

94
2

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO

NIT : 800176089-2

RECIBO OFICIAL DE CAJA : 05 - 40,332
FECHA : JUNIO 2 DE 2005

SUPERINTENDENCIA Y COMERCIO
Radicacion : 500005-01-01
Fecha (VNO) : 2005-06-23 16:48:30
Tramite : 002-0010005-01
Dependencia : 2005 DIVISION DE NUEVAS CREACIONES
Folios: 16

***** CONSIGNACION *****

DEPOSITANTE	TIPO PAGO	BANCO	CUENTA	No. PAGO	FECHA PAGO	Vr. PAGO
BRIGARD & CASTRO LTDA	CONSIGNACION	BANCO POPULAR	050-00110-6	28252183	02/06/2005	21,261,000.00

***** CONCEPTO *****

CANT.	RENTISTICO	CONCEPTO	TOTAL CONCEPTO
1	50005-01-01	SOLICITUDES	
		05 EXAMEN DE PATENTABILIDAD DE INVEN	371,000.00
		TOTAL :	\$ 371,000.00

SOM: TRESCIENTOS SETENTA Y UNO MIL PESOS

RESPONSABLE : _____

RECIBO DE CAJA APLICADO AL EXPEDIENTE No. _____



República Bolivariana de Venezuela
MINISTERIO DEL INTERIOR Y JUSTICIA

NOTARIA PUBLICA

**DEL MUNICIPIO GUAICAIPURO
DEL ESTADO MIRANDA**

Notario Público: Abogado María Gabriela Vielma Díaz

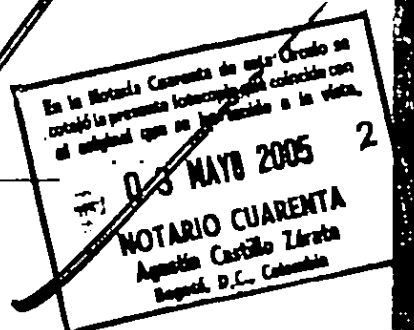
AUTENTICACION

Número:

49

Tomo:

32



De fecha:

27/03/2003

GRACIAS POR PERMITIRNOS SERVIRLES. TLF: 364-16-86

(1) 35994

2

Blanca Navarro
Blanca M. Navarro Laguna
Inpre 27.979

NOTARIA PUBLICA DEL MUNICIPIO
GUACAIPURO DEL ESTADO MIRANDA
R.M. 28.03.03
PL. 28.03.03
VALIDO PARA EL DIA 28.03.03

32

Verónica V. (03)

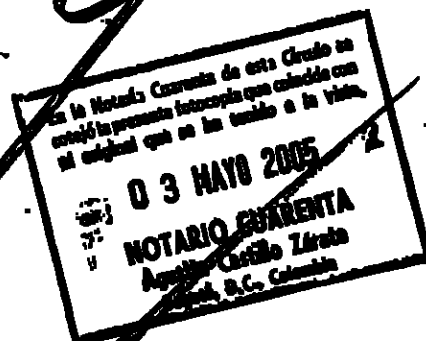
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772
40.000,00
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ilen

Yo, **BLANCA MATILDE NAVARRO LAGUNA**, venezolana, abogada en ejercicio, mayor de edad, domiciliada en Caracas, titular de la Cédula de Identidad N° 3.829.465 inscrita en el Instituto de Previsión Social del Abogado, bajo el N° 27.979, actuando en este acto en mi carácter de Apoderada Especial de **INTEVEP, S.A.**, Sociedad Mercantil domiciliada en Caracas, debidamente inscrita en el Registro Mercantil Primero de la Circunscripción Judicial del Distrito Federal y Estado Miranda, el treinta y uno (31) de mayo de 1979, bajo el N° 15, Tomo 65-A Segundo, reformada su Acta Constitutiva-Estatutos en diversas oportunidades, siendo su última reforma parcial la inscrita en el Registro Mercantil Segundo de la citada Circunscripción Judicial, el día 17 de Agosto de 1999, bajo el N° 17, Tomo 227-A Sgdo. y, finalmente, refundido en un solo texto dicho documento Constitutivo-Estatutos, según consta de documento inscrito ante la citada oficina de Registro, el día cinco (5) de junio de dos mil (2000), bajo el N° 72, Tomo 128-A Sgdo., inscrita en el Registro de Información Fiscal, N° J-00110848-3, en ejercicio de la facultad que me confiere la Cláusula VEINTINUEVE, del documento Constitutivo-Estatutos de la Compañía, debidamente autorizada para este acto, según consta en documento poder, debidamente autenticado por la Notaría Pública del Municipio Guacaipuro del Estado Miranda, el día 8 de marzo de 2003, bajo el N° 92, Tomo 27, de los Libros de Autenticaciones llevados por esa Notaría, por medio del presente documento declaro: Que sustituyo parcialmente y, en los términos expresamente descritos en el presente documento, las facultades que me han sido conferidas en los señores **RAMIRO CASTRO DUQUE** y/o **JUAN PABLO CADENA SARMIENTO** y/o **BEATRIZ JARAMILLO S.**, de Bogotá, Colombia, apoderados verdaderos y legales con poder especial, amplio y suficiente, para recabar de las oficinas y autoridades colombianas administrativas y de policía, en cualquier instancia o recurso administrativos, la obtención de patentes de invención, registros de marcas, diseños industriales, modelos de utilidad, depósitos de nombres comerciales y enseññas, registros de derechos de autor y contratos sobre los mismos, obtención de certificados de obtentor de variedades vegetales; así como, sus prórrogas, renovaciones, anotaciones de traspaso, cambios de nombre y/o domicilio; elaborar, tramitar y registrar contratos de licencia y licencias de cualesquiera clases. A efectos del ejercicio del presente poder, lo(s) faculto(s) para elevar solicitudes, formular descripciones, enmiendas, protestas, declaraciones, oposiciones, cancelaciones,

La presente fue dada fe y se otorgó en la ciudad de Bogotá, D.C., el día 03 de mayo de 2005.
NOTARIO CUARENTA
Angela Castillo Zárate
C.C. 1.000.000

nulidades, apelaciones administrativas y reclamos; pagar impuestos, cuotas y gravámenes prescritos por la ley; recibir toda clase de documentos y valores, dando el descargo respectivo y, en general, para dar ante dichas autoridades todos los pasos necesarios al efecto indicado y tomar todas las medidas que creyeren conducentes al resguardo de los intereses de mi poderdante, con todas las demás facultades legales necesarias. Este poder comprende la facultad de ratificar o confirmar en nombre de mi otorgante lo actuado; así como, la facultad de renunciar, desistir o transigir sobre derechos concedidos o en curso de concesión, previa autorización del otorgante. Asimismo, nombro, en representación de **INTEVEP, S.A.**, a: **RAMIRO CASTRO DUQUE y/o JUAN PABLO CADENA SARMIENTO y/o BEATRIZ JARAMILLO S.**, todos domiciliado(s) en la Carrera 7, N° 16-56, Piso 9, apoderados especiales en Colombia, con facultades para recibir notificaciones y las previamente establecidas en este documento. En Los Teques, a la fecha de su presentación y autenticación.

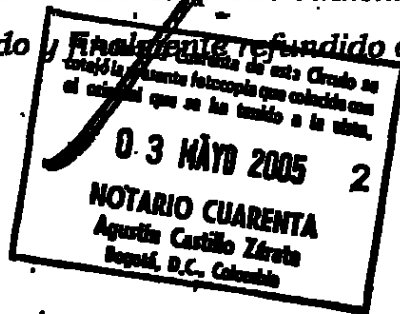
Beatriz Jaramillo



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REPÚBLICA BOLIVARIANA DE VENEZUELA. Dra. MARIA GABRIELA VIELMA DIAZ. NOTARIO PUBLICO TITULAR DE LA NOTARIA PUBLICA DEL MUNICIPIO GUAICAIPURO. ESTADO MIRANDA. Los Teques, VEINTIOCHO (28) DE MARZO del DOS MIL TRES (2.003).- 192° y 144°. El anterior documento redactado por el Abogado: BLANCA NAVARRO LAGUNA Inscrito en el inpreabogado bajo el N° 27.979 Fue presentado para su Autenticación y Devolución según planilla N° 158113 de fecha: 28-03-2003. Presente (s) su (s) otorgante (s) dijo (eron) .ser y llamarse: BLANCA MATILDE NAVARRO LAGUNA mayor (es) de edad, domiciliado (s) en: CARACAS, de nacionalidad: VENEZOLANA, de estado civil: DIVORCIADA portador (es) de la (s) Cédula (s) de Identidad No. V-3.829.465 Leído y confrontado con sus fotocopias, firmado en estas y en el presente original, en presencia del Notario el(los) Otorgante(s) expusieron) "SU CONTENIDO ES CIERTO Y MIA(NUESTRAS) LA(S) FIRMA(S) QUE LO AUTORIZA(N)". El Notario en tal virtud, da Fe Pública del presente documento y de las copias firmadas en originales que formaran el Tomo Principal y el Tomo Duplicado en presencia de los testigos: LOURDES PERDOMO y MARIA RAMIREZ, titulares de las Cédulas de Identidad Nros: V-8.682.840 y V-5.450.592 dejándolo inserto bajo el Nro. 49 Tomo 32 de los libros de Autenticaciones llevados por esta Notaría. El Notario que suscribe hace constar que ha dado cumplimiento al Artículo 78 del Decreto Ley de Registro y del Notariado e informó a las partes del contenido, naturaleza, trascendencia y consecuencias legales de los actos o negocios otorgados en su presencia, los cuales manifestaron su plena conformidad. FUE INUTILIZADOS TIMBRES FISCALES POR BOLIVARES 20000,00. Igualmente le fue presentado Registro Mercantil de INTEVEP S.A, debidamente en el Registro Mercantil Primero de la Circunscripción Judicial del Distrito Federal y Estado Miranda de fecha: 31-5-1979, bajo el No: 15 Tomo: 65-A Segundo, reformada su Acta Constitutiva Estatutos en diversas oportunidades, siendo la ultima reforma parcial la inscrita en el Registro Mercantil Segundo de la citada circunscripción Judicial en fecha 17-8-1999 bajo el No. 17 Tomo 227-A Segundo y finalmente refundido en un solo

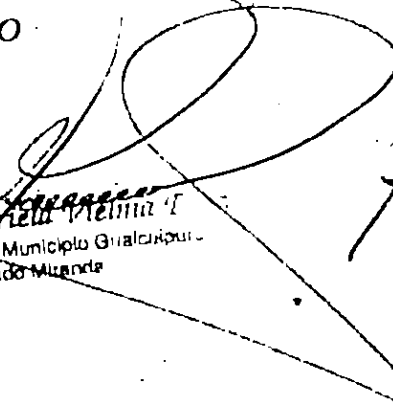


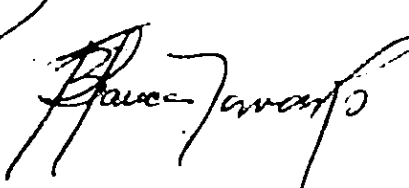
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texto dicho documento Constitutivo Estatutos según consta de documento inscrito ante la citada Oficina de Registro en fecha: 5-6-2000 bajo el No. 72 Tomo 128-A Sgdo. 2) Documento Poder autenticado por ante esta misma Notaria en fecha: 18-3-2003 bajo el No. 92, Tomo 27

EL NOTARIO PUBLICO

EL (LOS) OTORGANTE (S)


Dra. Maria Gabriela Velazquez
Notario Publico del Municipio Guacara
del Estado Miranda

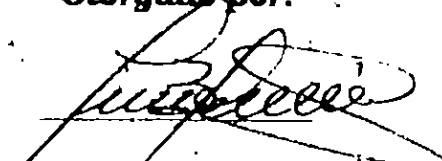


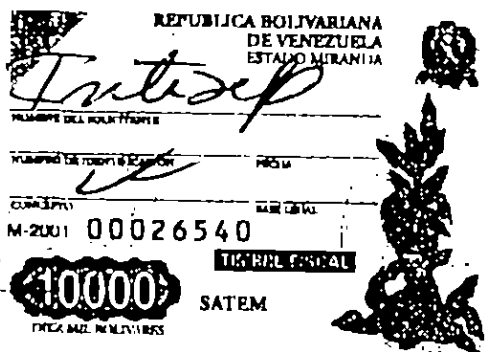
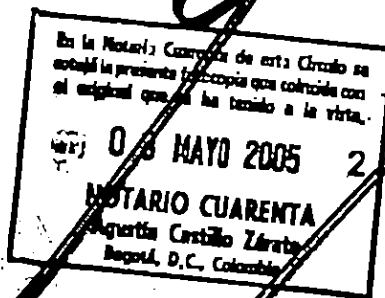
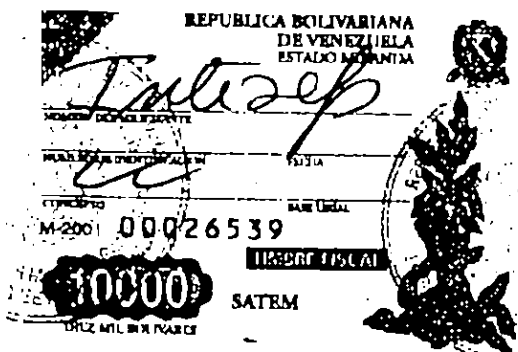


LOS TESTIGOS

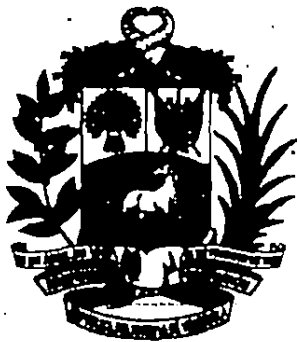



Otorgado por:





Nº. 721186 AB



REPUBLICA BOLIVARIANA DE VENEZUELA
MINISTERIO DEL INTERIOR Y JUSTICIA

OFICINA PRINCIPAL DE REGISTRO PUBLICO DEL ESTADO
MIRANDA

Los Teques, veinte y ocho (28) Marzo de 2003

AÑOS: 192º Y 143º

La Suscrita Registradora Principal del Estado Miranda, Dra. Mireya Rubio de Gámez, CERTIFICA que la firma que legaliza del anterior documento es autentica y la misma que utiliza en todos sus actos Públicos la ciudadana: **Dra. MARIA GABRIELA VIELMA DIAZ**. Quien para la fecha de la expedición del anterior documento a los Veinte (28) días del mes de Marzo del año 2003, era Notario Público del Municipio Guaicaipuro Los Teques, Estado Miranda. La presente **LEGALIZACIÓN** se expide sin prejuzgar acerca de ningún otro extremo de fondo ni de forma. Causó Derechos de Registro y Tímbres Fiscales. El presente documento fue elaborado por Juana Lorca Funcionaria autorizada quién firma conjuntamente conmigo.

FUNCIONARIA

JUANA LORCA

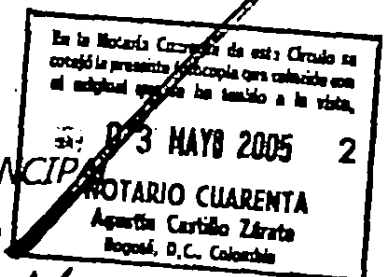
Para el día: 31/3/03

Planilla: Nº. 35994



LA REGISTRADORA PRINCIPAL

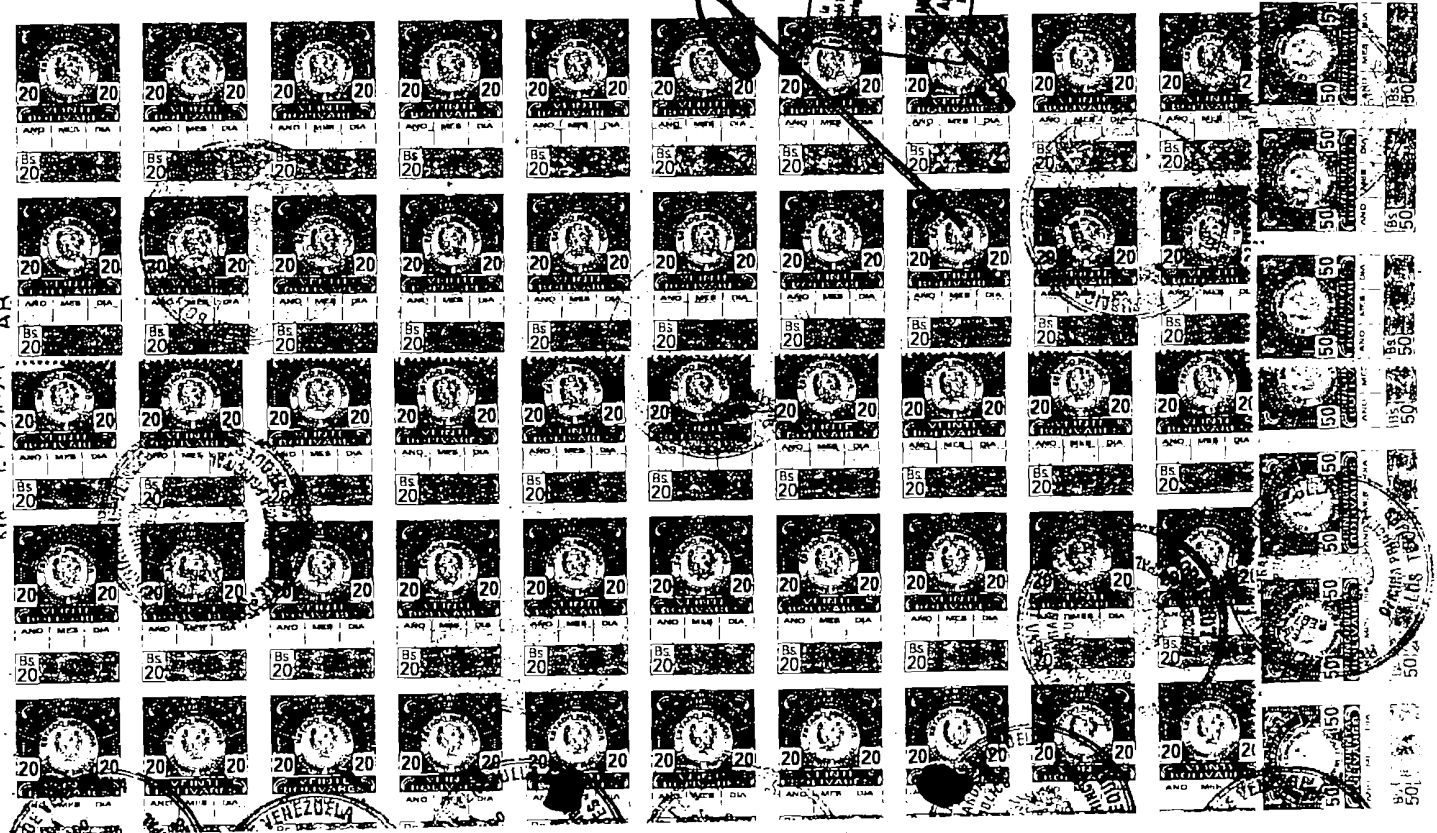
Dra. MIREYA RUBIO DE GAMEZ



Handwritten signature or initials.

La Notaría General de la Ciudad de Caracas se
encuentra habilitada para otorgar todo tipo de
instrumentos que se requieran en la vida.
03 MAY 2005 2
NOTARIO CUARENTA
Agencia Cuatitbo Zúñiga
Impulsa, D.C. Colombia

NOT. C10000 AR



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15-11

John D. Tindley

31 REPUBLICA DE VENEZUELA
Ministerio de Hacienda
32 Nombre del Contribuyente
33 Número de Identificación
34 Cédula
35 H-99
36 5000 CINCO MIL BOLIVARES
37 REPUBLICA DE VENEZUELA
Ministerio de Hacienda
38 Nombre del Contribuyente
39 Número de Identificación
40 Cédula
41 H-99 4713617
42 5000 CINCO MIL BOLIVARES
43 SENIAT

En la Notaría Cuarenta se otorgó la presente Autógrafa que se otorga con el original que se le adjunta a la vista.
03 MAY 2005 2
NOTARIO CUARENTA
Angela Castillo Zárate
Bogotá, D.C., Colombia

REPUBLICA DE VENEZUELA
Ministerio de Hacienda

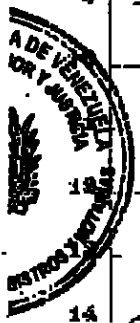
REPUBLICA DE VENEZUELA
Ministerio de Hacienda

REPUBLICA DE VENEZUELA
Ministerio de Hacienda

100
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Nº 26075734



3 MAYO 2005 2
NOTARIO CUARENTA
Agustín-Carillo-Lázaro
Bogotá, D.C., Colombia



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República Bolivariana de Venezuela



MINISTERIO DEL INTERIOR Y JUSTICIA

Se legaliza la firma que antecede de la ciudadana

MIREYA RUBIO DE GAMEZ

quien es como se titula, Registradora Principal del Estado Miranda

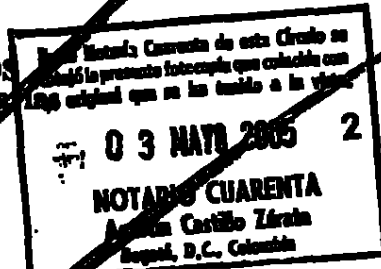
Se advierte que la presente legalización no prejuzga acerca de
ningún otro extremo de fondo ni de forma.

Caracas, 01 ABR. 2003

Años 192º y 144º

Por el Ministro,

JOSE G. VELASQUEZ CAMPOS
Director General de Registros y Notarías





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HA

REPUBLICA BOLIVARIANA DE VENEZUELA
MINISTERIO DE RELACIONES EXTERIORES
DIRECCION GENERAL DE RELACIONES CONSULARES

APOSTILLE

Convention de La Haye du 5 Octobre 1961

1- País: VENEZUELA

El presente documento público :

2- Ha sido suscrito por: JOSE G. VELAZQUEZ CAMPOS

3- Actuando en su calidad de: DIRECTOR GENERAL DE REGISTROS Y NOTARIAS

4- Llevando el sello/timbre de: MINISTERIO DEL INTERIOR Y JUSTICIA

Certificado

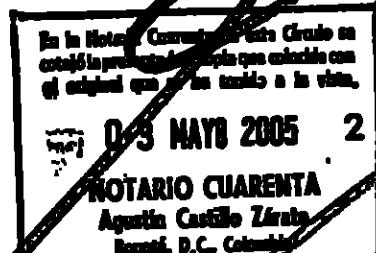
5- En Caracas: 04 de Abril de 2003

6- Por el Ministro:

7- N°: 026972

8-Sello/Timbre

9- Firma



[Firma manuscrita]

Dante Virasola
CONSULERO
REC. N° 00711-19.03.01

112 107
18

En la Notaría Cuarenta de la Ciudad de Bogotá se otorgó el presente instrumento que coincide con el original que se encuentra en la vida.

06 MAYO 2005 2

NOTARIO CUARENTA
Agustín Castillo Zárate
Bogotá, D.C., Colombia

REPUBLICA DE VENEZUELA
Ministerio de Hacienda

Nombre del Titular

Apellido de Identificación Fecha

Provincia

H-99 4736329

5000 CINCO MIL BOLIVARES

SENIAF

REPUBLICA DE VENEZUELA
Ministerio de Hacienda

Apellido de Identificación

Provincia

H-99 4239436

5000 CINCO MIL BOLIVARES

SENIAF

108 117

REGISTRO CIVIL DE DEFUNCIÓN

**Indicative
Serial**

5562241

Datos de la oficina de registro									
Clase de oficina: ..	Registraduría	Notaria	X	Consulado	Corregimiento	Insp. de Policía	Código	9795	
Folio: Documento - Partida - Corregimiento de Inmigración de Policía									
COLOMBIA CUNDINAMARCA BOGOTÁ D.C. NOTARIA 32.									

Datos del Inscrito		Apellidos y nombres completos	
CASTRO DUQUE RAMIRO			
Documento de Identificación (Clase y número)		Sexo (en Letras)	
C.C. No. 170322 DE BOGOTÁ		MASCULINO	

Orden de la defunción Lugar de la Defunción País - Departamento - Municipio - Corregimiento o de Inspección de Policía COLOMBIA CUNDINAMARCA BOGOTA D.C.														
Fecha de la defunción										Hora			Número de certificado de defunción	
Año	2	0	0	4	Mes	1	0	Día	3	0	04:10 PM	A- 2094375.		
Presunción de muerte														
Lugar que profiere la sentencia										Fecha de la sentencia				
-- -- -- -- -- -- -- -- -- --										Año -- -- -- -- -- Mes -- -- -- -- -- Día -- -- -- -- --				
Documento presentado										Nombre y cargo del funcionario				
Autenticación Judicial ☐ Certificado Médico ☒										ANDRES DIAZ CAMPOS.- R. M. No. 79982662				

Fecha del denunciante		Apellidos y nombres completos	
EDGAR DAVID REGINO II.			
Documento de identificación (Clase y número)		Firma	
C.C.No. 15.030.154 DE LORICA/ CORDOBA			

Primer testigo	
Apellidos y nombres completos	
Documentos de identificación (Clase y número)	
Firma	

Segundo testigo	
Apellidos y nombres completos	

Documentos de identificación (Clase y número)	Firma
-----	-----

Fecha de inscripción				Nombre y apellido del asegurado que autoriza	
Año	2	0	0	Mes	1
	4			Día	0
					2
BLANCA ROSARIO DE LOS RESTRÉPOL NOTARIA					

PADRES: ALFONSO CASTRO
MERCEDES DUQUE

9-2500 14. 57. 00. 00. 00. 00.

NOTARIA 32

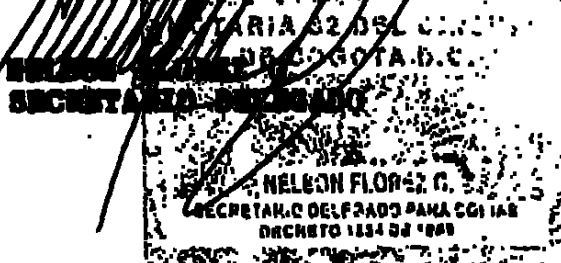
DEL CIRCULO DE SANTA FE DE BOGOTA, D.C.

Germán Eleázar Moreno L.
Notario

COMO SECRETARIO DELEGADO EN LA NOTARIA TREINTA Y DOS (32) DEL
CIRCULO DE BOGOTA

CERTIFICO, QUE:

La presente acta es fiel copia del original tomada del registro
civil de defunciones serial indicativa número: 556224
que expido en la ciudad de Bogotá D.C. hoy: 05 NOV. 2004



DIVISION DE NUEVAS CREACIONES

RADICACIÓN EXPEDIENTE No. 04-1055

EL EXTRACTO DE LA PRESENTE SOLICITUD DE PATENTE DE INVENCION
FUE PUBLICADO EN LA GACETA DE PROPIEDAD INDUSTRIAL No 554, DE
FECHA 29 DE JULIO DE 2005, EL TERMINO HABIL SEÑALADO POR LA LEY
EXPIRA EL 25 DE OCTUBRE DE 2005.

NOTA: Dentro del plazo de los seis (6) meses siguientes a partir de la fecha de publicación en la gaceta de Propiedad Industrial, deberá solicitar y cancelar el examen de patentabilidad so pena de que la solicitud caiga en abandono, de acuerdo con lo establecido en el Artículo 44 de la Decisión 486/2000.

SE PRESENTARON OPOSICIONES POR PARTE DE TERCEROS.

SI _____

NO **X** _____

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

2020

Bogotá, D. C., 13 de Junio de 2006

Doctor

JUAN PABLO CADENA SARMIENTO

Representante INTEVEP, S. A.

ASUNTO

Radicación No. 04-01055

Trámite 002

Evento 001

Actuación 430

Oficio

Folios 043

06693

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:

- a) Para el presente estudio se tendrán en cuenta el capítulo descriptivo, comprendido en los folios 9 a 18 de la solicitud en estudio.
- b) Para el presente estudio se tendrán en cuenta los dibujos comprendidos en los folios 33 a 38 de la solicitud en estudio.
- c) Para el presente estudio se tendrá en cuenta el capítulo reivindicatorio que comprende 20 reivindicaciones en los folios 29 a 32 de la solicitud en estudio.
- d) Conforme lo establece los artículos 9, 10 y 11 de la decisión 486 de la Comisión de la Comunidad Andina, la presente solicitud en estudio fue presentada el 8 de enero de 2004, y en el momento de la radicación SI se reclamo prioridad de la primera solicitud presentada en Estados Unidos US 10/342852

2) Objeto de la invención

- a) Las reivindicaciones 1 a 20 de la solicitud en estudio se refieren a
 - i) (1.-) Un fluido de perforación comprende: un fluido base; y un paquete de aditivos que reducen la pérdida de circulación comprende un polisacárido, un derivado de celulosa y un componente controlador del pH.

- ii) (17.-) Un paquete de aditivos reduciendo la pérdida de circulación comprende un polisacárido, un derivado de celulosa y un componente controlador del pH.
- b) El anterior producto busca mejorar las propiedades de pozos de perforación.
- c) Según la Clasificación Internacional de Patentes, la codificación para esta solicitud corresponde a C 09 K 7/00

3) Claridad de la Solicitud

- a) El artículo 28 de la Decisión 486 de la Comisión de la Comunidad Andina de Naciones 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"

La descripción no es clara toda vez que las unidades no corresponden al Sistema Internacional de Unidades y los dibujos se encuentran muy mal presentados; estos últimos deben suministrarse en original, en tinta negra indeleble y siguiendo las normas del dibujo técnico.

- b) 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 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 reivindicación dependiente múltiple."

El capítulo reivindicatorio no es claro toda vez que no se encuentra correctamente redactado. Por su estructura todas las reivindicaciones deben constar de dos partes. Una primera parte, el preámbulo, sirve para situar el objeto de la invención dentro de un contexto técnico, es lo que se conoce y sobre lo que no se reclama ningún privilegio. La segunda parte, o parte característica, define lo que se considera novedoso y se desea proteger. Estas dos partes están separadas por expresiones como 'caracterizado por' o similares. Debe ser más explícito lo que el solicitante considera como nuevo de lo que considera como conocido, en especial en las reivindicaciones independientes

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 este incluido en la solicitud de fecha anterior cuando ella se publique o hubiese transcurrido el plazo previsto en el artículo 40."

Consultadas las bases de datos y los archivos con que cuenta la entidad, especialmente bajo las clasificaciones C 09 K 7/00 y las más cercanas a ellas, se encontró que antes del 15 de enero de 2003 (fecha para determinar el estado de la técnica) habían sido publicados los documentos que se enumeran en la siguiente tabla los cuales se relacionan con composiciones empleadas en fluidos de perforación.

De acuerdo con lo establecido en el artículo 16 se determinó el estado de la técnica y se encontró el siguiente antecedente:

Nº	Documento	Título	Fecha de Publicación
D1	EP1 207 267	An oil water fracturing fluid emulsion, method of preparation and use for fracturing a subterranean formation	2002.05.22
D2	US 5 514 644	Polysaccharide containing fluids having enhanced thermal stability	1996.05.07
D3	US 4 620 596	Well drilling workover and completion fluids	1986.11.04
D4	US 6 180 571	Fluid loss control additives and subterranean treatment fluids containing the same	2001.01.30
D5	US 5 612 294	Scleroglucan based drilling mud	1997.03.18
D6	US 6 001 158	Dry biocide	1999.12.14
D7	US 3 971 734	Sulfite compositions, aqueous sulfite solutions and method of decreasing their rate of oxidation	1976.07.27

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 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.

a) Evaluación de la novedad y el del Nivel Inventivo

El art. 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 prioridad de la solicitud de patente que se estuviese examinando, siempre que dicho contenido esté incluido en la solicitud de fechas de prioridad cuando ella se publique o hubiese transcurrido el plazo previsto en el artículo 40."

El art. 18 de la Decisión 486 de la Comisión de la Comunidad Andina establece:

"Se considerará que una invención tiene nivel inventivo, si para una persona del oficio normalmente versada en el arte en la materia técnica correspondiente, esa invención no hubiese resultado obvia ni se hubiese derivado de manera evidente del estado de la técnica".

Los cinco primeros documentos revelan lo que el solicitante desea proteger para Colombia.

(D1) EP1 207 267 muestra un fluido de perforación que comprende un fluido base; y un conjunto de compuestos que reducen la pérdida de circulación y pueden comprender polisacáridos, derivados de celulosa y un componente controlador del pH. Lo mismo sucede con (D2) US 5 514 644, (D3) US 4 620 596, (D4) US 6 180 571, y (D5) US 5 612 294.

(D6) US 6 001 158 y (D7) US 3 971 734 muestran biocidas que al combinarse con cualquiera de los primeros cinco documentos permiten encontrar exactamente lo mismo que lo esbozado en la presente solicitud.

b) Resumen

En conclusión los requisitos de patentabilidad de la presente solicitud se podrían ver afectados así:

Nº	Documento	Relvindicaciones afectadas	Requisito que afecta
D1	EP1 207 267	1 - 20	Novedad
			Nivel inventivo
D2	US 5 514 644	1 - 20	Novedad
			Nivel inventivo
D3	US 4 620 596	1 - 20	Novedad
			Nivel inventivo
D4	US 6 180 571	1 - 20	Novedad
			Nivel inventivo
D5	US 5 612 294	1 - 20	Novedad
			Nivel inventivo
D6	US 6 001 158	15, 18, 20	Nivel inventivo
D7	US 3 971 734	15, 18, 20	Nivel inventivo

6) Notificación

En cumplimiento del artículo 45 de la Decisión 486 de la Comisión de la Comunidad Andina, se le indica que dentro del término de sesenta días contados a partir de la fecha de la notificación de la presente comunicación debe responder a la notificación. 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 por el numeral 5.2, literal e) del capítulo quinto del título primero de la Circular Única N° 10 de 2001


ALIX CARMENZA CÉSPEDES DE VERGEL
Jefe División de Nuevas Creaciones

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

22 JUN. 2006

Concepto Técnico N°	EXAMINADOR TÉCNICO	EXAMINADOR JURÍDICO
943	Código No. 202003	Código No.



(12) EUROPEAN PATENT APPLICATION

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(54) Designated Contracting States: AT BE CH CY DE DK ES FR GB GR IE IT LI LU MC NL PT SE TR Designated Extension States: AL LT LP MK NO RO	• Pessier, Oscar Colonne de Carrière Eau Minérale (VE) • Marquet, Rosalinde Eau Antiseptique des Lacs Alpins Eau Minérale (VE) • Simon, Jean La Rosalinde Bar, Eau, Minérale (VE)
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(54) An oil in water fracturing fluid emulsion, method of preparation and use for fracturing a subterranean formation

(57) An oil in water fracturing fluid emulsion includes a dispersed oil phase; and a continuous water phase in the form of a solution of cross-linkable polymer in water. A method for forming the emulsion, as well as a fracturing method using the emulsion, are also disclosed.

Description

[0001] The invention relates to the field of fracturing fluids and, more particularly, to a fracturing fluid useful in fracturing a subterranean formation for enhancing production from same.

[0002] The use of fracturing fluids for enhancing production from subterranean formations is well known. In such endeavors, a fluid is pumped into a well with the intent of fracturing a particular formation so as to increase permeability of the formation so that fluids can flow more readily from the formation into a production well.

[0003] Important concerns when evaluating and formulating a fracturing fluid are pumpability, viscosity, cost and recoverability among others. Numerous different types of fluids have been used as fracturing fluids. Conventionally used fluids include aqueous viscousified with guar, gelled oils, linear gelled water, cross-linked gelled water and foamed gels.

[0004] In connection with pumpability and viscosity, it is desirable that the fluid be easily pumpable at low pumping pressures while sufficiently viscous that the fluid, when pumped into a well, will break-up a subterranean structure and increase the permeability of the structure as desired.

[0005] It is also desirable, once the subterranean formation is fractured, that the fluid be easily recovered from the well.

[0006] Conventional fluids utilize expensive additives in large amounts so as to meet these requirements, and the need remains for an acceptable fracturing fluid which is inexpensive in preparation and use, and which yields the desired results.

[0007] It is therefore the primary object of the present invention to provide a fracturing fluid which performs well as a fracturing fluid and has reduced cost for preparation.

[0008] It is a further object of the present invention to provide a method for preparing such a drilling fluid.

[0009] It is a still further object of the present invention to provide a method for fracturing a formation utilizing such a fracturing fluid.

[0010] Other objects and advantages of the present invention will appear hereinafter.

[0011] The problems are solved by the teaching according to the independent claims. Particular developments are given in the dependent claims. Within the frame of the invention are all combinations of at least two of the descriptive elements and technical features disclosed in the claims and/or in the description.

[0012] In accordance with the present invention, the foregoing objects and advantages have been readily attained.

[0013] In accordance with the invention, an oil in water fracturing fluid emulsion is provided, which emulsion comprises a dispersed oil phase, and a continuous water phase comprising a solution of cross-linkable polymer in water.

[0014] In further accordance with the present invention, an oil in water fracturing fluid emulsion is prepared according to a method which comprises the steps of providing a water phase comprising a solution of a cross-linkable polymer in water; providing an oil phase; forming an oil in water emulsion from said water phase and said oil phase; adjusting pH of said emulsion to a pH of between about 8.0 and about 13.0; and cross-linking said polymer solution so as to provide a cross-linked emulsion.

[0015] In accordance with another aspect of the present invention, a method is provided for fracturing a subterranean formation through a well, which method comprises the steps of providing an oil in water fracturing fluid emulsion comprising a dispersed oil phase; a continuous water phase comprising a solution of cross-linkable polymer in water; and a propping agent carried by said emulsion; pumping said emulsion into a well comminuted with a subterranean formation so as to form cracks in said formation; and removing said emulsion whereby said propping agent is positioned in said cracks.

[0016] Further advantages, characteristics and details of the invention are apparent from the following detailed description of preferred embodiments of the invention with reference to the attached drawings schematically illustrating same:

Figure 1 graphically illustrates viscosity over time for emulsions in accordance with the present invention when subjected to different amounts of breaker; and

Figure 2 graphically illustrates viscosity at different temperatures for a cross-linked emulsion in accordance with the present invention as compared to a polymer free gel.

[0017] The invention relates to an oil in water fracturing fluid emulsion which is useful for fracturing subterranean formations so as to improve permeability of same and, thereby, to improve production of hydrocarbons. In accordance with the present invention, the fracturing fluid is prepared utilizing inexpensive and readily available ingredients, and further utilizing reduced amounts of ingredients which increase the cost of conventional fracturing fluids.

[0018] In accordance with the present invention, the fracturing fluid is provided as an emulsion of a dispersed oil phase in a continuous water phase. As will be further discussed below, the water phase is provided as a polymer in water solution, and the emulsion is treated with a cross-linking agent which serves to cross-link the polymer and in-

increase viscosity of the overall emulsion. This advantageously allows for using the emulsion as a fracturing fluid as well as a carrier of propping agents or proppants which are left behind in the formation to keep fractures or cracks formed in the formation open, thereby enhancing production of hydrocarbons and other desired fluids.

[0010] The oil phase of the emulsion of the present invention may advantageously be any hydrocarbon which is preferably inexpensive and readily available such as, for example, diesel, mineral oil and mixtures thereof. Of course other suitable oil or hydrocarbon phases could be utilized so long as they are compatible with the well and formation, as well as the polymer solution and its cross-linking agent. Diesel and mineral oil are particularly desirable because they are readily available at reasonable cost and are compatible with the well.

[0010] The water phase is preferably formed by mixing a solution of the desirable cross-linkable polymer in water. The water can be obtained from any acceptable source, and may include brine, fresh water, etc.

[0011] The emulsion may advantageously be prepared having a ratio by volume of oil to water of between about 80: 20 and about 90:10. The proper ratio should be selected depending upon the expected fracturing force required for fracturing the well, as well as various pumping parameters particular to a subject well. The emulsion is preferably prepared having an average droplet size of less than about 80 micrometers, more preferably between about 8 micrometers and about 3 micrometers.

[0012] In accordance with the present invention, the emulsion preferably includes a cross-linking agent which cross-links the polymer so as to increase viscosity of the overall emulsion, thereby rendering the emulsion ideal for use as a fracturing fluid and as a carrier of a propping agent. In this regard, various polymers are suitable. Preferred polymers include polyacrylamides, cellulose derivatives, carboxy gums, and *big blue*, and hydroxy propyl guar, *one example* of a suitable polymer. The polymers are preferably present in the polymer solution in an amount between about 10 and about 70 lbs of polymer per 1000 gallons of water.

[0013] The cross-linking agent in accordance with the present invention may suitably be any agent which will produce or serve as a source of desired ions which act to cross-link the various chains or branches of polymer present in the water phase of the emulsion. Preferred cross-linking agents include aluminum, titanium, zirconium, antimony, chromium, borate and mixtures thereof, all of which can serve as the source of free ions as desired. Borate and any source of free borate ions is preferred.

[0014] The water phase of the emulsion of the present invention may also advantageously be mixed with a salt such as potassium chloride and the like so as to avoid excessive clay swelling which would adversely impact upon the activities of the emulsion.

[0015] Emulsions according to the invention also preferably include a suitable surfactant so as to facilitate forming of the emulsion as well as to improve stability of same. Suitable surfactants are discussed below.

[0016] The emulsion is preferably mixed with sand serves as an excellent carrier for a propping agent, as mentioned above. The propping agent should be selected as any granular substance having a desirable particle or grain size which will serve to lodge in cracks and fractures induced into the formation, and thereby hold such cracks or fractures open so as to enhance hydrocarbon production from same. Such proppants are well known to the person of ordinary skill in the art.

[0017] Before cross-linking, the emulsion may suitably have a viscosity of between about 80 and about 180 cP at 511 μ^2 and 80°F. The cross-linking of the emulsion provides an increase in emulsion viscosity, preferably to a viscosity of between about 180 and about 750 cP at 170 μ^2 and 180°F. This allows the emulsion to be used as an excellent carrier for the propping agent so as to advantageously deliver the propping agent to the formation as it is fractured. This advantageously allows for the formation to be fractured and propping agent delivered all utilizing a single emulsion fracturing fluid and process step.

[0018] Through use of an oil in water emulsion and cross-linking of polymer in the water phase of the emulsion, a fluid is provided which has the desired viscosity and pumpability, and which also serves as an excellent propping agent carrier. The combination of oil in water emulsion with cross-linked polymer advantageously provides for reduced amounts of polymer and cross-linking agent which results in reduced cost.

[0019] In accordance with the present invention, an oil in water fracturing fluid emulsion can be prepared as follows.

[0020] The water phase is prepared by mixing the selected polymer to water until a solution is formed.

[0021] The oil phase, such as diesel, mineral oil and the like, is obtained and an emulsion is formed of the oil phase in the water phase, preferably utilizing a surfactant. Suitable surfactants include a combination of suitable, alkaline metal sulfonates and non-ionic surfactants selected from the group consisting of alkyl phenols, aliphatic-ethoxylated alcohols, and mixtures thereof. A surfactant package is preferably provided having a ratio of anionic surfactant to non-ionic surfactant, by volume, of between about 70:30 and about 90:10.

[0022] Once the emulsion is formed, it has been found in accordance with the invention that the pH may frequently need to be adjusted so as to allow for the desired cross-linking. In order to obtain the desired cross-linking, a pH of between about 8.5 and about 13.0, preferably between about 9.5 and about 12.0, is critical. The pH can be adjusted by mixing with any suitable and well-known pH controller such as monoethanolamine, sodium hydroxide, potassium hydroxide and the like. Once the suitable pH is obtained, the emulsion is then cross-linked by mixing with a suitable

cross-linking agent such as an agent selected from the group consisting of aluminum, titanium, zirconium, antimony, chromium, borate and mixtures thereof. In accordance with the present invention, borate compounds are most preferred, as are compounds which generate borate ions in solution in the water phase, as such borate ions appear to enhance the cross-linking process so as to obtain the desired viscosity of the emulsion in accordance with the present invention. If the emulsion is to be transported by flowing through conduits before use, it may be desirable to add the cross-linking agent after such transport. Thus, the cross-linking agent can be added at the time the emulsion is formed, just before or simultaneously with addition of the propping agent, or any point thereafter.

[0023] Once the emulsion is complete, any desired propping agent or proppant can be mixed into the emulsion as desired, and the emulsion serves as an excellent carrier for carrying the propping agent down through a well and to a subterranean formation which is to be the subject of a fracturing process. Typically, the propping agent is not added to the emulsion until just before use.

[0024] Once the formation is fractured, it is desirable to remove the fracturing fluid, especially any polymers and the like which remain after the process. In order to facilitate removal of the fracturing fluid, it is desired to break the cross-link of the polymer so as to reduce viscosity and allow for pumping of the broken fracturing fluid back to the surface. Breaking can be accomplished utilizing breakers such as sulfur dioxide, peroxides and azobisisobutyronitrile. Such breaking agents or breakers are well known to a person of ordinary skill in the art.

[0025] Once the cross-linking is broken, the reduced viscosity emulsion advantageously retrogrades remaining or residual polymer so as to facilitate removal of the entire fracturing fluid including polymers, while nevertheless leaving propping agents behind, in cracks or fractures in the formation, so as to enhance hydrocarbon production from the formation as desired.

[0026] The fracturing fluid in accordance with the present invention is advantageous in that viscosities up to 750 cP are provided at temperatures between about 110°F and about 220°F, which provides for excellent propping agent transport. Further, the system uses very low polymer concentration, providing excellent results utilizing 14-18 lbs. of polymer per 1000 gallons of water and providing satisfactory results up to temperatures of about 180°F and potentially up to about 220°F. This is a reduced concentration and improvement in temperature tolerance as compared to conventional fracturing fluids.

[0027] In addition, the oil phase is low cost, and all additives are commercially available.

Example

[0028] This example demonstrates preparation of a fracturing fluid in accordance with the present invention, as well as analysis of same.

[0029] 0.5 barrels of a diesel-mineral oil mixture were obtained for use as the oil phase.

[0030] The water phase was provided as 0.5 barrels of fresh water mixed with polymer hydroxy propyl guar (HPG) polymer at a rate of 50 lbs. polymer per 1000 gallons of water, and 6 lbs. of potassium chloride per barrel were added to the water. During emulsion formation, a commercial surfactant was used at a rate of 80 lbs. of surfactant per barrel of total emulsion. This surfactant is an anionic/nonionic surfactant having a ratio of 75:25, and is selected so as to be compatible with drilling fluid and other well fluids to be encountered. The emulsion was formed at 511 μ^2 and 80°F, and the resulting emulsion had a viscosity of 120 cP. Sodium hydroxide and monoethanolamine were then added to the emulsion until a pH resulted that was in the range of between about 9.5 and about 12, in this case 11.5.

[0031] Boric acid was then added to the pH-adjusted emulsion so as to induce cross-linking in the polymer. Boric acid was added at the rate of 0.5 lbs/1000 gallons of emulsion. The emulsion as formed was then tested for rheological behavior, particularly when treated with pseudosolvents of ammonium bromide over time. The results are set forth in Table 1 below showing pseudo plastic index (PI) and consistency index (K'). Table 1 shows that the cross-linked emulsion is a highly pseudoplastic fluid at different concentrations of breaker, and therefore has lower viscosity at high shear rate and high viscosity at low shear rate as desired.

Table 1

Time (min)		Breaker (lbs./1000 gal)							
		0				1.0			
		PI'	PI'	PI'	PI'	PI'	PI'	PI'	PI'
0	1	0.4108	0.3709	0.3680	0.3175	0.3646	0.1877	0.3386	0.1888
30	2	0.7118	0.5346	0.4680	0.5467	0.4684	0.0800	0.3138	0.3148
74	3	0.7118	0.5346	0.4687	0.0813	0.438	0.0808	0.4678	0.3187

Table 1 (continued)

170°F								
Breaker (lbs./1000 gal)								
Time (min)	0		0.5		0.75		1.0	
	a'	b'	a'	b'	a'	b'	a'	b'
110	0.3888	0.5808	0.4652	0.3814	0.3515	0.4505	0.5716	0.5119
140	0.4171	0.1180	0.3883	0.0883	0.4481	0.0548	0.4388	0.0148
180	0.5793	0.1911	0.5483	0.0803	0.5889	0.0481	0.6883	0.0388

[0042] The emulsion prepared in this example was also tested utilizing different amounts of breaker so as to illustrate viscosity change over time. Figure 1 shows the emulsion of the present invention when treated with different amounts of breaker, and the resulting viscosity at 170°F. As shown, 0.5 lbs/1000 gallons of breaker and greater provided for excellent reduction in viscosity after an initial high-viscosity period which is ideal for utilizing the emulsion of the present invention as a fracturing fluid. The high viscosity in the initial period allows the fluid to be utilized for forming fractures, while the break in cross-linking and reduction in viscosity allows for the emulsion, with encapsulated polymer, to be readily recovered from the well, leaving propping agent behind.

[0043] Figure 8 further shows the emulsion as prepared in this example as compared to a conventional polymer-free gel in viscosity at different temperatures, which further demonstrates the benefit of the cross-linking of the present invention in providing for use as a fracturing fluid, as well as a propping agent transport. As shown, at temperatures between 110°F and 170°F, the cross-linked emulsion has a greater viscosity in all cases, with the degree of magnitude of improvement in viscosity of the cross-linked emulsion being greater as temperature increases.

[0044] It should readily be appreciated that in accordance with the present invention, an emulsion and method for forming same have been provided which allow for an effective and inexpensively prepared fracturing fluid. Further, methods are provided for use of this fracturing fluid in fracturing formations so as to enhance hydrocarbon and other desired fluid production.

[0045] This invention may be embodied in other forms or carried out in other ways without departing from the spirit or essential characteristics thereof. The present embodiments are therefore to be considered as in all respects illustrative and not restrictive, the scope of the invention being indicated by the appended claims, and all changes which come within the meaning and range of equivalency are intended to be embraced therein.

Claims

1. An oil in water fracturing fluid emulsion, comprising:

a dispersed oil phase; and

a continuous water phase comprising a solution of cross-linkable polymer in water;

2. The emulsion of claim 1, wherein said emulsion has a viscosity of between about 80 and about 150 cP at 811 μ s² and 80°F;

3. The emulsion of claim 1, wherein said polymer is cross-linked and said emulsion has viscosity of between about 150 cP and about 750 cP at 170 μ s² and 180°F;

4. The emulsion of claim 1, wherein said oil phase is selected from the group consisting of gasoil, mineral oil and mixtures thereof;

5. The emulsion of claim 1, wherein said water phase contains said polymer in an amount between about 10 and about 70 lbs. of said polymer per 1000 gallons of water;

6. The emulsion of one of the claims 1 to 5, wherein said polymer is selected from the group consisting of polysaccharides, cellulose derivatives, xanthan gum and combinations thereof, preferably wherein said polymer is hydroxy propyl guar;

7. The emulsion of claim 1 or 2 or 3, further comprising a propping agent carried by said emulsion.

8. A method for making a fracturing fluid emulsion, preferably an emulsion of one of the foregoing claims, comprising the steps of:

providing a water phase comprising a solution of a cross-linkable polymer in water;

providing an oil phase;

forming an oil in water emulsion from said water phase and said oil phase;

adjusting pH of said emulsion to a pH of between about 9.0 and about 13.0; and

cross-linking said polymer solution so as to provide a cross-linked emulsion;

9. The method of claim 8, wherein said cross-linked emulsion has a viscosity of between about 180 and about 750 cP at 170 μ s² and 180 °F;

10. The method of claim 8 or 9, wherein said oil phase is selected from the group consisting of gasoil, mineral oil and mixtures thereof and/or wherein said water phase contains said polymer in an amount between about 10 and about 70 lbs. of said polymer per 1000 gallons of water;

11. The method of claim 8 or 10, wherein said polymer is selected from the group consisting of polysaccharides, cellulose derivatives, xanthan gum and combinations thereof, preferably wherein said polymer is hydroxy propyl guar;

12. The method of one of the claims 8 to 11, wherein said cross-linking step comprises adding said emulsion with a cross-linking agent;

13. The method of one of the claims 8 to 12, wherein said cross-linking agent is selected from the group consisting of aluminum, titanium, zirconium, antimony, cerium, borate and mixtures thereof;

14. A method for treating a subterranean formation, comprising the steps of providing an oil in water fracturing fluid emulsion comprising a dispersed oil phase, a continuous water phase comprising a solution of cross-linkable polymer in water, and a propping agent carried by said emulsion;

pumping said emulsion into a well communicated with a subterranean formation so as to form cracks in said formation; and

removing said emulsion whereby said propping agent is positioned to said cracks;

15. The method of claim 14, wherein said emulsion is cross-linked and wherein said removing step comprises breaking cross-linking of said polymer so as to provide a reduced viscosity emulsion, and recovering said reduced viscosity emulsion from said well;

16. The method of claim 14 or 15, wherein said reduced viscosity emulsion encapsulates said polymer whereby said removing step removes said polymer.

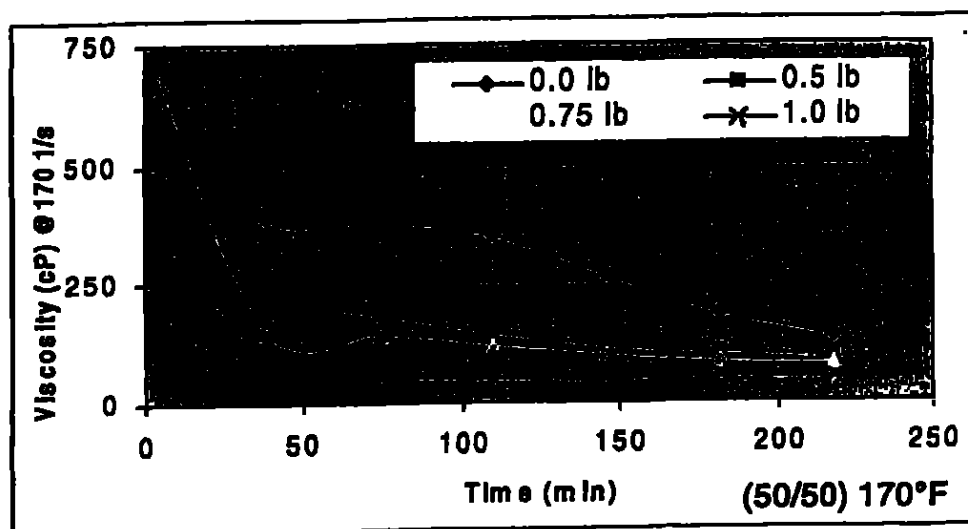


Fig.1

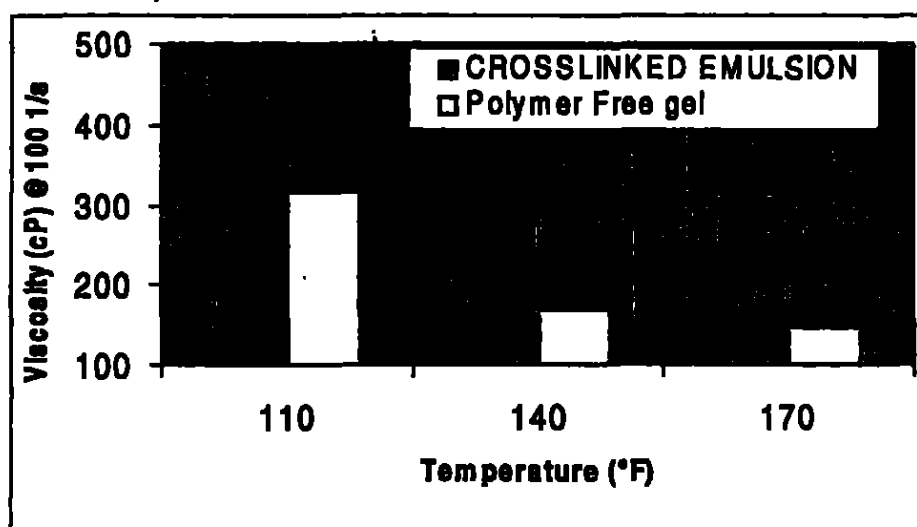


Fig. 2

[75] **Investor:** James W. Dobson, Houston, Tex.

5,637,025 4/18/85 Lohmeyer et al. 3,971,141
Primary Examiner—Philip Tisher
Attorney Agent, or Firm—Ray F. Hixon
(57) **ABSTRACT**
The invention provides (1) a method of measuring the

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(57) Int. Cl.⁶ _____ CINK 7/00
(52) U.S. Cl. _____ 807/113; 807/114
(58) Field of Search _____ 807/111, 113

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The invention provides (1) a method of increasing the thermal stability of an aqueous polyacrylate-containing emulsion by mixing dodecyl magnesium salt and a thioethanol salt; (2) a defined emulsion of water-soluble solid comprising an aqueous liquid, a water soluble polyacrylate, magnesium, and a thioethanol salt; and (3) an additive for increasing the thermal stability of an aqueous polyacrylate-containing fluid which comprises magnesium and a thioethanol salt in a weight ratio of magnesium to thioethanol salt from about 0.15/1 to about 6.5/1. The preferred magnesium salt has an activity index less than 100, most preferably less than 30. The preferred thioethanol salt is sodium thioethanol. The preferred polyacrylate is selected from the group consisting of methacryl group, acryloylcarboxylic acid, acryloyl, and acrylamide groups and substituted groups. The preferred aqueous liquid is a saturated sodium chloride solution.

16. Chlorine Gas Production

**POLYACRYLAMIDE CONTAINING FLUORINE
HAVING ENHANCED THERMAL STABILITY**

FIELD OF THE INVENTION

The invention pertains to aqueous fluids containing water-soluble polysaccharides such as oil and gas well drilling fluids, completion fluids, workover fluids, and well servicing fluids.

BACKGROUND OF THE INVENTION

The use of Platts (and their compositions, characteristics and functions) during the drilling of wells is well known. See for example the book "Composition and Properties of Oil Well Drilling Fluids," Fourth Edition, 1980, George E. Gray et al., Gulf Publishing Co., or Third Edition, 1963, McGraw-Hill.

The use of fluids for controlling various operations in the branches of subterranean oil and gas wells which contact producing formations are well known. These fluids or fluids are utilized when initially drilling into producing formations. Completion fluids are utilized when constructing various completion operations in the producing formations. Workover fluids are utilized when conducting workover operations of completely completed wells.

One of the most important functions of these fields is to shed off the face of the weldment so that the field is not lost to the formation. Ideally this is accomplished by depositing a thin coat of the weld in the field over the surface of the burr without any loss of weld to the fracture. In other words, the weld in the field covers over the formation pores rather than unnecessarily obscuring the same.

Many shop-floor fights have been provoked by questioning the producing means of oil and gas wells. See, for example, the following U.S. patents: Jackson et al. U.S. Pat. No. 3,783,438; Alexander U.S. Pat. No. 3,772,079; Fletcher et al. U.S. Pat. No. 3,652,009; Walker U.S. Pat. No. 3,696,141; Bunting U.S. Pat. No. 3,686,964; Jackson et al. U.S. Pat. No. 4,029,858; Moncrieff U.S. Pat. No. 4,175,062; Moncrieff U.S. Pat. No. 4,186,809; Moncrieff U.S. Pat. No. 4,369,843; Moncrieff U.S. Pat. No. 4,626,596; and Dobson, Jr. et al. U.S. Pat. No. 4,622,592.

[illegible]

It is well known that the polyamides are degraded by heat and alcohols. These studies lend credence to the temperatures of 300° F. (150° C.) and above, gear case bearing temperatures, and the temperatures of 150° F. (65° C.) and above, drive shaft temperatures. The temperatures of 150° F. (65° C.) and above, the thermal degradation of carbonylhydrazide polymers is accelerated as temperature approaches 300° F. (150° C.). As the polyamides degrade, the properties of the fluids containing them degrade. Thus fluids containing polyamides experience decreases in viscosity, and fluids containing polyamide fluids lose solubility characteristics and solvent fluid properties.

Johnson U.S. Pat. No. 3,853,301 discloses the use of magnesium oxide (magnesia) to stabilize Sulfide containing hydroxyacyl sulfonates in suspension at high or 275°F. Jackson U.S. Pat. No. 3,853,335 discloses the use of magnesium oxide to enhance the effectiveness of hydroxyacyl sulfonates over a higher temperature range and over a longer time period. Hurdell U.S. Pat. No. 3,888,266 discloses the

use of magnesium oxide to stabilize fluids containing ketone peroxide derivatives such as acetone peroxide. The fluids also included various starch derivatives as water phase emulsifier additives. Johnson U.S. Pat. 3,622,043 discloses the use of magnesium oxide to stabilize fluids containing hydroxyalkyl ester gases. Chen-Barnes U.S. Pat. No. 4,900,437 discloses the use of a borate salt to enhance the thermal stability of aqueous polyacrylate solutions.

SUMMARY OF THE INVENTION

I have found that the thermal stability of fluids containing polyacrylates is enhanced by incorporating into the fluids conjugated acids and a thiol/thiol salt selected from the group consisting of sodium thiosulfate, ammonium thiosulfate, potassium thiosulfate, calcium thiosulfate, magnesium thiosulfate, ferrous thiosulfate, and zincous thiosulfate. The thiosulfates were by themselves or isolated.

Thus it is an object of this invention to provide aqueous polysaccharide-containing fluids having enhanced thermal stability. It is another object of this invention to provide a method of increasing the thermal stability of aqueous fluids containing one or more polysaccharides by incorporating salts. Another object of this invention is to provide an additive for increasing the thermal stability of an aqueous polysaccharide-containing fluid selected from the group consisting of drilling fluids, completion fluids, wellbore fluids, and well servicing fluids, which comprises aqueous salts and a thixotropic salt, the thixotropic salt partially being selected from the group consisting of sodium thiosulfate, ammonium thiosulfate, potassium thiosulfate, sodium tetrathionate, ammonium tetrathionate, potassium tetrathionate, and sodium trithionate. These and other objects of the invention will be readily apparent to one skilled in the art as the description of the preferred embodiments follows.

While the invention is susceptible of various modifications, those and alternative forms, specific embodiments thereof will hereinafter be described in detail and shown by way of example. It should be understood, however, that it is not intended to limit the invention to the particular forms disclosed, but, on the contrary, the invention is to cover all modifications and alterations falling within the spirit and scope of the invention as expressed in the appended claims.

The compositions can comprise, consist essentially of, or consist of the stated materials. The method can comprise, consist essentially of, or consist of the stated steps with the stated materials.

DESCRIPTION OF THE PROPOSED REORGANIZATION OF THE DIVISION

The Solids of the present invention consists an aqueous phase which may be either fresh water, a brine, sea water, or any combination thereof. The brine, if used, may be naturally occurring brine or a manufactured brine obtained by the dissolution of one or more water soluble salts in water, a brine, sea water, or natural brine. Soluble water soluble salts include sodium chloride, potassium chloride, calcium chloride, sodium acetate, potassium acetate, zinc acetate, sodium formate, potassium formate, sodium borate, calcium borate, zinc borate, potassium borate, sea water, and the like and mixtures thereof.

The concentration of the water soluble salt in the brine may be very increased up to and including the amount required to form a saturated solution. Any salt present in the fluid is a source of the amount required to form a saturated solution. It is preferably present as a clear solution to Sweden as

TABLE 2

Completion Fields Agent M. Brown at 3:25 P.

11

1.25 gph sodium persulfate, 2.75 gph quaternary ammonium salt, 4.5 gph orthophosphoric acid, 20 gph citric acid, sodium chloride, and 2.0 gph MgO (2:1 = 3) in 0.50 l of a 15.0 gph sodium chloride bath.

Field No. E2799, 196	5 1.5		6 2.5		7 7.0		8 10.0	
	Initial	Agel	Initial	Agel	Initial	Agel	Initial	Agel
TV	44	78	47	38	48	31	46	41
TP	37	11	66	23	48	26	67	31
Chl	15979	30	14208	8911	16500	11413	16478	586
Chl	18.0	8.9	16.6	9.3	16.1	8.2	16.6	9.1
SP	23,000	4,000	45,000	4,000	45,000	18,000	23,000	3,000

Page = Number Transmitted

TABLE 3

Completion Fields Aged 18 Hours at 320° F

Public

0.01 ml of a 100 µg/ml sodium chloride solution, 0.25 µg/ml sodium phosphate, 0.25 µg/ml sodium chloride, 0.25 µg/ml sodium chloride, and 0.25 µg/ml sodium chloride.

[illegible]

TABLE 4

Printed April 16, 1966 at N.Y.C.

0.05 mole Pb(NO₃)₂ salt, 1.50 gph sodium gum, 1.50 gph epichlorohydrin emulsified hydrazine, 4.5 gph methoxyphenyl methanes, and 25 gph dried solvent petroleum.

[illegible]

TABLE 5

Philip A. and M. E. Brown of D.C.P. Inc.

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[illegible][illegible]

What is claimed is:

1. A method of increasing the thermal stability of a field comprising a surface polymerizable monomer and at least one group capable of forming a crosslink with the monomer, the monomer consisting of starch disubstituted, methylolphenyl, and chloromethyl phenyl, oligomeric thiocarbonyl groups which react with the monomer, and a thiolate ion salt selected from the group consisting of sodium thiosulfate, ammonium thiosulfate, potassium thiosulfate, sodium thiosulfate, magnesium thiosulfate, barium thiosulfate, and calcium thiosulfate, the concentration of the monomer and the thiosulfate salt being sufficient to synergistically increase the thermal stability of the field.

2. The method of claim 1 wherein the manganese has an activity index less than 100 and wherein the thioethers are in molten thioethers.

3. The method of claim 1 wherein the polymacrolide is selected from the group consisting of malonylcapryl starch, hydroxycapryl starch, hydroxycaproyl starch, epichlorohydrin crosslinked hydroxycapryl starch, carboxyl gum, gallic gum, wicker gum, and croton gum.

4. The method of claim 3 wherein the compound has an activity index less than 100 and wherein the fibronectin adsorbent is a collagen fibronectin.

5. The method of chain 1 wherein the polymacrolide is obtained from the group consisting of monomers glycol, epichlorohydrin, crosslinked hydroxypropyl starch, and substituted thiophen, wherein the thiophene has an activity factor less than 30 and wherein the substitution rate is random chlorination.

6. The method of claim 1, 2, 3, 4 or 5 wherein the concentration of compounds is from about 1.5 to about 10 pounds per 42 gallon barrel of fluid and wherein the concentration of tolouene salt is from about 1.5 to about 10 pounds per 42 gallon barrel of fluid.

7. An aqueous feed selected from the group consisting of drilling fluids, completion fluids, and workover fluids which comprises a substituted sodium chloride solution, a water-soluble polysaccharide selected from the group consisting of starch derivatives, biopolymers, and cellulose ethers, xanthane and a thixotropic salt, wherein the concentration of both the xanthane and thixotropic salt are from about 1.5 to about 10 pounds per 42 gallons barrel.

B. The field of claim 7 wherein the thiamine salt is selected from the group consisting of sodium thiamine, ammonium thiamine, potassium thiamine, calcium thiamine, magnesium thiamine, and zinc thiamine, and wherein the aqueous has an activity level less than 50.

9. The field of claim 8 wherein the polyacetaldehyde is selected from the group consisting of carboxymethyl starch, hydroxymethyl starch, hydroxypropyl starch, silylhydroxyethyl starch, acetylated hydroxypropyl starch, cationic gum, gallic gum, water gum and various blends.

18. The field of choice II wherein the thiazolidine unit is located thiazolidine, and wherein the polyanthracene is selected from the group consisting of anthracene, epichlorohydrin crosslinked hydroxypropyl starch, and methacrylate.

II. An additive for increasing the thermal stability of an aqueous field comprising a saturated sodium chloride solution and a water soluble polyacrylamide selected from the group consisting of starch derivatives, bioglycymer, and styrene-thene, which contains anionic and a cationic

ethers, which comprises ergosterol and a cholesterol not selected from the group consisting of ergosterol, cholesterol, lanosterol, stigmasterol, yamasterol, sitosterol, campesterol, stigmasterol, and lanosterol, wherein the weight ratio of ergosterol to cholesterol is less than 0.5/1 to about

12. The addition of chain 11 reduces the magnitude but not activity index less than 30 and reduces the thickness rate by medium thickness.

14. The additive of claim 11 wherein the weight ratio of tetragnone to sodium chlorate is from about 0.5/1 to about 3/1.

15. The method of claim 1 wherein the fluid additionally contains carbonylmethylolurea.

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United States Patent (19)

[11] Patent Number: 4,620,596
[45] Date of Patent: Nov. 4, 1986

[54] WELL DRILLING, WORKOVER AND COMPLETION FLUIDS
[75] Inventor: Thomas C. Muehleisen, Houston, Tex.
[73] Assignee: Texas United Chemical Corp., Houston, Tex.
[21] Appl. No.: 879,376
[22] PCT Filed: Sep. 24, 1983
[23] PCT No.: PCT/US83/05408
[37] Date: Oct. 31, 1984
[37] Date: Oct. 31, 1984
[37] Date: Oct. 31, 1984
[37] Date: Oct. 31, 1984

[31] Int. Cl. 2: E21B 33/12
[32] U.S. Cl.: 166/283; 166/281; 173/72; 252/1.31
[33] Field of Search: 252/1.1 A, 1.1 B, 1.1 C, 1.1 D, 1.1 E, 1.1 F, 1.1 G, 1.1 H, 1.1 I, 1.1 J, 1.1 K, 1.1 L, 1.1 M, 1.1 N, 1.1 O, 1.1 P, 1.1 Q, 1.1 R, 1.1 S, 1.1 T, 1.1 U, 1.1 V, 1.1 W, 1.1 X, 1.1 Y, 1.1 Z, 1.1 AA, 1.1 AB, 1.1 AC, 1.1 AD, 1.1 AE, 1.1 AF, 1.1 AG, 1.1 AH, 1.1 AI, 1.1 AJ, 1.1 AK, 1.1 AL, 1.1 AM, 1.1 AN, 1.1 AO, 1.1 AP, 1.1 AQ, 1.1 AR, 1.1 AS, 1.1 AT, 1.1 AU, 1.1 AV, 1.1 AW, 1.1 AX, 1.1 AY, 1.1 AZ, 1.1 BA, 1.1 BB, 1.1 BC, 1.1 BD, 1.1 BE, 1.1 BF, 1.1 BG, 1.1 BH, 1.1 BI, 1.1 BJ, 1.1 BK, 1.1 BL, 1.1 BM, 1.1 BN, 1.1 BO, 1.1 BP, 1.1 BQ, 1.1 BR, 1.1 BS, 1.1 BT, 1.1 BU, 1.1 BV, 1.1 BW, 1.1 BX, 1.1 BY, 1.1 BZ, 1.1 CA, 1.1 CB, 1.1 CC, 1.1 CD, 1.1 CE, 1.1 CF, 1.1 CG, 1.1 CH, 1.1 CI, 1.1 CJ, 1.1 CK, 1.1 CL, 1.1 CM, 1.1 CN, 1.1 CO, 1.1 CP, 1.1 CQ, 1.1 CR, 1.1 CS, 1.1 CT, 1.1 CU, 1.1 CV, 1.1 CW, 1.1 CX, 1.1 CY, 1.1 CZ, 1.1 DA, 1.1 DB, 1.1 DC, 1.1 DD, 1.1 DE, 1.1 DF, 1.1 DG, 1.1 DH, 1.1 DI, 1.1 DJ, 1.1 DK, 1.1 DL, 1.1 DM, 1.1 DN, 1.1 DO, 1.1 DP, 1.1 DQ, 1.1 DR, 1.1 DS, 1.1 DT, 1.1 DU, 1.1 DV, 1.1 DW, 1.1 DX, 1.1 DY, 1.1 DZ, 1.1 EA, 1.1 EB, 1.1 EC, 1.1 ED, 1.1 EE, 1.1 EF, 1.1 EG, 1.1 EH, 1.1 EI, 1.1 EJ, 1.1 EK, 1.1 EL, 1.1 EM, 1.1 EN, 1.1 EO, 1.1 EP, 1.1 EQ, 1.1 ER, 1.1 ES, 1.1 ET, 1.1 EU, 1.1 EV, 1.1 EW, 1.1 EX, 1.1 EY, 1.1 EZ, 1.1 FA, 1.1 FB, 1.1 FC, 1.1 FD, 1.1 FE, 1.1 FF, 1.1 FG, 1.1 FH, 1.1 FI, 1.1 FJ, 1.1 FK, 1.1 FL, 1.1 FM, 1.1 FN, 1.1 FO, 1.1 FP, 1.1 FQ, 1.1 FR, 1.1 FS, 1.1 FT, 1.1 FU, 1.1 FV, 1.1 FW, 1.1 FX, 1.1 FY, 1.1 FZ, 1.1 GA, 1.1 GB, 1.1 GC, 1.1 GD, 1.1 GE, 1.1 GF, 1.1 GG, 1.1 GH, 1.1 GI, 1.1 GJ, 1.1 GK, 1.1 GL, 1.1 GM, 1.1 GN, 1.1 GO, 1.1 GP, 1.1 GQ, 1.1 GR, 1.1 GS, 1.1 GT, 1.1 GU, 1.1 GV, 1.1 GW, 1.1 GX, 1.1 GY, 1.1 GZ, 1.1 HA, 1.1 HB, 1.1 HC, 1.1 HD, 1.1 HE, 1.1 HF, 1.1 HG, 1.1 HH, 1.1 HI, 1.1 HJ, 1.1 HK, 1.1 HL, 1.1 HM, 1.1 HN, 1.1 HO, 1.1 HP, 1.1 HQ, 1.1 HR, 1.1 HS, 1.1 HT, 1.1 HU, 1.1 HV, 1.1 HW, 1.1 HX, 1.1 HY, 1.1 HZ, 1.1 IA, 1.1 IB, 1.1 IC, 1.1 ID, 1.1 IE, 1.1 IF, 1.1 IG, 1.1 IH, 1.1 II, 1.1 IJ, 1.1 IK, 1.1 IL, 1.1 IM, 1.1 IN, 1.1 IO, 1.1 IP, 1.1 IQ, 1.1 IR, 1.1 IS, 1.1 IT, 1.1 IU, 1.1 IV, 1.1 IW, 1.1 IX, 1.1 IY, 1.1 IZ, 1.1 JA, 1.1 JB, 1.1 JC, 1.1 JD, 1.1 JE, 1.1 JF, 1.1 JG, 1.1 JH, 1.1 JI, 1.1 JJ, 1.1 JK, 1.1 JL, 1.1 JM, 1.1 JN, 1.1 JO, 1.1 JP, 1.1 JQ, 1.1 JR, 1.1 JS, 1.1 JT, 1.1 JU, 1.1 JV, 1.1 JW, 1.1 JX, 1.1 JY, 1.1 JZ, 1.1 KA, 1.1 KB, 1.1 KC, 1.1 KD, 1.1 KE, 1.1 KF, 1.1 KG, 1.1 KH, 1.1 KI, 1.1 KJ, 1.1 KK, 1.1 KL, 1.1 KM, 1.1 KN, 1.1 KO, 1.1 KP, 1.1 KQ, 1.1 KR, 1.1 KS, 1.1 KT, 1.1 KU, 1.1 KV, 1.1 KW, 1.1 KX, 1.1 KY, 1.1 KZ, 1.1 LA, 1.1 LB, 1.1 LC, 1.1 LD, 1.1 LE, 1.1 LF, 1.1 LG, 1.1 LH, 1.1 LI, 1.1 LJ, 1.1 LK, 1.1 LL, 1.1 LM, 1.1 LN, 1.1 LO, 1.1 LP, 1.1 LQ, 1.1 LR, 1.1 LS, 1.1 LT, 1.1 LU, 1.1 LV, 1.1 LW, 1.1 LX, 1.1 LY, 1.1 LZ, 1.1 MA, 1.1 MB, 1.1 MC, 1.1 MD, 1.1 ME, 1.1 MF, 1.1 MG, 1.1 MH, 1.1 MI, 1.1 MJ, 1.1 MK, 1.1 ML, 1.1 MN, 1.1 MO, 1.1 MP, 1.1 MQ, 1.1 MR, 1.1 MS, 1.1 MT, 1.1 MU, 1.1 MV, 1.1 MW, 1.1 MX, 1.1 MY, 1.1 MZ, 1.1 NA, 1.1 NB, 1.1 NC, 1.1 ND, 1.1 NE, 1.1 NF, 1.1 NG, 1.1 NH, 1.1 NI, 1.1 NJ, 1.1 NK, 1.1 NL, 1.1 NM, 1.1 NN, 1.1 NO, 1.1 NP, 1.1 NQ, 1.1 NR, 1.1 NS, 1.1 NT, 1.1 NU, 1.1 NV, 1.1 NW, 1.1 NX, 1.1 NY, 1.1 NZ, 1.1 OA, 1.1 OB, 1.1 OC, 1.1 OD, 1.1 OE, 1.1 OF, 1.1 OG, 1.1 OH, 1.1 OI, 1.1 OJ, 1.1 OK, 1.1 OL, 1.1 OM, 1.1 ON, 1.1 OO, 1.1 OP, 1.1 OQ, 1.1 OR, 1.1 OS, 1.1 OT, 1.1 OU, 1.1 OV, 1.1 OW, 1.1 OX, 1.1 OY, 1.1 OZ, 1.1 PA, 1.1 PB, 1.1 PC, 1.1 PD, 1.1 PE, 1.1 PF, 1.1 PG, 1.1 PH, 1.1 PI, 1.1 PJ, 1.1 PK, 1.1 PL, 1.1 PM, 1.1 PN, 1.1 PO, 1.1 PP, 1.1 PQ, 1.1 PR, 1.1 PS, 1.1 PT, 1.1 PU, 1.1 PV, 1.1 PW, 1.1 PX, 1.1 PY, 1.1 PZ, 1.1 QA, 1.1 QB, 1.1 QC, 1.1 QD, 1.1 QE, 1.1 QF, 1.1 QG, 1.1 QH, 1.1 QI, 1.1 QJ, 1.1 QK, 1.1 QL, 1.1 QM, 1.1 QN, 1.1 QO, 1.1 QP, 1.1 QQ, 1.1 QR, 1.1 QS, 1.1 QT, 1.1 QU, 1.1 QV, 1.1 QW, 1.1 QX, 1.1 QY, 1.1 QZ, 1.1 RA, 1.1 RB, 1.1 RC, 1.1 RD, 1.1 RE, 1.1 RF, 1.1 RG, 1.1 RH, 1.1 RI, 1.1 RJ, 1.1 RK, 1.1 RL, 1.1 RM, 1.1 RN, 1.1 RO, 1.1 RP, 1.1 RQ, 1.1 RR, 1.1 RS, 1.1 RT, 1.1 RU, 1.1 RV, 1.1 RW, 1.1 RX, 1.1 RY, 1.1 RZ, 1.1 SA, 1.1 SB, 1.1 SC, 1.1 SD, 1.1 SE, 1.1 SF, 1.1 SG, 1.1 SH, 1.1 SI, 1.1 SJ, 1.1 SK, 1.1 SL, 1.1 SM, 1.1 SN, 1.1 SO, 1.1 SP, 1.1 SQ, 1.1 SR, 1.1 SS, 1.1 ST, 1.1 SU, 1.1 SV, 1.1 SW, 1.1 SX, 1.1 SY, 1.1 SZ, 1.1 TA, 1.1 TB, 1.1 TC, 1.1 TD, 1.1 TE, 1.1 TF, 1.1 TG, 1.1 TH, 1.1 TI, 1.1 TJ, 1.1 TK, 1.1 TL, 1.1 TM, 1.1 TN, 1.1 TO, 1.1 TP, 1.1 TQ, 1.1 TR, 1.1 TS, 1.1 TT, 1.1 TU, 1.1 TV, 1.1 TW, 1.1 TX, 1.1 TY, 1.1 TZ, 1.1 UA, 1.1 UB, 1.1 UC, 1.1 UD, 1.1 UE, 1.1 UF, 1.1 UG, 1.1 UH, 1.1 UI, 1.1 UJ, 1.1 UK, 1.1 UL, 1.1 UM, 1.1 UN, 1.1 UO, 1.1 UP, 1.1 UQ, 1.1 UR, 1.1 US, 1.1 UT, 1.1 UY, 1.1 UZ, 1.1 VA, 1.1 VB, 1.1 VC, 1.1 VD, 1.1 VE, 1.1 VF, 1.1 VG, 1.1 VH, 1.1 VI, 1.1 VJ, 1.1 VK, 1.1 VL, 1.1 VM, 1.1 VN, 1.1 VO, 1.1 VP, 1.1 VQ, 1.1 VR, 1.1 VS, 1.1 VT, 1.1 VU, 1.1 VV, 1.1 VW, 1.1 VX, 1.1 VY, 1.1 VZ, 1.1 WA, 1.1 WB, 1.1 WC, 1.1 WD, 1.1 WE, 1.1 WF, 1.1 WG, 1.1 WH, 1.1 WI, 1.1 WJ, 1.1 WK, 1.1 WL, 1.1 WM, 1.1 WN, 1.1 WO, 1.1 WP, 1.1 WQ, 1.1 WR, 1.1 WS, 1.1 WT, 1.1 WY, 1.1 WZ, 1.1 XA, 1.1 XB, 1.1 XC, 1.1 XD, 1.1 XE, 1.1 XF, 1.1 XG, 1.1 XH, 1.1 XI, 1.1 XJ, 1.1 XK, 1.1 XL, 1.1 XM, 1.1 XN, 1.1 XO, 1.1 XP, 1.1 XQ, 1.1 XR, 1.1 XS, 1.1 XT, 1.1 XU, 1.1 XV, 1.1 XW, 1.1 XX, 1.1 XY, 1.1 XZ, 1.1 YA, 1.1 YB, 1.1 YC, 1.1 YD, 1.1 YE, 1.1 YF, 1.1 YG, 1.1 YH, 1.1 YI, 1.1 YJ, 1.1 YK, 1.1 YL, 1.1 YM, 1.1 YN, 1.1 YO, 1.1 YP, 1.1 YQ, 1.1 YR, 1.1 YS, 1.1 YT, 1.1 YU, 1.1 YV, 1.1 YW, 1.1 YX, 1.1 YY, 1.1 YZ, 1.1 ZA, 1.1 ZB, 1.1 ZC, 1.1 ZD, 1.1 ZE, 1.1 ZF, 1.1 ZG, 1.1 ZH, 1.1 ZI, 1.1 ZJ, 1.1 ZK, 1.1 ZL, 1.1 ZM, 1.1 ZN, 1.1 ZO, 1.1 ZP, 1.1 ZQ, 1.1 ZR, 1.1 ZS, 1.1 ZT, 1.1 ZU, 1.1 ZV, 1.1 ZW, 1.1 ZX, 1.1 ZY, 1.1 ZZ

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Primary Examiner—Harbert B. Oryen
Attorney Agent, or Firm—Roy P. Hines

[57] ABSTRACT
Muehleisen, "Completion Fluids for Drilling, Workover, and Completion Operations," *Oil and Gas Journal*, Aug. 22, 1977.
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Gray et al, "Composition and Properties of Oil Well Drilling Fluids," 4th edition, 1980, pp. 497-511, 522-523.
Primary Examiner—Harbert B. Oryen
Attorney Agent, or Firm—Roy P. Hines

Well treatment may be practiced by pumping or discharging the fluid or a slug or pill of the fluid into an oil, gas, water, injection or storage well where operations are to be conducted in which it is desired to temporarily plug the permeable zone while such operations are carried out. Thereafter, the hydrated borate bridging agent is removed by means of water from the permeable zone, or by a non-aqueous brine wash, or ordinary water or acid obtained in the well.

28 Claims, No Drawings

WELL DRILLING, WORKOVER AND COMPLETION FLUIDS
FIELD OF THE INVENTION

The invention relates to a method of completing a well after it has been drilled, or of servicing a well by workover operations. More particularly, it relates to a method of completing and workover of a well by suspending a subterranean formation which produces hydrocarbons with aqueous well completion and workover fluids to maintain the hydrocarbons in the producing well formation or formations under control while at the same time inhibiting or preventing damage to the producing formation or formations during the completion or workover operations.

BACKGROUND OF THE INVENTION

After a well has been drilled from the earth's surface, one or more subterranean producing formations may be encountered. It is then desirable to complete the well so as to obtain the maximum hydrocarbon production from such subterranean producing formations, and to complete such well in a manner so that the pressure in the subterranean producing formations is controlled during completion operations, while bridging or sealing off the producing formations to inhibit damage thereto and to maintain field loss into the formations which might inhibit or in some cases substantially reduce the production of hydrocarbons from the subterranean producing formations.

Also, it is desirable or necessary after a period of time to perform workover or other service operations on a previously drilled well, and during such workover or service operations, it is desirable to control the pressure in the subterranean producing formations or formations while at the same time bridging or sealing off the formations in a manner so as to maintain particle invasion and field loss into the producing formation or formations and thereby reduce if not substantially eliminate damage to the formations.

In addition to the necessary required density characteristics of a workover and completion fluid, it is desirable to seal off or temporarily plug the face of the subterranean producing formations or formations in the well bore so that during the completion and workover operations field and water in the field are not lost to the producing formation which might cause damage thereto.

Heretofore various types of workover and completion fluids with components thereof of a particle size to bridge and seal off the producing formations have been employed. Workover and completion fluids should have field loss (filter loss) control to prevent substantial field invasion of the formation. This is achieved by a combination of a field loss control agent and a bridging agent.

Various types of soluble or dispersible bridging materials are available commercially, and the choice between them depends on reservoir conditions and type of operation. Most particles of oil-soluble salts or waxes have been used as bridging agents for oil reservoirs. Such particles must be removed by dissolving them in oil when used to dry gas reservoirs or water hydrates, wells. Calcium carbonate was the first dispersible bridging particles to be used in workover and completion fluids. On completion of the job, they are removed with acid if necessary. Addition is an extra operation

and additional expense, except in carbonate reservoirs that must be acidized. Furthermore, the acid may dissolve loss on the way down to the sealing zone and introduce iron compounds into the formation. Thus, when the acid is spent, the pH rises, iron hydroxide is precipitated, and formation damage results. All of the carbonate particles may not be contained by the acid. To avoid this problem, alternate slugs of acid and filtering agent are necessary.

I have found that workover and completion fluids can be formulated utilizing about particles of a water-soluble salt as a bridging agent suspended in a saturated brine solution in which the salt is substantially insoluble. (U.S. Pat. Nos. 4,179,882; 4,184,882; and 4,388,841.)

The treating fluid comprises a saturated aqueous solution with at least one water-soluble salt which is substantially insoluble in the saturated saline solution, the water-soluble salt having a particle size range of about 5 microns to about 800 microns with greater than 5 percent of the particles being coarser than 60 microns to control the pressure in the formation while bridging and sealing it, and also substantially particle invasion to the formation. A minor amount of field loss additive to inhibit loss of fluid into the subterranean producing formations, and a suspension additive to prevent settling of the water-soluble salt particles is included in the treating fluid. The water-soluble salt which is substantially insoluble in the saline solution is added in sufficient quantity to control the pressure in the producing formation by increasing the density of the treating fluid.

The bridging and sealing salt particles used in the well completion and workover method can be dissolved by the flow of produced fluid below or by the injection of water or an un-aqueous brine solution. This eliminates the undesirable use of acid or acid solutions to remove the bridge from the subterranean hydrocarbon-producing formations. The saturated saline solution is formed by dissolving a salt or mixture of salts in water and normally the minimum density of the saturated saline solution is approximately at least 1.20 grams per cubic centimeter.

SUMMARY OF THE INVENTION

The present invention broadly comprises an improved well completion and workover fluid and method wherein a subterranean formation or formations is contacted with a fluid having a density less than about 1.26 g/cm³ the controlling formation pressure and also for temporary bridging and sealing off the formation or formations in the well bore to maintain field loss or damage to the formation. The treating fluid comprises an aqueous liquid having a density in the range from about 1.0 to about 1.20 g/cm³ (8.33-10.0 ppg) in which there is suspended a bridging agent comprising a hydrated borate of sodium and/or calcium to control the pressure in the formation while bridging and sealing it. One substantially particle invasion to the formation. A minor amount of field loss additive to inhibit loss of fluid into the formation, and a suspension additive to prevent settling of the borate particles is included in the treating fluid. The hydrated borate is added in sufficient quantity to control the pressure in the formation, in the density range from about 1.007 to about 1.26 g/cm³ by increasing the density of the treating fluid, and in sufficient quantity to effectively seal the formation.

The hydrated borate particles used in these novel well completion and workover fluids and methods have

a desired solubility in water which is insufficient to appreciably dissolve the particles in the aqueous liquid in which it is sufficient, however, to allow the particles to be dissolved by the flow of produced fluid into or by the injection of water or other non-aqueous aqueous solution. This facilitates the removal of oil or solid solutions to remove the bridge from the formation. However, aqueous acid can be used if desired.

Thus the invention provides for the temporary control of fluid loss to productive formations during completion or workover operations where desirable ranging from about 1.007 to about 1.26 g/cm³ are needed to control the formation pressure. The invention further provides for a readily removable bridging or filter cake, i.e., one that is solubilized by contacting with an aqueous liquid during workover or completion operations. Formation damage caused by excessive fluid invasion of the formation is minimized, reducing the pressure loss.

While the invention is susceptible of various modifications and alternative forms, specific embodiments thereof will hereinafter be described in detail and shown by way of example. It should be understood, however, that it is not intended to limit the invention to the particular forms disclosed, but, on the contrary, the invention is to cover all modifications and alternatives falling within the spirit and scope of the invention as expressed in the appended claims.

The composition can comprise, consist essentially of, or consist of the stated materials. The method can comprise, consist essentially of, or consist of the stated steps with the stated materials.

DESCRIPTION OF THE PREFERRED EMBODIMENT

The present invention is based on my discovery that certain naturally occurring hydrated borates of sodium and/or calcium are uniquely applicable for providing water-soluble or acid-soluble completion and workover fluids in the density range from about 1.007 to about 1.26 g/cm³. Ullrich and Proberts are generally considered to have first described the use of these borates in the density range from about 1.007 to about 1.26 g/cm³. Ullrich and Proberts are generally considered to have first described the use of these borates in the density range from about 1.007 to about 1.26 g/cm³.

These materials have the ability to form a distribution ranging from about 1 micron to about 100 microns with at least 1% of the particles being greater than 44 microns to adequately bridge and seal typical formations during workover and completion operations. Preferably the most workover and completion operations, the particles also distributed will be such that at least 5% of the particles will be greater than 44 microns, at least 20% of the particles will be greater than 20 microns, and less than 10% of the particles will have a particle size less than 10 microns.

In gravel pack operations, such as described in U.S. Pat. No. 3,674,717, less than about 5% by weight of the particles can be greater than about 44 microns for a successful gravel pack. Thus, it is at least 95% by weight of the particles must not exceed about 44 microns in size. It is essential in gravel packing operations that the concentration and particle size of the carrier fluid not have any effect on the spacing of the gravel particles and be such that it will flow through the voids between the gravel to enable the gravel to be properly placed. If more than about 5% by weight of the hydrated borate particles in the gravel packing carrier fluid exceeds about 44 microns in size, the gravel bed will become plugged while causing proper placement of the gravel itself, if not impossible.

A coarse particle size hydrated borate can be used both as a weighting material and as a bridging agent for controlling lost circulation in higher permeability type formations. In extremely high permeability formations, fractured formations, or vuggy type formations, the particles also should be expanded to hydrate particles as high as 2000 microns for effective bridging.

The amount of hydrated borate added to the aqueous suspension medium, which may contain dissolved inorganic salts, having a density in the range from about 1.0 to about 1.26 g/cm³, need only be sufficient to effectively bridge and seal off the desired formation. Generally, the amount will vary from about 14 kg/m³ to about 370 kg/m³ of the aqueous suspension medium depending on the density desired in the treating fluid and the density of the aqueous suspension medium, preferably from about 20 kg/m³ to about 385 kg/m³. Thus the treating fluid resulting from the combination of the aqueous suspension medium and the hydrated borate need have a density sufficient to balance or exceed the formation pressure in the well bore, and it is well known to those skilled in the art how to calculate the amount of hydrated borate and aqueous suspension medium required to obtain such density, and most certainly hydrated borate particles to effectively bridge and seal the desired subterranean formation.

The aqueous suspension medium with the hydrated borate described as above described may be employed with any suitable viscosifier to provide the desired viscosity and suspension characteristics to the treating fluid to retain the hydrated borate particles in suspension in the aqueous liquid.

One suitable additive for obtaining desired viscosity and suspension is hydroxyethyl cellulose. Hydroxyethyl cellulose is prepared by treating cellulose with caustic and time creating the caustic treated cellulose with about 1 to 3 moles of ethylene oxide for each hydroxyl group unit in the cellulose molecule. The viscosity of an aqueous solution of hydroxyethyl cellulose depends upon the concentration and molecular weight of the hydroxyethyl cellulose. Typically, the hydroxyethyl cellulose employed in the practice of this invention has about 1 to 3 moles of substituted ethylene oxide per anhydroglucose unit and is characterized by a Brookfield viscosity of about 1,500 to 2,500 centipoises at 25° C. for a 1 weight percent solution. A preferred hydroxyethyl cellulose has about 2.3 moles of substituted ethylene oxide per anhydroglucose unit and is characterized by a viscosity of about 1,500 to 2,500 centipoises at 25° C. for a 1 weight percent solution. A suitable hydroxyethyl cellulose is marketed by Union Carbide under the trademark Calcelec HEC-34. Hydroxy-

ethyl cellulose is employed to increase the viscosity of the fluid and to increase the stability of the dispersion.

In general, most of the water soluble cellulose ethers can be used as a viscosifier and to provide suspension for the borate particles of the invention. The cellulose ethers which can be used include, among others, the various carboxymethyl cellulose ethers, e.g., carboxymethyl cellulose and carboxymethyl cellulose (CMC), methyl cellulose and methylhydroxyethyl cellulose (MHCE), hydroxyethyl cellulose and hydroxyethyl cellulose, and hydroxypropyl cellulose, alkylhydroxyethyl cellulose such as methylhydroxypropyl cellulose, alkyl cellulose such as methyl cellulose, ethyl cellulose, and propyl cellulose; alkylcarboxymethyl cellulose such as alkylcarboxymethyl cellulose, alkylalkyl cellulose such as methylalkyl cellulose, and hydroxyalkylalkyl cellulose such as hydroxyethylalkyl cellulose, hydroxypropylalkyl cellulose, and the like. Many of the cellulose ethers are available commercially in various grades. The carboxymethylated cellulose ethers are available in the ethyl ester salt, usually the sodium salt. However, the actual is sodium referred to and they are commonly referred to as CMC, MHCE, etc. For example, water soluble CMC is available in various degrees of carboxymethylation ranging from about 0.1 up to the maximum degree of substitution of 3.0. In general, CMC having a degree of substitution in the range of 0.45 to 0.95 is preferred, CMC having a degree of substitution in the range of 0.85 to 0.95 is a more preferred cellulose ether. CMC having a degree of substitution less than the above preferred ranges usually provides too low a viscosity and is thus less desirable. The degree of substitution of CMC is commonly designated in practice as CMC-1, CMC-2, CMC-3, etc., where the 1, 2, and 3 refer to a degree of substitution of 0.1, 0.5, and 1.3 respectively. For example, in CMHEC it is preferred that the carboxymethyl degree of substitution be at least 0.4. The degree of hydroxyethyl substitution is less important and can range widely, e.g., from about 0.1 or lower to about 4 or higher.

Kaoline gum, which is used as a suspending agent, is also available commercially. It is a hydrophilic colloid produced by bacterium of the species *Xanthomonas campestris*. The colloid is a polymer consisting of mucous, glucose, glucuronic acid salts such as potassium gluconate, sodium gluconate, or the like, and acetyl radicals. Other *Xanthomonas* bacteria have been found which produce the hydrophilic gum and any of the mucous gums and their derivatives can be used in this invention.

Kaoline gum is a high molecular weight linear polysaccharide that is readily soluble in water to form a viscous fluid. Exemplary of the mucous gums that can be employed is an industrial grade of mucous gum marketed by the Kelco Company under the trademark Kelco XG mucous gum. Kaoline gum increases the gel strength of the fluid without appreciably increasing its viscosity.

Other suitable viscosifiers and suspension agents can be employed other than those specifically mentioned above, and I have found that any one of such viscosifiers and suspension agents, or any combination of others of suitable viscosifiers and suspension agents can be employed, including those mentioned above in any amount in any be desired and preferably in the range of about 0.1 kg/m³ to about 14 kg/m³ of treating fluid.

In general, polymers which complex and cross-link in the presence of the borate under an alkaline pH should not be used in the treating fluids of this invention. Polymers which contain two hydroxyl (OH) groups positioned in the borate portion of the invention. The cellulose ethers which can be used include, among others, the various carboxymethyl cellulose ethers, e.g., carboxymethyl cellulose and carboxymethyl cellulose (CMC), methyl cellulose and methylhydroxyethyl cellulose (MHCE), hydroxyethyl cellulose and hydroxyethyl cellulose, and hydroxypropyl cellulose, alkylhydroxyethyl cellulose such as methylhydroxypropyl cellulose, alkyl cellulose such as methyl cellulose, ethyl cellulose, and propyl cellulose; alkylcarboxymethyl cellulose such as alkylcarboxymethyl cellulose, alkylalkyl cellulose such as methylalkyl cellulose, and hydroxyalkylalkyl cellulose such as hydroxyethylalkyl cellulose, hydroxypropylalkyl cellulose, and the like. Many of the cellulose ethers are available commercially in various grades. The carboxymethylated cellulose ethers are available in the ethyl ester salt, usually the sodium salt. However, the actual is sodium referred to and they are commonly referred to as CMC, MHCE, etc. For example, water soluble CMC is available in various degrees of carboxymethylation ranging from about 0.1 up to the maximum degree of substitution of 3.0. In general, CMC having a degree of substitution in the range of 0.45 to 0.95 is preferred, CMC having a degree of substitution in the range of 0.85 to 0.95 is a more preferred cellulose ether. CMC having a degree of substitution less than the above preferred ranges usually provides too low a viscosity and is thus less desirable. The degree of substitution of CMC is commonly designated in practice as CMC-1, CMC-2, CMC-3, etc., where the 1, 2, and 3 refer to a degree of substitution of 0.1, 0.5, and 1.3 respectively. For example, in CMHEC it is preferred that the carboxymethyl degree of substitution be at least 0.4. The degree of hydroxyethyl substitution is less important and can range widely, e.g., from about 0.1 or lower to about 4 or higher.

Field loss control additives which are well known in the art may be employed including by way of example only, cellulose lignosulfonates, clays or bentonite clays, lignosulfonates, starches such as corn, potato and lupine and their derivatives and carboxymethyl cellulose having a degree of substitution in the range of 0.4 through 0.9. The field loss control compositions may be added in any amount desired and preferably in the range of about 0.1 kg/m³ to about 28 kg/m³ of treating fluid alone or in any combination.

Where any of the lignosulfonates are used other alone or with any of the other field loss control agents the amount may be in the range of about 0.1 kg/m³ to about 31 kg/m³ of treating fluid. Also, it is well known in the art that when any of the lignosulfonates are employed it is desirable to neutralize the acidic nature of the lignosulfonates. This may be done by adding a material to raise the pH of the completion fluid to at least 7. Any one or more of the alkaline salts, such as sodium carbonate or sodium citrate may be employed. Sodium hydroxide may also be used. The amount of material used to adjust the pH of the completion fluid is in the range of about 0.4 to about 14 kg/m³ of treating fluid. The invention can be used in the various applications involved in completion and workover operations where densities from about 1.007 g/cm³ to about 1.26 g/cm³ are required. Such applications include:

- Completion and Workover Systems with Field Loss Control
- Kill Fluids to Control Pressure
- Lost Circulation Pills to Prevent Loss of Brine
- Unconventional Seals
- Microfractures
- Matrix Fractures and Vagular Perforations
- Drilling into Productive Formations
- Matrix Perforation Damage
- Prevent Water and Oil Resistive Formations
- Eliminate Solids Invasion
- Control Water Invasion
- Perforating
- Post Perforating Lost Circulation Pills
- Perforating Pills to Prevent Invasion in Overlapped Perforating
- Gravel Packing
- Underdrilling
- Bed Washing of Cased Hole Perforations
- Plugging for Two-Stage Gravel Placement
- Bedding Underdrain or Bed Washed Hole for Production Screen Placement
- Drill Carrier Fluid
- PH Placement to Control Loss of Clay Solubles During Gravel Placement
- Fracturing
- Controlling Fluid Loss
- Drilling for Acid Treatment

EXAMPLE 7

The compatibility of saturated Uricolic solutions (in fresh water, 3% by weight potassium chloride, and 1.09 g/cm³ sodium chloride brine) with various aqueous solutions containing either sodium nitrate, sodium bi-

[illegible]

	Example 5	Comparative Example A
<u>Fluid Composition</u>		
1.5% phos ¹ NaCl brine, m ³	1.0	1.0
Hydroxyethyl Cellulose, kg	1.87	1.87
2.5% Lignin, kg	1.0	1.0
Carboxymethyl Cellulose, kg	1.0	1.0
Polyacetylene Slurries, kg	11.43	11.43
Lime, kg	0	1.43
Alkalies (< 1% alkalies), kg	26.57	0
Calcium Carboxylate (< 1% alkalies),	0	26.57
<u>Test Conditions</u>		

the range of 0.4 through 0.9, and subareas there.

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18. The method of claim 17 wherein said bridging agent is selected from the group consisting of alcohols, carbonates, phosphates, and esters thereof.
19. The well treating method of claim 17 wherein the fluid has additive is in the amount of about 0.5 kg/m³ to about 11 kg/m³ of said treating fluid, and wherein said

impregnation additive is in the amount of about 0.5 kg/m³ to about 14 kg/m³ of said treating fluid.
20. The well treating method of claim 19 wherein said fluid has additive is selected from the group consisting of calcium lignosulfonates, calcium lignosulfonates, ferric chloride lignosulfonates, alkali, alkali derivatives, carboxymethyl cellulose having a degree of substitution in the range of 0.4 through 0.9, and mixtures thereof.

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(56) FLUID LOSS CONTROL ADDITIVES AND SUBTERRANEAN TREATMENT FLUIDS CONTAINING THE SAME

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ABSTRACT

Effectively cross-linked starches are disclosed that are useful as fluid loss control additives in subterranean treatment fluids comprising starches that are cross-linked in a three-breaker peak viscosity of about 800 to about 1250 Brinkman units after about 40 to about 70 minutes at about 97° C. and provide good fluid loss control over a temperature range of from about 20° C. to about 160° C. (68° F. to 320° F.).

28 Claims, No Drawings

(*) Notice: This patent issued on a continued prosecution application filed under 37 CFR 1.53(d), and is subject to the twenty year patent term provisions of 35 U.S.C. 154(a)(2).

Under 35 U.S.C. 154(b), the term of this patent shall be extended by 0 days.

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(2) Filed: Jul. 28, 1997

(3) Int. Cl. 7: C08K 7/02; C08K 7/06

(52) U.S. Cl.: 267/118; 267/111; 267/114; 267/134

(56) Field of Search: 267/110, 111, 267/134, 134

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FLUID LOSS CONTROL ADDITIVES AND
SUBTERRANEAN TREATMENT FLUIDS
CONTAINING THE SAME

BACKGROUND OF THE INVENTION

1. Field of the Invention
This invention relates to cross-linked starches that are useful as fluid loss control additives for aqueous-based subterranean treatment fluids, such as drilling, workover and completion fluids.

2. Related Background Art

The cross-linked starches of this invention may be advantageously used in oil field applications. Particularly, the starches may be incorporated into fluids used in operations where there is contact with a subterranean formation. Drilling, workover, and completion fluids are examples of fluids used in subterranean formations.

Drilling fluids may be used for any of several functions that allow evaluating or producing a reservoir (formation) for oil, gas, or water. The drilling fluid may be pumped into the wellbore during the drilling operation to cool the drill bit and to flush out the rock particles that are stirred off by the drill bit. A "drill-bit" fluid is often used while drilling the production zone.

Workover fluids may be used to perform one or more of a variety of successful operations on a producing oil well with the intention of restoring or increasing production. Examples of workover operations include, but are not limited to, descaling, plugging back, pulling and setting a liner, squeeze cementing, shooting and acidizing.

Completion fluids may be used to perform one or more of a variety of oil field applications. Completion fluids are used to treat the wellbore, such as cementing, setting sleeves, perforating, gravel packing, installing casing, sandscreening, milling and a variety of stimulation techniques such as acidizing and the like.

Subterranean treatment fluids are used in well operations, particularly of well operations, for various purposes. The subterranean treatment fluids are generally prepared at the well site by adding a viscousifying agent and a base fluid. The viscousifying agent thickens or viscosifies the base fluid, thereby increasing the ability of the fluid to suspend or flush out the rock particles. The subterranean treatment fluid may also advantageously contain other additives that are conventionally used in well treatment operations, as needed, based upon the specific site requirements and environmental conditions.

A common problem associated with the use of subterranean treatment fluids is the loss of fluid into the surrounding formation near the wellbore. Fluid loss control additives are added to the subterranean treatment fluids to limit exposure of the formation and also control leak off of the fluid components to the surrounding subterranean formation. As a result, the subterranean treatment fluids that are used in well operations possess adequate high water retention capacity. Desirably, the subterranean treatment fluid should retain high water retention capacity under the often adverse environmental conditions encountered during use. For example, high temperatures could be encountered in deep wells, where operating temperatures frequently exceed 200° F. Low temperature conditions are encountered in shallow wells or in some of a well that are closer to the earth's surface. High salt conditions are created when brine-containing subterranean treatment fluids are used. Accordingly, the fluid loss control additives used in sub-

terranean treatment fluids should preferably be stable in both high temperature and high salinity environments. More preferably, the fluid loss control additives should be stable over a range of temperatures and should function in environments of either high or low salinity.

Natural starches are a well known and important class of materials useful as fluid loss control additives. However, it is also well known that starches do not possess long term stability and tend to degrade when maintained at elevated temperatures. For example, at temperatures in excess of 225° F., natural or conventional starches begin to degrade, and will fail to provide adequate fluid loss control.

Several approaches have been used to increase the stability of starches to provide more stable well drilling fluids. For example, U.S. Pat. No. 4,090,568 discloses the use of quaternary ammonium starch derivatives as fluid control additives that are stable at high temperatures. These derivatives were prepared by reaction of starch with epichlorohydrin and a tertiary amine.

A heterocyclic three-component well drilling fluid, consisting of a cross-linked potato starch, a heteropolysaccharide derived from a carboxydextran by reaction of the gum Xanthomonas, and hydroxypropyl cellulose, providing improved water loss control is disclosed in U.S. Pat. No. 4,422,947.

U.S. Pat. No. 4,453,384 discloses the use of substituted cross-linked starches to provide fluid loss control at elevated temperatures. The starch, which is cross-linked in a rather high degree under specified conditions, requires activation at elevated temperatures for over four hours in order to achieve suitable effectiveness.

Other well treating fluid blends have been prepared by incorporating Xanthomonas gum and a heteropolysaccharide cross-linked hydroxypropyl starch, as described in U.S. Pat. No. 4,823,800. This particular combination of additives interact synergistically to enhance suspension characteristics and decrease fluid loss.

U.S. Pat. No. 5,008,267 discloses fluid loss control well-treating fluid formulations composed of blends of two or more modified starches, starches or blends of one or more natural starches with one or more modified starches.

Although many of the cross-linked starch compositions described above offer improvements over conventional starch, there remains a need in the industry for a readily degradable starch additive that can provide good fluid loss control over a wide temperature range and that is stable in brine-containing fluids.

SUMMARY OF THE INVENTION

This invention is directed to selectively cross-linked starches and blends of these cross-linked starches that are useful as fluid loss control additives that provide good fluid loss control over a wide temperature range. More particularly, this invention is directed to fluid loss control additives for use in subterranean treatment fluids comprising starches which are cross-linked and have a Brinkman peak viscosity of about 800 to about 1250 Brinkman units after about 40 to about 70 minutes at about 97° C. (198° F.) and provide good fluid loss control over a wide temperature range of from about 20° C. to about 160° C. (68° F. to 320° F.). This invention is also directed to the selectively cross-linked starches that are spray-dried to further improve the starch properties. Additionally, this invention covers subterranean treatment fluids containing the disclosed cross-linked starches.

DETAILED DESCRIPTION OF THE INVENTION

In this invention, the ability to provide a fluid loss control additive which is effective over a wide temperature range by

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using a selectively cross-linked starch is contemplated. This result is surprising and unexpected as evidenced by a review of the literature and commercially available products which show the use of various starches and modified starches, none of which suggest the particular starches of this invention or the degree of field loss control exhibited over an extended temperature range.

An important feature of this invention is the amount of cross-linking that the starch receives, i.e., the amount of treatment or the degree of cross-linking. While it is difficult to measure this characteristic of the treated starch, particularly at low levels, one of the best ways to determine the amount of cross-linking is to measure the viscosity of the starch. It is well known to measure the viscosity of cross-linked starch using a C. W. Brabender Visco-Amylog Graph. Using this measuring device and method, the starches of this invention are cross-linked to provide a Brabender peak viscosity of about 800 to about 1200, preferably about 920 to about 1150 Brabender units (about 40 to about 70 cSt) at about 52° C. The test procedure for measuring this feature is provided below.

The cross-linked starches used in this invention may include starch treated with a mixture of multi-functional cross-linking agents. More particularly, the cross-linking agents used in this invention include epichlorohydrin, phosphorus oxychloride, allyl glycid ether, isocyanates and isocyanate-epichlorohydrin. Epichlorohydrin and phosphorus oxychloride are preferred cross-linking agents and epichlorohydrin is most preferred.

The starches which may be used in the base material in preparing the cross-linked starch of this invention may be derived from any plant source including corn, potato, wheat, rice, sago, lupine, waxy maize, waxy rice, and mugwort. Also useful are the conversion products derived from any of the above base materials including, cross-linked starches, prepared by treatment with oxidants such as sodium hypochlorite, and dextrin or dextrin-starch, prepared by enzyme conversion or mild acid hydrolysis. Protein and starch are even, waxy maize, potato, wheat and lupine, with waxy maize being especially preferred.

The cross-linked starches of the present invention are generally prepared using known techniques by reacting starch with an appropriate cross-linking agent in aqueous solution under alkaline conditions. The desired cross-linked starch will have a specified activity low degree of cross-linking defined by Brabender viscosity as described earlier. The amount of cross-linking agent used to achieve this degree of cross-linking will vary somewhat depending on the conditions and materials used. Typically, the amount of cross-linking agent used is from about 0.05% to 0.15%, and preferably about 0.1%, by weight of the starch.

In order to using the selectively cross-linked starches as defined herein, it has been found that preagitating the starch using a spray-drying process provides a product which has enhanced properties. It is believed that the spray-dried starches possess more uniform particle size which leads to more uniform and controlled seedling. The use of the spray-dry preagitation technology provides starch that possesses uniform particle size without the effect of significant degradation that occurs when drying and gelatinizing by freeze-drying or extrusion methods.

Preagitation of the cross-linked starches of this invention may be accomplished by spray-drying using a steam-injection method or single-spray-drying process described in U.S. Pat. No. 4,380,951, U.S. Pat. No. 4,600,472, or U.S. Pat. No. 5,149,799, the disclosure of which are

incorporated by reference herein. In this process, a mixture of the granular starch is coated or gelatinized in a controlled state. The starch which is to be coated is injected through an extruder aperture in the starch assembly into the spray of cross-linked starch so as to coat the starch in a temperature effective to gelatinize the starch. An extruder chamber surrounds the extruder and heating medium injection apertures and defines a vent aperture positioned to enable the heated spray of starch to exit the chamber. The arrangement is such that the heated spray enters passage of the spray of starch through the chamber, i.e., from the extruder chamber and through the vent aperture, defines the gelatinization time of the starch. The resulting spray-dried preagitated starch comprises uniformly gelatinized starch in the form of individual granules, with a majority of the granules being whole and subwhole and which would upon rehydration, remain suitable for use in the preparation of those starches as described in U.S. Pat. No. 4,610,780 which is incorporated by reference herein.

The steam injection/gelatinization process as referred to above may be more particularly described as preagitation of the starch by:

- a) adding the starch to an aqueous solvent,
- b) surrounding the mixture with an extruder chamber, and
- c) injecting a heating medium into the extruder chamber to the extruder chamber to cook the starch, the size and shape of the chamber being effective to maintain the temperature and moisture control of the starch for a period of time sufficient to cook said starch.

A steam injection/gelatinization process for cooking and spray-drying starch is disclosed in the U.S. Pat. No. 5,149,799 patent referred to above and incorporated herein by reference.

- a) spraying the starch in an aqueous medium,
- b) making a stream of the starch slurry as a pressure from about 50 to about 200 psig, low to an extruder chamber within a spray nozzle,
- c) injecting a heating medium into the extruder chamber at a pressure from about 50 to about 150 psig,
- d) substantially cooking and sterilizing the starch slurry as the heating medium forces the starch through a vent at the bottom of the chamber, and
- e) drying the sterilized starch.

It is to be noted that blends of the selected cross-linked starches may be used. For example, a blend of epichlorohydrin cross-linked starch and phosphorus oxychloride cross-linked starch may be used. The proportions of the two cross-linked starches are not limited but generally a weight ratio of about 4:1 to about 1:4 of epichlorohydrin cross-linked starch to phosphorus oxychloride cross-linked starch is used. Preferably, the blend comprises a mixture of about 1:1, by weight, of the starches. The blends of the epichlorohydrin and phosphorus oxychloride cross-linked starch may be prepared by dry-mixing the separately prepared, spray-dried starches. Alternatively, the blends may be prepared by simultaneously spray-drying wet mixtures of the cross-linked starches.

The cross-linked starches of the present invention are employed in subterranean treatment fluids to an effective amount to provide field loss control and reduce field loss over a broad temperature range. The effective amount of cross-linked starches will vary depending on the other components of the subterranean treatment fluid, as well as the geological characteristics and conditions of the subterranean formation in which it is employed. Typically, the cross-linked starch blend has control additive may be used in an amount of from about 1 pound to about 10 pounds (lb)

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of starch per barrel (bbl) of the subterranean treatment fluid, preferably from about 3 to about 6 pounds per barrel. The term "barrel" as used herein means a barrel that contains 42 U.S. gallons of fluid.

In addition to the cross-linked starches, the subterranean fluids may contain other components such as a base fluid and other a viscosity agent. The base fluid may be an aqueous system containing fresh water, seawater, and/or brine. Brine is an aqueous solution containing soluble salts of potassium, sodium, calcium, zinc, and/or cesium and the like. The viscosity agent may be a surface active agent, polymer, or other polymer under shear such as a cellulose derivative of these and the like. Other additives known to be used in these subterranean fluids include, but are not limited to, corrosion inhibitors, oxygen scavengers, surfactants, biocides, breakers, sequestrants as well as materials chosen and the like.

The oxygen scavengers and surfactants may be added to subterranean treatment fluids to reduce the deleterious effects of oxygen, i.e., the oxidative degradation of the fluid has control additive, viscosity agent, and/or other additive. Biocidal oxygen scavengers include sodium sulfite, sodium dithionite, potassium metabisulfite, and the like. Exemplary surfactants include magnum surfactant, triethanolamine (TEA), tetrahydrofuran (THF), and the like. The addition of oxygen scavengers or surfactants to subterranean treatment fluids may provide fluids possessing enhanced viscosity and field loss control properties, such that enhanced field loss control may be maintained over a broad range of temperatures.

The amount or proportion of each of the components and additives used in the subterranean treatment fluid will vary greatly depending on the intended use and purpose of the treatment fluid as well as the geological characteristics and conditions of the subterranean formation in which the fluid is employed. However, the amount of base fluid generally present in the fluid is about 25% to about 95% by weight of the fluid. The viscosity agent may be present in an amount of about 0% to about 20% by weight of the fluid. Other additives, such as those listed above, may be present in a treatment fluid generally in an amount of about 0% to about 10% by weight of the fluid.

Subterranean treatment fluids for specific purposes require special additives. For instance, drilling fluids may also have weighting agents, such as barite, to control the pressure of the formation. Further information on the composition of drilling fluids can be found in the Fifth Edition (1980) of "Composition and Properties of Drilling and Completion Fluids" by Drury and Gray, the disclosure of which is incorporated by reference herein. Oil well cement slurries may also be classified as subterranean fluids and other cements Portland cement, oil cement, accelerators and retarders. Weighting agents in drilling fluids and cementing agents in slurries or spacer fluids may be used to increase up to about 50% or more, by weight of the fluid, depending on the requirements of the geological formation. Further information on the composition of cement slurries can be found in the 1987 SPE Monograph on "Cementing" by D. K. Smith, the disclosure of which is incorporated by reference herein. Adding fluids would include acid, typically in amounts of about 1% to about 3% by weight, to reach the formation. The 1978 SPE Monograph "Acidizing Fundamentals" by Williams et al., the disclosure of which is incorporated by reference herein, further describes the use and composition of acidizing fluids. Similarly, other special purpose additives could be used for other applications.

The subterranean treatment fluid of this invention includes the cross-linked starch or starch blend, and any viscos-

ifying agent, base fluid and other additive components, present in such proportions that are appropriate for the specific well use as determined by those skilled in the art. For example, a typical drilling fluid containing the fluid loss control additive of the present invention may be prepared by adding 4 pounds of the cross-linked starch of this invention, 0.8 pounds of high viscosity polyacrylamide, 1.1 pounds of calcium carbonate and 50 pounds of calcium carbonate into 1 barrel (42 U.S. gallons) of water or brine.

As described above, the cross-linked starch fluid loss additives of this invention provide good field loss control over a broad temperature range and in an environment where salinity, shear and high temperature resistance are often required. While the degree of field loss is a relative term depending on actual conditions of operation, a field loss of less than about 100 g, as shown by the low temperature-low pressure (LTP) API and the high temperature-high pressure (HTHP) API tests as described herein, has resulted when using the cross-linked starch additives of this invention. This level of field loss control has been found to occur over a broad temperature range of about 20° F. to about 150° F. (6° C. to 60° C. to 100° F.) in the presence of high salinity environments of sea water or saturated sodium chloride solution, mud or base fluids. Addition of oxygen scavengers or surfactants to subterranean treatment fluids containing the cross-linked starches of this invention may provide enhanced field loss control over a wider temperature range, e.g., up to about 160° C. (320° F.). Use of higher concentrations of fluid loss control additive under viscousifying agents in the subterranean treatment fluids of this invention may similarly increase field loss control at very high temperatures.

The examples which follow are intended as an illustration of certain preferred embodiments of the invention, and no limitation of the invention is implied. In these examples, the concentrations of reagents and components are expressed as parts by weight, unless otherwise provided. All temperatures are reported in degrees Celsius unless otherwise noted.

The following test procedures were used in evaluating cross-linked starch fluid loss material additives in accordance with this invention.

Brabender Viscometer Test
A Brabender Visco-Amylog Graph is used in this procedure. This is a standard device, readily available in the open market, and is a recording, rotating cup viscometer that measures and records apparent viscosity at fixed temperatures and reported in dynes/cm² unless otherwise noted.

The procedure for evaluating the cross-linked starch is as follows:

- 1) A sample of the cross-linked starch, prior to preagitation, is added to a solution containing distilled water and glacial acetic acid (1.66% by weight of total charge) to 6.7% methanol while stirred by hand.
- 2) The sample is transferred to the Brabender cup. The cup is then heated with the viscometer.
- 3) The glass viscosity thermometer is set at 52° C. (125° F.) and the sample is heated at a rate of four degrees per minute to 52° C. The sample is then held at about 52° C. until the sample reaches the peak viscosity.
- 4) The peak viscosity is recorded. Also recorded is the time, in minutes, that it takes for the sample to reach peak viscosity after it reaches 52° C. (Note: the total time the sample is at 52° C. until the sample reaches peak viscosity).

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FLUID LOSS TESTING PROCEDURE

Field Preparation

The starch field loss control additives were tested in two systems: upstream separator and 30% (w/w) saturated NaCl brine. The separator was prepared by dissolving 18.85 g of dry "Sea-Salt" (ASTM D-1141-32, Lake Products Company, Maryland Heights, Mo.) into 450 g prepared tap water (the prepared tap water is dechlorinated water containing 1000 ppm NaCl and 1.0 ppm CaCl_2). The 30% NaCl brine field was prepared by dissolving 141.4 g of NaCl into 298.6 g of dechlorinated water.

Prior to salt addition, prepared tap water or dechlorinated water was added to Hachette Beach salt mixing cups and stirred at approximately 4000 rpm with a Hachette Beach salt mixer A-1.1. A fixed amount of machine gun (1-C) 3-XCD, a product of Micro-Sonics Koko Co., a unit of Micro-Sonics Company, St. Louis, Mo.) was added into each mixing cup and allowed to mix for approximately 3-5 minutes. One drop of 5 M potassium hydroxide was added to each mixing cup to raise the pH to between 8.5-9 and the mixture stirred for 20 minutes at 11,000-200 rpm. At the end of the 30 minutes of stirring, the appropriate amount of either "Sea-Salt" or NaCl was added and the field was stirred an additional 10 minutes at 11,000 rpm.

A 0.8 fluid ounce of Aquapack-Bio-Logic, which is a high viscosity polyacrylic colloid used as a viscosity and filtration control aid (1.07 g, a product of Aquapack Co., Houston, Tex.) and a 4 fluid ounce sample (5.14 g), prepared as described above, were dry blended together with a spatula, then added in the field mixture. Mixing was continued at 11,000 rpm for 15 minutes. The mixing container was removed from the mixer and 50 Beblor CC-10 (54.29 g, calcium carbonate, a product of the ECI International Co., Sylacauga, Ala.) was added. The mixing cup was removed to the mixer and added for an additional 5 minutes at 11,000 rpm. (Note: two drops, dechlorinated) was added and the resulting mixture was stirred for an additional minute. Finally, the pH of the field was adjusted with 5 M potassium hydroxide to obtain a pH between 8.5 and 9.

Low Temperature/Low Pressure (LTL/P) API Field Loss Test Procedure

Unaged samples of the field prepared above were tested for field loss using a standard American Petroleum Institute (API) low temperature-low pressure (LTL/P) Fluid Loss Test at room temperature (77°F/22°C).

Samples of test fluid (200 mL) were re-mixed using a Hachette Beach Mixer for approximately 1 minute at 11,000 rpm, then poured into an API Fluid Loss Filter Cell (Parr Instrument Company, Houston, Tex., Model 128, No. 5051) to assess a half-hour field loss from the top of the cell. As 1/4-oz and Wetmore 50 filter paper was placed in the cell prior to sealing the cell.

The API LTL/P Fluid Loss Test was performed at room temperature as follows. The cell was placed on a filter press, pressurized at 100 psi using nitrogen pressure, and pressurized for 30 minutes. Field loss from the pressurized cell was collected in a sealed beaker and weighed.

High Temperature/High Pressure (HTH/P) Fluid Loss Test Procedure

Prior to conducting the HTH/P API field loss test, the samples were aged for 16 hours at elevated temperatures, as follows.

Flow Rating Procedure

The field containing the test starch sample was poured into a 200 mL high-temperature aging cell (Parr Instrument Co., Houston, Tex., Part No. 75000). The cell is made of stainless steel. The fluid (fluid, the cell) is approximately

one-quarter inch from the top of the cell. The cell was pressurized to about 150-200 psi and then the valve stem was carefully tightened. The cell was then placed in the roller oven (Parr Instrument Co., Houston, Tex., Part No. 7000) that had been preheated to the test temperature. The roller oven is a standard API roller oven except that downstream temperature controllers (Bendix Corp., Boston, Virginia, Model 800) were added to adjust the temperature variance during aging. The cell was cooled at the test temperature for 16 hours (overnight). The sample was removed from the oven, cooled to room temperature, depressurized, then tested for high temperature/high pressure (HTH/P) fluid loss as described below.

The cooled sample was placed in a cool 175 mL HTH/P fluid loss cell (Parr Instrument Co., Part No. 36750) containing a Wetmore 50 (or equivalent) filter paper. The bottom valve stem of the cell was closed to prevent loss of the fluid prior to test up. The top cap was attached and the cell placed in a pressurized cell holder. A nitrogen pressure line was attached to the top valve stem and the cell was pressurized to approximately 200 psi to prevent leaking of the fluid during test up. Once the cell reached temperature, a condenser was added to the bottom valve stem of the cell and a back pressure of 100 psi nitrogen pressure was added to the condenser. The bottom valve stem of the cell was then opened to allow field loss to occur and the pressure of the top valve stem was increased to 400 psi (to provide 500 psi differential pressure). Field loss was measured over a 30 minute time period or until complete field loss occurred, whichever comes first. The field loss was measured by weight. The field loss reported was exactly two times the field loss collected (as per API procedures) to compensate for the smaller surface area of the filter paper compared to the low temperature-low pressure fluid loss cell.

Differences between LTL/P and HTH/P Testing

Testing was conducted as per "API Recommended Practice, Standard Procedures for Field Testing Water-Based Drilling Fluids," API RP 13B-1, Part 1 Edition, June 1, 1990. Room temperature (77°F/22°C) field loss tests were conducted using the API low-temperature/low-pressure (LTL/P) test procedure (API Proc. RP 13B-1 Sect. 3.3). All field loss testing above room temperature was done using the API high-temperature/high-pressure (HTH/P) test procedure (API Proc. RP 13B-1 Sect. 3.5). The HTH/P testing was different equipment than the LTL/P test, which allows for heating of the filter press and higher differential pressure. The LTL/P apparatus was 500 psi differential pressure whereas the HTH/P apparatus was 100 psi differential. Also, the LTL/P test used filter paper that is one-half the surface area of the LTL/P test and, therefore, the field loss reported for LTL/P testing is doubled the collected.

EXAMPLE 1

Preparation and Testing of Spikethiolite Cross-Linked Starch

At room temperature, 1000 g of waxy maize starch was slurried in 1500 g of water. To the slurry, sodium hydroxide, as a 3% solution, was slowly added to a pH of about 12.0 (25 mL of reactive slurry should require 18-20 mL of 0.1 N HCl to neutralize at the phenolphthalein end point). Spikethiolite (0.15% by weight) was added to the slurry.

The reaction mixture was allowed to react at 40°C for 17 hours cooled to room temperature, and neutralized to a pH of 6.0 with 10-30% solution of hydrochloric acid. The starch was then filtered, washed and dried to provide a sugar-free

starch dry powder. A sample of the cross-linked starch was analyzed to determine its peak viscosity using a C. W. Brabender Viscosity-Amylo Graph, as described above, and found to have a peak viscosity of 1000 Brabender units after 52 minutes at 52°C.

The dried cross-linked starch was slurried in water to 20-30% solids by weight. The starch was spray-dried to granules, using the process described above, and in U.S. Pat. No. 4,280,253 and U.S. Pat. No. 4,500,472.

The resulting dried, spray-dried powder was tested for field loss using both the API LTL/P fluid loss test (room temperature of 77°F/22°C) and the API HTH/P test, described above. The test was in both seawater and saturated NaCl solution (20%) and gave the results shown below in Tables 1 and 2.

TABLE 1

Spikethiolite Cross-Linked Starch: 0.15% Solution	
Temperature (°F)	Field Loss (g)
72 (22° C)	6.4
100 (38° C)	6.8
150 (66° C)	12.5
170 (66° C)	18.3
200 (93° C)	46.1
200 (117° C)	46.1
200 (147° C)	64.8

TABLE 2

Spikethiolite Cross-Linked Starch: 0.15% Solution	
Temperature (°F)	Field Loss (g)
72 (22° C)	4.9
100 (38° C)	8.1
150 (66° C)	21.2
200 (93° C)	46.1
200 (117° C)	64.7
200 (147° C)	66.2

Standard seawater NaCl (20%) solution

EXAMPLE 2

Preparation and Testing of Phosphorus Trichloride Cross-Linked Starch

At room temperature, 1000 g of waxy maize starch was slurried into an aqueous solution of sodium chloride (1500 g water, 0.5% NaCl by weight of starch). To this slurry, a 3% solution of sodium hydroxide was slowly added to a pH of about 12.0 (25 mL of reactive slurry should require 18-20 mL of 0.1 N HCl to neutralize at the phenolphthalein end point). Phosphorus trichloride (0.15%) was added and the reaction mixture allowed to react for 35 minutes. The resulting reaction mixture was neutralized to a pH of 6.0 with a 10-30% solution of hydrochloric acid. The starch was then filtered, washed and dried. A sample of the cross-linked starch was analyzed to determine its peak viscosity using a C. W. Brabender Viscosity-Amylo Graph and found to have a peak viscosity of 1000 Brabender units after about 40 minutes at 52°C. The cross-linked starch was spray-dried and tested for field loss as in Example 1 with the results shown below in Tables 3 and 4.

TABLE 3

Phosphorus Trichloride Cross-Linked Starch: 0.15% Solution	
Temperature (°F)	Field Loss (g)
72 (22° C)	6.3
100 (38° C)	8.1
200 (147° C)	13.8

TABLE 4

Phosphorus Trichloride Cross-Linked Starch: 0.15% Solution	
Temperature (°F)	Field Loss (g)
72 (22° C)	6.3
100 (38° C)	12.8
200 (147° C)	16.8

Standard seawater NaCl (20%) solution

EXAMPLE 3

A blend (1:1 wt. ratio) of spikethiolite (wt) cross-linked starch and phosphorus trichloride cross-linked starch (both prepared as in Examples 1 and 2) was made and tested for field loss in sea water and saturated NaCl solution as in the previous Examples. The results are shown below in Tables 5 and 6.

TABLE 5

Blend of Spikethiolite Cross-Linked Starch and Phosphorus Trichloride Cross-Linked Starch (1:1)	
Temperature (°F)	Field Loss (g)
72 (22° C)	6.9
100 (38° C)	8.1
150 (66° C)	18.7
200 (93° C)	47.8

Standard seawater NaCl (20%) solution

TABLE 6

Blend of Spikethiolite Cross-Linked Starch and Phosphorus Trichloride Cross-Linked Starch (1:1)	
Temperature (°F)	Field Loss (g)
72 (22° C)	8.0
100 (38° C)	9.7
200 (147° C)	13.2

Other variations or modifications, which will be obvious to those skilled in the art, are within the scope and teachings of this invention. This invention is not to be limited except as set forth in the following claims.

We claim:

1. A field loss control additive for use in a subterranean wellbore, said additive comprising a pre-gelatinized cross-linked starch, wherein said starch provides field loss control over a temperature range of from about 20°C to about 160°C, and prior to pre-gelatinization, said starch has a Brabender peak viscosity of from about 800 to about 1250 Brabender

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viscosity units after about 40 to about 70 minutes at about 92° C. when subjected to a Brabender viscometer test.

2. The fluid loss control additive according to claim 1 wherein the starch is cross-linked with an agent selected from the group consisting of epichlorohydrin, phosphorus oxychloride, adipic-acetic anhydride and another triester phosphate.

3. The fluid loss control additive according to claim 2 wherein the starch is selected from the group consisting of corn, waxy maize, potato, wheat and tapioca.

4. The fluid loss control additive according to claim 3 wherein the cross-linking agent is epichlorohydrin or phosphorus oxychloride.

5. The fluid loss control additive according to claim 4 wherein the starch is waxy maize.

6. The fluid loss control additive according to claim 3 wherein the cross-linked starch has a Brabender peak viscosity of from about 920 to about 1150 Brabender units after about 40 to about 70 minutes at about 92° C.

7. The fluid loss control additive according to claim 6 wherein the cross-linked starch exhibits a fluid loss of less than about 100 g when subjected to a low-temperature-low pressure (LTLF) or high temperature high pressure (HTHP) American Petroleum Institute Fluid Loss Test over a temperature range of from about 20° C. to about 160° C.

8. The fluid loss control additive according to claim 7 wherein the starch is cross-linked with an epichlorohydrin and the starch is waxy maize.

9. The fluid loss control additive according to claim 3 wherein the cross-linked starch is about a 4:1 to about a 1:4 by weight blend of epichlorohydrin cross-linked starch and phosphorus oxychloride cross-linked starch.

10. The fluid loss control additive according to claim 9 wherein the cross-linked starch is about a 1:1 by weight blend of epichlorohydrin cross-linked starch and phosphorus oxychloride cross-linked starch.

11. The fluid loss control additive according to claim 10 wherein the starch is the epichlorohydrin cross-linked starch and the phosphorus oxychloride cross-linked starch is waxy maize starch.

12. The fluid loss control additive according to any of claims 1-11 wherein the cross-linked starch is pregelatinized by spray-drying.

13. A subterranean treatment fluid treatment fluid composition comprising a base fluid, a viscosifying agent and an effective amount of a fluid loss control agent, wherein said fluid loss control agent comprises a pre-gelatinized cross-linked starch that provides fluid loss control over a temperature range of from about 20° C. to about 160° C. and prior to pre-gelatinization, said starch has a Brabender peak viscosity of from about 800 to about 1250 Brabender, viscosity units after about 40 to about 70 minutes at about 92° C. when subjected to a Brabender viscometer test.

14. The subterranean treatment fluid composition according to claim 13 wherein the subterranean treatment fluid is a drilling fluid, a workover fluid or a completion fluid.

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15. The subterranean treatment fluid composition according to claim 14 wherein the starch is cross-linked with an agent selected from the group consisting of epichlorohydrin, phosphorus oxychloride, adipic-acetic anhydride and sodium trimetaphosphate.

16. The subterranean treatment fluid according to claim 15 wherein the starch is selected from the group consisting of corn, waxy maize, potato, wheat and tapioca.

17. The subterranean treatment fluid according to claim 16 wherein the cross-linking agent is epichlorohydrin or phosphorus oxychloride.

18. The subterranean treatment fluid according to claim 17 wherein the starch is waxy maize.

19. The subterranean treatment fluid according to claim 16 wherein the cross-linked starch has a Brabender peak viscosity of from about 920 to about 1150 Brabender units after about 40 to about 70 minutes at about 92° C.

20. The subterranean treatment fluid according to claim 19 wherein the cross-linked starch exhibits a fluid loss of less than about 100 g when subjected to a low-temperature-low pressure (LTLF) or high temperature high pressure (HTHP) American Petroleum Institute Fluid Loss Test over a temperature range of from about 20° C. to about 160° C.

21. The subterranean treatment fluid according to claim 20 wherein the starch is cross-linked with an epichlorohydrin and the starch is waxy maize.

22. The subterranean treatment fluid according to claim 16 wherein the cross-linked starch is present in an amount of from about 1 pound per barrel to about 10 pounds per barrel of subterranean treatment fluid.

23. The subterranean treatment fluid according to claim 22 wherein the cross-linked starch is present in an amount of from about 3 pounds per barrel to about 5 pounds per barrel of subterranean treatment fluid.

24. The subterranean treatment fluid according to claim 23 wherein the cross-linking agent is epichlorohydrin and the starch is waxy maize starch.

25. The subterranean treatment fluid according to claim 16 wherein the cross-linked starch is about a 4:1 to about a 1:4 by weight blend of epichlorohydrin cross-linked starch and phosphorus oxychloride cross-linked starch.

26. The subterranean treatment fluid according to claim 25 wherein the cross-linked starch is about a 1:1 by weight blend of epichlorohydrin cross-linked starch and phosphorus oxychloride cross-linked starch.

27. The subterranean treatment fluid according to claim 26 wherein the starch is the epichlorohydrin cross-linked starch and the phosphorus oxychloride cross-linked starch is waxy maize starch.

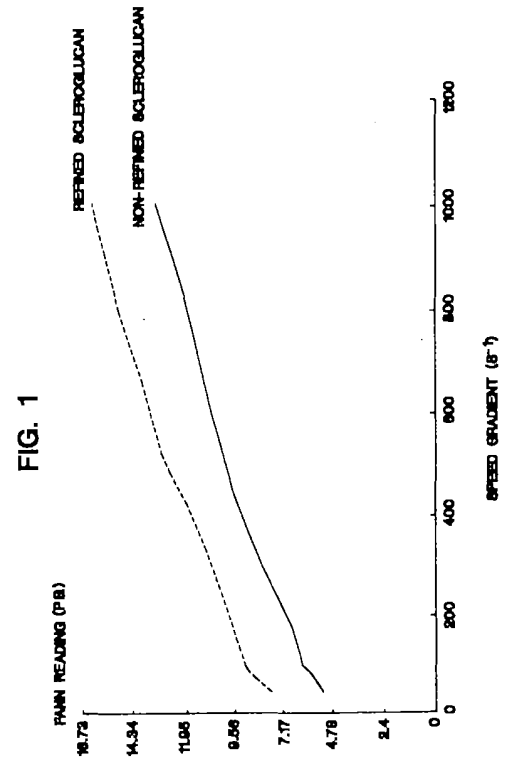
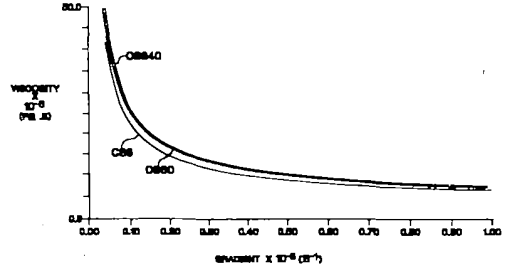
28. The subterranean treatment fluid according to any of claims 13-27 wherein the cross-linked starch is pregelatinized by spray-drying.

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[54] SCLEROGUCCAN BASED DRILLING MUD
[72] Inventors: Alain Vassard, Parc Alain Lombard, 13005 La Ciotat, France; Alain Lombard, 13005 La Ciotat, France
[73] Assignee: Elf Aquitaine, Courbevoie, France
[52] Int. Cl. C09K 8/00
[51] U.S. Cl. 267/112, 213, 214
[58] Field of Search: 267/112, 213, 214
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Primary Examiner—Philip Tucker
Attorney Agent, or Firm—Blick, Stewart, Kitchin & Birch, LLP
[57] ABSTRACT
This composition for water-based drilling muds showing the rheology and the amount of the other constituents of the mud to be combined. In addition to the base polymer, fresh water, sea water or salt water, the said base composition comprises a scleroguccan as viscosity agent, an organophilic which produces a thickening and an equivalent to fluid loss control.



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FIG. 2

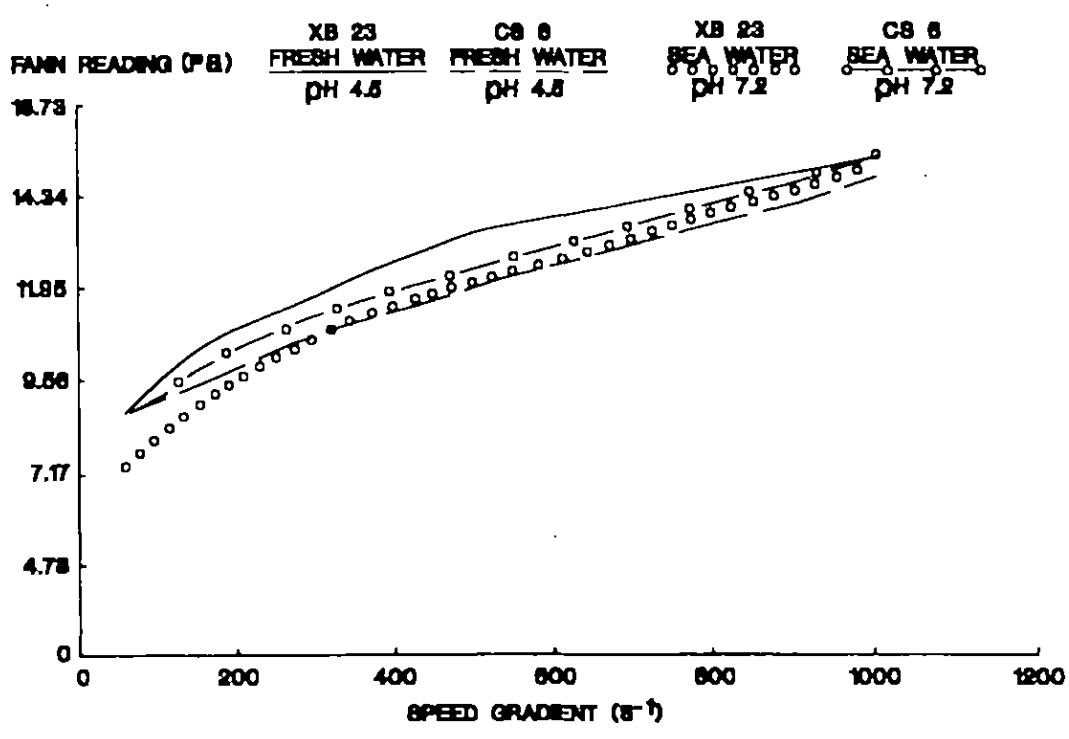


FIG. 3

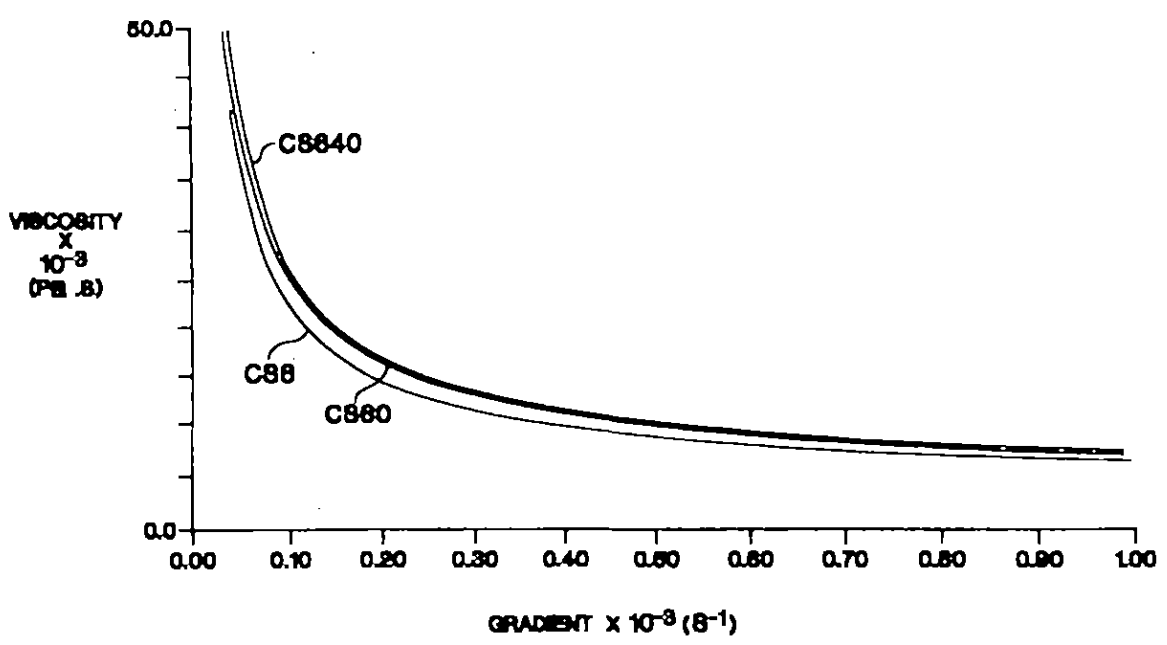


FIG. 4

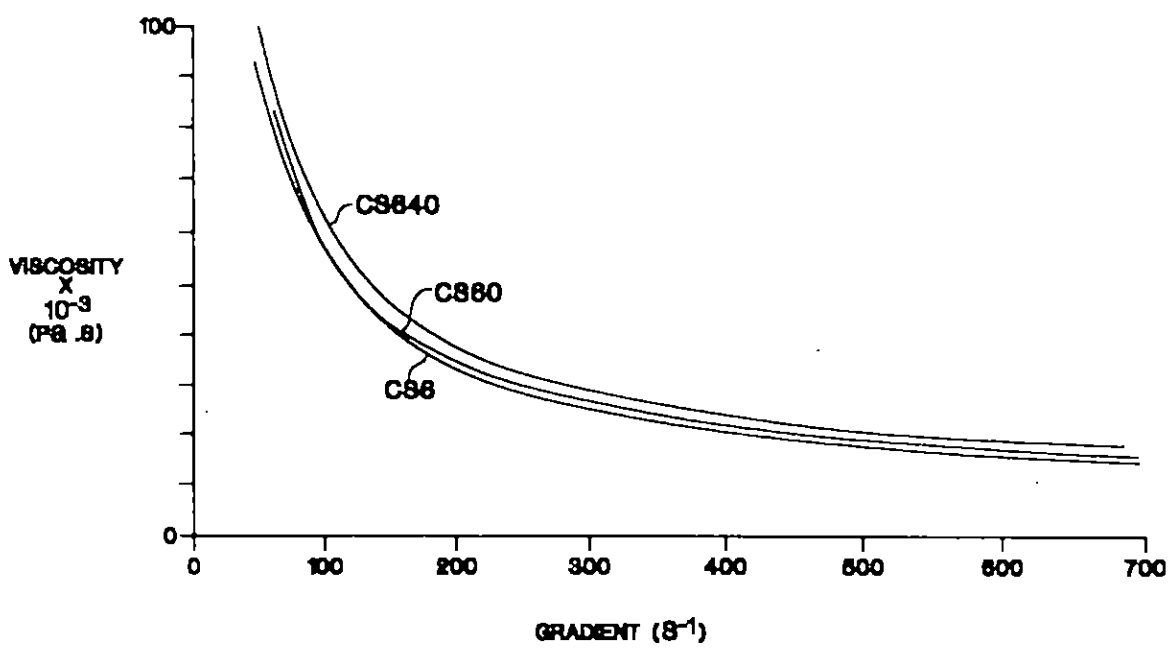
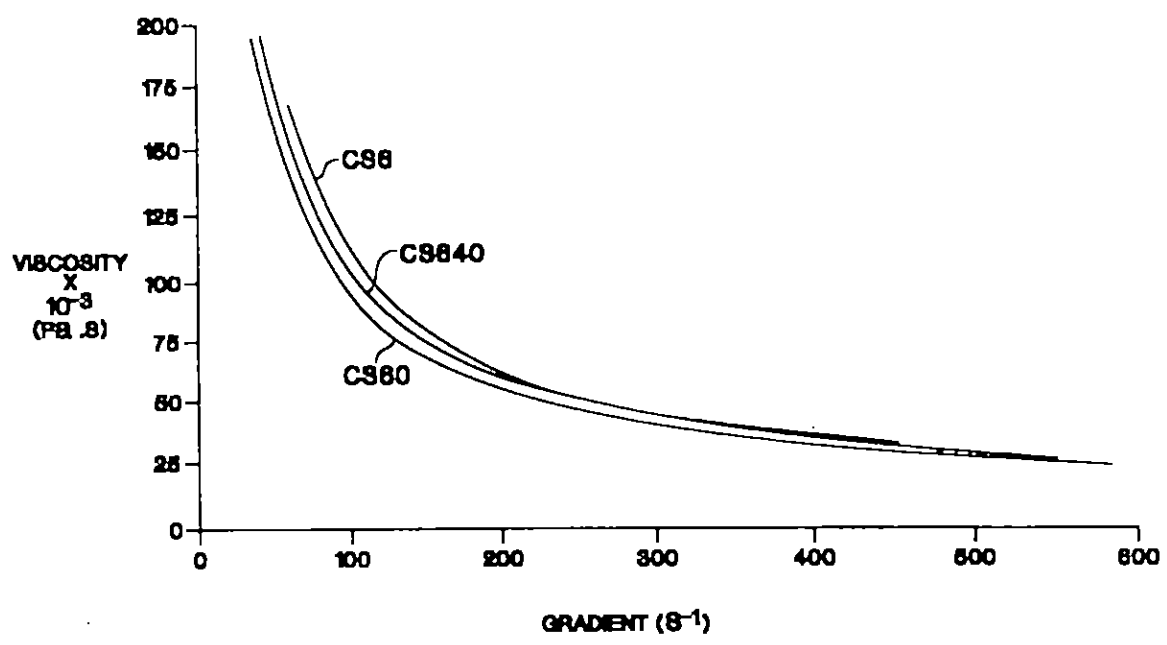


FIG. 5



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FIG. 6

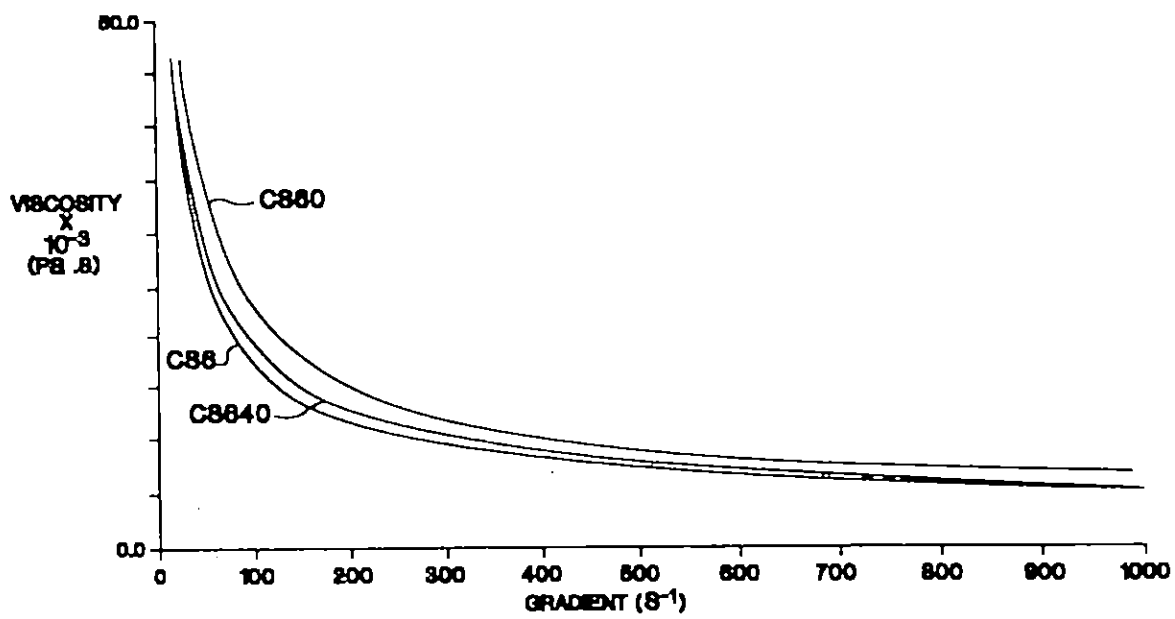
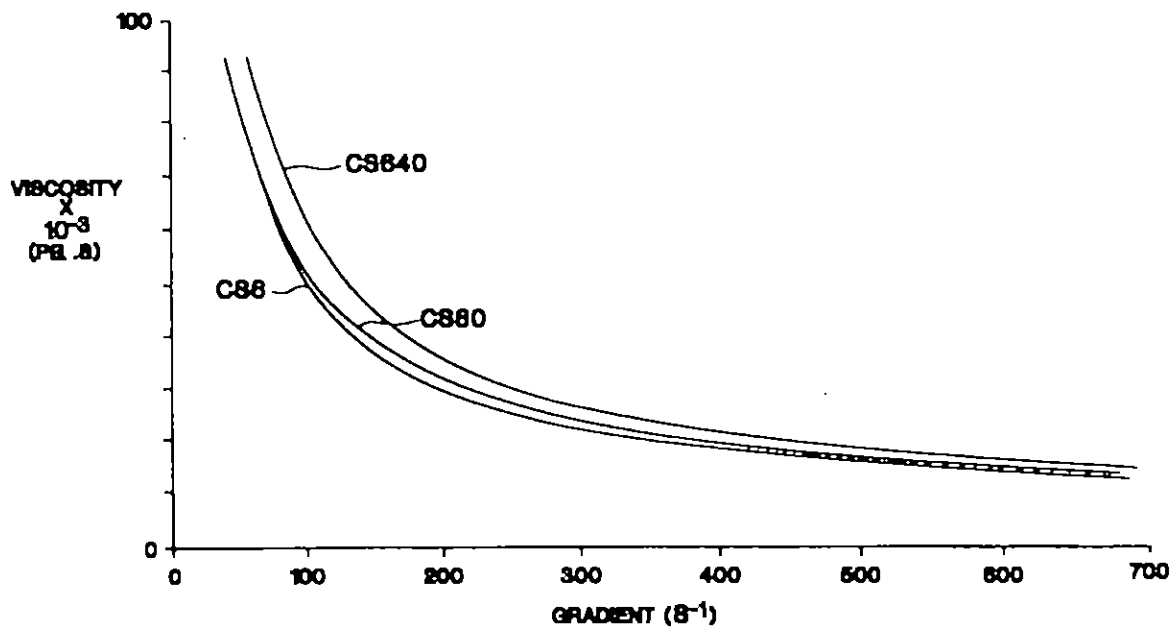


FIG. 7



DEL

FIG. 8

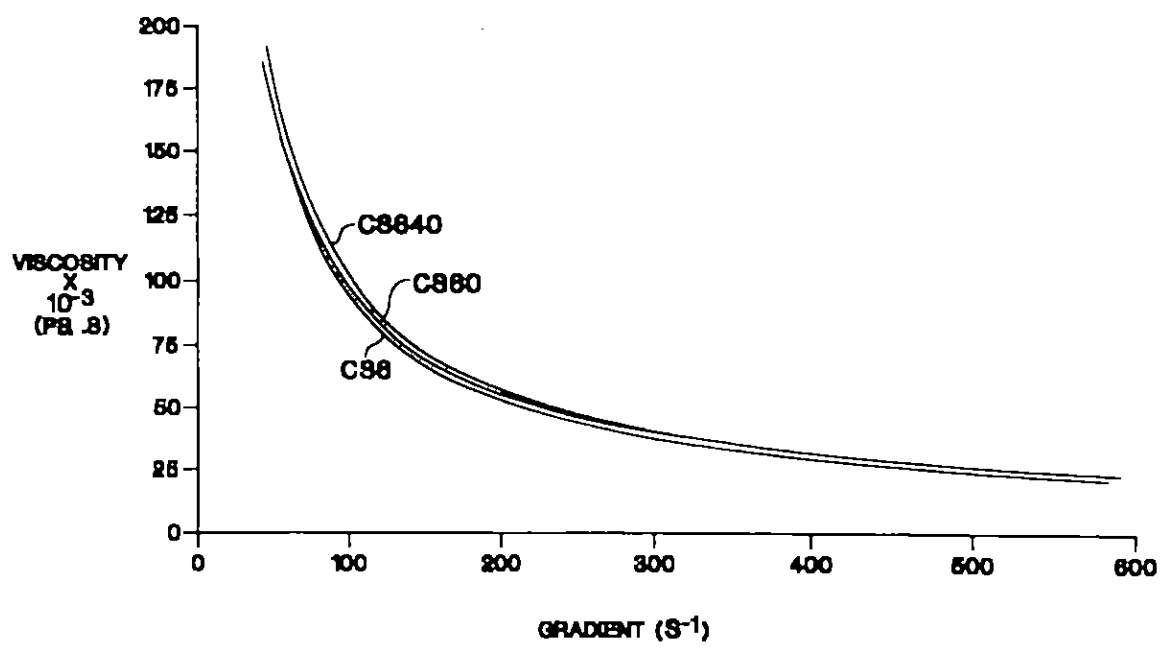


FIG. 9

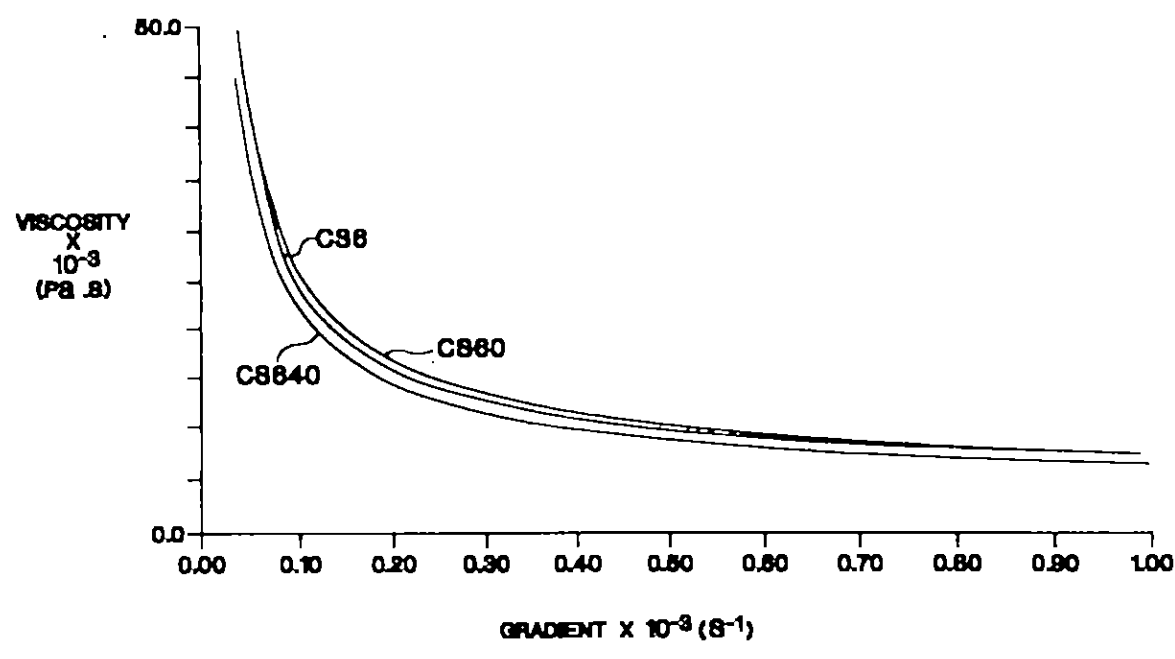


FIG. 10

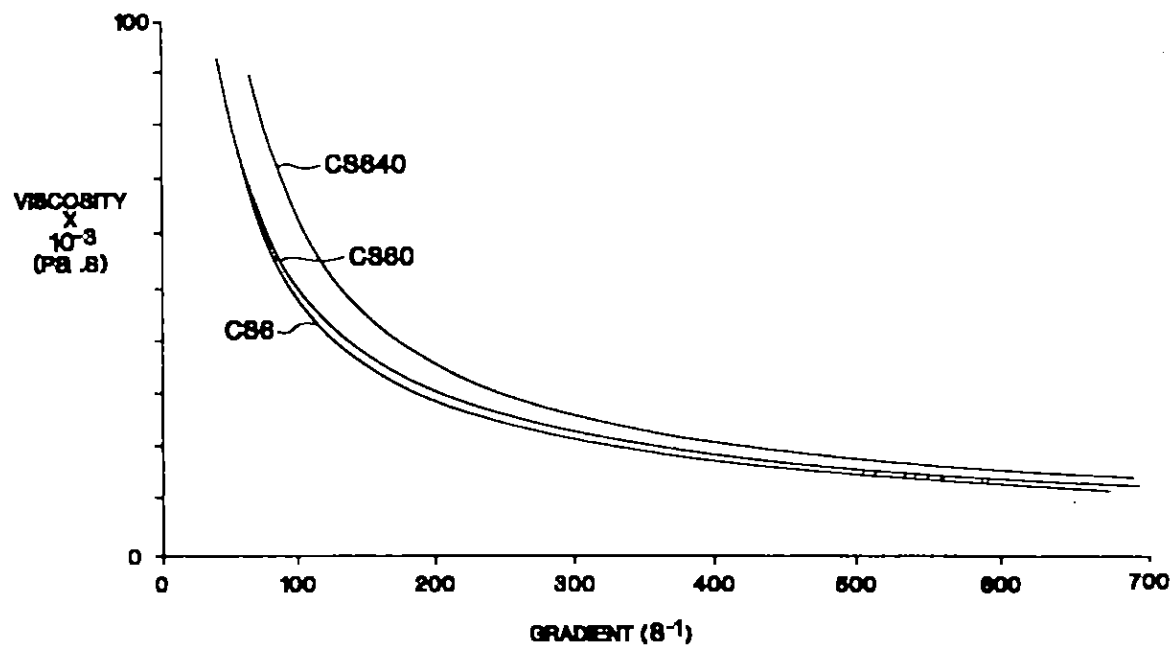
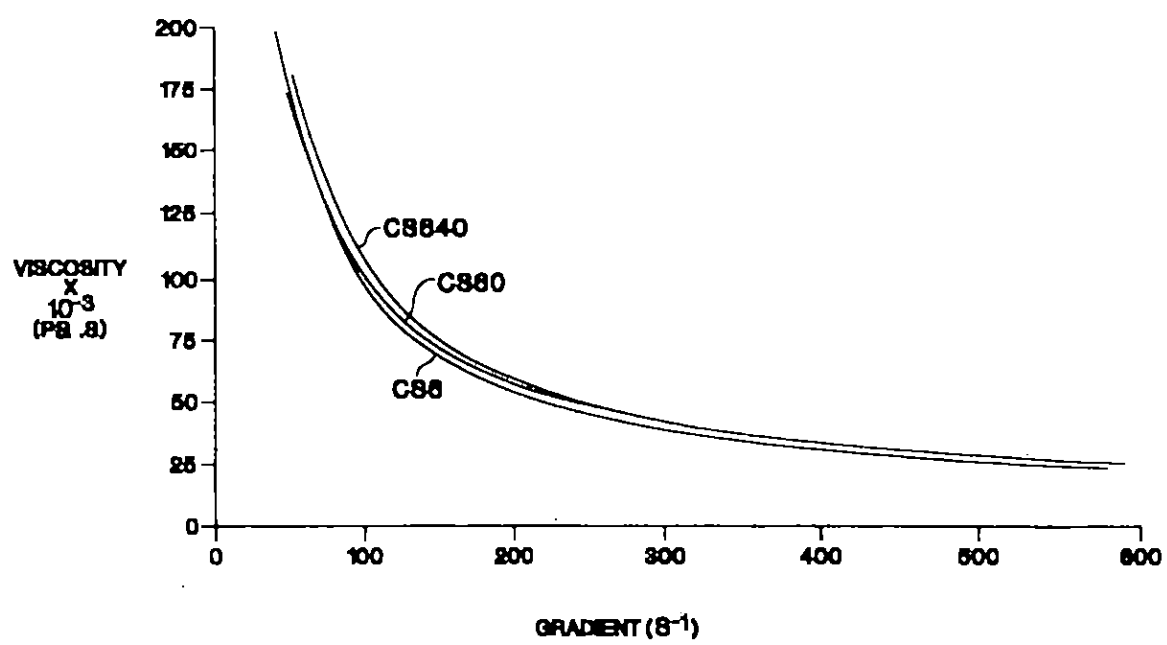


FIG. 11



OP1

XANTHOGUCCAN BASED DRILLING MUD

This application is a continuation of application Ser. No. 890,776 filed on Jan. 31, 1993 now abandoned, which is a continuation of Ser. No. 07,088,055, filed on Apr. 15, 1991, now abandoned.

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a water-based drilling mud comprising a combination of speckles, known as xanthoguccans, which contain, in particular, the cellular residues of the producing organisms.

2. Description of the Related Art

Drilling mud is a more or less complex mixture most often based on a water-based or oil-based colloidal suspension used for drilling wells. This mud, injected into the section of drill pipe, circulates by means of an ascending movement in the annular space delimited between the walls of the geological formations drilled and the section of pipe. It has multiple functions: in addition to cooling and lubricating without exceeding the drilling tool, the mud must be able to rise to the surface the cuttings stripped from the formations. For this purpose it is necessary for the mud to be sufficiently viscous and for its pH to be such that the cuttings are able to remain in suspension in the mud when the flow rate of the latter is zero. The density of the mud must be sufficiently high so as to equilibrate the pressure in the pores of the formations and thus to prevent the formations from breaching the well. However, this density must not be too high so as not to prevent the progress of drilling, or to fracture the formations.

Another function of the mud is to maintain the wall of the well such that there is no collapse. This function is usually ensured by virtue of the formation of a deposit of a solid of clay particles contained in the mud, this deposit being termed "cake" and covering the wall of the well. The quality of the cake is dependent on the composition of the mud and must be adapted to the nature of the various drilled mud of water. A good quality cake not only permits the wall to be maintained but also permits a filtration control such that the ingress of water under head into the formations is limited. However, plugging of the formations and in particular of the productive formations must be avoided.

A good quality mud must also be inert with respect to the formations which it passes through, in particular if the latter contain salts or reactive dyes. The high sensitivity of the components of the mud with the components of the formations in fact gives rise to reactions in the quality of the wall of the well and a pollution of the mud such as the physical characteristics, such as, for example, its viscosity, are modified, with the consequence that it is no longer able to perform its functions.

The multiple functions of the mud, some of which are contradictory, are the reason why a large variety of muds currently exists. These muds are usually highly complex mixtures of from two to ten or more constituents, the composition of which changes, becoming more complex as drilling progresses, and the use of which necessitates the involvement of specialists. The role of the specialist is to define the mud composition at the start of drilling and to monitor the physical and physico-chemical properties of the mud during operation in order to maintain the mud properties under to adapt them progressively to the drilling conditions

by adding suitable components, such as agents for increasing the weight, rheology-modifying agents, viscosity agents, dispersants, plugging agents or lubricants, mud-forming agents, neutralizing agents and other specific or chemical components.

However, suitable because the viscosities and gelling, rheology, for example, which is often used to reach desired as from water, also contributes to the formation of a cake protecting the walls of the well against collapse and makes it controlling the flow.

Among the organic solids, most are used as rheology-modifying agents, others as viscosity agents and yet others as dispersants. The introduction of these into the mud composition is necessary when the viscosities become inadequate under the effect of an increase in the clay loading, for example.

Carboxymethylcellulose (CMC), for example, which is a cellulose derived from cellulose, is commonly used as additive when it is necessary to improve the carrying capacity of the mud by increasing the apparent viscosity. An improvement in the carrying capacity by means of such a procedure is often by an increase in pressure loss. Cellulose derivatives, among other compounds, may also be present in the composition of the mud in field use conditions.

Rheology or other chemical compounds may also be introduced into the composition of the mud, in order to modify the pH, such as sodium hydroxide for example, or in order to maintain the reactions between the components of the mud and those of the formations.

It is well known that biopolymers may be present in the composition of a mud as a viscosity agent. Apart from non-reducible viscosity-improving properties, the biopolymers commonly used for drilling muds have a good compatibility with drilling agents and are also biodegradable, which has the effect of reducing the problems of clogging and removal of polluted water.

The quoted document U.S. Pat. No. 4,561,883 describes drilling muds in which there is a water-soluble cross-linked polyelectrolyte, selected from the family of cellulose derivatives or gum derivatives, or a water-soluble anionic polyelectrolyte, selected from the group of carboxymethylcellulose or the group of polyacrylates obtained from Xanthomonas campestris, or a mixture of these polyelectrolytes is incorporated as the viscosity agent.

Xanthan is particularly an anionic heteropolysaccharide obtained by fermentation from the action of a microorganism of the Xanthomonas type. Its molecular weight exceeds one million and it is commonly very often used in the composition of drilling muds. This hydrophilic colloid not only has the property of thickening but also of stabilizing the water-based systems and conferring on them a particularly high viscosity of the order of 1.4 to 1.8 Pa.s measured at 30 seconds on a Brookfield viscometer for a solution containing 10% by weight of xanthan, in the presence of 5 g/l of NaCl. In addition it has low sensitivity to significant variations in temperature, pH or salinity.

However, the introduction of xanthan into the composition of a drilling mud as the viscosity agent does not enable the other constituents usually added to the mud composition in order to ensure its other functions to be improved.

Xanthoguccan is another polyelectrolyte produced by fermentation of a fungus of the Botrytis type, some applications of which are known in the petroleum field. Thus, the quoted document EP 0216461 A1 describes an application of xanthoguccan in the field of muded recovery of petroleum.

The quoted document FR 2,570,754 also other possible applications of this product in the field of the treatment of hydrocarbon wells, in particular as completion fluid or cleaning agent for oil or gas transport pipes or as fracturing fluid.

Some properties of xanthoguccans are known. Thus, xanthoguccan, like xanthan, is a hydrophilic colloid which has the property of thickening and stabilizing water-based systems by conferring on them a particularly high viscosity, higher than that obtained in the case of xanthan, the identical concentrations of active components, and in particular a high independence of these viscosities with respect to variations in pH and temperature within a very wide range, and also rheological properties of the pseudoplastic type. Thus, the viscosity of a xanthoguccan solution is virtually independent of the pH between pH 1 and pH 12.5 and of the temperature up to a limit which is located in the vicinity of 130°C. With xanthoguccan the viscosity is also highly independent of the salinity.

The xanthoguccan or xanthoguccans continuously used in the applications in the petroleum field are refined materials which are in the form of a white powder obtained by chemical purification of a fermentation broth after filtration in order to remove the residues of the producing organism. It is necessary in the known applications of xanthoguccans in the field of well treatment to purify or refine the liquid reaction mixture resulting from the fermentation and maintaining the biopolymer in solution so as to require off all or most of the residues which it contains, by filtering or centrifuging or concentrating the said reaction mixture, so that the treatment agents do not contain more than 10 to 15% of the said residues, consisting of mycelium in the case of xanthoguccan.

Xanthan is produced by a bacterium which has a slow rate of only a few milligrams. The known and cross-linked xanthoguccan mycelium is of considerable size. Once after drying, the cellular residues remain of the order of one milligram.

SUMMARY OF THE INVENTION

It has now been found that by using xanthoguccans to make up at least part of the viscosity agent for drilling mud, it was possible to reduce the concentration of the other constituents of the mud or even to suppress them. In fact, the introduction of xanthoguccan as main constituent permits the preparation of a water-based mud containing a combination of constituents ensuring its functions to a satisfactory manner in a large number of cases, especially if the xanthoguccan mud contains all or part of the organisms which produced it, so the extent that the presence of this mycelium in the mud improves some of the functions of the latter. Thus, for example, a mud containing non-refined xanthoguccan appears to preserve the self-healing functions better than a mud containing refined xanthoguccan or a very drilling mud having stable physical and chemical characteristics. The self-healing functions are thus less sensitive to the effect of erosion and mechanical destruction and the presence of mycelium allows a better preservation of the walls of the well and, in a way, inhibits the erosion of the clay in the formations.

The mycelium associated to the xanthoguccan mud may even play the role of plugging agent in certain cases.

Moreover, the presence of the mycelium modifies the interaction between the polymer and the solids and makes the viscosity of a solution containing non-refined xanthoguccan even less sensitive to the clay content.

It is also found that the presence of mycelium improves the control of the flow and in certain cases may even avoid the specific use of a rheology-modifying agent, or at least allow the mud to be stored in its container.

The presence of xanthoguccan gives rise to an unexpected phenomenon of the reactive dyes, for example contained in the mud, and the presence of mycelium, in combination with the excellent carrying capacity of the xanthoguccan containing xanthoguccan, permits the removal of cuttings originating from drilling, which aggregates and causes the clogging or the removal by mechanical means at the surface more effective. In fact, in the presence of mycelium the phenomenon of clogging in a mud containing xanthoguccan is not observed. It appears that mycelium observed phenomenon, that the cuttings related to the surface by the mud during drilling is to a lesser and therefore better preserved state with a mud containing non-refined xanthoguccan than with a mud of different nature and in thickness of greater when in the production when study it.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a graph of the results produced in Example 1. FIG. 2 is a graph of the results produced in Example 2. FIGS. 3-11 are such a graph of the results produced in Example 6.

DETAILED DESCRIPTION OF THE INVENTION

The subject of the invention is therefore a less complex mud for drilling mud comprising at least of a useful amount of xanthoguccan in order to obtain the desired viscosity, mixed with a production waste, which may be found water, sea water or brine or any other type of water (and water or water containing sodium or potassium salts etc.), a cross-linked heteropolysaccharide in an amount which may vary from 0 g/l to 50 g/l and, if necessary, a bactericide in an amount sufficient to prevent any biodegradation phenomenon. The amount of bactericide, which is less than that of xanthoguccan, may, for example, represent between 0.01 and 0.5% of the weight of the composition according to the invention. The bactericide, for example of the PRECOCOL type, produced by ICI, will be introduced into the composition according to the invention for quantities which will be, for example, more than two or three days, in order to control bacterial degradation and its effects.

The xanthoguccan, which are present in the composition of muds according to the invention, are anionic water-soluble heteropolysaccharides having molecular weights in excess of 300,000, the molecules of which consist of a main straight chain formed of D-glucose units which are bonded by 1-3 bonds and one to three of which is bonded to a side D-glucose unit by means of a 1-6 bond. These polyelectrolytes are obtained by fermentation of a medium based on sugar and inorganic salts under the action of a microorganism of the Botrytis type. A more complete description of the xanthoguccans and their preparation may be found in the quoted document U.S. Pat. No. 3,507,848, the content of which is incorporated by reference in the present description. In various studies, the xanthoguccan chains are associated in triple helix, which explains the high rigidity of the biopolymer and consequently its high viscosity-increasing power and its resistance to shearing stress.

According to the invention, it is possible to use, as source of xanthoguccan, the xanthoguccan isolated from the fermentation medium, the said product being in the form of a

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powder or of a more or less concentrated solution in an aqueous medium, aqueous-alkaline solution, or to use the liquid medium mixture resulting from the dissemination and considering the rheological behavior. According to the invention, thicker suitable rheological agents are used, for example, those of the type of polyacrylamide, for example, those of the type of polyacrylamide with a chelating agent, such as glycyl, the said treatment being carried out, for example, by bringing the rheological agent in contact, in solution, in suspension or in emulsion with 0.5% to 10% by weight of the chelating agent, relative to the rheological agent.

Preferably, the rheological agent in the composition of the mud according to the invention will contain all or part of the crystalline of the preceding group. Advantageously, the rheological agent in the composition of the mud according to the invention will contain more than 15% by weight of crystalline.

Advantageously the base composition for the mud according to the invention will contain 1 g/l to 10 g/l of rheological agent and preferably 2 g/l to 5 g/l of non-collated rheological agent.

Advantageously, in order to ensure better rheological control, the base composition of the drilling mud according to the invention contains as rheological colloid such as bentonite or substituted calcium carboximate, the particle size of which has been adapted, preferably between 5×10^{-4} m and 100×10^{-4} m, in proportions less than are used for water-based drilling muds in which the viscosity agent consists of a dispersant rather than the rheological agent. In the composition according to the invention, the proportion of bentonite is preferably between 0 g/l and 30 g/l and the proportion of substituted calcium carboximate between 0 g/l and 50 g/l.

The water present in the mud composition may be of any type and of any pH. For example, it is possible to use fresh water, brackish or even water in which any salt, such as an alkali metal salt or alkaline earth metal salt, such as sodium carbonate, sodium chloride, potassium chloride, etc., has been added.

Although this is not indispensable with the composition according to the invention, it may be necessary to adjust the pH of a drilling mud. An alkaline mud having a high pH has no self-conservative action and assists in the swelling of the reactive clays, which are a constituent of the mud, which is necessary for ensuring that the mud performs its functions as well as possible. Moreover, the property of compressions or additives which it may be desired to add to the composition of a base mud have a better stability in an alkaline medium.

A compound having an alkaline reaction, for example NaOH or KOH , will therefore advantageously be included in the base composition of a mud according to the invention, in a proportion such that the pH of the mud thus obtained is between 8 and 10 and preferably between 9 and 9.5.

The drilling mud according to the invention may also contain diverse additives more or less commonly used for the composition of drilling muds.

A composition of this type according to the invention, containing, in solution, in suspension or in colloidal solution, as any production water, rheological agent, is a sufficient amount as an inorganic colloid in a mud, to which a base mud or a bentonite has been added if appropriate, constitutes a base composition for ready-to-use drilling mud having certain advantages. A composition of this type may itself constitute a drilling mud which is used as such, to the extent that it ensures the main functions of a mud such as viscosity agent, transport agent, rheological control agent and suspending agent.

A composition according to the invention provides a very good viscosity agent, substantially similar amounts of viscosity agent than those customarily used, and which is also beneficial to the mud, in particular, stability and clay content. Moreover, if the rheological agent in the composition is non-collated, a composition is obtained which ensures constant control of the rheology, good preservation of the mud and good cleaning of the well without perturbing the rate of progress of drilling.

The use of this composition in fact makes it possible to economize on the amount of compounds used, such as the viscosity agent or the rheological colloid. By way of example, the amount of bentonite necessary for a water-based mud in which the viscosity agent is similar, in composition, between 20 and 40 grams per liter, whereas in the composition according to the invention amounts not exceeding 30 grams per liter suffice in order to obtain equivalent effects. Similarly, in some cases it may be possible to restrict and even suppress the use of calcium derivatives used as plugging agent, the quantities contained in the composition according to the invention at least partly making this function. Similarly, the use of PAM (polyacrylamide colloidal) or of CMC used in order to increase the apparent viscosity at low transport speeds and to improve the carrying capacity to achieve better removal of the waste is no longer justified when the composition according to the invention is used.

Similarly, finally, the use of some chemical products to treat some pollution by NaCl or calcium salts for example is no longer necessary with the composition according to the invention, because of the greater tolerance of the mud pollution.

Apart from the fact that this mud contains a limited number of compounds which are simple to use, this mud may be used without any particular precautions in a wide range of wells and for drilling any type of formation and is more particularly suitable for drilling at high temperatures under slight added costs.

A high temperature is understood to be temperatures which may reach 120°C . In the case of temperatures going beyond this limit, favorable gelling phenomena may appear after a certain aging of the mud, in the laboratory, of 16 h for a temperature $T=140^\circ\text{C}$, and of more than 100 h for $T=120^\circ\text{C}$. The phenomenon is produced, for example, for 5 g/l solution in fresh water which is also alkaline or quasi-alkaline with sodium chloride or calcium chloride, or in the presence, and only in the presence, of solids. In a solid-free solution, the polymer degrades without gelling at temperatures higher than $T=120^\circ\text{C}$.

The base composition for drilling mud according to the invention is prepared by mixing, with stirring, the rheological agent, which may be in any form, solid or solution or suspension, in appropriate amounts to obtain the above-mentioned concentrations, with the amount of water necessary for the production of the mud. As a general rule, it is recommended to prepare a solution containing 1% of rheological agent, which after adding 20 volumes is brought to the desired concentration. The mechanical stirring must be sufficiently vigorous to supply the indispensable shearing stress, while avoiding the breakage of it. It is pointed out that the shearing stress, which is necessary to achieve a good dispersion, improves the viscosity, in contrast to the majority of known colloids. After evening, the solution is brought to the desired concentration, if a viscosity higher than 0.1 Pa.s is desired, the concentration must be higher than 0.5% by weight. The respective amounts of rheological

colloid and bentonite, if used, added to the water are chosen such that the concentrations of these constituents in the resulting suspension are within the ranges defined above. The amount of the compound having an alkaline reaction, if used, is adjusted so as to bring the pH of the suspension to the chosen value. The consequence, that is to say the rheological agent, the rheological colloid and, if appropriate, the bentonite and the compound having an alkaline reaction which are added to the water may be added in any order. However, it is preferable first to dissolve the compound having an alkaline reaction, if this compound is, in particular, sodium hydroxide or potassium hydroxide, in the water intended to form the aqueous phase of the suspension before incorporating the rheological colloid, then the agent based on rheological agent and finally the bentonite into the solution obtained.

Compared with a composition containing similar amounts in equal amount, the composition according to the invention has some advantages. Apart from a very good rheological yield, at least equal to that of a composition containing similar amounts, the composition according to the invention has very good stability within a wide pH range and better temperature stability, at least up to 120°C . In rheological characterization conducted under these temperatures, when aged for 16 h at 120°C , a solution containing 5 g/l of the polymer Rhodopol XE3 from Rhone-Poulenc, for example, loses all of its viscosity-decreasing properties, both in fresh water and in sea water. In the presence of rheological agent it will be produced, however, in a neutral or alkaline medium. It has also been found that the composition according to the invention has a good stability in the presence of significant clay content of up to 150 g/l and more, in respect of clays of low conductivity, to the extent that the rheological characteristics of these compositions remain work to the presence of loading and comparable to those of an unconfined base solution, in contrast to what occurs in the case of reactive-based compositions.

In the presence of reactive clay, such as the bentonite CLAROL P82 or atropite, the effect produced by the composition based on non-collated rheological agent in the composition of these clays in the form of mud aggregates which can be destroyed by violent agitation or shearing stress.

It has also been found that the composition according to the invention has good stability in electrolytes, the polymer rhodopol having sodium chloride or potassium chloride solution of 120 g/l without any problem, with slight variations in the rheological characteristics, including the presence of clay mud. The stress curve is appropriate in the presence or absence of diverse reactive clays and of diverse concentrations by electrolyte or calcium for example. Experiments carried out on samples based on fresh water or sea water show that these results are virtually independent of the type of water used. The stress curve, however, appears to be better in fresh water than in sea water, while supplementary concentration by sodium chloride, calcium chloride or clays for example appears to be better without from the rheological viewpoint by the polymer in sea water rather than by that in fresh water.

The base compositions for drilling mud according to the invention are very particularly suitable for the drilling of any type of well whatever the field of application, for example petroleum, mining, civil engineering or any other field of application, for example drilling for water.

The invention is illustrated by the following examples which are given without any restriction being implied.

The equipment used for the measurements is manufactured (API standard RP 15). The rheological behavior of the

solutions tested was evaluated using a FANN 35 viscometer with six speeds, that is to say 600-300-200-100-60 and 30 revolutions per minute (rpm), each corresponding to a speed gradient expressed in reciprocal seconds (s^{-1}) of, respectively, 1000, 510, 340, 170, 85 and $31 s^{-1}$. This apparatus provides a measurement of the shear stress levels, which is termed FANN reading, expressed here in Pascals. FANN is a make of equipment to which particular procedures are applied.

The FANN viscometer is an apparatus having concentric cylinders, the rotor of which is driven with the aid of an electric motor (a mechanical viscometer also exists to which the rotor is driven by hand). The resistance to shear of the mud, contained in a bucket into which the concentric cylinders are immersed, is measured. The resistance to shear at various speeds of rotation of the rotor is read off (FANN reading) on the graduated dial. The viscosity of the mud comes a rotation of the rotor which is indicated on the reading dial.

The rheological measurements are carried out at the end of 30 minutes using an API three press and are expressed in centipoises.

The rheological agent used is produced by RANFOL RHO INDUSTRIES from a Rhodopol R82 8 mud. Two grades of rheological agent are used in the following examples: a refined grade containing less than 10% of crystalline residues, marketed under the name ACTIUM CB11, and a non-refined grade containing of the order of 25% of crystalline residues, marketed under the name ACTIUM CB8. The muds used for the tests described below are marked by RHOPOLENT under the name RHODOPOL XE3 (CB83 below) and contains about 90% of active substance. The rheological agent was hydrated with stirring in the RAYNOR for 2 hours.

All of the following experiments were carried out using rheological agent previously treated with 1 to 2% of working agent, that is to say a surface active, to facilitate hydration. The experiments were carried out on 5 g/l solutions in fresh water or sea water, without adjusting the pH, unless indicated in the contrary, obtained from the same base solution (composition of a 2.0-0.5 sample for all the experiments).

EXAMPLE 1

The curves in FIG. 1 show comparison of the rheological behavior, in FANN reading, of a refined rheological agent and a non-refined rheological agent, the same concentration, that is to say 3 g/l, in fresh water at pH 10.5. It is found that the efficiency (in the refined rheological agent) is about 20% higher than that for the non-refined rheological agent. This discrepancy is due to the sole difference in concentration of active compound between the rheological agents.

EXAMPLE 2

The rheological efficiency of a suspension of non-collated CB8 rheological agent and a suspension of XE3 muds is compared for a given concentration of 3 g/l, on the one hand in fresh water at pH 4.5 and on the other hand in sea water of pH 7.2. The curves in FIG. 2 show comparison of the results obtained in FANN readings. It is found that for an equal weight of active substance the efficiency, in viscosity, of fresh water, are largely equivalent and that in sea water the efficiency is better for the rheological agent.

EXAMPLE 3

The rheological behavior of 5 g/l suspensions of non-collated CB8 rheological agent in fresh water or in sea water is compared for various loadings of non-reactive clays. The

are given in Table 4 below. The behavior of the three solutions is very similar, with, however, a better stability of the CSM. A very good stability of the sludge up to 130° C. will be noted.

The drilling values for run is between 130 and 140° C. for the three types of sclerogelans.

TABLE 4

Pore measurements	Composition of the mud				
	SP RT 1: CSM (80) 3.3 g/l + fresh water pH 9				
	SP RT 2: CSM (80) 4 g/l + fresh water pH 9				
	SP RT 3: CSM (80) 4.5 g/l + fresh water pH 9				
	30 bar 90° C.	30 bar 90° C.	30 bar 110° C.	30 bar 130° C.	30 bar 140° C.
SP RT 1					
PLUSE 800 Pa.	8.24	8.1	8.1	7.3	3.18
PLUSE 800 Pa.	1.3	1.3	1.3	4.26	1.43
PLUSE 800 Pa.	6.88	6.88	6.88	4.3	8.88
PLUSE 800 Pa.	1.74	1.74	1.5	1.81	6.48
PLUSE 80 Pa.	4.3	4.38	4.38	3.35	
PLUSE 80 Pa.	4.3	3.82	3.82	3.87	
PLUSE 5 Pa.	3.38	2.87	2.87	1.8	
PLUSE 1 Pa.	3.77	3.88	3.88	1.43	
AV Pa. ±	8.25 ± 10 ⁻⁴	8.1 ± 10 ⁻⁴	8.1 ± 10 ⁻⁴	7.3 ± 10 ⁻⁴	3.15 ± 10 ⁻⁴
PV Pa. ±	1.5 ± 10 ⁻⁴	1 ± 10 ⁻⁴	1 ± 10 ⁻⁴	1 ± 10 ⁻⁴	1.5 ± 10 ⁻⁴
VV Pa.	3.5	6.31	6.31	3.38	1.18
SP RT 2					
PLUSE 800 Pa.	8.1	7.65	7.3	5.1	4.3
PLUSE 800 Pa.	7.3	6.88	6.88	6.11	1.88
PLUSE 800 Pa.	6.88	6.31	6.31	5.74	3.35
PLUSE 800 Pa.	1.74	1.38	1.38	1.38	1.37
PLUSE 80 Pa.	4.78	3.82	3.82	3.35	3.38
PLUSE 80 Pa.	4.3	3.82	3.82	3.87	1.8
PLUSE 5 Pa.	3.88	3.35	3.35	3.88	1.87
PLUSE 1 Pa.	3.88	3.35	3.35	1.8	1.43
AV Pa. ±	8.1 ± 10 ⁻⁴	7.6 ± 10 ⁻⁴	7.3 ± 10 ⁻⁴	5.1 ± 10 ⁻⁴	4.3 ± 10 ⁻⁴
PV Pa. ±	1.5 ± 10 ⁻⁴	1 ± 10 ⁻⁴	1 ± 10 ⁻⁴	1 ± 10 ⁻⁴	1 ± 10 ⁻⁴
VV Pa.	4.31	3.74	6.31	3.38	3.35
SP RT 3					
PLUSE 800 Pa.	8.38	8.88	8.8	5.74	3.38
PLUSE 800 Pa.	8.1	7.65	8.1	3.38	1.43
PLUSE 800 Pa.	7.65	7.3	7.3	4.78	8.88
PLUSE 800 Pa.	7.3	6.88	6.88	4.3	6.88
PLUSE 800 Pa.	1.74	6.31	5.74	3.82	6.88
PLUSE 80 Pa.	3.38	3.38	3.38	3.38	3.38
PLUSE 5 Pa.	4.38	4.38	4.38	3.35	3.88
PLUSE 1 Pa.	4.3	4.3	4.3	3.38	6.88
AV Pa. ±	10 ± 10 ⁻⁴	9.3 ± 10 ⁻⁴	9 ± 10 ⁻⁴	6 ± 10 ⁻⁴	3.5 ± 10 ⁻⁴
PV Pa. ±	1.5 ± 10 ⁻⁴	1 ± 10 ⁻⁴	1 ± 10 ⁻⁴	1 ± 10 ⁻⁴	1 ± 10 ⁻⁴
VV Pa.	4.88	6.31	7.65	1.43	6.48

EXAMPLE 8

Phonetic study. Influence of the biomass on the API filtrate. The experiment was first carried out using the sclerogelans on its own. The three types of sclerogelans were dispersed in fresh water at pH 9. The measurements were carried out by applying the API standard test described in Example 4, at ambient temperature, for various concentrations of pore product, that is to say 1.5 g/l, 3.3 g/l and 4.8 g/l. The results are grouped in the following table 5.

CSM Concentration Filterate	CSM Concentration Filterate		CSM 48 Concentration Filterate	
	1.5 g/l	3.3 g/l	3.3 g/l	4.8 g/l
1.5 g/l	3.3	3.3	3.3	3.3
3.3 g/l	4.8	4.8	4.8	4.8
4.8 g/l	6.3	6.3	6.3	6.3

It is found that a 30% concentration of biomass (CSM) creates a filter bed. The biomass therefore improves the control of filtration. The addition of 20% of biomass which has been subjected to an extraction process does not significantly improve the control of the filtrate.

EXAMPLE 9

Phonetic study. Influence of the biomass on the API filtrate. This time the filtrate measurements were carried out on fresh water solutions at pH 9 containing 30 g/l of WYOMING WFO leucocidin, in which solutions CSM, CSM and CSM48 were dispersed in an amount of, respectively, 3.3 g/l, 4 g/l and 4.8 g/l. The results are grouped in the following table 6.

CSM Concentration Filterate	CSM Concentration Filterate		CSM48 Concentration Filterate	
	3.3 g/l	4 g/l	4.8 g/l	12 ml
3.3 g/l	3.3	3.3	3.3	3.3
4 g/l	4.8	4.8	4.8	4.8
4.8 g/l	6.3	6.3	6.3	6.3

The results can be compared with those of example 8. It is found that in the presence of a filter bed the influence of the biomass is not significant.

We claim:

1. A base composition for a water-based drilling mud comprising a mixture of (1) water, (2) sclerogelans, and (3) a non-erective inorganic colloidal solid, wherein said colloidal solid is contained in an amount greater than 0 but less than or equal to 30 g/l and wherein said sclerogelans has been produced by carrying out fermentation of a producing fungus and said composition further comprises at least 1.5% by weight of the superoxide of said producing fungus.
2. The composition according to claim 1, wherein said sclerogelans is contained in an amount between 1 g/l and 10 g/l.
3. The composition according to claim 1, wherein said base composition contains 2 g/l to 5 g/l of non-erective sclerogelans.
4. The composition according to claim 1, wherein said inorganic colloidal solid is bentonite.
5. The composition according to claim 1, wherein said water is selected from fresh water, brine and water in which a salt has been added.
6. The composition according to claim 1, which further comprises an alkaline compound in an amount sufficient to obtain a pH of said composition of between 8 and 10.

7. A water-based drilling mud, consisting essentially of the base composition according to claim 1 or 6.
8. A process for drilling petroleum wells which comprises applying a drilling mud which contains the composition according to claim 1 to the drill.
9. A process for drilling a well which comprises applying a drilling mud which contains the composition according to claim 1 to the drill.
10. A process for drilling a water well which comprises applying a drilling mud which contains the composition according to claim 1 to the drill.
11. The composition according to claim 1, which further comprises calcium carbonate in an amount of up to 50 g/l.
12. The composition according to claim 1, which further comprises a bactericide.
13. The composition according to claim 13, wherein said bactericide is contained in an amount up to 0.5% by weight.
14. The composition according to claim 11 which further comprises a bactericide.
15. The composition according to claim 14, wherein said bactericide is contained in an amount up to 0.5% by weight.

[54] DRY BIOCIDES
[75] Inventors: Eugene A. Ephraïm, Missouri; City, Frank B. Winkler, Houston, both of Tex.
[73] Assignee: Baker Hughes Incorporated, Houston, Tex.
[21] Appl. No.: 09/243,133
[22] Filed: Feb. 18, 1999
[51] Int. Cl.⁷: A01N 25/00; A01N 31/00; A01N 37/00
[52] U.S. Cl.: 106/18.31; 106/18.34; 210/784; 252/78; 432/28; 434/409; 434/417; 434/421; 506/153; 514/126; 514/129
[56] Field of Search: 106/18.31, 18.34; 504/153, 514/126, 129; 432/28; 434/409, 417, 421; 210/784; 252/78
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Albright & Wilson, "TOLCLOD 95", Technical Bulletin 235, undated.
Primary Examiner—Anthony Christ
Attorney, Agent, or Firm—Blacks, Mowatt & Smith, P.C.
[57] ABSTRACT
A method has been discovered for controlling bacterial growth using a dry biocide. Triclor-4-hydroxyphenyl-phosphonate sodium (THPS) is adsorbed on a solid, particulate substrate through a spraying technique. The THPS in a dry form colonizes or reduces areas involved in bacterial and algal growth. The normally liquid THPS

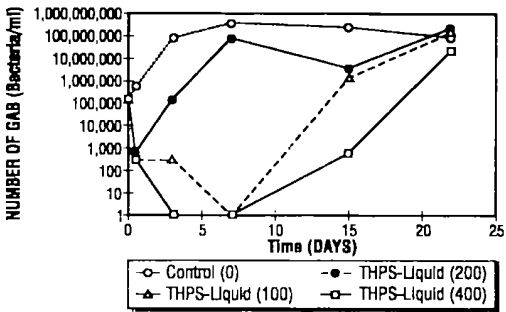


FIG. 1A

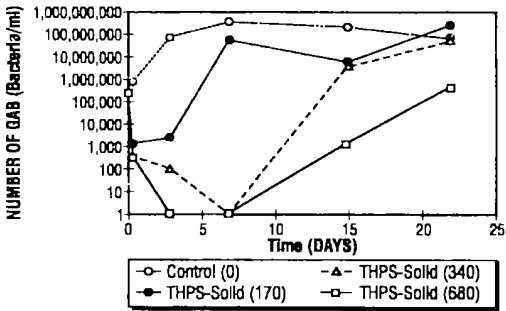


FIG. 1B

14

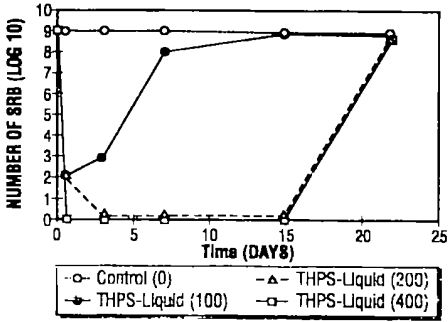


FIG. 2A

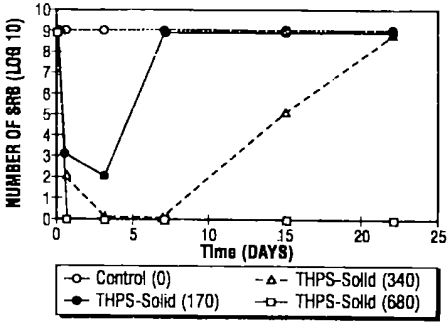


FIG. 2B

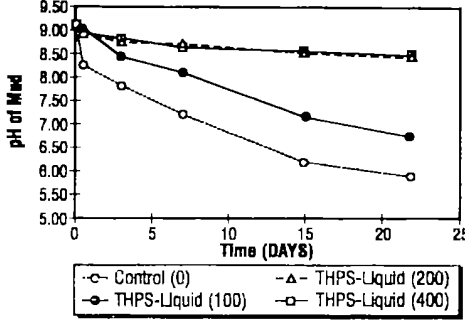


FIG. 3A

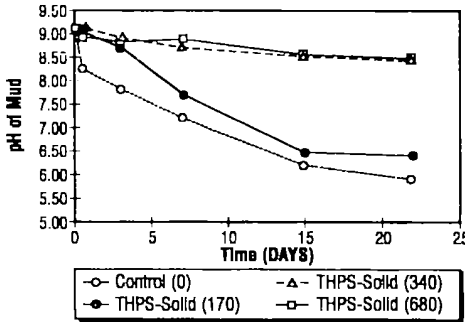


FIG. 3B

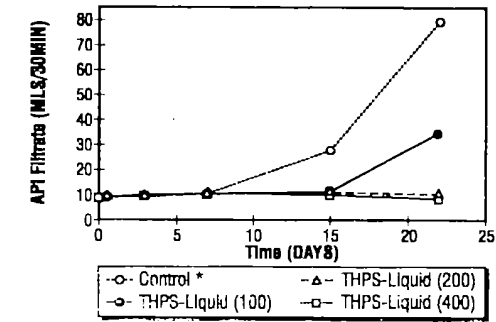


FIG. 4A

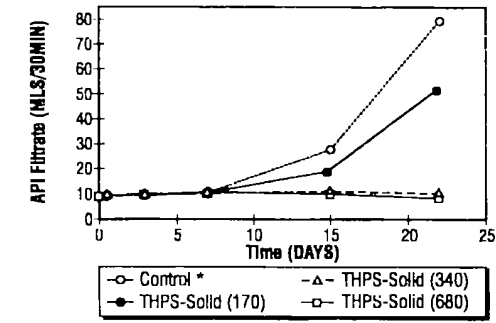


FIG. 4B

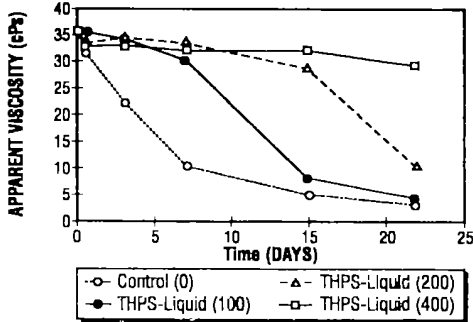


FIG. 5A

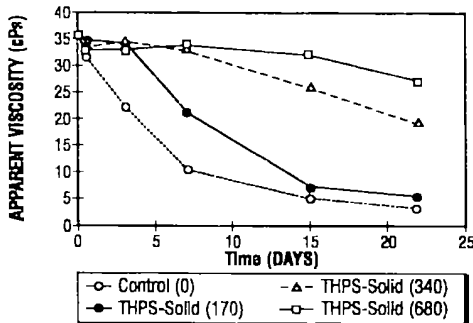


FIG. 5B

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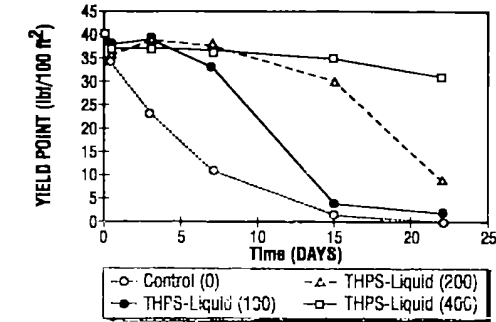


FIG. 6A

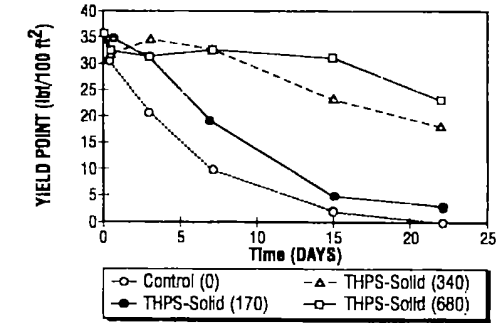


FIG. 6B

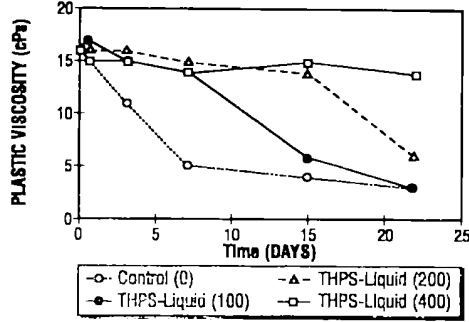


FIG. 7A

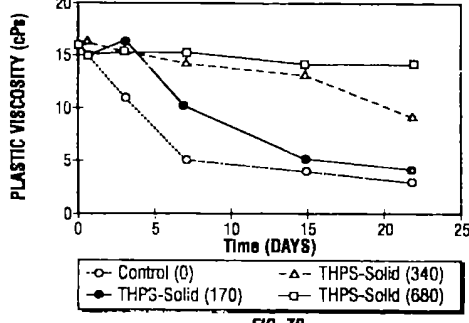


FIG. 7B

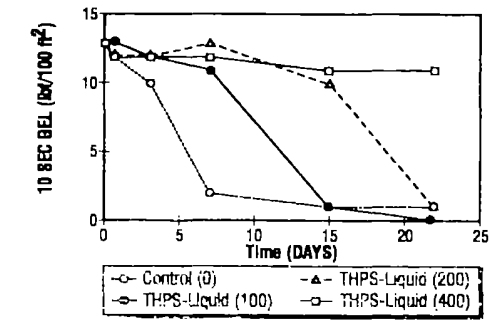


FIG. 8A

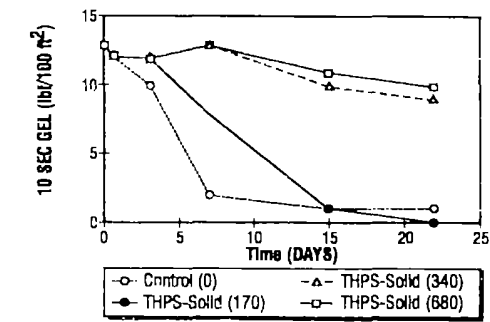


FIG. 8B

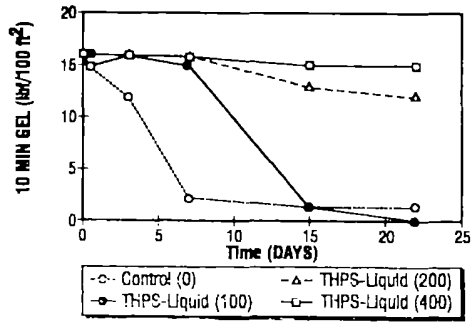


FIG. 9A

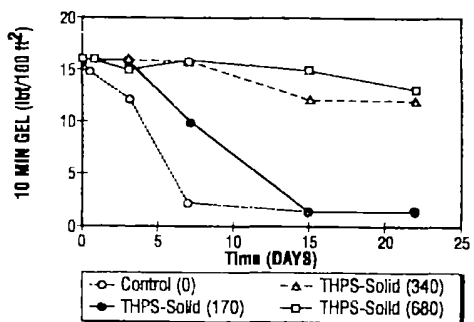


FIG. 9B

[Handwritten mark]

TABLE 4

Block	Conc.	Time Interval					
		0	0.5	3	7	15*	22
Control	—	40	34	23	11	2	0
TIIPS	100	40	48	46	33	4	2
Liquid	300	40	34	36	36	30	0
Liquid	600	40	37	37	37	28	0
TIIPS	150	40	39	39	23	3	2
Solid	340	40	34	36	37	28	28
Solid	680	4	24	30	37	30	36

*subculture

TABLE 7

Block	Conc.	Time Interval					
		0	0.5	3	7	15*	22
Control	—	18	13	11	3	4	2
TIIPS	100	16	17	15	14	6	2
Liquid	300	18	14	14	15	11	4
Liquid	600	18	13	13	14	23	14
TIIPS	150	18	17	16	18	5	4
Solid	340	18	11	15	18	11	9
Solid	680	18	12	14	15	14	14

*subculture

(a) Strength

Micro-sections of the solid (10 sec.) and 10 minute gel strengths of the sample results are presented in Tables 8-9 and 10 (CA, RA, RA, RA, RA, RA).

As observed with the other rheological properties, Liquid TIIPS at 400 ppm and solid TIIPS at 680 ppm were generally equivalent to the strength of the XCD gel strength for the duration of the performance study. Liquid TIIPS at 200 ppm and solid TIIPS at 340 ppm also maintained gel strength for the entire 3 weeks, although not as effectively as the liquid class.

TABLE 8

Block	Conc.	Time Interval					
		0	0.5	3	7	15*	22
Control	—	13	11	10	7	1	0
TIIPS	100	13	13	12	11	1	0
Liquid	300	13	12	12	12	11	11
Liquid	600	13	12	12	12	11	11
TIIPS	150	13	12	12	12	1	0
Solid	340	13	12	12	13	10	6
Solid	680	13	12	12	13	11	10

*subculture

TABLE 9

Block	Conc.	Time Interval					
		0	0.5	3	7	15*	22
Control	—	18	15	12	2	1	1

TABLE 5-continued

Block	Conc.	Time Interval					
		0	0.5	3	7	15*	22
TIIPS	100	18	18	18	18	1	0
Liquid	300	18	15	18	18	12	12
Liquid	600	18	15	18	18	12	12
TIIPS	150	18	18	18	18	12	12
Solid	340	18	18	18	18	12	12
Solid	680	18	18	18	18	12	12

*subculture

As demonstrated, a rigorous test of block performance in drilling fluids was conducted using XCD polymer as the test drilling fluid. XCD polymer was selected because it is highly conducive to bacterial growth. Inoculation of the drilling fluid with 10⁷ CAH and 10⁷ SAR had no effect on physical integrity within 3 days. Liquid TIIPS and solid TIIPS performed effectively as quick killing biocides, decreasing the CAH and SAR populations dramatically within 12 hours. However, neither biocide was able to maintain long term control on the bacterial populations. Reduced 10⁷ CAH and 10⁷ SAR by the end of the 22 day study. The surprising exception to this line of control was the 680 ppm solid TIIPS, which suppressed CAH growth to 10⁴ and SAR growth to below detectable levels until the end of the study. It is noteworthy that TIIPS in solid or liquid form was by far the most effective biocide against both.

In the foregoing specification, the invention has been described with reference to specific embodiments thereof, and it will be understood that various modifications can be made therein without departing from the spirit and scope of the invention as set forth in the appended claims. Accordingly, the specification is to be regarded in this respect as illustrative rather than restrictive. For example, specific substrates, proportions of TIIPS on the substrate, and concentrations listed, other than those specifically listed, falling within the claimed parameters, but not specifically identified or used in a particular application to control bacteria, are within the scope of this invention. Similarly, it is expected that the innovative dry form of TIIPS will find utility as a biocide in other fluids and solid biocides those specifically listed herein.

1. A method of inhibiting bacterial growth in a composition comprising adding thereto an effective bacterial inhibiting amount of a biocide comprising tetra-alkyl-hydroxyamyl-phosphonium sulfate (TIIPS) adsorbed on a solid, particulate, flowable substrate selected from the group consisting of silica, sodium sulfate, sodium carbonate, sodium chloride, potassium chloride, and borax.

2. The method of claim 1 where the TIIPS is sprayed onto the solid, particulate substrate.

3. The method of claim 1 where the solid, particulate substrate is silica.

4. A dry biocide comprising tetra-alkyl-hydroxyamyl-phosphonium sulfate (TIIPS) adsorbed on a solid, particulate, flowable substrate selected from the group consisting of silica, sodium sulfate, sodium carbonate, sodium chloride, potassium chloride, and borax.

5. The dry biocide of claim 4 where the dry biocide is made by the process of spraying TIIPS onto the solid, particulate substrate.

6. The dry biocide of claim 4 where the solid, particulate substrate is silica.

7. The dry biocide of claim 4 where the proportion of TIIPS on the substrate ranges from about 1 to about 90 wt %.

8. A composition (adsorbed against bacterial growth comprising a composition selected from the group consisting of fluid and solids, and an effective bacterial inhibiting amount of a biocide comprising tetra-alkyl-hydroxyamyl-phosphonium sulfate (TIIPS) adsorbed on a solid, particulate, flowable substrate selected from the group consisting of silica, sodium sulfate, sodium carbonate, sodium chloride, potassium chloride, and borax.

9. The method of claim 8 where the TIIPS is sprayed onto the solid, particulate substrate before it contacts the solid, particulate substrate.

10. The method of claim 8 where the solid, particulate substrate is silica.

11. A method for producing a dry biocide comprising spraying tetra-alkyl-hydroxyamyl-phosphonium sulfate (TIIPS) onto a solid, particulate, flowable substrate for adsorption thereon where the substrate is selected from the group consisting of silica, sodium sulfate, sodium carbonate, sodium chloride, potassium chloride, and borax.

12. The method of claim 11 where the TIIPS is sprayed onto the solid, particulate substrate before it contacts the solid, particulate substrate.

13. The method of claim 11 where the solid, particulate substrate is silica.

(54) SULFITE COMPOSITIONS, AQUEOUS SULFITE SOLUTIONS AND METHOD OF DECREASING THEIR RATE OF OXIDATION
(75) Invention: Harley E. Bush, Houston, Tex.
(73) Assignee: NL Industries, Inc., New York, N.Y.
(22) Filed: Mar. 5, 1975
(21) Appl. No.: 555,070

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Primary Examiner—Seymour W. Eagle
Assistant Examiner—Donald P. Walsh
Attorney, Agent, or Firm—Roy F. Housar, Debra H. Lussan, Robert L. Latham

(57) **ABSTRACT**
The invention provides compositions and aqueous solutions containing a sulfite compound chosen from at least one water soluble stabilizing compound which is an organic phosphonate containing at least two phosphonic acid groups per molecule. Also provided is a method of reducing the oxidation rate of aqueous sulfite solutions caused by oxygen in the atmosphere and a method of decreasing the corrosiveness to ferrous metals of aqueous systems containing dissolved oxygen and at least one electron acceptor derived from iron, cobalt, copper, manganese, and nickel.

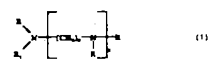
10 Claims, No Drawings

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SULFITE COMPOSITIONS, AQUEOUS SULFITE SOLUTIONS AND METHOD OF DECREASING THEIR RATE OF OXIDATION

DESCRIPTION OF THE INVENTION

The rate of oxidation of aqueous sulfite solutions can be decreased by adding to such solutions a water soluble stabilizing compound which is an organic phosphonate containing at least two phosphonic acid groups per molecule. Preferred stabilizing compounds are selected from the group consisting of the free acids and water soluble salts of:



where each R₁ is independently selected from the group consisting of hydrogen, —CH₂PO₃(OH)₂, and —(C₂H₅)₂PO₃H wherein n is 2 to 4 and c is 1 to 3; R₂ is



where X and Y are independently selected from the group consisting of hydrogen and lower alkyl radicals having 1 to 4 carbon atoms; n is 2 to 4 and c is 0 to 6; provided that at least 14 of the radicals represented by R₂ are —CH₂PO₃(OH)₂.



where R₄ is —CH₂PO₃(OH)₂; R₅ is selected from the group consisting of hydrogen, hydroxyl, and —(C₂H₅)₂PO₃H wherein n is an integer from 2 to 4 and c is an integer from 1 to 3; and where R₆ is selected from the group consisting of lower alkyl radicals containing 1 to 5 carbon atoms and:



where n is an integer from 0 to 6; and



where R₇ is —CH₂PO₃(OH)₂; each R₈ is independently selected from the group consisting of hydrogen, —CH₂PO₃(OH)₂, and —(C₂H₅)₂PO₃H wherein n is an integer from 2 to 4 and c is an integer from 1 to 3; and where R₉ is selected from the group consisting of lower alkyl radicals containing 1 to 5 carbon atoms and

RELATED APPLICATION

This application is a division of co-pending application Ser. No. 992,344, filed Aug. 28, 1973, now U.S. Pat. No. 3,899,293.

BACKGROUND OF THE INVENTION

1. Field
This invention relates to the art of decreasing the corrosion of ferrous metals and to the art of decreasing the rate of oxidation of aqueous solutions of sulfite and monosulfite and bisulfite upon exposure to a source of oxygen such as the atmosphere.

2. Prior Art
Over the years many investigators have studied the oxidation of sulfite and the effect of various substances on the oxidation of sulfite. Known catalysts for the reaction are certain heavy metal cations, particularly chromate, cobalt, copper, iron, manganese, and nickel. Heavy chemicals are known to either inhibit or retard the oxidation. These are generally free radical scavengers.

It is well known to use sulfite and monosulfite and bisulfite, preferably sodium sulfite, as corrosion inhibitors in aqueous systems containing dissolved oxygen which contain ferrous metals. The sulfite reacts with the oxygen to eliminate it from the system thus preventing its reaction with the ferrous metal. Two books which discuss the corrosion of ferrous metals and the use of sulfite for corrosion protection are: *Handbook Corrosion Inhibitors and Protection*, Ulick R. Evans, Longmans, Green and Co. (New York), 1946; *Corrosion and Corrosion Control*, Herbert H. Uhlig, John Wiley and Sons, Inc. (New York), 1963.

SUMMARY OF THE INVENTION

I have now found that the stability of aqueous sulfite solutions to oxidation by oxygen in the atmosphere is increased by adding to such solutions a water soluble organic phosphonate compound containing at least two phosphonic acid groups per molecule. Solutions containing one or more sulfite and a polyphosphonic acid more particularly described hereinafter remain useful for longer periods of time and are especially effective in decreasing the corrosion of ferrous metals which are contacted by large volumes of water containing dissolved oxygen and which thus tend to be continuously treated with an oxygen scavenging inhibitor.

Accordingly it is an object of this invention to provide aqueous sulfite solutions having increased resistance to oxidation by atmospheric oxygen. It is another object of this invention to provide a sulfite composition which is useful in preparing aqueous sulfite solutions having increased resistance to oxidation by atmospheric oxygen. It is still another object of this invention to provide a method of decreasing the rate of atmospheric oxidation of aqueous sulfite solutions. Another object of this invention is to provide a method of reducing the corrosion of ferrous metals contacted by aqueous systems containing dissolved oxygen and a dissolved cation selected from the group consisting of iron, cobalt, copper, manganese, and nickel.

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not intended to be used in this sulfate composition. Other polyphosphates as disclosed herein may also be used.

The aqueous sulfate solutions of this invention are particularly useful in reducing the corrosion of ferrous metals which are in contact with an aqueous system containing dissolved oxygen and at least one metallic cation selected from the group consisting of ferrous (Fe²⁺), cobaltous (Co²⁺), nickelous (Ni²⁺), manganese (Mn²⁺), and cupric (Cu²⁺).

The corrosion of ferrous metals in contact with such a system is decreased by the removal of the oxygen from the system. This is preferably accomplished by adding to the aqueous system sufficient of the aqueous sulfate solution described herein to provide an excess sulfate (SO₄²⁻) concentration in the system of from 20 parts per million parts by weight (ppm) to 100 ppm above the concentration of sulfate required to react with the oxygen in the system. Thus for (X) ppm of oxygen in the aqueous system to be treated, the amount of sulfate to be added is (X/2) ppm plus 10 to 100 ppm.

The corrosion of a ferrous metal controlled by the aqueous system will be reduced in proportion to the amount of oxygen removed from the system. Total removal of the molecular oxygen in the system will effectively eliminate the corrosion of the ferrous metal which is caused by the presence of the oxygen in the system. Thus it is preferable that the sulfate compound and the oxygen react to remove essentially all of the oxygen from the system before contacting the ferrous metal with the system.

It is well known that metallic cations such as the ferrous, cobaltous, nickelous, manganese, and cupric cations act as catalysts to speed up the rate of reaction between the sulfate solution and oxygen. I have discovered that the aqueous system to be treated must contain a concentration of at least one of these cations which is sufficient to catalyze the reaction of the sulfate compound with the oxygen in the system in order to provide a fast reaction rate when the treated system is used in a reacting tank or other device.

The concentration of sulfate solution needed to effectively catalyze the reaction is dependent upon the concentration of other multivalent cations in the aqueous system. Thus in a relatively pure water to be treated, the catalytic metallic cation is the only cation present, the concentration of the sulfate solution required for the reaction is much greater than would be required if the stabilizing compound were not present. In this case the concentration of catalytic metallic cation in the system is about 5 ppm. At the concentration of other multivalent cations in the system however, particularly the ferrous cation, the concentration of the sulfate solution needed to effectively catalyze the reaction between the sulfate and oxygen decreases. Oil field brines containing high concentrations of ferrous cations need only about 0.5 ppm or more of the catalytic metallic cation to produce a fast reaction rate. Apparently these other multivalent cations complex with the stabilizing compound preventing the stabilizing compound from complexing with the catalytic metallic cation or at least delaying its reaction with the catalytic metallic cation until after the metallic cation has catalyzed the reaction between the sulfate compound and the oxygen.

The preferred aqueous system to be treated with the aqueous sulfate solution of this invention are low sulfate water base drilling fluids, flood waters used in treating subterranean formations, and waste effluents pumped into disposal wells.

Low sulfate drilling fluids contain less than about 6% sulfate and generally contain one or more polymers which function as viscosifiers, suspending agents, borehole breakers and sealable thickeners. Representative low sulfate drilling fluids are disclosed in the following United States patents, incorporated herein by reference: U.S. Pat. Nos. 3,070,343 (Scott), 3,335,803 (Lamson et al.), 3,338,330 (Olson et al.), 3,340,461 (Anderson et al.).

The use of sulfate to reduce the corrosion of well drilling tools, drill pipe and other ferrous surface during drilling operations is disclosed in U.S. Pat. No. 3,301,323 (Parsons), incorporated herein by reference.

Flood waters used in treating subterranean formations in secondary recovery operations to increase the yield of petroleum from such formations are generally either fresh ground waters or obtained from lakes, rivers, wells and the like, and brine waters obtained from producing wells. The use of sulfate in flood waters is described in the following United States patents, incorporated herein by reference: U.S. Pat. Nos. 3,119,447 (Raffertier et al.), 3,234,072 (Proffitt).

The following examples will further illustrate the invention and are not intended to limit the invention. The results of the invention are incorporated into the appended claims.

EXAMPLE I

An aqueous solution containing 10% by weight of analytical reagent grade sodium sulfate was prepared and divided into three separate solutions. To one solution was added 0.1% by weight (1.5 g. by weight based on the concentration of sodium sulfate) of the pentasodium salt of sodium triethylenephosphonate acid while to another solution was added 1.0% by weight of the same polyphosphonate. One solution was not further treated. One hundred grams of each of these solutions were placed in separate 1 pint covered jars. These solutions were aged at room temperature (R.T.) for 4 days after which the jars were removed and the solutions aged as additional 10 days. The residual sulfate concentration remaining in the solutions after different aging periods was determined by the following procedure: 12 ml. of the aqueous sulfate solution was diluted with 100 ml. of distilled water; 5-8 drops of 0.5% phenolphthalein indicator solution was added followed by 2 ml. of 15% hydrochloric acid and 2 ml. of starch indicator solution. The solution was then stirred until the red color disappeared; the solution was stirred with 0.0125 N iodine iodine solution (1 ml. is equivalent to 0.5 mg. SO₄²⁻) until a faint permanent blue color developed in the solution; the concentration of residual sulfate in the diluted solution in ppm was obtained by multiplying the ml. of the iodine iodine solution used by 5.

The results obtained are given in Table I. These results indicate that the concentration of sulfate in the untreated aqueous solution decreased at a faster rate than did the concentration of sulfate in the treated solutions. Thus the addition of the polyphosphonate stabilizing compound significantly decreased the rate

of atmospheric oxidation of the aqueous sulfate solution.

Table I

Stabilizing Compound	10% Sodium Sulfate Solution				% of Initial Sulfate Remaining After 7 Days
	Stabilizing Compound	Days Aging at Room Temperature	Days Aging at Room Temperature	Days Aging at Room Temperature	
None	0	0	0	0	75
0.1	1.5	1.5	1.5	1.5	62
1.0	15	15	15	15	56

EXAMPLE II

An aqueous solution containing 10% by weight of

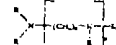
the results obtained are given in Table II. These results indicate that the polyphosphonate reduced the rate of oxidation of the sulfate compound. The sulfate polyphosphonate was not effective at higher concentrations upon aging the solutions at 120°F., however.

Table II

Stabilizing Compound	10% Na ₂ SO ₄ Solution				% of Initial Sulfate Remaining After 7 Days
	Stabilizing Compound	Days Aging at Room Temperature	Days Aging at Room Temperature	Days Aging at Room Temperature	
None	0	0	0	0	75
A	0.1	75	150	225	52
A	1.0	75	150	225	52
B	2.0	75	150	225	46
B	1.0	75	150	225	46
B	0.1	75	150	225	39
A	0	120	240	360	31
A	0.1	120	240	360	65
A	1.0	120	240	360	62
A	2.0	120	240	360	62
B	1.0	120	240	360	61
B	2.0	120	240	360	57

A = pentasodium salt of sodium triethylenephosphonate acid
B = sodium diethylenephosphonate

analytical grade sodium sulfate was prepared. To separate aliquots of this solution were added various concentrations of either the pentasodium salt of sodium triethylenephosphonate acid or a mixture of polyphosphonate acids having the formula:



where R = -CH₂CH₂CH₂OH and n is 2 to 4, as indicated in Table II. These solutions were then aged for 2 days and sealed as indicated in Example I except that the solutions remained unsealed while aging at room temperature. Aqueous solutions of sodium triethylenephosphonate acid were also aged at a temperature of 120°F. Any water which evaporated during aging was replaced prior to measuring the sulfate solution for residual sulfate testing.

EXAMPLE III

An aqueous solution containing 10% by weight of analytical grade sodium sulfate (commercially used in water treating) was prepared. To separate aliquots of this solution were added 1 ppm of catalytic cation in the form of sodium acetate. Various amounts of the pentasodium salt of sodium triethylenephosphonate acid (TRISOL 2025) was added to these solutions as indicated in Table III. The solutions were aged 1 day at room temperature and the sulfate concentrations determined as indicated in Example I.

The results obtained are given in Table III. These results indicate that at concentrations greater than about 9% by weight, based on concentrations of sulfate in the solution, the polyphosphonate drastically reduced the rate of oxidation of the sulfate cation in the presence of the catalytic cation catalyst, Co²⁺.

Table III

Stabilizing Compound	10% Na ₂ SO ₄ Solution Containing 1 ppm CO ²⁺				% of Initial Sulfate Remaining After 1 Day
	Stabilizing Compound	Days Aging at Room Temperature	Days Aging at Room Temperature	Days Aging at Room Temperature	
None	0	0	0	0	8
REQUIST 2025	0.1	0	0	0	8
REQUIST 2025	0.5	0	0	0	8
REQUIST 2025	1.0	0	0	0	8
REQUIST 2025	1.5	0	0	0	8

EXAMPLE IV

A sulfite composition was prepared by mixing together 90% technical grade sodium sulfite and 10% of the pentasodium salt of triethylenetriamphosphonic acid. This composition was used to prepare a 9% aqueous sulfite solution (10% solution of the sulfite composition). Thirty ppm of CoSO_4 was added to an oil field brine water which contained 2.4 ppm oxygen. This aqueous system at 70°F was treated with 30 ppm $\text{K}_2\text{S}_2\text{O}_8$ (17.3 ppm of the sulfite composition = 17.3 ppm of the sulfite solution). The concentration of oxygen in the system and the corrosivity of the system were then measured over the next 15 minutes.

The data obtained are given in Table IV. The results indicate that the stabilized sulfite solution decreased the concentration of oxygen in the oil field brine and decreased the corrosivity of the brine water.

Table IV

Time min.	Dissolved Oxygen ppm	Corrosion Rate mpy
0	2.4	1.6
5	1.9	1.1
10	0.95	0.4
15	0.1	0.4
20	0.3	0.2
25	0.15	0.2
30	0.1	0.2

Note: ppm parts per million

EXAMPLE V

A sulfite composition was prepared by mixing together 90% technical grade sodium sulfite and 10% of the pentasodium salt of triethylenetriamphosphonic acid. An oil field brine water composition was prepared by mixing together 90% sodium sulfite and 10% of the pentasodium salt of triethylenetriamphosphonic acid. Aqueous sulfite solutions were prepared by dissolving 10% of each of these sulfite compositions in tap water. Three sulfite solutions were evaluated at 70°F in oxygen corrosion tests at a concentration of 57 ppm $\text{K}_2\text{S}_2\text{O}_8$ in an oil field brine water which contained 1845 ppm calcium, 57 ppm magnesium, 6.3 ppm iron, 121434 ppm sodium, 48.4 ppm nickel, 1000 ppm copper, 100 ppm zinc, 3174 ppm sulfur, 11210 ppm total dissolved solids, pH = 7.1. Also evaluated for comparison, at the same concentration of $\text{K}_2\text{S}_2\text{O}_8$, was sodium bisulfite and a commercial sodium sulfite oxygen scavenger which contained 0.5 ppm CO_3^{2-} as CaSO_3 .

The results obtained are given in Table V. These results indicate that the sulfite compositions are excellent oxygen scavengers for treating aqueous systems, to the system they reacted in that or better than the untreated system sulfite and better than sodium bisulfite.

Table V

Oxygen Scavenger	Time min.	Dissolved Oxygen ppm
Sodium Bisulfite	0	2.5
	5	0.5
	10	0.4
	15	0.2
	20	0.2
S10 Sodium Sulfite/STP	0	2.5
	5	0.2
	10	0.1
	15	0.1
	20	0.1

Table V continued

Oxygen Scavenger	Time min.	Dissolved Oxygen ppm
Sodium Sulfite + 0.5 ppm CO_3^{2-}	0	2.5
	5	1.8
	10	0.9
	15	0.2
	20	0.1
S10 Sodium Sulfite/STP	0	2.5
	5	0.2
	10	0.1
	15	0.1
	20	0.1

STP: Pentasodium salt of triethylenetriamphosphonic acid

EXAMPLE VI

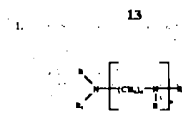
A sulfite composition containing 90% technical grade sodium sulfite and 10% of the pentasodium salt of triethylenetriamphosphonic acid was used to prepare a 9% aqueous sulfite solution (10% solution of the sulfite composition). This aqueous sulfite solution was continuously added to a brine water drilling fluid (while it was circulating) at a rate of 25 pounds per hour (2.5 pounds per hour of the sulfite composition). The brine water drilling fluid was prepared from the brine water of Example V. It contained some solids passed up during drilling of the well. The drilling fluid to the surface plus contained 1.8 p.p.m. of dissolved oxygen. After treatment with the aqueous sulfite composition the concentration of oxygen in the drilling fluid was less than 0.1 p.p.m. and the corrosion rate as determined from corrosion coupons attached to the drill pipe was decreased from 18.4 mpy per year to 2.7 mpy per year. The corrosion coupons after treatment of the drilling fluid were bright whereas before treatment the coupons were dark and exhibited pitting.

EXAMPLE VII

An aqueous sulfite composition containing 9% technical grade sodium sulfite and 1% of the pentasodium salt of triethylenetriamphosphonic acid was added to a low solids polymer mud containing a complex of vinyl acetate and maleic anhydride (U.S. Pat. No. 3,770,143 - Scott). The aqueous sulfite composition was added at the rate of 25 pounds per hour at its Example VI. Before treatment corrosion coupons attached to the drill pipe at a depth of 4700 feet were dark, exhibited pitting, and corroded at the rate of 304 mpy per year. After treatment with the aqueous sulfite composition corrosion coupons attached to the drill pipe at a depth of 13,300 feet were bright, exhibited no pitting, and corroded at the rate of only 10 mpy per year.

1. A sulfite composition which comprises a major proportion of a sulfite compound selected from the group consisting of alkali metal sulfites, alkali metal bisulfites, ammonium sulfites, ammonium bisulfites, and sulfites thereof, and from 1 to 50% by weight, based on the concentration of said sulfite compound, of a stabilizing compound which consists of a water soluble salt of an organic polyphosphoric acid containing at least two phosphoric acid groups per molecule, wherein said composition does not contain any metallic cations which function as catalysts for reacting said sulfite compound with oxygen.

2. The composition of claim 1 wherein said polyphosphoric acid is selected from the group consisting of:



where each R is independently selected from the group consisting of hydrogen, $-\text{CH}_2\text{PO}_3(\text{OH})_2$, and $-(\text{C}_6\text{H}_4)_n\text{O}_2\text{H}$ wherein n is 2 to 4 and c is 1 to 5; R₁ is



where X and Y are independently selected from the group consisting of hydrogen and lower alkyl radicals having 1 to 4 carbon atoms; a is 2 to 6 and b is 0 to 6; provided that at least N of the radicals represented by R₁ are $-\text{CH}_2\text{PO}_3(\text{OH})_2$.



where R₁ is $-\text{CH}_2\text{PO}_3(\text{OH})_2$, R₂ is selected from the group consisting of hydrogen, hydroxyl, and $-(\text{C}_6\text{H}_4)_n\text{O}_2\text{H}$ wherein n is an integer from 2 to 4 and c is an integer from 1 to 3; and where R₃ is selected from the group consisting of lower alkyl radicals containing 1 to 5 carbon atoms and



wherein a is an integer from 0 to 6; and



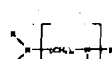
where R₁ is $-\text{CH}_2\text{PO}_3(\text{OH})_2$, each R₂ is independently selected from the group consisting of hydrogen, $-\text{CH}_2\text{PO}_3(\text{OH})_2$, and $-(\text{C}_6\text{H}_4)_n\text{O}_2\text{H}$ wherein n is an integer from 2 to 4 and c is an integer from 1 to 3 and where R₃ is selected from the group consisting of lower alkyl radicals containing 1 to 5 carbon atoms and



wherein a is an integer from 0 to 6.

3. The composition of claim 2 wherein the concentration of said water soluble salt is from 1 to 50% by weight of the concentration of said sulfite compound, wherein said water soluble salt is in the sodium form, and wherein said sulfite compound is sodium sulfite.

4. The composition of claim 3 wherein the stabilizing compound is



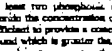
where R is $-\text{CH}_2\text{PO}_3(\text{OH})_2$, R₁ is $-\text{CH}_2\text{PO}_3(\text{OH})_2$, a is either 2 or 6 and b is 0 to 4.

5. The composition of claim 4 wherein a is 0, to 6.

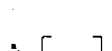
6. The composition of claim 4 wherein a is 6 and b is 1 to 4.

7. An aqueous sulfite solution which comprises from 3% up to saturation of a sulfite compound selected from the group consisting of alkali metal sulfites, alkali metal bisulfites, ammonium sulfites, ammonium bisulfites, and sulfites thereof, and from 1 to 20% by weight, based on the concentration of said sulfite compound, of a water soluble organic polyphosphoric acid containing at least two phosphoric acid groups per molecule, wherein the concentration of said polyphosphoric acid is sufficient to provide a concentration of said sulfite compound which is greater than in the absence of said polyphosphoric acid upon exposing said solution to the atmosphere for 2 days, and wherein said solution does not contain any metallic cations which function as catalysts for reacting said sulfite compound with oxygen.

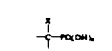
8. The solution of claim 7 wherein said polyphosphoric acid is selected from the group consisting of the free acids and water soluble salts of:



where X and Y are independently selected from the group consisting of hydrogen, $-\text{CH}_2\text{PO}_3(\text{OH})_2$, and $-(\text{C}_6\text{H}_4)_n\text{O}_2\text{H}$ wherein n is 2 to 4 and c is 1 to 3; R₁ is



where R₁ is $-\text{CH}_2\text{PO}_3(\text{OH})_2$, each R₂ is independently selected from the group consisting of hydrogen, $-\text{CH}_2\text{PO}_3(\text{OH})_2$, and $-(\text{C}_6\text{H}_4)_n\text{O}_2\text{H}$ wherein n is an integer from 2 to 4 and c is an integer from 1 to 3 and where R₃ is selected from the group consisting of lower alkyl radicals containing 1 to 5 carbon atoms and



wherein a is an integer from 0 to 6; and



where R₁ is $-\text{CH}_2\text{PO}_3(\text{OH})_2$, each R₂ is independently selected from the group consisting of hydrogen, $-\text{CH}_2\text{PO}_3(\text{OH})_2$, and $-(\text{C}_6\text{H}_4)_n\text{O}_2\text{H}$ wherein n is an integer from 2 to 4 and c is an integer from 1 to 3 and where R₃ is selected from the group consisting of lower alkyl radicals containing 1 to 5 carbon atoms and



wherein a is an integer from 0 to 6.

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where R is $-\text{CH}_2\text{PO}(\text{OH})_2$, R is selected from the group consisting of hydrogen, hydroxyl, and $-\text{C}_n\text{H}_{2n+1}$ where n is an integer from 2 to 4 and c is an integer from 1 to 3, and where R₂ is selected from the group consisting of lower alkyl radicals containing 1 to 5 carbon atoms and



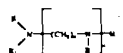
where a is an integer from 0 to 5; and



where R is $-\text{CH}_2\text{PO}(\text{OH})_2$, each R₁ and R₂ is independently selected from the group consisting of hydrogen, $-\text{CH}_2\text{PO}(\text{OH})_2$, and $-\text{C}_n\text{H}_{2n+1}$ where n is an integer from 2 to 4 and c is an integer from 1 to 3, and where R₂ is selected from the group consisting of lower alkyl radicals containing 1 to 5 carbon atoms and



where a is an integer from 0 to 5.
5. The method of claim 1 wherein the concentration of acid organic polyphosphonate is from 1 to 20% by weight based on the concentration of acid sulfate compound, wherein acid organic polyphosphonate is in the sulfate form, and wherein acid sulfate compound is sodium sulfate.
18. The method of claim 9 wherein the organic polyphosphonate is



where R is $-\text{CH}_2\text{PO}(\text{OH})_2$, R₁ is $-\text{CH}_2\text{PO}(\text{OH})_2$, a is either 2 or 5 and b is 0 to 4.
11. The method of claim 10 wherein b is 0.
12. The method of claim 10 wherein a is 5 and b is 1 to 4.
13. The method of determining the rate of atmospheric corrosion of a compound selected from the group consisting of alkali metal sulfates, alkali metal bisulfates, ammonium sulfate, ammonium bisulfate, and mixtures thereof which comprises adding acid sulfate compound in effective amount from 1 to 20%

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by weight, based on the concentration of acid sulfate compound, of a water soluble organic polyphosphonate containing at least two phosphonic acid groups per molecule.

14. The method of claim 13 wherein acid organic polyphosphonate is selected from the group consisting of the two acids and water soluble salts of



where each R is independently selected from the group consisting of hydrogen, $-\text{CH}_2\text{PO}(\text{OH})_2$, and $-\text{C}_n\text{H}_{2n+1}$ where n is 2 to 4 and c is 1 to 3; R₂ is



wherein X and Y are independently selected from the group consisting of hydrogen and lower alkyl radicals having 1 to 4 carbon atoms; a is 2 to 6 and b is 0 to 6; provided that at least 16 of the radicals represented by R₂ are $-\text{CH}_2\text{PO}(\text{OH})_2$.



where R is $-\text{CH}_2\text{PO}(\text{OH})_2$, R₁ is selected from the group consisting of hydrogen, hydroxyl, and $-\text{C}_n\text{H}_{2n+1}$ where n is an integer from 2 to 4 and c is an integer from 1 to 3, and where R₂ is selected from the group consisting of lower alkyl radicals containing 1 to 5 carbon atoms and



where a is an integer from 0 to 5; and



where R is $-\text{CH}_2\text{PO}(\text{OH})_2$, and R₂ is independently selected from the group consisting of hydrogen, $-\text{CH}_2\text{PO}(\text{OH})_2$, and $-\text{C}_n\text{H}_{2n+1}$ where n is an integer from 2 to 4 and c is an integer from 1 to 3, and where R₂ is selected from the group consisting of lower alkyl radicals containing 1 to 5 carbon atoms and

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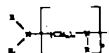


wherein a is an integer from 0 to 5.

18. The method of claim 14 wherein the concentration of acid organic polyphosphonate is from 1 to 20% by weight based on the concentration of acid sulfate compound, wherein acid organic polyphosphonate is in the sulfate form, and wherein acid sulfate compound is sodium sulfate.

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14. The method of claim 13 wherein the polyphosphonate is



where R is $-\text{CH}_2\text{PO}(\text{OH})_2$, R₁ is $-\text{CH}_2\text{PO}(\text{OH})_2$, a is either 2 or 5 and b is 0 to 4.

17. The method of claim 16 wherein b is 0.

18. The method of claim 16 wherein a is 6 and b is 1 to 4.

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