of copper salt solution cobalt salt solution, iron salt solution and chromium salt solution is flushed over the filtercake.

In one preferred method for removing filtercake from a subterranean borehole, the steps for removal of the filtercake comprise drilling the borehole with a drilling fluid to form a filtercake comprising an oxidation-degradable component and an activating agent for activating a precursor of an oxidizing agent, wherein the filtercake is free of the precursor, contacting the filtercake with a precursor of oxidizing agent, allowing the precursor to remain in contact with the filtercake to form an oxidizing agent to degrade the oxidation-degradable agent and decompose the filtercake, and flushing away the decomposed filtercake. Preferably, the oxidation-degradable component is a polymer. The polymer can comprise starch, cellulose or xanthan. The activating agent can comprise a tertiary amine. Preferably, the tertiary amine comprises triethanolamine. Alternatively, the activating agent is a polymer comprising pendant tertiary amine

moieties. The oxidation-degradable polymer can be functionalized with the amine moieties. In one aspect, the precursor is selected from alkali metal and ammonium salts of persulfates, perborates, permanganates and percarbonates. Alternatively, the precursor is selected from the group consisting of t-butyl hydroperoxide, cumene hydroperoxide, t-butyl dihydroperoxide, and amylhydroperoxide. Preferably, additional steps for this preferred method include: installing gravel pack screens and tool assemblies into the borehole prior to the step of contacting the filtercake with the precursor, determining fluid losses and adding sand in a nonviscous carrier to the borehole.

DETAILED DESCRIPTION OF THE INVENTION

In the method of this invention, filtercake formed on the walls of a subterranean borehole is removed by contacting the filtercake with a precursor to an oxidizing agent. In one preferred embodiment, a catalyst is included in the filtercake-forming fluid to accelerate the conversion of the precursor to the oxidizing agent. Filtercakes are tough, almost water insoluble coatings that reduce permeability of formation walls. Formed during the drilling stage to limit losses from the wellbore and protect the formation from possible damage by fluids and solids within the wellbore, filtercake layers must be removed so that the formation wall is restored to its natural permeability to allow for hydrocarbon production or cementing.

Filtercakes can be formed with polymers that encapsulate particles or solids which form a bridge over the pores of the formation. Drilling fluids as well as any bridging agents and polymers contained within the drilling fluid are well known in the art. In the method of this invention, the preferred drilling fluid is a brine, more preferably, a calcium bromide brine with additives, preferably polymers, salts, carbonates and other soluble solids. An example of a suitable drilling fluid according to the present invention comprises a calcium bromide brine with a cationic starch, a cross-linked, non-cationic starch, sodium thiosulfate, magnesium oxide, and xanthan biopolymer. The bridging agent within the drilling fluid may include either water soluble or acid soluble materials, for example: sized salt solids in salt saturated solutions, finely ground carbonates found in limestone, marble, or dolomite; or oil soluble such as resins, waxes and the like. Polymers can be either natural or synthetic polymers. Preferred polymers comprise starches and xanthans. Alternatively, the polymer can be selected from starch derivatives, cellulose derivatives and biopolymers such as hydroxypropyl starch, hydroxyethyl starch, carboxymethyl starch and their corresponding crosslinked derivatives; carboxymethyl cellulose, hydroxyethyl cellulose, hydroxypropyl cellulose, methyl cellulose, dihydroxypropyl cellulose, and their corresponding crosslinked derivatives; xanthan gum, gellan gum, welan and the like.

In the drilling and completion of a well, several operations may be required after the drilling process before the well is produced. For these stages it is usually desirable to maintain the filtercake on the wellbore thereby limiting fluid losses to the formation. Immediate degradation or removal of the filtercake is not desired. The drilling or completion fluid is displaced without removing the filtercake. Known procedures which are designed to achieve this displacement are believed to be compatible with the invention. In other situations, such as the cementing of a cased hole, the drilling fluid and the filtercake are removed together. The preferred practice is to completely displace the drilling fluid first, and then treat to remove the filtercake.

According to the filtercake removal method of this invention, a filtercake is formed with an oxidation-degradable component, preferably a polymer as described above. Oxidizing agents, or preferably precursors to oxidizing agents, attack and decompose the oxidation-degradable component. In one embodiment of the method of filtercake removal, the filtercake is treated or flushed with a precursor to an oxidizing agent, for example an organic peroxide or hydroperoxide. Preferably the precursor remains in contact with the filtercake as a soak for a time period of from one to six or more hours. Preferably the organic peroxide or hydroperoxide is soluble or dispersible in aqueous mixtures and relatively inert at ambient temperatures. Because of these properties, the organic peroxide or hydroperoxide can be included in the final treating flush of weighted brines with little oxidation of the halide to the free element. At downhole temperatures, however, the oxidative activity increases. Organic peroxides and hydroperoxides are selected for the characteristic of increasing reactivity with increasing temperature. Commercially, they are described as having a declining half-life at various increasing temperatures that correspond to this increasing oxidative activity. Consequently the preferred precursor to an oxidizing agent is selected so that an oxidizer is rapidly generated at reservoir formation temperatures although stable in storage at ambient conditions.

Preferred precursors having such properties comprise t-butylhydroperoxide, tertiary dibutyl hydroperoxide, cumene hydroperoxide, or amyl-hydroperoxide, especially t-butylhydroperoxide. They can be used as precursors in dilute concentrations. Some chlorite solutions are also stable until activated at particular temperatures, including chlorinated isocyanurates, such as, for example, dichloro-s-triazine-2,4,6-trione or dichloroisocyanuric acid. Thus the formation temperature activates the precursors in the degradation of filtercake. Preferably, the formation or borehole temperature is at least 80° C.

In another embodiment of this invention, the filtercake is flushed with a fluid containing a catalyst prior to the soak with a precursor. The catalyst functions as an activating agent for forming the oxidizing agent from the precursor. Various activating agents can be selected to catalyze the decomposition of precursors. Preferably, specific catalysts are used with specific precursors, for example, tertiary amines and ascorbic acid act as catalysts to degrade t-butylhydroperoxide. In one aspect, the catalyst is included in the drilling fluid displacement stage and the oxidizing precursors are then included in a later flush or flushes intended to dissolve and disperse the filtercake. The later flushes can include surfactants and other materials designed to displace the polymeric components from the surfaces of the drill solid materials, such as, for example, lactose or methyl glycoside.

Oxidizing agents formed from the precursors attack polymers encapsulating the bridging particles and break down the filtercakes by removing the polymeric coat, with the effect that the residual filtercake solids are no longer bridged or bonded by polymers. Preferably, the polymer is completely dissolved so that the carbonate particles do not bond to each other. These bridging solids can then easily be dispersed as individual particles, not clustered films. The removal of the filtercake particles can then occur either particle by particle as production fluid flows out of the formation into the wellbore, or by the addition of a solubilizing flush to dissolve the bridging solids. Although no acid is required, since the filtercake particles are small enough to flow through as production fluids flow into the bore, an acid flush

is preferably injected into the bore to dissolve the carbonate bridging component. The acid can be applied immediately, or alternatively, flushed over the filtercakes at a later time. Alternatively, the acid can be generated in place, for example, by the decomposition of a polyglycolic acid.

In an alternative embodiment, a catalyst or activating agent for the precursor is incorporated into the filtercake. The catalyst is included in the drilling fluid along with other filtercake building materials to deposit into the filtercake as it is formed. Oxidation of the filtercakes occurs when a precursor is flushed over the filtercake and decomposes, upon activation by the catalyst, into an oxidizing agent. Even though the catalyst is within the filtercakes, no oxidative attack on the polymers of the filtercake takes place until the filtercake is contacted with the oxidizing precursor. Specific catalysts are used with specific precursors as described above, preferably tertiary amines or ascorbic acid with t-butylhydroperoxide. Preferably, the catalyst is chemically bonded as an adduct with targeted polymers, tertiary amines as adducts on starches or xanthan for example. For that reason, the decomposition of the oxidizing precursor occurs locally, in the molecular region where the oxidative attack of the polymer is desired.

In one aspect, the catalyst is a tertiary amine or aminoalkanol, such as, for example, triethanolamine, diethylaminoisopropanol, or the like. In another embodiment, the catalytic materials are polymeric and become part of the polymeric component of the filtercakes, as functional moieties dependent from the polymeric backbone e.g., thereby limiting catalyst loss with brine or fluids that are lost to the formation from the filtercakes building fluid. Preferably, the catalytic moiety can be a component of one or any combination of the polymers chosen for use in the formation. The activating agent or catalyst can be a polymer comprising pendant tertiary amine moieties. One preferred activating agent comprises an amine adduct to a starch or viscosifying polymer. In a preferred embodiment, the catalyst is a diethylaminoisopropanol adduct to either a starch or xanthan.

When the catalyst or activating agent is incorporated within the filtercakes, decomposition of the filtercakes begins as the precursor is placed in contact with the filtercakes and then remains in contact as a soak until the filtercake is decomposed. Preferably, the precursor is one that is stable at ambient temperatures and decomposes to the oxidizing agent at downhole temperatures, between 40° C. and 120° C. The oxidizing agent breaks down the polymeric coating on the carbonate particles of the filtercakes thereby destroying the bridging feature of the filtercakes. The particles can be further reduced or dissolved by the use of a separate acid wash after the precursor soak.

In a preferred method of filtercake removal, a well is drilled using a drilling fluid that includes an amine-substituted starch and an amine-substituted xanthan thickening agent. Preferably the amine is diethylaminoisopropanol. Alternatively, a polymer containing tertiary and quaternary functional groups, such as a copolymer of poly-ethylenimine and ethylene oxide may be included. The preferred amounts of polymer are 0.14 g/l to 28.6 g/l. The fluid preferably contains about 85.7 g/l of sized carbonate, as well as drill solids resulting from the drilling operations. Other additives, such as gel stabilizers, clay treating additives, pH control agents, anti-oxidants, lubricants, non-emulsifying agents, iron control agents and the like can be included as desired.

Following the drilling of a well, when fluid losses are acceptable for the proposed pumping pressures, gravel or

sand packing can begin. First the drill-in fluid is displaced with a first clear fluid, which is otherwise similar to the drilling fluid. The wellbore is maintained in a slightly overbalanced state. Gravel pack screens and tool assemblies are run into the bore. During this stage, it is desirable to maintain the filtercake with as little fluid loss to the production formation as possible. Following displacement of the drilling fluid, the well is gravel packed. In a preferred procedure, the gravel, preferably sized sand, about 20-30 U.S. mesh, is placed into a nonviscofied carrier, such as a brine. As the low viscosity fluid cannot transport a significant amount of solids, the concentrations are usually about 60 g/l to 360 g/l of sand per gallon of fluid and pump rates approach 1 m³/min. The hydrostatic overbalance that arises from the pumping pressure necessary to achieve these rates is desirable since the overbalance holds the filtercake in place. An oxidative precursor, preferably t-butyl hydroperoxide, can be added during the sand packing. A preferred practice starts with small concentrations, approximately 0.1-0.5%, and increases the concentration of the precursor if there are no fluid loss responses.

Once the gravel pack sand is in place, it becomes more difficult to insure contact of the filtercake with acidic or other flushes. Treating fluids, particularly acids, tend to dissolve all of the filtercake in small areas so that the remaining treating fluid leaks off, or leaves, the wellbore at those points. In one aspect of the present invention, the problem of a flush completely dissolving a small area of the filtercake is overcome by including the activator in the filtercake. The precursor is flushed in at a later time. Alternatively, the precursor of the oxidizer is included in the gravel pack carrier fluid itself, combining two treatment steps with resultant savings in rig time. In another aspect of the invention, after the drill zone is completely filled with sand and flushed with a precursor, the gravel pack can be filled with an acid-containing fluid to dissolve the carbonate.

Prior to the acid flush and after the gravel pack is in place, the first replacement fluid is usually displaced with a spacer (buffer) or series of spacers, so that a clear fluid is left in the bore. In an alternative method, this fluid can contain about 0.014 g/l to 2.86 g/l by weight of a copper salt. The copper ions, with a strong affinity for tertiary amines, are retained in the filtercake and function as an additional activator to catalyze the breakdown of some oxidizing agents, particularly organic peroxides and hydroperoxides. Alternatively, ascorbic acid is used as the activating agent for the precursor. Ascorbic acid with the addition of the copper salt will rapidly reduce the precursor to an oxidizing agent. Other metal ions, such as cobalt, nickel, iron, and chromium could be substituted for the copper. If fluid losses are too great during this step, additional sized carbonate can be injected to reduce such losses.

The additional benefit of the copper catalytic effect is important at temperatures below 60° C. as the amines in the filtercake can catalyze the decomposition of many oxidizing precursors, including sodium persulfate and t-butyl hydroperoxide more effectively. Amines alone with no additional catalyst are sufficient above this bottom hole temperature.

Interaction of the oxidative precursors and the catalysts embedded in the filtercake generates the oxidation-degradable agent needed to decompose the polymers of the filtercake. The residual filtercake solids, no longer bridged or bonded by polymer, can be easily dispersed. The removal of the particles can then be by either particle by particle as the well is flowed in the production direction, or by a solubilizing flush such as an acid injected to dissolve carbonate. The acid can be immediately applied, squeezed at a

later time, or generated in place, such as by decomposition of polyglycolic acid.

EXAMPLES

Drill in fluid formulations with a Specific Gravity (SG) equaling 1.44 based upon a CaBr₂ based brine were used for the tests.

Formulations

Drill-in Fluid Based Upon CaBr₂

Component	Quantities in grams/liter Part 2	
	1	2
Water	424.9	424.9
CaBr ₂ (80 = 1.70) brine	920.9	920.9
Cationic Starch	0	13.7
Crosslinked, Non-Cationic starch (FL7+)	13.7	0
Sodium Thiosulfate	2.86	2.86
Magnesium Oxide	2.86	2.86
Xanthan biopolymer	3.14	3.14
Sized Marble powder #1	16	16
Sized Marble powder #2	16	16
Sized Marble powder #3	2.86	2.86
Tertiary Amine polymer, #1	0	0.29
Tertiary Amine polymer, #2	0	0.29
Xanthan biopolymer	3.14	3.14

Sized Marble powder #1 (1 μ to 400 μ)

Sized Marble powder #2 (1 μ to 36 μ)

Sized Marble powder #3 (1 μ to 4 μ)

Tertiary amine polymer #1, Polyethylenimine copolymer with ethylene diglycol

Tertiary amine polymer #2, Polyethylenimine copolymer with epichlorohydrin

The CaBr₂ brine was a stock commercial solution marketed by TETRA Technologies. The cationic starch used was also commercially available from TETRA Technologies as TETRA HPS. It is an epichlorohydrin crosslinked, pregelatinized corn starch which has been reacted with diethanolamino-methane. Levels of substitution are about 0.20 to 0.40 moles amine per mole amylose. The non-cationic starch was commercially obtained as FL 7 PLUS, a trademarked product of TBC-Brinnadd. It is an epichlorohydrin crosslinked starch which can be substituted with propylene oxide. The sodium thiosulfate and magnesium oxide were USP grade. The xanthan biopolymer is available from several suppliers, that used was supplied by Drilling Specialties. The sized marble powders are available from TETRA Technologies under the trade designation TETRA Carb-Prime, TETRA Carb-Fine, and TETRA Carb-Ultra, respectively. The tertiary amine polymer #1 was a homopolymer of ethylene-imine with about 40% of the available nitrogen reacted with ethylene oxide. Molecular weight was 60,000-80,000. Tertiary amine polymer #2 was a homopolymer of ethylene-imine with about 40% of the available nitrogen reacted with epichlorohydrin. Molecular weight was about 40,000.

This mixing procedure was followed for all laboratory tests. After adding the starch, and before adding the next ingredients, the mixture was sheared with a high shear (Silvermen type) mixer for 30 seconds, and then mixed at 500 RPM using a low shear Servodyne unit for 30 minutes. This is intended to simulate mixing with a high shear centrifugal pump, and then slow mechanical rolling of a field mixing unit. This mixing procedure was repeated after the addition of the next three ingredients, the thiosulfate, magnesium oxide and xanthan. A third mixing for 30 minutes was run after adding the carbonates and tertiary amines.

Rheological properties were then measured (heating only the sample used for testing to 49° C.), and the samples were "hot-rolled" at 93° C. in a Baroid roller oven for 48 hours. Following the "hot rolling", the rheological properties were again tested, and the samples were then tested for "filtercake removal" in the following manner.

The permeability of a 5 μ Aloxide disk was first determined in both directions of flow. This test was run at 35 kPa and 21° C. Next, a filtercake was built using a standard high temperature, high pressure cell (HTHP cell). Penn Instruments and OPI, both in Houston Tex., market this equipment. The 5 μ Aloxide disk was used as the filtering medium and the chamber was run upside down so that any solids separating from the drill-in fluid might fall to the bottom and not become part of the filtercake. The cell itself was filled with the test drill-in fluid and a higher density fluid was run on bottom from a reservoir attached to the cell, so that the drill-in fluid might be displaced upward.

The test was run at 93° C. for 39 hours, with a squeeze pressure of 3,500 kPa applied to the fluid. The filtrate was collected and measured during this time. The objective for producing a filtercake was to allow an initial spurt fluid loss as the filtercake is building, but then have a rapid decline as the filtercake limits further fluid loss. At the end of the cake building time, the cell was cooled and pressure released. Remaining fluid was drained from the cell and the filtercake which had been formed was examined.

Following the visual examination, the chemical treatment for removal of the filtercake and recovery of the permeability of the Aloxide disk was performed. This part of the testing was run in the normal direction, with the disk (and filtercake on it) at the cell bottom and the treating fluid carefully poured in on top of it. This fluid was injected in the same direction as the drill-in fluid to simulate the injection of a clean-up fluid in field practice. Consequently the permeability determined in this direction is called the recovered injection permeability. The test is repeated in the opposite direction, again at 35 kPa and ambient temperature. This flow was in the production direction of an actual well and is called the recovered production permeability.

Test 1

A filtercake as described above was prepared using formulation #1 at 38° C. for heat aging and permeability testing. An initial soak of 3 hours was tried using 2% by weight of tertiary-butyl hydroperoxide and 0.3% of an ethoxylated nonylphenol surfactant. This soak was run at room temperature and 3500 kPa differential pressure. After 3 hours, less than 4 ml of fluid filtrate had been produced and the injection permeability was essentially zero. The cell was loaded again with 2% t-butyl hydroperoxide and the 3 hour test repeated. No additional breakthrough of fluid was noted, and permeability, both injection and production directions was less than 2%.

Test 2

A filtercake and test similar in all respects to Test 1 above, except that the temperature of the test was 93° C. In this case the treating fluid broke through in 45 minutes, flowing at about 1 ml/min. In about 15 minutes additional time, this rate had increased to about 5 ml/min. and the test was terminated after 80 ml of the treating fluid had been displaced through the cell. The cell was allowed to cool and pressure was released. The filtercake was visually inspected and found to be composed of discrete carbonate particles with no evidence of starches or polymers. A recovered permeability test was run in the injection direction, with 34% recovered permeability. A recovered permeability test was run in the production direction, with 67% of the original permeability recovered.

Following this step and prior to an acid flush, 50 ml of an iron control agent (2-thioethanol) and 0.3% surfactant were flushed through in the injection direction. This was done as actual field practice would call for a spacer fluid to separate the oxidizing agent stages from the hydrochloric or hydrobromic acids, which are reducing in nature. Another purpose of such a stage is to complex any Fe⁺⁺⁺ that may have been generated. Obviously a wide variety of other agents could be used.

After this buffer or spacer stage, a 5% solution of HCl in 1.32 g/ml CaBr₂ was poured into the cell. The cell was sealed and pressurized to 3,500 kPa, which was intended to simulate the spotting (but not injection) of acid in a balanced hydrostatic condition. After 3 hours, the bottom valve was opened and the acid flushed from the cell. It was noted that the time of this acid soak was one half that of the acid soaks in Tests 6 & 7 below, and only one acid soak was required. The recovered permeability was 91% in the production direction and 95% in the injection direction.

Test 3

A test similar to Test 1 was run, except in this case, formulation #2 was used; this included a cationic starch as well as amine polymers. Small amounts of fluid broke through after about 2 hours. The total fluid loss was about 30 ml during the first three hour test run. After the first 3 hour run, the cell was opened, emptied of treating solution, and a fresh 60 ml of treating solution added. Again, slow fluid loss was noted at 72.5 mPa and 38° C. over the next 3 hours resulting in a total of 30 ml displaced from the cell. Visual inspection of the filtercake showed that a top layer of the polymer had been dissolved, though not completely through. This in contrast to Test 1 that showed no such polymer attack. Permeabilities were less than 2% in both directions. Again, an iron control agent was added as in Test 2. Following this step, the cell was loaded with a 5% HCl in 1.34 g/ml CaBr₂ brine and allowed to soak for 6 hrs. Recovered permeability in the injection direction was 4%. After a second, similar 6 hour acid soak, recovered permeabilities were 77% in the production direction and 72% in the injection direction.

Test 4

A test similar to Test 1 using formulation #1, except that heat aging, filtercake build-up and treatment soaks were performed at 65° C. After 3 hours, no significant leak-off of fluid had been observed. The test chamber was refilled with a fresh 2.3% solution and the test run for another 3 hours. During the final hour of this test, fluid began to leak off, amounting to about 50 ml at the end of the test. The filtercake was powdery on top and the polymer appeared to be completely removed. Permeabilities were run in both directions, with the recovered injection permeability being 3% and the recovered production permeability being 37%.

Following this test, a mixture of 5% HCl in 1.34 g/ml CaBr₂ was loaded in the chamber for 6 hours—as described in Test 2. Recovered permeabilities following this treatment were 23% in the injection direction and 54% in the production direction.

Test 5

A test similar to Test 4 above was run, however in the formulation included amine substituted polymers with the substituted starch. The formulations were the same as those described in Test 3 using formulation #2. Heat aging, filtercake build-up, and precursor soaks (as well as acid soaks) were again run at 66° C. Fluid breakthrough was noted just after a second 3 hour soak, as fresh 2.3% t-butyl hydroperoxide was started, and then stopped after the first hour (4 hours total) when fluid totaled 60 ml. The injection

recovered permeability was 4% and the production recovered permeability was 45%. Following a single 6 hour acid soak similar to that in Test 4, the recovered permeabilities were 89% in the injection direction and 72% in the production direction.

Test 6 (for comparison to Test 2)

A test using formulation #1 was prepared, heat aging, filtercake build-up, and acid soaks were run at 93° C. No oxidizer or oxidative precursor was included. Recovered permeability after 6 hrs. soak with a 5% HCl solution in 1.34 g/ml CaBr₂ brine at 93° C. was less than 50% in both directions. After a second 6 hr. treatment with fresh acid solutions, the recovered permeability was 92% in the injection direction and 90% in the production direction.

Test 7 (also for comparison to Test 2)

A test using formulation #2 was prepared, heat aging, filtercake build-up, and acid soaks were run at 93° C. No oxidizer or oxidative precursor was run. Recovered permeability after 6 hrs. soak with a 5% HCl solution in 1.34 g/ml CaBr₂ brine at 93° C. was less than 50% in both directions. After a second 6 hr. treatment with fresh acid solutions, the recovered permeability was 88% in the injection direction and 93% in the production direction.

Test #8 (for comparison to #1 and 3)

A filtercake as described above was prepared using formulation #1 at 38° C. for heat aging and permeability testing. Two soaks of 6 hours each were run using 5% HCl in 1.34 g/ml CaBr₂ brine at room temperature and 3,500 kPa differential pressure. After the second soak, some acid was displaced through the Alconite disk and permeabilities were tested. These were essentially zero in both directions. The cell was loaded again with 5% HCl in 1.34 g/ml CaBr₂ brine and a third 6 hour soak repeated. Recovered injection permeability was 81% and recovered production permeability was 90%.

The foregoing description is illustrative and explanatory of preferred embodiments of the invention, and variations in the size, shape, materials and other details will become apparent to those skilled in the art. It is intended that all such variations and modifications which fall within the scope or spirit of the appended claims be embraced thereby.

What is claimed is:

1. A method for removing filtercake from a subterranean borehole, comprising:

drilling the borehole with a drilling fluid to form a filtercake comprising an oxidation degradable component;

contacting the filtercake with a fluid containing a soluble organic hydroperoxide stable at ambient temperature and thermally activatable at the downhole temperature of the filtercake;

allowing the organic hydroperoxide to remain at the downhole temperature for a period of time effective to form an oxidizing agent to degrade the oxidation degradable agent and decompose the filtercake;

flushing away the decomposed filtercake.

2. The method of claim 1 wherein the oxidation-degradable component is a polymer.

3. The method of claim 2 wherein the polymer comprises starch, cellulose or xanthan.

4. The method of claim 1 wherein the organic hydroperoxide is t-butylhydroperoxide and the borehole temperature is at least about 80° C.

5. The method of claim 1 wherein the organic hydroperoxide is selected from the group consisting of cumene hydroperoxide, t-butyl dihydroperoxide, and amyldihydroperoxide, and the borehole temperature is at least about 80° C.

6. The method of claim 1 wherein an activating agent for the organic hydroperoxide is flushed over the filtercake prior to contacting the filtercake with the organic hydroperoxide.

7. The method of claim 1 wherein the filtercake comprises an activating agent for activating the organic hydroperoxide.

8. The method of claim 7 wherein the activating agent comprises an ascorbic acid.

9. A method for removing filtercake from a subterranean borehole, comprising:

drilling the borehole with a drilling fluid to form a filtercake comprising an oxidation degradable component and an activating agent for activating a precursor of an oxidizing agent, wherein the filtercake is free of the precursor;

contacting the filtercake with a fluid containing the precursor of the oxidizing agent, wherein the precursor is soluble in the fluid, stable at ambient temperature and thermally activatable at the downhole temperature of the filtercake to form the oxidizing agent;

allowing the precursor to remain in contact with the filtercake to form the oxidizing component to degrade the oxidation degradable agent and decompose the filtercake;

flushing away the decomposed filtercake.

10. The method of claim 9 wherein the oxidation-degradable component is a polymer.

11. The method of claim 10 wherein the polymer comprises starch, cellulose or xanthan.

12. The method of claim 9 wherein the precursor is selected from the group consisting of t-butyl hydroperoxide, cumene hydroperoxide, t-butyl dihydroperoxide, and amyldihydroperoxide.

13. The method of claim 9 further comprising the steps of installing gravel pack screens and tool assemblies into the borehole prior to the step of contacting the filtercake with the precursor;

determining fluid losses; and

adding sand in a nonviscosified carrier to the borehole.

14. A method for removing filtercake from a subterranean borehole, comprising:

drilling the borehole with a drilling fluid to form a filtercake comprising an oxidation degradable component and an activating agent comprising a tertiary amine for activating an organic hydroperoxide;

thereafter contacting the filtercake with a fluid containing a solution of the organic hydroperoxide;

allowing the organic hydroperoxide to remain at the downhole temperature in contact with the activating agent in the filtercake for a period of time effective to form an oxidizing agent to degrade the oxidation degradable component and decompose the filtercake;

flushing away the decomposed filtercake.

15. The method of claim 14 wherein the tertiary amine comprises triethanolamine.

16. The method of claim 15 wherein the tertiary amine comprises diethylaminoisopropanol.

17. The method of claim 14 wherein the activating agent is a polymer comprising pendant tertiary amine moieties.

18. The method of claim 14 wherein the oxidation degradable component is functionalized with the amine moieties.

19. A method for removing filtercake from a subterranean borehole, comprising:

drilling the borehole with a drilling fluid to form a filtercake comprising an oxidation degradable component and an activating agent for activating an organic hydroperoxide;

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flushing over the filtercake with an additional activating agent comprising a metal salt solution wherein the metal is selected from the group consisting of copper, cobalt, nickel, chromium, iron and combinations thereof;

thereafter contacting the filtercake with a fluid containing a solution of the organic hydroperoxide;

allowing the organic hydroperoxide to remain at the downhole temperature in contact with the activating agents in the filtercake for a period of time effective to form an oxidizing agent to degrade the oxidation degradable component and decompose the filtercake;

flushing away the decomposed filtercake.

20. A method for removing filtercake from a subterranean borehole, comprising the steps of:

drilling the borehole with a drilling fluid to form a filtercake comprising an oxidation degradable component and an activating agent for activating a precursor of an oxidizing agent, wherein the filtercake is essentially free of the precursor;

installing gravel pack screens and tool assemblies into the borehole;

determining fluid losses;

adding sand in a non-viscosified carrier to the borehole after the screen installation step, contacting the filtercake with the precursor of the oxidizing agent;

allowing the precursor to remain in contact with the filtercake for a period of time effective to form the

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oxidizing agent to degrade the oxidation degradable component and decompose the filtercake;

flushing away the decomposed filtercake.

21. A method for removing filtercake from a subterranean borehole, comprising:

drilling the borehole with a drilling fluid to form a filtercake comprising an oxidation degradable component and an activating agent comprising a tertiary amine for activating a precursor of an oxidizing agent, wherein the filtercake is essentially free of the precursor;

contacting the filtercake with the precursor of the oxidizing agent;

allowing the precursor to remain in contact with the filtercake to be activated by the tertiary amine and form the oxidizing agent to degrade the oxidation degradable component and decompose the filtercake;

flushing away the decomposed filtercake.

22. The method of claim 21 wherein the tertiary amine comprises triethanolamine.

23. The method of claim 21 wherein the activating agent is a polymer comprising pendant tertiary amine moieties.

24. The method of claim 23 wherein the oxidation-degradable polymer is functionalized with the amine moieties.

25. The method of claim 21 wherein the precursor is selected from alkali metal and ammonium salts of persulfates, permanganates and percarbonates.

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[54] **WELL DRILLING AND SERVICING FLUIDS WHICH DEPOSIT AN EASILY REMOVABLE FILTER CAKE**

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[57] **ABSTRACT**

The invention provides alkaline water base well drilling and servicing fluids which deposit an easily degradable and removable filter cake on the sides of a borehole during well drilling and servicing operations. The fluids contain one or more polysaccharide polymers, sized bridging particles, and a peroxide selected from the group consisting of alkaline earth metal peroxides, zinc peroxide, and mixtures thereof. The fluids deposit a filter cake containing the peroxide. The invention also provides processes for enhancing the removal of the filter cake which comprises depositing a peroxide-containing filter cake on the sides of the borehole, or on the filter cake already present on the sides of the borehole, and thereafter contacting the peroxide-containing filter cake with an acidic solution to activate the peroxide which thereafter degrades the polysaccharide polymers in the filter cake. Preferably the filter cake containing the degraded polymer is washed with a fluid in which the bridging particles are soluble to remove the entire filter cake(s) from the sides of the borehole.

17 Claims, No Drawings