

HUMBERTO RUBIO & CIA.

ABOGADOS

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SUPERINDUSTRIA Y COMERCIO

Radicacion : 02015140 00000003

Folios: 10

Fecha (AMD): 2002-04-11 15:04:39

Tramite : 002 PATENTES D 1 REGISTRO/ 444 REPUESTA

Dependencia: 2020 DIVISION DE NUEVAS CREACIONES

Señor
SUPERINTENDENTE DE INDUSTRIA Y COMERCIO
DIVISIÓN DE NUEVAS CREACIONES
E. S. D.

REF. Expediente:
Patente de Invención:

02-015.140

"METODOS Y COMPOSICIONES PARA
EL TRATAMIENTO DE FORMACIONES
SUBTERRÁNEAS CON FLUIDOS
HIDROCARBUROS GELIFICADOS"
HALLIBURTON ENERGY SERVICES,
INC.

Titular:

DESTINO: 09

HUMBERTO RUBIO CAMACHO, mayor de edad, vecino de Bogotá, D.C., identificado con la cédula de ciudadanía numero 17'192.062 de Bogotá, abogado en ejercicio portador de la Tarjeta Profesional No. 50.007, expedida por el Consejo Superior de la Judicatura, en carácter de apoderado de la Sociedad HALLIBURTON ENERGY SERVICES, INC; encontrándome dentro del termino legal para dar contestación al auto proferido por su Despacho, notificado por Estado de 21 de Marzo de 2.002, me permito anexar y manifestar:

- 1.- El documento de cesión expedido por el inventor a la sociedad Peticionaria, debidamente legalizado, fue radicado ante su Despacho el 5 de Marzo de 2.002, de conformidad con la copia que se anexa.
- 2.- Para dar cumplimiento con el artículo 27-C de la Decisión 486, me permito manifestar que la Sociedad solicitante se encuentra legalmente constituida bajo las leyes de OKLAHOMA.
- 3.- Nuevo Capitulo Reivindicatorio con las modificaciones sugeridas.

Habiendo dado respuesta a las observaciones del primer examen de forma, manifiesto que renuncio al termino concedido en el auto y respetuosamente solicito se continúe con el trámite correspondiente, ordenándose la publicación del extracto de la patente en la Gaceta de la Propiedad Industrial.

Del Señor Superintendente,


HUMBERTO RUBIO CAMACHO
C.C. 17'192.062 de Bogotá.
T.P. 50.007 Consejo Superior
de la Judicatura.
COD. 4134

01/448-10/PI

Señor

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

E. S. D.

SUPERINDUSTRIA Y COMERCIO

Radicación: 02015140 00000001

Folios: 104

Fecha (AMD): 2002-03-05 15:44:17

Trámite: 002 PATENTES D 1 REGISTRO/ 333 COMPLETOS

Dependencia: 2020 DIVISION DE NUEVAS CREACIONES

REF. Expediente:

02-015.140

Patente de Invención:

**"METODOS Y COMPOSICIONES
PARA EL TRATAMIENTO DE
FORMACIONES SUBTERRÁNEAS
CON FLUIDOS
HIDROCARBUROS
GELIFICADOS"**

Titular:

**HALLIBURTON ENERGY
SERVICES, INC.**

DESTINO: 09

HUMBERTO RUBIO CAMACHO, mayor de edad, vecino de Bogotá, D.C., identificado con la cédula de ciudadanía número 17'192.062 de Bogotá, abogado en ejercicio portador de la Tarjeta Profesional No. 50.007, expedida por el Consejo Superior de la Judicatura, en carácter de apoderado de la Sociedad HALLIBURTON ENERGY SERVICES, INC; encontrándome dentro del término legal establecido por los Artículos 10 y 39 de la Decisión 486 de la Comunidad Andina, me permito anexar los siguientes documentos:

- 1.- Copia certificada de la Solicitud No. 09/792,109 del 23 de Febrero de 2.001 de Estados Unidos de América, expedida por la Autoridad Competente, junto con su respectiva traducción al Castellano; base de la prioridad reivindicada en la solicitud de registro de la Patente de Invención citada en la referencia; todo de conformidad con el Artículo 4º del Convenio de la Unión de París.
- 2.- Original de Documento de Cesión del Inventor al Solicitante, debidamente traducido por traductor oficial y legalizado por Apostille.

Teniendo en cuenta lo anterior, solicito se continúe con su respectivo trámite.

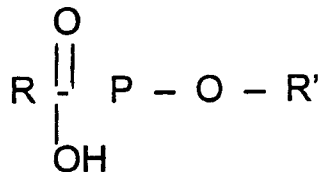
Atentamente,


HUMBERTO RUBIO CAMACHO
C.C. 17'192.062 de Bogotá
T.P. 50.007 Consejo Superior
de la Judicatura
COD 4134

REIVINDICACIONES

1. Un método para la fracturación de una formación subterránea que comprende las etapas de:

(a) la preparación de un fluido de fracturación de hidrocarburo líquido gelificado compuesto de un hidrocarburo líquido, una sal metálica polivalente de aluminio o hierro férrico de un éster de ácido fosfónico, teniendo el ácido fosfónico la fórmula:



donde R es un grupo alquilo que tiene desde aproximadamente 8 hasta aproximadamente 24 átomos de carbono y R' es un grupo alquilo que tiene desde aproximadamente 1 hasta aproximadamente 4 átomos de carbono, un material de consolidación, agua y una cantidad de un agente fracturador en gel retrasado efectiva para romper dicho fluido gelificado de fracturación;

(b) contactar dicha formación subterránea con dicho fluido para fracturación de hidrocarburo gelificado bajo condiciones efectivas para crear por lo menos una fractura en dicha formación subterránea.

2. El método de la reivindicación 1, donde dicho líquido hidrocarburo es seleccionado a partir del grupo compuesto por olefinas, keroseno, diesel oil, gasoil, fuel oil, destilados de petróleo y petróleos crudos.

3. El método de la reivindicación 1, donde dicha sal metálica polivalente de un éster de ácido fosfónico es producida por medio de la reacción de dicho éster de ácido fosfónico con un compuesto de hierro férrico.

4. El método de la reivindicación 1, donde dicha sal metálica polivalente de un éster de ácido fosfónico es producida por medio de la reacción de dicho éster de ácido fosfónico con un compuesto de aluminio.

5. El método de la reivindicación 1, donde dicha sal metálica polivalente de aluminio o hierro férrico de un éster de ácido fosfónico está presente en dicho líquido hidrocarburo en una cantidad dentro del rango desde aproximadamente 0,1% hasta aproximadamente 2,5% en peso de dicho líquido hidrocarburo.

6. El método de la reivindicación 1, donde dicho agente fracturador retrasado en gel es seleccionado a partir del grupo que consiste de óxidos de metales alcalinotérreos incluyendo óxido de magnesio, carbonatos de metal alcalino, bicarbonatos de metal alcalino, acetatos de metal alcalino, hidróxidos de metal alcalino, aminas y ácidos débiles que son lentamente solubles en agua o son encapsulados con un material lentamente soluble en agua u otro material de encapsulación similar.

7. El método de la reivindicación 1, donde dicho agente fracturador retrasado en gel es óxido de magnesio quemado duro lentamente soluble en agua.

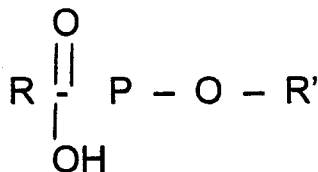
8. El método de la reivindicación 3, donde dicho agente fracturador retrasado en gel es un agente de reducción que reduce el hierro férrico a hierro ferroso.

9. El método de la reivindicación 8, donde dicho agente de reducción es seleccionado a partir del grupo compuesto por cloruro estannoso, ácido tioglicólico y sus sales, sulfato de hidracina, dietilditiocarbamato de sodio, dimetilditiocarbamato de sodio, hipofosfita

de sodio, clorhidrato de hidroxilamina, tioglicol, ácido ascórbico y sus sales, tiosulfato de sodio y sulfito de sodio.

10. El método de la reivindicación 1, donde dicho agente fracturador retrasado en gel está presente en una cantidad en el rango desde aproximadamente 0,01% hasta aproximadamente 3% en peso de dicho hidrocarburo líquido.

11. Un método para la preparación de fluidos hidrocarburos líquidos gelificados, el cual comprende agregar un éster de ácido fosfónico a un líquido hidrocarburo, el éster de ácido fosfónico tiene la fórmula:



donde R es un grupo alquilo que tiene desde aproximadamente 8 hasta aproximadamente 24 átomos de carbono y R' es un grupo alquilo que tiene desde aproximadamente 1 hasta aproximadamente 4 átomos de carbono, por lo menos una cantidad estequiométrica de una fuente de metal polivalente, seleccionada a partir de sales de hierro férrico y compuestos de aluminio, que reacciona con dicho éster del ácido fosfónico para formar una sal metálica polivalente de aluminio o hierro férrico del mismo, agua y una cantidad de un agente fracturador retrasado en gel efectivo para romper dicho fluido de fracturación de hidrocarburo gelificado.

12. El método de la reivindicación 11, donde dicho líquido hidrocarburo es seleccionado a partir del grupo compuesto por olefinas, keroseno, diesel oil, gasoil, fuel oil, destilados de petróleo y petróleos crudos.

13. El método de la reivindicación 11, donde dicha sal metálica polivalente de aluminio o hierro férrico de dicho éster de ácido fosfónico en dicho líquido hidrocarburo está presente en una cantidad en el rango desde aproximadamente 0,1% hasta aproximadamente 2,5% en peso de dicho hidrocarburo líquido.

14. El método de la reivindicación 11, donde dicho agente fracturador en gel retrasado es seleccionado a partir del grupo que consiste de óxidos de metales alcalinotérreos incluyendo óxido de magnesio, carbonatos de metal alcalino, bicarbonatos de metal alcalino, acetatos de metal alcalino, hidróxidos de metal alcalino, aminas y ácidos débiles que son lentamente solubles en agua o son encapsulados con un material lentamente soluble en agua u otro material de encapsulación similar.

15. El método de la reivindicación 11, donde dicho agente fracturador retrasado en gel es óxido de magnesio quemado duro lentamente soluble en agua.

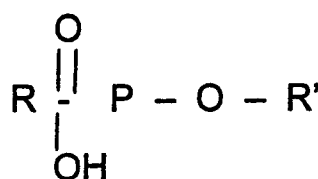
16. El método de la reivindicación 11, donde dicho agente fracturador retrasado en gel es un agente de reducción que reduce el hierro férrico a hierro ferroso.

17. El método de la reivindicación 16, donde dicho agente de reducción es seleccionado a partir del grupo compuesto por cloruro estannoso, ácido tioglicólico y sus sales, sulfato de hidracina, dietilditiocarbamato de sodio, dimetilditiocarbamato de sodio, hipofosfita de sodio, clorhidrato de hidroxilamina, tioglicol, ácido ascórbico y sus sales, tiosulfato de sodio y sulfito de sodio.

18. El método de la reivindicación 11, donde dicho agente fracturador en gel está presente en dicho líquido hidrocarburo en una

cantidad dentro del rango desde aproximadamente 0,01% hasta aproximadamente 3% en peso de dicho líquido hidrocarburo.

19. Un agente de gelificación de hidrocarburo líquido que comprende una sal metálica polivalente de aluminio o hierro férrico de un éster de ácido fosfónico, dicho éster de ácido fosfónico tiene la fórmula:



donde R es un grupo alquilo que tiene desde aproximadamente 8 hasta aproximadamente 24 átomos de carbono y R' es un grupo alquilo que tiene desde aproximadamente 1 hasta aproximadamente 4 átomos de carbono.

20. El agente de gelificación de la reivindicación 19, donde R es un grupo alquilo que tiene desde 14 hasta 24 átomos de carbono.

21. El agente de gelificación de la reivindicación 19, donde R¹ es un grupo alquilo que tiene desde 1 átomo de carbono hasta 2 átomos de carbono.

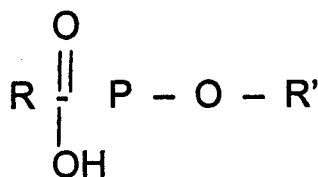
22. El agente de gelificación de la reivindicación 19, donde R es tetradecilo y R¹ es metilo.

23. El agente de gelificación de la reivindicación 19, donde dicho metal polivalente es hierro férrico.

24. Un fluido de hidrocarburo líquido gelificado que comprende:

un hidrocarburo líquido;

un agente de gelificación que comprende una sal metálica polivalente de un éster de ácido fosfónico producida a partir de un éster de ácido fosfónico y un compuesto de aluminio o una sal de hierro férrico, dicho éster de ácido fosfónico tiene la fórmula:



donde R es un grupo alquilo que tiene desde aproximadamente 8 hasta aproximadamente 24 átomos de carbono y R' es un grupo alquilo que tiene desde aproximadamente 1 hasta aproximadamente 4 átomos de carbono;

agua; y

un agente fracturador retrasado en gel presente en una cantidad efectiva para fracturar el gel formado por dicho agente de gelificación y dicho líquido hidrocarburo.

25. La composición de la reivindicación 24, donde R es un grupo alquilo que tiene desde 14 hasta 24 átomos de carbono.

26. La composición de la reivindicación 24, donde R¹ es un grupo alquilo que tiene desde 1 hasta 2 átomos de carbono.

27. La composición de la reivindicación 24, donde R es tetradecilo y R¹ es metilo.

28. La composición de la reivindicación 24, donde dicho líquido hidrocarburo es seleccionado a partir del grupo compuesto por olefinas, keroseno, diesel oil, gasoil, fuel oil, destilados de petróleo y petróleos crudos.

29. La composición de la reivindicación 24, donde dicha sal de hierro férrico es seleccionada a partir del grupo que consiste de sulfato férrico y cloruro férrico.

30. La composición de la reivindicación 24, donde dicho compuesto de aluminio es seleccionado a partir del grupo que consiste de cloruro de aluminio, sulfato de aluminio e isopropóxido de aluminio.

31. La composición de la reivindicación 24, donde dicha sal metálica polivalente de aluminio o hierro férrico de dicho éster de ácido fosfónico está presente en dicho líquido hidrocarburo en una cantidad dentro del rango desde aproximadamente 0,1% hasta aproximadamente 2,5% en peso de dicho líquido hidrocarburo.

32. La composición de la reivindicación 24, donde dicho agente fracturador retrasado en gel es seleccionado a partir del grupo que consiste de óxidos de metales alcalinotérreos incluyendo óxido de magnesio, carbonatos de metal alcalino, bicarbonatos de metal alcalino, acetatos de metal alcalino, hidróxidos de metal alcalino, aminas y ácidos débiles que son lentamente solubles en agua o son encapsulados con un material lentamente soluble en agua u otro material de encapsulación similar.

33. La composición de la reivindicación 24, donde dicho agente fracturador retrasado en gel es óxido de magnesio quemado duro lentamente soluble en agua.

34. La composición de la reivindicación 24, donde dicho agente fracturador retrasado en gel es un agente de reducción que reduce el hierro férrico a hierro ferroso encapsulado con un material de encapsulación lentamente soluble en agua u otro material de encapsulación similar.

35. La composición de la reivindicación 34, donde dicho agente de reducción es seleccionado a partir del grupo compuesto por cloruro estannoso, ácido tioglicólico y sus sales, sulfato de hidracina, dietilditiocarbamato de sodio, dimetilditiocarbamato de sodio, hipofosfita de sodio, clorhidrato de hidroxilamina, tioglicol, ácido ascórbico y sus sales, tiosulfato de sodio y sulfito de sodio.

36. La composición de la reivindicación 24, donde dicho agente fracturador retrasado en gel en dicho líquido hidrocarburo gelificado está presente en una cantidad en el rango desde aproximadamente 0,01% hasta aproximadamente 3% en peso de dicho hidrocarburo líquido.



2° EXAMEN DE FORMA, PATENTE DE INVENCION

Folio 172

Radicación N° 02-15140

Concepto Técnico N° 108

Clasificación Internacional de Patentes: C09K 7/06, C10G 3/00

Practicado el examen de acuerdo a lo establecido en el Art. 38 de la Decisión 486, se determinó que esta solicitud de **Patente**:

- SI ☒ NO ☐ Contiene un resumen de la invención (Art. 26-e)
- SI ☒ NO ☐ Contiene el título o nombre de la invención (Art. 27-d)
- SI ☒ NO ☐ Contiene la descripción de la invención (Art. 26-b)
- SI ☐ NO ☐ NO ES APLICABLE ☒ Contiene los dibujos necesarios para comprender la invención (Art. 26-d)
- SI ☒ NO ☐ Contiene una o más reivindicaciones (Art. 26-c)
- SI ☐ NO ☐ NO ES APLICABLE ☒ Han sido desarrollados los productos a partir de recursos genéticos o de sus productos derivados de los que cualquiera de los Países Miembros es país de origen (Art. 26-h)
- SI ☐ NO ☐ NO ES APLICABLE ☒ Los productos y o procedimientos han sido obtenidos o desarrollados a partir a partir de los conocimientos tradicionales de las comunidades indígenas, afro americanas, o locales de los Países Miembros, de acuerdo a lo establecido en la Decisión 391 y sus modificaciones y reglamentaciones vigentes (Art. 26-i)
- SI ☐ NO ☒ La invención se refiere a un producto relativo a un material biológico (Art. 26-j)
- SI ☒ NO ☐ NO ES APLICABLE ☐ La prioridad coincide con la materia reivindicada.
- SI ☒ NO ☐ **CUMPLE LOS REQUISITOS TÉCNICOS**

OBSERVACIONES Y OTROS: SI ☐ NO ☐ Ver hoja(s) anexa(s)

- Nuevo capítulo reivindicatorio, folios: 164 - 171

EXAMINADOR TÉCNICO: 202051

Bogotá D C, enero 30 de 2004.

2020
Bogotá D C

Doctor(a)
HUMBERTO RUBIO CAMACHO
Apoderado(a)

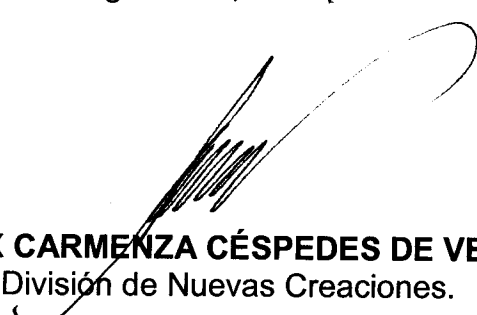
REFERENCIA:	Radicación N°	02-15140
	Trámite	002
	Evento	001
	Actuación	416
	Oficio N°	107
	Folios	001

Teniendo en cuenta que la solicitud de privilegio de patente que se tramita bajo el expediente indicado en la referencia, reúne los requisitos de forma establecidos en los artículos 26 y 27 de la Decisión 486, de la Comisión de la Comunidad Andina, y en las demás disposiciones vigentes sobre la materia, se envía el extracto de la solicitud a la oficina de comunicaciones para efecto de su publicación en la Gaceta de Propiedad Industrial, conforme lo establece el artículo 40 de la Decisión 486.

Cúmplase

Dado en Bogotá D C,

30 ENE 2004


ALIX CARMENZA CÉSPEDES DE VERGEL
Jefe División de Nuevas Creaciones.

202051

DIVISION DE NUEVAS CREACIONES

RADICACIÓN EXPEDIENTE No. 02-15140

EL EXTRACTO DE LA PRESENTE SOLICITUD DE **PATENTE DE INVENCION** FUE PUBLICADO

EN LA GACETA DE PROPIEDAD INDUSTRIAL No **538**, DE FECHA **31 DE MARZO DE 2004**, EL

TERMINO HABIL SEÑALADO POR LA LEY EXPIRA EL **01 DE JULIO DE 2004**.

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.

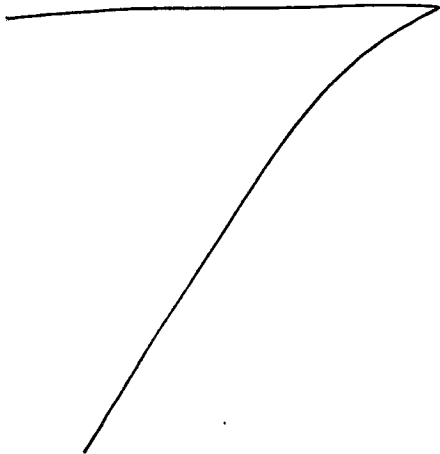
SE PRESENTARON OPOSICIONES POR PARTE DE TERCEROS.

SI _____

NO **X** _____

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ACCION: Consultar Siguiente Anterior Primero Ultimo Salir									
Ver el Siguiente Registro									
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SUPERINDUSTRIA Y COMERCIO					SISTEMA DE TRAMITES				
Fecha: 06/12/2005									
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CONSULTA RADICACION TRAMITES DIAS ANTERIORES									
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No. radicacion	2	15140	0	Sec_eve	0	Sec_act	4		
+-----+									
Tramite	2	PATENTES DE INVENCION							
Evento	1	REGISTRO/DEPOSITO/CONCESION/DEPOSITO							
Actuacion	538	PETICION DE EXAMEN							
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Dep. Origen									
Dep. Destino	2020	DIVISION DE NUEVAS CREACIONES							
Solicit/Destinat	RUBIO CAMACHO HUMBERTO								
Tipo Documento	1	CARTA	Fecha	04/06/2004					
Folios	2								
Fecha radicacion	2004-06-04 14:57:37			Tipo Radicacion	EN				
Observaciones									
+-----+									
Encontrados (5/5) registro(s)									
+-----+									



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

2020

Bogotá, D. C., 6 de Diciembre de 2005

Doctor

HUMBERTO RUBIO CAMACHO

Representante **HALLIBURTON ENERGY SERVICES, INC.**

ASUNTO	Radicación No.	02-15140
	Trámite	002
	Evento	001
	Actuación	430
	Oficio	
	Folios	036

13465

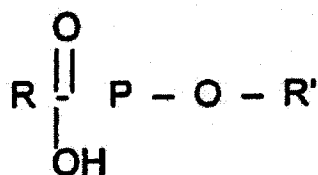
Como resultado del examen de fondo, realizado con fundamento en el artículo 45 de la Decisión 486 de la Comisión de la Comunidad Andina, se le comunica

1) Documentos estudiados:

- a) Para el presente estudio se tendrán en cuenta el capítulo descriptivo, comprendido en los folios 9 a 45 de la solicitud en estudio.
- b) Para el presente estudio se tendrá en cuenta el capítulo reivindicatorio que comprende 36 reivindicaciones en los folios 164 a 171 de la solicitud en estudio.
- c) 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 22 de febrero de 2002, y en el momento de la radicación **SI** se reclamo prioridad de la primera solicitud presentada en Estados Unidos US 09/792109

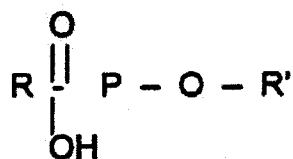
2) Objeto de la invención

- a) Las reivindicaciones 1 a 36 de la solicitud en estudio se refieren a:
 - i) (1.-) Un método para la fracturación de una formación subterránea que comprende las etapas de: (a) la preparación de un fluido de fracturación de hidrocarburo líquido gelificado compuesto de un hidrocarburo líquido, una sal metálica polivalente de aluminio o hierro férrico de un éster de ácido fosfónico, teniendo el ácido fosfónico la fórmula:



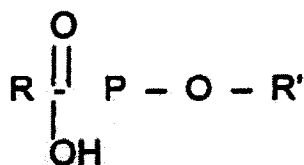
donde R es un grupo alquilo que tiene desde aproximadamente 8 hasta aproximadamente 24 átomos de carbono y R' es un grupo alquilo que tiene desde aproximadamente 1 hasta aproximadamente 4 átomos de carbono, un material de consolidación, agua y una cantidad de un agente fracturador en gel retrasado efectiva para romper dicho fluido gelificado de fracturación; (b) contactar dicha formación subterránea con dicho fluido para fracturación de hidrocarburo gelificado bajo condiciones efectivas para crear por lo menos una fractura en dicha formación subterránea.

- ii) (11.-) Un método para la preparación de fluidos hidrocarburos líquidos gelificados el cual comprende agregar un ester de ácido fosfónico a un líquido hidrocarburo, el ester de ácido fosfónico tiene la fórmula:



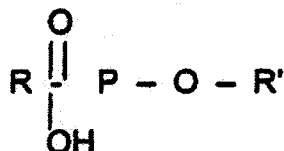
donde R es un grupo alquilo que tiene desde aproximadamente 8 hasta aproximadamente 24 átomos de carbono y R' es un grupo alquilo que tiene desde aproximadamente 1 hasta aproximadamente 4 átomos de carbono, *por lo menos una cantidad estequiométrica de una fuente de un metal polivalente, seleccionada a partir de de sales de hierro férrico y compuestos de aluminio que reacciona con dicho ester de ácido fosfónico para formar una sal metálica polivalente de aluminio o hierro férrico del mismo*, agua y una cantidad de un agente fracturador **retrasado** en gel efectiva para romper dicho fluido de fracturación de hidrocarburo gelificado;

- iii) (19.-) Un agente de gelificación de hidrocarburo líquido que comprende, una sal metálica polivalente de aluminio o hierro férrico de un éster de ácido fosfónico, teniendo el ácido fosfónico la fórmula:



Donde R es un grupo alquilo que tiene desde aproximadamente 8 hasta aproximadamente 24 átomos de carbono y R' es un grupo alquilo que tiene desde aproximadamente 1 hasta aproximadamente 4 átomos de

- iv) (24.-) Un fluido de hidrocarburo líquido gelificado que comprende: un hidrocarburo líquido. Un agente de gelificación que comprende una sal metálica polivalente de un ester de ácido fosfónico producida a través de un ester de ácido fosfónico y un compuesto de aluminio o una sal de hierro férrico, teniendo el ácido fosfónico la fórmula:



Donde R es un grupo alquilo que tiene desde aproximadamente 8 hasta aproximadamente 24 átomos de carbono y R' es un grupo alquilo que tiene desde aproximadamente 1 hasta aproximadamente 4 átomos de carbono,

Agua y

Un agente fracturador en gel retrasado en gel presente en una cantidad efectiva para fracturar el gel formado por dicho agente de gelificación y dicho líquido hidrocarburo.

- b) El anterior producto y sus procedimientos buscan mejorar el tratamiento de formaciones subterráneas penetradas por pozos de perforación.
- c) Según la Clasificación Internacional de Patentes, la codificación para esta solicitud corresponde a C 10 G 3/00

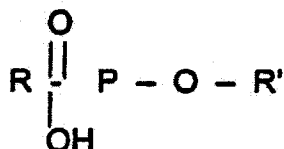
3) Claridad de la Solicitud

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

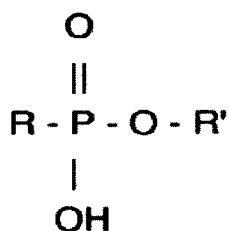
"La descripción deberá divulgar la invención de manera suficientemente clara y completa para su comprensión y para que una persona capacitada en la materia técnica correspondiente pueda ejecutarla"

La descripción no es clara toda vez que emplea unidades de medida que no corresponden al Sistema Internacional de Unidades. Las tablas están dadas en centipoises cuando esta unidad no corresponden a las que deben darse en el mencionado sistema.

También en todo el documento se encuentra mal empleada la formula estructural



Cuando la que debe aparecer es.



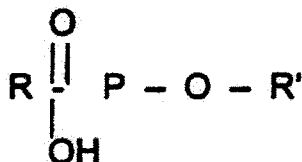
Debe enviarse un nuevo capítulo descriptivo completo con las correcciones aquí pedidas.

- b) El artículo 30 de la Decisión 486 de la Comisión de la Comunidad Andina establece que

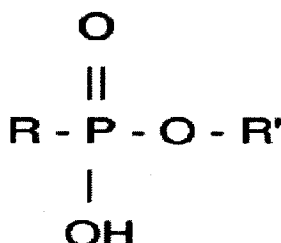
“Las reivindicaciones definirán la materia que se desea proteger mediante la patente. Deben ser claras y concisas y estar enteramente sustentadas por la descripción. Las reivindicaciones podrán ser independientes o dependientes. Una reivindicación será independiente cuando defina la materia que se desea 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:

- i) No se pueden aceptar palabras o frases ambiguas tales como “aproximadamente” pues no precisan el objeto a ser protegido. Deben eliminarse.
- ii) En todo el documento se encuentra mal empleada la fórmula estructural



Cuando la que debe aparecer es.



- iii) No se precisa la materia sobre la cual se solicita protección. Cómo se explicará en el punto 4), la presente solicitud no posee unidad de invención, por lo que no está definida la materia sobre la cual se solicita protección.
- iv) Las reivindicaciones 1 y 11 y sus dependientes, corresponden al uso que se le va a dar a las composiciones que el solicitante considera como nuevas. Aunque las encabeza como método es un simple uso que se le va a dar a las composiciones. Por tanto, deberán eliminarse todas esas reivindicaciones y centrarse en el producto o procedimiento que el solicitante considera nuevo, en este caso en el agente de gelificación de hidrocarburo líquido y el fluido que lo contiene. También debe cambiarse el título de la solicitud.

De acuerdo a lo anterior, el capítulo reivindicatorio no cumple con el requisito de claridad de acuerdo a lo establecido en el Art. 30 de la Decisión 486.

4) Evaluación de la Unidad de Invención

El artículo 25 de la Decisión 486 de la Comisión de la Comunidad Andina establece

"La solicitud de patente sólo podrá comprender una invención o un grupo de invenciones relacionadas entre sí, de manera que conformen un único concepto inventivo"

La presente solicitud carece de unidad de invención toda vez que configura diferentes objetos. La definición de la materia que caracteriza a cada una de las reivindicaciones independientes es muy diferente entre sí. Todo el problema radica en configurar varias reivindicaciones independientes con materia diferente. Existe un objeto dirigido al uso de una composición en una fractura de una formación subterránea (uso), otra para agregar un compuesto a otro (uso), una para un agente de gelificación y otra para un hidrocarburo líquido gelificado. El solicitante debe establecer una sola reivindicación independiente dirigida al **producto** en la forma más simple de la solicitud de invención. Partiendo de allí establecer reivindicaciones dependientes que amplíen esa forma más simple hasta su forma más compleja. Como se dijo antes deben eliminarse las reivindicaciones de uso.

De acuerdo a lo anterior, la presente solicitud no cumple con el requisito de unidad de invención de acuerdo al Art. 25 de la Decisión 486.

5) 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

“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 10 G 3/00**, **C 09 K 7/06** y las más cercanas a ellas, se encontró que antes del 23 de febrero de 2001 (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 para el tratamiento de formaciones subterráneas.

De acuerdo con o 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	US 4622155	Method for fracturing subterranean formations	1986.11.11
D2	US 5529125	Acid treatment method for siliceous formations	1996.06.25

6) 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 del Nivel Inventivo

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”.

El documento D1 (US 4622155) muestra un agente de gelificación de

formula estructurales, el principio es el mismo y podría considerarse que D1 es una anticipación de la presente solicitud.

D2 US 5529125 muestra otra composición que incorpora derivados del ácido fosfórico junto con compuestos de aluminio. Aunque también lleva otros elementos, podría considerarse como una anticipación del presente documento.

b) Resumen

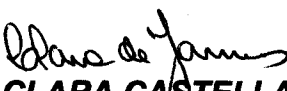
En conclusión los requisitos de patentabilidad de la presente solicitud se podrían ver afectados así:

Nº	Documento	Reivindicaciones afectadas	Requisito que afecta
D1	US 4622155	1 - 36	Nivel inventivo
D2	US 5529125	1 - 36	Nivel inventivo

7) 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


CLARA CASTELLANOS DE JAIMES
Jefe División de Nuevas Creaciones (E)

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

22 DIC. 2005

Concepto Técnico N°	EXAMINADOR TÉCNICO Código No.	EXAMINADOR JURÍDICO Código No.
1963	202003	

United States Patent [19]

Harris et al.

[11] Patent Number: 4,622,155

[45] Date of Patent: Nov. 11, 1986

[54] METHOD FOR FRACTURING SUBTERRANEAN FORMATIONS

[75] Inventors: Lawrence E. Harris; Marlin D.
Holtmyer; Richard W. Pauls, all of
Duncan, Okla.

[73] Assignee: Halliburton Company, Duncan, Okla.

[21] Appl. No.: 764,972

[22] Filed: Aug. 12, 1985

Related U.S. Application Data

[63] Continuation of Ser. No. 589,188, Mar. 13, 1984, abandoned.

[51] Int. Cl.⁴ E21B 43/26

[52] U.S. Cl. 252/8.551; 166/308

[58] Field of Search 252/8.55 R, 8.5 M, 315.1;
166/308

[56] References Cited

U.S. PATENT DOCUMENTS

3,757,864 9/1973 Crawford et al. 166/308

4,174,283 11/1979 Griffin 252/8.55
4,200,539 4/1980 Burnham et al. 252/8.55
4,200,540 4/1980 Burnham 252/8.55
4,316,810 2/1982 Burnham 252/8.55

Primary Examiner—Herbert B. Gwynn

Attorney, Agent, or Firm—Robert A. Kent

[57] ABSTRACT

The present invention provides a method of forming an easily pumpable gelled fluid which is capable of yielding an apparent viscosity of in excess of about 100 centipoise at a shear rate of 40 sec⁻¹ for in excess of about six hours at a temperature in excess of 250° F. An initial gel is formed by adding a selected basic aluminum compound and a phosphoric acid ester to a hydrocarbon liquid. This mixture is aged to form the initial gel and an additional quantity of a basic aluminum compound then is admixed with the initial gel. The crosslinked gel then is introduced into a subterranean formation at a rate and pressure sufficient to fracture the formation.

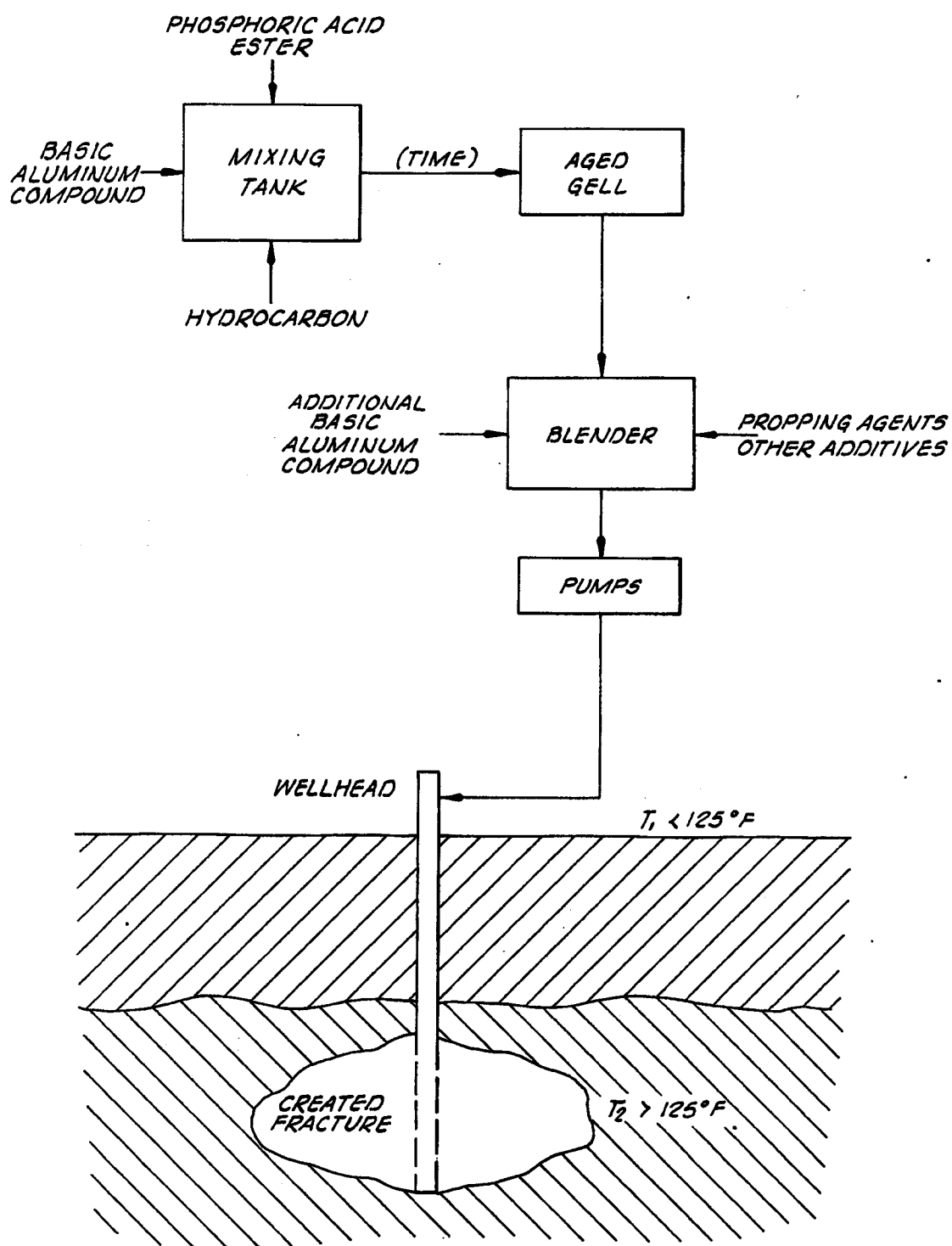
13 Claims, 1 Drawing Figure

184
182

U.S. Patent

Nov. 11, 1986

4,622,155



METHOD FOR FRACTURING SUBTERRANEAN FORMATIONS

This is a continuation of application Ser. No. 589,188, filed Mar. 13, 1984, now abandoned.

This invention relates to methods for fracturing subterranean formations to enhance oil and gas production, and more particularly, to methods for fracture stimulation of either or both oil and gas wells in which the temperature at the location where the fracture is to be stimulated is in excess of about 200° F.

Hydraulic fracturing is a widely used method for stimulating petroleum producing subterranean formations. Fracturing is commonly performed by contacting a subterranean formation with a viscous fracturing fluid having particulated solids, hereinafter referred to as propping agents, suspended therein, applying sufficient pressure to the fracturing fluid to open a fracture in the subterranean formation and maintaining this pressure while injecting the fracturing fluid into the fracture at a sufficient rate to extend the fracture into the subterranean formation. When the pressure on the fracturing fluid is reduced, the propping agent prevents the complete closure of the fracture.

Viscous liquids are desirably used as fracturing fluids because they have been found to remain in the fracture long enough to permit buildup and maintenance of sufficient pressure to open a fracture. Additionally, a viscous fracturing fluid can support propping agents suspended therein.

A significant problem is encountered where the bottom hole temperature or the environmental temperature at the locus of the fracture which is to be propagated or enlarged exceeds about 200° F. At such elevated temperature, many types of fluids introduced into the formation for the purpose of fracturing the formation undergo a reduction in viscosity, and therefore in their fracturing capability. For example, significant decreases in viscosity at temperatures exceeding 200° F. have been observed in the case of fracturing fluids prepared from hydratable polysaccharides and hydratable polyacrylamides. If an attempt is made to increase the viscosity of an oil base fracturing fluid as it is made up and prior to pumping it into the subterranean location, the increased viscosity results in difficulty in pumping the fluid, and other problems also are encountered in handling the relatively high viscosity fluid at the surface. These difficulties are especially acute where it is undertaken to add a solid propping agent to the fracturing fluid.

In one specific type of formation fracturing which heretofore has been practiced, an oil base fracturing fluid which consists essentially of a refined hydrocarbon containing an aluminum aliphatic phosphate has been used, and the fracturing method is carried out as described in U.S. Pat. No. 3,757,864. The fracturing fluid is prepared in the form of a pumpable gel by mixing the hydrocarbon with an aluminum salt of an aliphatic phosphate, and after the gel has been permitted to age for a selected period of time, the fracturing fluid is pumped downhole to the location of the formation to be fractured and, by application of pressure, a fracture then is developed or propagated due to the hydraulic pressure exerted by the fluid. The effectiveness of the fracturing treatment is directly related to the viscosity of the gel utilized. Generally, fracturing treatments are more effective when the viscosity of the fluid used is

higher. The described oil base fracturing fluid containing an aluminum salt of an aliphatic phosphate is usually limited in the concentration of the aluminum salt gelling agent to about 20 to about 200 pounds while it has been disclosed that the gelling agent can be present in an amount of up to about 400 pounds per 1000 gallons of fluid, since above this concentration, the viscosity of the gel becomes sufficiently high that the fluid is very difficult or impossible to manipulate on the surface, and is difficult to pump into the well conduit and into the formation. The recommended concentration of the aluminum salt depends upon the type of oil base liquid utilized. When the concentration of the aluminum salt gelling agent is maintained at a level sufficient to produce a fluid viscosity in the range of 100-500 centipoise, which is tolerable from the standpoint of handling and pumping, a significant decrease in the viscosity of the fluid generally is experienced when this fracturing fluid is introduced into a formation having a temperature above about 150° F.

The present invention relates to a method for fracturing subterranean formations which are at relatively higher temperatures, that is, above 125° F. The method is especially effective for fracturing formations in which the temperature at the location to be fractured exceeds about 200° F.

BRIEF DESCRIPTION OF THE DRAWINGS

The single drawing FIGURE diagrammatically illustrates the method of the present invention.

SUMMARY OF THE INVENTION

The method of the invention can be broadly described as initially forming an aged gel by blending an aluminum salt of a phosphate ester with a hydrocarbon base liquid in a sufficiently low concentration of salt to enable the apparent viscosity of the gel to remain in the range of 100-500 centipoise at a shear rate of 40 sec⁻¹ so that the gel can be relatively easily handled and pumped. To the aged gel then is added a quantity of a basic aluminum compound which results in additional crosslinking of the gel to yield a higher viscosity fluid at elevated formation temperatures. The preparation of the gel, and the addition of the basic aluminum compound is carried out at above-ground ambient temperatures and, in any event, at a temperature which is less than about 125° F. After formulation, it is pumped downhole to the subterranean formation to be fractured, and is employed, while under elevated pressure, for creating or propagating a fracture in the formation. At the relatively higher temperature of the formation, and particularly at a temperature above about 200° F., the fracturing fluid substantially maintains its viscosity.

DESCRIPTION OF THE PREFERRED EMBODIMENT

When the described procedure for fracturing of the present invention is employed, no difficulty is encountered in handling and pumping the materials required to make up the fluid at the ambient temperatures generally encountered at the surface over the formation to be fractured. Moreover, the additional crosslinking of the fluid effectively maintains the viscosity of the fluid at a level sufficient to effectively transport a propping agent at the higher temperatures encountered at the underground fracturing location. Surprisingly, the higher viscosity fracturing fluid does not break down or become deleteriously affected at temperatures above

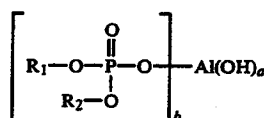
high as about 250° F. By controlling the quantity of the basic aluminum compound added to the aged gel in making up the fluid, the viscosity of the gel can be selectively determined and controlled.

The methods by which the aged gel prepared in the initial steps of the process of the invention is made up are generally well known in the art. One such procedure is that described in *Industrial and Engineering Chemistry*, Vol. 34, page 20 et seq. Other methods are alluded to in U.S. Pat. No. 3,757,864. In general, the procedure entails reacting a phosphorous compound, such as phosphorous pentoxide or phosphorous oxychloride, with a selected alcohol or mixture of alcohols to form the phosphoric acid ester precursor of the salt desired. The ester then is reacted with a basic aluminum compound. Typical usable aluminum compounds are sodium aluminate, aluminum isopropoxide, hydrated alumina, and any other aluminum compound which is capable of reacting with the ester.

The aluminum salt as thus synthesized is next added, also in accordance with well understood procedures, to an oil base or hydrocarbon-type liquid suitable for use in fracturing. The hydrocarbon liquid can be any of various previously used hydrocarbon materials, including kerosene, diesel oil, gas oil, fuel oil and certain types and mixtures of crude oil. Crude oil having in excess of 40 API gravity, condensates, kerosene and diesel are the preferred base materials. The salt can be made up prior to adding to the hydrocarbon liquid, or can be formed in situ by addition of the phosphate ester and aluminum compound concurrently to the hydrocarbon liquid with concurrent mixing.

The amount of the aluminum salt placed in the hydrocarbon liquid in making up the initial aged gel in the preliminary steps of the process can be varied in accordance with a number of factors. In general, however, the concentration of the aluminum salt in the hydrocarbon liquid should be sufficient to yield an apparent viscosity to the fluid in the range of from about 100 to about 500 centipoise at a shear rate of 40 sec⁻¹. If the prescribed concentrations are exceeded, the viscosity of the aged gel under preparation may be so high that the gel will be very difficult to handle, and to pump to the subterranean fracture location, and one of the major objectives of the invention will thus be largely defeated.

The aluminum salts used in initially making up the aged gel, in practicing the method of the invention, are broadly aluminum aromatic phosphates, aluminum oxoalkyl phosphates, aluminum oxaalkyl alkyl phosphates and the aluminum aliphatic salts described in Crawford U.S. Pat. No. 3,757,864. The salts employed in the preparation of the aged gel are selected from the group of salts having the structural formulae:



where

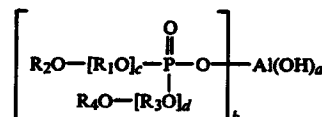
a=0 to 2,
b=1 to 3,

and the sum of a+b=3;

R₁=an aryl or aliphatic-aryl group containing from 6 to 24 carbon atoms, and

R₂=an aryl, aliphatic-aryl or aliphatic group containing from 1 to 24 carbon atoms, or H;

provided, however, that where R₁ is an aryl group, then R₂ must be either an aliphatic group containing at least six carbon atoms, or an aliphatic-aryl group containing at least twelve carbon atoms; and provided that if R₂ is an aryl group, then R₁ is an aliphatic-aryl group containing at least 12 carbon atoms; and provided that if both R₁ and R₂ are aliphatic-aryl groups; one of R₁ and R₂ contains at least 12 carbon atoms; and provided that where R₁ is an aliphatic-aryl containing less than 12 carbon atoms and R₂ is aliphatic, R₂ must contain at least six carbon atoms; and



where

a=0 to 2,

b=1 to 3,

c=1 to 5,

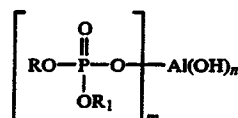
d=1 to 5,

and the sum of a+b=3;

R₁O and R₃O=an alkyloxy, alkenyloxy or alkynyloxy group containing from 1 to 18 carbon atoms, or CH₂CH(CH₃)O, or CH₂CH₂O, and

R₂O and R₄O=an alkyloxy, alkenyloxy or alkynyloxy group containing from 1 to 18 carbon atoms.

R₁O and R₂O may differ from each other but shall together contain from 1 to 24 carbon atoms, and R₃O and R₄O may differ from each other but shall together contain from 1 to 20 carbon atoms, provided that at least one of R₁O and R₃O shall be either CH₂CH(CH₃)O or CH₂CH₂O and provided further that where either R₁O or R₃O is neither CH₂CH(CH₃)O nor CH₂CH₂O, then the respective R₂O or R₄O group otherwise bonded thereto shall be deleted; and



where

m=1 to 3,

n=0 to 2,

and the sum of n+m=3; and

R and R₁ are independently C₁ to C₂₀ alkyls, or C₂ to C₂₀ alkenyls, or C₂ to C₂₀ alkynyls, or R or R₁, but not both, may be H;

provided, however, that where either the R or R₁ contains fewer than six carbon atoms, then the other of R or R₁ contains at least seven carbon atoms.

The aluminum aromatic phosphates having the structural formula (1) appearing above include aluminum aryl phosphates, aluminum aliphatic-aryl phosphates, aluminum aryl aliphatic phosphates, aluminum aliphatic-aryl aliphatic phosphates and aluminum aryl aliphatic-aryl phosphates. In these compounds the term "aliphatic" is used to mean saturated, olefinic and/or acetylenic straight and/or branched chain constituents. The

term "aryl" is defined as a phenyl group, and the term "aliphatic-aryl" is defined as including phenyl groups substituted by an aliphatic hydrocarbon substituent as this term is defined. In each case, the aromatic phosphate constituting the precursor of the aluminum salts includes an aryl or aliphatic hydrocarbon-aryl substituent containing from about 6 to about 24 carbon atoms. The most preferred salts within this group are aluminum aryl aliphatic phosphates in which the aliphatic hydrocarbon substituent contains from 6 to 18 carbon atoms.

A partial listing of aluminum phosphate salts constituting additives of the invention includes aluminum phenyl hexadecyl phosphate, aluminum bis(4-dodecylphenyl)phosphate, aluminum 4-dodecylphenyl ethyl phosphate, aluminum tolyl octadecyl phosphate, aluminum phenyl 2-tetradecyl phosphate, aluminum 3-octadecylphenyl phosphate, and aluminum 2-ethylphenyl tetradecyl phosphate.

The aluminum salts which conform to structural formula (2) above can be the aluminum salts of both mono- and diesters having either one or two oxaalkyl substituents, with the term "alkyl" included within the term "oxaalkyl" being used in the generic sense to include straight and branched chain, saturated and unsaturated aliphatic groups. The most preferred salts of this type are the aluminum salts of phosphate diesters in which the oxaalkyl substituent contains from about 16 to about 24 carbon atoms and the second ester substituent in the salt contains from about 1 to about 16 carbon atoms.

A partial listing of aluminum salts constituting compounds of the type contemplated by structural formula (2) above includes: aluminum bis(7,10-dioxadodecyl)phosphate; aluminum 4-methyl-2-oxabutyl hexyldecyl phosphate; aluminum 4,7-dioxanonyl oxadecyl phosphate; aluminum octadecyl 2-oxabutyl phosphate; aluminum bis(14-oxahexadecyl)phosphate; aluminum 3-oxapentyl octadecyl phosphate; aluminum 5-methyl-7,10-dioxadodecyl tetradecyl phosphate; aluminum 11,14-dimethyl 9,12-dioxatetradecyl phosphate and aluminum 6-butyl-12-methyl-10-oxadodecyl hexadecyl phosphate.

Examples of aluminum salts conforming to formula (3) above are the aluminum salts of octylethylorthophosphoric acid ester, propynyldecynylorthophosphoric acid ester, methyltetradecylorthophosphoric acid ester, methyl-dodecylorthophosphoric acid ester, ethyltetradecylorthophosphoric acid ester and octyl-dodecylorthophosphoric acid ester.

If a solid aluminum salt is employed, a quantity of a phosphate ester may, if desired, also be admixed with the aged gel in an amount sufficient to react with additional quantities of a basic aluminum compound upon admixture with the aged gel.

Preferably, the salts are formed in situ in the hydrocarbon liquid by initially adding to the hydrocarbon liquid a phosphate ester in appropriate amount, followed by the addition of a selected quantity of the aluminum compound which is to be reacted therewith to form the aluminum salt. At the time of addition of the aluminum compound to the hydrocarbon, it is beneficial to add a small amount of sodium hydroxide and water. For purposes of illustration, the use of an aliphatic phosphate ester of the type employed as a precursor in the preparation of a compound conforming to structural formula (3) above is referred to in the schematic illustration of the process. It will be understood, of course, that compounds of the sort defined by structural formulae

(1) and (2) can also be used pursuant to the process scheme with equal facility.

In the preparation of the aged gel, the phosphate ester and aqueous solution of sodium aluminate or other suitable aluminum compound are added to a mixing tank which contains crude oil, kerosene or diesel, and the aluminum aliphatic phosphate compound is formed in situ in the hydrocarbon liquid. As previously indicated, the amounts of the aluminate and phosphate ester which are added to the hydrocarbon are limited such that, at the ambient temperature at the mixing site and prevailing in the vicinity of the pumps used for pumping the final dispersion downhole, the dispersion formed will be of sufficiently low viscosity that no difficulty in handling and pumping is experienced. That is, the fluid will have an apparent viscosity in the range of from about 100 to about 500 centipoise at a shear rate of 40 sec⁻¹. Where an aluminum aliphatic phosphate conforming to structural formula (3) above is utilized, the amounts of aliphatic phosphate ester and aluminate compound added to the hydrocarbon are such that the aluminum salt formed in situ preferably does not exceed a concentration of about 2 weight percent of the fluid. Generally, the phosphoric acid ester will be admixed in an amount of from about 25 pounds to about 200 pounds per 1000 gallons of the aged gel and, most preferably, from about 75 pounds to about 175 pounds per 1000 gallons. The basic aluminum compound initially is admixed in an amount of from about 1 pound to about 15 pounds per 1000 gallons of aged gel and, preferably, from about 1 pound to about 10 pounds per 1000 gallons.

After thoroughly mixing the hydrocarbon and reactants, the mixture is permitted to age for a period in excess of about three minutes. No detrimental effect has been noted when the fluid has been aged in excess of up to about 30 days. During this time, reaction of the ester and aluminate compounds occurs to produce the aluminum salt which is dissolved in the hydrocarbon and the resulting system undergoes an increase in viscosity as the reaction proceeds.

When the aged gel has been prepared in the manner described, the next step of the process of the invention involves adding to this gel an additional quantity of the basic aluminum compound to effect additional cross-linking of the aged gel as it is introduced into the subterranean formation. An additional quantity of from about 0.5 to about 15 pounds per 1000 gallons of aged gel and, preferably, from about 1 to about 10 pounds is added to the aged gel. Typically, the basic aluminum compound is admixed with the aged gel as an aqueous solution containing from about 2 to about 5 pounds of the compound per gallon of solution. The total additional quantity of the basic aluminum compound admixed with the aged gel will depend upon the formation temperature. In this instance, from about 1 to about 5 gallons of the solution are admixed with each 1000 gallons of the aged gel immediately prior to or substantially simultaneously with introduction of the gel into the well bore communicating with the subterranean formation which is to be treated. The addition of the basic aluminum compound to the aged gel will provide the fluid with a viscosity in excess of that otherwise achievable by the aged gel at a temperature in excess of about 125° F.

The addition of the aqueous solution of the basic aluminum compound generally is made at ambient temperature in any suitable blending device. Numerous conventional devices are well known by individuals

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skilled in the art. The amount of the basic aluminum compound which is used will be determined in part by the ultimate downhole viscosity of the fracturing fluid that is desired and also, in part, by the quantity of propping agent which it may be desired to incorporate in, and have carried by, the hydrocarbon liquid comprising the principal component of the aged gel. Typical propping agents can comprise sand, resin-coated sand, resin-coated sintered bauxite, glass beads, ceramic beads, sintered bauxite and the like. The propping agent typically is admixed with the aged gel in an amount of from about $\frac{1}{2}$ to about 20 pounds per gallon of gel. The propping agent may be admixed with the gel in any suitable conventional blending device. Other types of fracturing fluid additives such as surfactants, corrosion inhibitors and the like well known in the art also can be added to the aged gel when the propping agent is added.

After thoroughly blending the propping agent and any other additives with the aged gel, the additional crosslinking agent is admixed with the gel and pumped into the well bore where it is ultimately caused to enter the subterranean formation which is to be treated. The gelled fluid is pumped at a sufficient rate and pressure to effect a fracture and propagate the same in the subterranean formation. The temperature in the formation is generally higher than the ambient temperature at the well head where the fluid is introduced. The method of the present invention is particularly advantageous when the formation is at a temperature level in excess of about 200° F. and, most particularly, when the temperature is in excess of about 225° F. Surprisingly, it has been found that the method of the present invention will produce a fluid which is capable of maintaining an apparent viscosity in excess of about 100 centipoise at a shear rate of 40 sec⁻¹ for in excess of six hours at a temperature in excess of 250° F.

To further illustrate the present invention, and not by way of limitation, the following examples are provided.

EXAMPLE I

The following tests were performed to compare the process of the present invention to the known prior art technique for gelling hydrocarbon fluids. A first example of a crude oil is gelled utilizing the known technique. The sample is placed in a Waring Blender and a quantity of a phosphoric acid ester is admixed with the crude oil in a proportionate amount of about 91 pounds per 1000 gallons of crude oil. A quantity of a basic aluminum compound comprising sodium aluminate then is admixed in a dropwise manner to provide a proportionate amount of about 6.5 pounds per 1000 gallons of crude oil. The fluid then was permitted to continue mixing for about 15 minutes at the maximum rate without significant air entrainment. The fluid then was placed in a tightly sealed glass jar and allowed to age for about 12 hours.

A second sample also is prepared utilizing the above technique in which the proportionate amount of the phosphoric acid ester was about 91 pounds per 1000 gallons of crude oil and the basic aluminum compound was about 10 pounds per 1000 gallons of crude oil.

A third sample is prepared in accordance with the method of the present invention. A quantity of crude oil is placed in the Waring Blender and a quantity of the phosphoric acid ester is admixed with the crude oil in a proportionate amount of about 91 pounds per 1000 gallons of crude oil. A quantity of the basic aluminum compound then is admixed in a dropwise manner to

provide a proportionate amount of about 6.5 pounds per 1000 gallons of crude oil. Mixing is continued for about 15 minutes as previously described after which the fluid is aged for about 12 hours as previously described. The aged sample then is returned to the Waring Blender and an additional quantity of the basic aluminum compound is admixed with the aged fluid in an amount sufficient to provide a proportionate amount of about 3.5 pounds per 1000 gallons of aged fluid.

Thereafter, 40 ml aliquots of each of the three samples are tested on a Model 50 Fann Viscometer. The fluid is tested on the viscometer at a 300 rpm sample cup speed using a standard bob. The maximum heating rate is utilized to heat the fluid sample to 250° F. The sample is maintained under a nitrogen gas blanket maintained at a 300 psi overpressure. The data is set forth in the following Tables I, II and III corresponding to samples 1, 2 and 3.

TABLE I

Temp °F.	Time at Temp. (min.)	Apparent Viscosity at 40 sec ⁻¹ , cp
80	0	368
250	0	40
250	30	32
250	60	29
250	90	23
250	120	19
250	150	15
250	180	8

TABLE II

Temp °F.	Time at Temp. (min.)	Apparent Viscosity at 40 sec ⁻¹ , cp
80	0	79
250	0	87
250	30	117
250	60	125
250	90	142
250	120	132
250	150	104
250	180	91

TABLE III

Temp °F.	Time at Temp. (min.)	Apparent Viscosity at 40 sec ⁻¹ , cp
80	0	203
250	0	168
250	30	171
250	60	126
250	90	108
250	120	103
250	150	95
250	180	95

The data set forth above clearly illustrates the superior performance of the fluid of the present invention in comparison to the fluid prepared by prior art techniques.

The fluid produced by the method of the present invention provides sufficient initial viscosity to the gelled hydrocarbon to readily support a propping agent without premature settling in comparison to a prior art fluid containing the same quantity of the gelling agent. The fluid produced by the method of the present invention also exhibits a significantly improved temperature stability in comparison to the fluid prepared in Table I.

EXAMPLE II

To illustrate the utility of the method of the present invention with various hydrocarbon fluids, the following tests were performed. A sample of a hydrocarbon is placed in a Waring Blender together with a quantity of the phosphoric acid ester described in Example I. The ester is admixed with the hydrocarbon in the proportionate amount set forth in each of the following tables. A quantity of the basic aluminum compound then is admixed in a dropwise manner to provide a proportionate amount in pounds per 1000 gallons of hydrocarbon as set forth in each of the following tables. After addition of the aluminum compound, the mixing is continued for about 15 minutes at the maximum rate achievable without causing significant air entrainment. The sample is placed in a tightly sealed glass jar and allowed to age for about 12 hours. The aged sample is returned to the Waring Blender and an additional quantity of the basic aluminum compound is admixed with the aged fluid sample. The aluminum compound is added in a proportionate amount as set forth in the following tables.

Thereafter, a 40 ml aliquot is tested on a Model 50 Fann Viscometer. The fluid is tested on the viscometer at a 300 rpm sample cup speed using a standard bob. The maximum heating rate is utilized to heat the sample to 250° F. The sample is maintained under a nitrogen gas blanket maintained at a 300 psi overpressure. The data from the tests is set forth in the following Tables IV, V, VI, VII and VIII.

TABLE IV

Hydrocarbon: crude oil		
Phosphoric acid ester: about 145 pounds/1000 gallons hydrocarbon		
Basic aluminum compound: about 7.1 pounds/1000 gallons hydrocarbon		
Additional aluminum compound: about 8.3 pounds/1000 gallons hydrocarbon		
Temp., °F.	Time at Temp., Min.	Apparent Viscosity at 40 sec ⁻¹ , cp.
75	0	265
250	0	251
250	60	350
250	120	322
250	180	293
250	240	265
250	300	201

TABLE V

Hydrocarbon: crude oil		
Phosphoric acid ester: about 127 pounds/1000 gallons hydrocarbon		
Basic aluminum compound: about 7.1 pounds/1000 gallons hydrocarbon		
Additional aluminum compound: about 5.3 pounds/1000 gallons hydrocarbon		
Temp., °F.	Time at Temp., Min.	Apparent Viscosity at 40 sec ⁻¹ , cp.
75	0	525
250	0	206
250	60	180
250	120	193
250	180	172
250	360	157
250	450	135

TABLE VI

Hydrocarbon: kerosene		
Phosphoric acid ester: about 145 pounds/1000 gallons hydrocarbon		
Basic aluminum compound: about 7.1 pounds/1000 gallons hydrocarbon		
Additional aluminum compound: about 7.1 pounds/1000 gallons hydrocarbon		
Temp., °F.	Time at Temp., Min.	Apparent Viscosity at 40 sec ⁻¹ , cp.
75	0	349
250	0	204
250	60	251
250	121	283
250	181	276
250	240	264
250	300	243
250	360	230

TABLE VII

Hydrocarbon: diesel		
Phosphoric acid ester: about 127 pounds/1000 gallons hydrocarbon		
Basic aluminum compound: about 5.9 pounds/1000 gallons hydrocarbon		
Additional aluminum compound: about 7.1 pounds/1000 gallons hydrocarbon		
Temp., °F.	Time at Temp., Min.	Apparent Viscosity at 40 sec ⁻¹ , cp.
80	0	116
250	0	311
250	60	285
250	120	253
250	180	224
250	240	203
250	300	185
250	360	162
250	420	147
250	600	128
250	696	108

TABLE VIII

Hydrocarbon: jet fuel		
Phosphoric acid ester: about 145 pounds/100 gallons hydrocarbon		
Basic aluminum compound: about 7.1 pounds/1000 gallons hydrocarbon		
Additional aluminum compound: about 8.3 pounds/1000 gallons hydrocarbon		
Temp., °F.	Time at Temp., Min.	Apparent Viscosity at 40 sec ⁻¹ , cp.
80	0	189
250	0	215
250	30	351
250	60	361
250	120	256
250	180	226
250	240	192

The data set forth above clearly illustrates the beneficial results obtained by practice of the process of the present invention.

EXAMPLE III

To illustrate the effect of the method of the present invention and the effect the concentration of the basic aluminum compound has upon the viscosity of the fluid, the following tests were performed. A sample of crude oil is placed in a Waring Blender together with a quantity of the phosphoric acid ester described in Example I. The ester is admixed with the crude in a proportionate amount of about 109 pounds per 1000 gallons of crude. A quantity of the basic aluminum compound then is

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admixed in a dropwise manner with the crude to provide a proportionate amount of about 5.9 pounds per 1000 gallons of crude. After addition of the aluminum compound, the mixing is continued for about 15 minutes at the maximum rate achievable without causing significant air entrainment. The sample is placed in a tightly sealed gas jar and allowed to age for about 12 hours. Aliquots of the aged sample are admixed with an additional quantity of the basic aluminum compound in the proportionate amount as set forth in the following tables.

Thereafter, 40 ml. of the fluid sample is tested on a Model 50 Fann Viscometer. The fluid is tested on the viscometer at a 300 rpm sample cup speed using a standard bob. The maximum heating rate is utilized to heat the sample to 250° F. The sample is maintained under a nitrogen gas blanket maintained at a 300 psi overpressure. The data from the tests is set forth in the following Tables IX, X, XI, XII, XIII, XIV and XV.

TABLE IX

Additional basic aluminum compound, about 3 pounds/1000 gallons crude		
Temp °F.	Time at Temp. (min.)	Apparent Viscosity at 40 sec ⁻¹ , cp
75	0	409
250	0	156
250	60	79
250	120	64
250	150	60

TABLE X

Additional basic aluminum compound, about 3.55 pounds/1000 gallons crude		
Temp °F.	Time at Temp. (min.)	Apparent Viscosity at 40 sec ⁻¹ , cp
75	0	449
250	0	97
250	60	66
250	120	77
250	181	63

TABLE XI

Additional basic aluminum compound, about 4.15 pounds/1000 gallons crude		
Temp °F.	Time at Temp. (min.)	Apparent Viscosity at 40 sec ⁻¹ , cp
75	0	402
250	0	163
250	60	211
250	120	206
250	180	176
250	240	156

TABLE XII

Additional basic aluminum compound, about 4.75 pounds/1000 gallons crude		
Temp °F.	Time at Temp. (min.)	Apparent Viscosity at 40 sec ⁻¹ , cp
75	0	183
250	0	151
250	60	159
250	120	164
250	180	156
250	240	147
250	285	143

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TABLE XIII

Additional basic aluminum compound, about 5.3 pounds/1000 gallons crude		
Temp °F.	Time at Temp. (min.)	Apparent Viscosity at 40 sec ⁻¹ , cp
75	0	147
250	0	84
250	60	130
250	120	154
250	180	144
250	240	121

TABLE XIV

Additional basic aluminum compound, about 5.9 pounds/1000 gallons crude		
Temp °F.	Time at Temp. (min.)	Apparent Viscosity at 40 sec ⁻¹ , cp
75	0	168
250	0	62
250	60	104
250	120	133
250	180	140
250	241	140
250	272	143

TABLE XV

Additional basic aluminum compound, about 6.5 pounds/1000 gallons crude		
Temp °F.	Time at Temp. (min.)	Apparent Viscosity at 40 sec ⁻¹ , cp
75	0	56
250	0	46
250	62	139
250	120	175

The data clearly illustrates the potential benefits to be derived from use of the method of the present invention. The present invention can be used to provide a fluid which is stable at elevated temperatures and thereby capable of supporting significant quantities of a propping agent. Known fluids having a similar viscosity at the elevated temperature of the formation have a viscosity at ambient temperature which makes them virtually impossible to pump from their containers into the subterranean formation. It is believed that, in the practice of the present invention, the solubility of the aluminum phosphate ester reaction product in the hydrocarbon increases as the temperature of the fluid increases. The method of the present invention permits the maintenance of a relatively constant viscosity in a fluid during heating or the ability to build viscosity in the fluid without the addition of more gelling agent to the fluid.

From the foregoing description of the invention, it will be perceived that a useful, relatively easily practiced method for fracturing subterranean formations has been proposed, and contemplates the usage of a substantially temperature stable fracturing fluid which is suitable for use at relatively elevated bottom hole temperatures. Although certain specific embodiments of the invention have been herein described in order to clearly illustrate the basic principles which underlie the invention, and to provide sufficient guidance to those skilled in the art to enable them to practice the invention without difficulty, it will be understood that various changes and alterations in the exemplary compositions and methods which are set forth herein can be effected without departure from the spirit or scope of the inven-

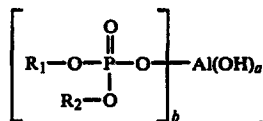
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tion. Changes and innovations of this type are therefore deemed to be circumscribed by the spirit and scope of the invention, except as the same may be necessarily limited by the appended claims.

What is claimed is:

1. A method for fracturing a subterranean formation having an elevated temperature comprising:

adding at a temperature of less than about 125° F. to a hydrocarbon liquid, a phosphoric acid ester in an amount sufficient to provide a concentration of from about 25 to about 200 pounds of ester per 1000 gallons of hydrocarbon liquid and a basic aluminum compound in an amount sufficient to provide a concentration of from about 1 to about 15 pounds of said compound per 1000 gallons of hydrocarbon liquid to form, in situ, at least one aluminum salt selected from the group having the structural formulae:



where

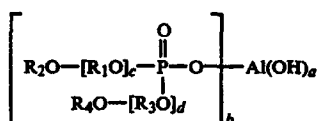
a=0 to 2,

b=1 to 3,

and the sum of a+b=3;

R₁=a phenyl or aliphatic hydrocarbon substituted-phenyl group containing from 6 to 24 carbon atoms, and

R₂=a phenyl, aliphatic hydrocarbon substituted-phenyl or aliphatic hydrocarbon group containing from 1 to 24 carbon atoms, or H; provided, however, that where R₁ is an phenyl group, then R₂ must be either an aliphatic hydrocarbon group containing at least six carbon atoms, or an aliphatic hydrocarbon substituted-phenyl group containing at least twelve carbon atoms; and provided that if R₂ is a phenyl group, then R₁ is an aliphatic hydrocarbon substituted-phenyl group containing at least 12 carbon atoms; and provided that if both R₁ and R₂ are aliphatic hydrocarbon substituted-phenyl groups; one of R₁ and R₂ contains at least 12 carbon atoms; and provided that where R₁ is an aliphatic hydrocarbon substituted-phenyl containing less than 12 carbon atoms and R₂ is aliphatic hydrocarbon, R₂ must contain at least six carbon atoms; and



where

a=0 to 2,

b=1 to 3,

c=1 to 5,

d=1 to 5,

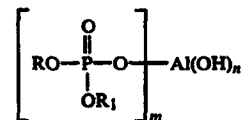
and the sum of a+b=3;

R₁O and R₃O=an alkyloxy, alkenyloxy or alkynyloxy group containing from 1 to 18 carbon atoms, and

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R₂O and R₄O=an alkyloxy, alkenyloxy or alkynyloxy group containing from 1 to 18 carbon atoms, and wherein

R₁O and R₂O may differ from each other but shall together contain from 1 to 24 carbon atoms, and R₃O and R₄O may differ from each other but shall together contain from 1 to 20 carbon atoms, provided that at least one of R₁O and R₃O shall be either CH₂CH(CH₃)O or CH₂CH₂O and provided further that where either R₁O or R₃O is neither CH₂CH(CH₃)O nor CH₂CH₂O, then the respective R₂O or R₄O group otherwise bonded thereto shall be deleted; and



where

m=1 to 3,

n=0 to 2,

and the sum of n+m=3; and

R and R₁ are independently C₁ to C₂₀ alkyls, or C₂ to C₂₀ alkenyls, or C₂ to C₂₀ alkynyls, or R or R₁, but not both, may be H; provided, however, that where either R or R₁ contains fewer than six carbon atoms, then the other of R or R₁ contains at least seven carbon atoms whereby the liquid hydrocarbon is caused to form a pumpable initial gel; aging said initial gel for a period of at least about twelve hours whereby said gel is caused to develop an initial apparent viscosity in the range of from about 100 to about 500 centipoise at a shear rate of 40 sec⁻¹;

adding to said aged initial gel, at a temperature below about 125° F., as an aqueous solution containing an additional quantity of a basic aluminum compound in an amount in the range of from about 0.5 to about 15 pounds per 1000 gallons of hydrocarbon liquid to react with said ester to effect additional gelling of said pumpable initial gel;

introducing said aged initial gel containing said additional basic aluminum compound into a well bore communicating with a subterranean formation having a temperature in excess of about 125° F. substantially simultaneously with said addition of said additional basic aluminum compound whereby said fluid is heated during said additional gelling to form a gelled fluid having a viscosity in the formation sufficient to transport a propping agent into a created fracture in said subterranean formation; and

fracturing said formation with said introduced gel.

2. The method of claim 1 wherein a solid particulate is admixed with at least a portion of said initial gel in an amount of from about 1/2 pound to about 20 pounds per gallon of said gel.

3. The method of claim 1 wherein said hydrocarbon comprises at least one member selected from the group consisting of diesel, kerosene, fuel oil, gas oil and crude oil.

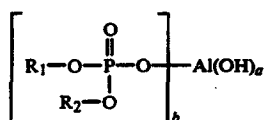
4. The method of claim 1 wherein the basic aluminum compound comprises sodium aluminate.

5. A method for fracturing a subterranean formation having an elevated temperature comprising:

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adding at a temperature of less than about 125° F. to a hydrocarbon liquid, a phosphoric acid ester in an amount sufficient to provide a concentration of from about 25 to about 200 pounds of ester per 1000 gallons of hydrocarbon liquid and a basic aluminum compound in an amount sufficient to provide a concentration of from about 1 to about 15 pounds of said compound per 1000 gallons of hydrocarbon liquid to form, in situ, at least one aluminum salt selected from the group having the structural formulae:



where

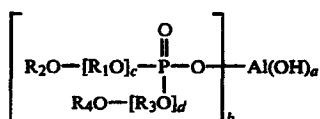
a=0 to 2,

b=1 to 3,

and the sum of a+b=3;

R₁=a phenyl or aliphatic hydrocarbon substituted-phenyl group containing from 6 to 24 carbon atoms, and

R₂=a phenyl, aliphatic hydrocarbon substituted-phenyl or aliphatic hydrocarbon group containing from 1 to 24 carbon atoms, or H; provided, however, that where R₁ is an aliphatic hydrocarbon group containing at least six carbon atoms, or an aliphatic hydrocarbon substituted-phenyl group containing at least twelve carbon atoms; and provided that if R₂ is a phenyl group, then R₁ is an aliphatic hydrocarbon substituted-phenyl group containing at least 12 carbon atoms; and provided that if both R₁ and R₂ are aliphatic hydrocarbon substituted-phenyl groups; one of R₁ and R₂ contains at least 12 carbon atoms; and provided that where R₁ is an aliphatic hydrocarbon substituted-phenyl containing less than 12 carbon atoms and R₂ is aliphatic hydrocarbon, R₂ must contain at least six carbon atoms; and



where

a=0 to 2,

b=1 to 3,

c=1 to 5,

d=1 to 5,

and the sum of a+b=3;

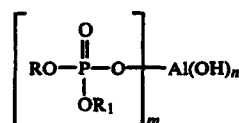
R₁O and R₃O=an alkyloxy, alkenyloxy or alkynyloxy group containing from 1 to 18 carbon atoms, or CH₂CH(CH₃)O, or CH₂CH₂O, and

R₂O and R₄O=an alkyloxy, alkenyloxy or alkynyloxy group containing from 1 to 18 carbon atoms, and wherein

R₁O and R₂O may differ from each other but shall together contain from 1 to 24 carbon atoms, and R₃O and R₄O may differ from each other but shall together contain from 1 to 20 carbon atoms, provided that at least one of R₁O and R₃O shall be either CH₂CH(CH₃)O or CH₂CH₂O and provided

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further that where either R₁O or R₃O is neither CH₂CH(CH₃)O nor CH₂CH₂O, then the respective R₂O or R₄O group otherwise bonded thereto shall be deleted; and



where

m=1 to 3,

n=0 to 2,

and the sum of n+m=3; and

R and R₁ are independently C₁ to C₂₀ alkyls, or C₂ to C₂₀ alkenyls, or C₂ to C₂₀ alkynyls, or R or R₁, but not both, may be H; provided, however, that where either R or R₁ contains fewer than six carbon atoms, then the other of R or R₁ contains at least seven carbon atoms whereby the liquid hydrocarbon is caused to form a pumpable initial gel; aging said initial gel for a period of at least about twelve hours whereby said gel is caused to develop an initial apparent viscosity in the range of from about 100 to about 500 centipoise at a shear rate of 40 sec⁻¹;

adding to said aged initial gel, at a temperature below about 125° F., an additional quantity of a basic aluminum compound comprising sodium aluminate in an amount in the range of from about 0.5 to about 15 pounds per 1000 gallons of hydrocarbon liquid to react with said ester to effect additional gelling of said pumpable aged initial gel and form a pumpable high viscosity gelled liquid; and

introducing said pumpable high viscosity gelled liquid into a formation having a temperature above about 125° F. under pressure sufficient to accomplish fracturing of said elevated temperature formation whereby said high viscosity gelled liquid maintains sufficient viscosity as it undergoes viscosity reduction as a result of heating in said formation that it remains capable of transporting a propping agent into the fracture created by said liquid.

6. The method of claim 5 wherein the additional quantity of basic aluminum compound is admixed as an aqueous solution with said initial gel.

7. The method of claim 5 wherein a solid particulate is admixed with at least a portion of said initial gel in an amount of from about 1/4 pound to about 20 pounds per gallon of said gel.

8. The method of claim 5 wherein said hydrocarbon comprises at least one member selected from the group consisting of diesel, kerosene, fuel oil, gas oil and crude oil.

9. A method for fracturing a subterranean formation at a location where the temperature exceeds about 200° F. comprising:

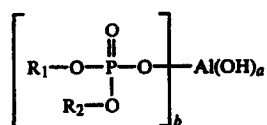
adding at a temperature of less than about 125° F. to a hydrocarbon liquid, a phosphoric acid ester in an amount sufficient to provide a concentration of from about 25 to about 200 pounds of ester per 1000 gallons of hydrocarbon liquid and a basic aluminum compound in an amount sufficient to provide a concentration of from about 1 to about 15 pounds of said compound per 1000 gallons of hydrocarbon

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liquid to form, in situ, at least one aluminum salt selected from the group having the structural formulae:



(1) 5

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where

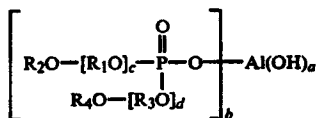
a=0 to 2,

b=1 to 3,

and the sum of a+b=3;

R₁=a phenyl or aliphatic hydrocarbon substituted-phenyl group containing from 6 to 24 carbon atoms, and

R₂=a phenyl, aliphatic hydrocarbon substituted-phenyl or aliphatic hydrocarbon group containing from 1 to 24 carbon atoms, or H; provided, however, that where R₁ is an phenyl group, then R₂ must be either an aliphatic hydrocarbon group containing at least six carbon atoms, or an aliphatic hydrocarbon substituted-phenyl group containing at least twelve carbon atoms; and provided that if R₂ is a phenyl group, then R₁ is an aliphatic hydrocarbon substituted-phenyl group containing at least 12 carbon atoms; and provided that if both R₁ and R₂ are aliphatic hydrocarbon substituted-phenyl groups; one of R₁ and R₂ contains at least 12 carbon atoms; and provided that where R₁ is an aliphatic hydrocarbon substituted-phenyl containing less than 12 carbon atoms and R₂ is aliphatic hydrocarbon, R₂ must contain at least six carbon atoms; and



(2)

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where

a=0 to 2,

b=1 to 3,

c=1 to 5,

d=1 to 5,

and the sum of a+b=3;

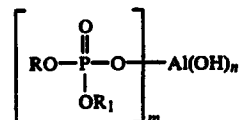
R₁O and R₃O=an alkyloxy, alkenyloxy or alkynyloxy group containing from 1 to 18 carbon atoms, or CH₂CH(CH₃)O, or CH₂CH₂O, and

R₂O and R₄O=an alkyloxy, alkenyloxy or alkynyloxy group containing from 1 to 18 carbon atoms, and wherein

R₁O and R₂O may differ from each other but shall together contain from 1 to 24 carbon atoms, and R₃O and R₄O may differ from each other but shall together contain from 1 to 20 carbon atoms, provided that at least one of R₁O and R₃O shall be either C₂CH(CH₃)O or CH₂CH₂O and provided further that where either R₁O or R₃O is neither

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CH₂CH(CH₃)O nor CH₂CH₂O, then the respective R₂O or R₄O group otherwise bonded thereto shall be deleted; and



(3)

where

m=1 to 3,

n=0 to 2,

and the sum of n+m=3; and

R and R₁ are independently C₁ to C₂₀ alkyls, or C₂ to C₂₀ alkenyls, or C₂ to C₂₀ alkynyls, or R or R₁, but not both, may be H; provided, however, that where either R or R₁ contains fewer than six carbon atoms, then the other of R or R₁ contains at least seven carbon atoms whereby the liquid hydrocarbon is caused to form a pumpable initial gel; aging said initial gel for a period of at least twelve hours whereby said gel is caused to develop an initial apparent viscosity in the range of from about 100 to about 500 centipoise at a shear rate of 40 sec⁻¹;

admixing a propping agent with at least a portion of said aged initial gel in an amount of from about 1 to about 20 pounds per gallon of initial gel;

adding to said aged initial gel, at a temperature below about 125° F., as an aqueous solution an additional quantity of a basic aluminum compound in an amount in the range of from about 0.5 to about 15 pounds per 1000 gallons of hydrocarbon liquid to react with said ester to effect additional gelling of said pumpable initial gel to form a pumpable high viscosity gelled liquid;

introducing said pumpable high viscosity gelled liquid into a formation having a temperature above about 125° F. under pressure sufficient to accomplish fracturing of said elevated temperature formation; and

depositing at least a portion of said propping agent in the fracture produced by said pumpable high viscosity gelled liquid.

10. The method of claim 9 wherein said basic aluminum compound is sodium aluminate.

11. The method of claim 9 wherein said basic aluminum compound is present in an amount of from about 1 to about 10 pounds per 1000 gallons of said initial gel prior to admixing with an additional quantity of a basic aluminum compound to form said high viscosity gelled liquid.

12. The method of claim 9 wherein said phosphoric acid ester is present in an amount of from about 75 to about 175 pounds per 1000 gallons of said initial gel.

13. The method of claim 9 wherein the additional quantity of basic aluminum compound added to said gel is an amount in the range of from about 1 to about 10 pounds.

* * * * *

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US005529125A

United States Patent [19]

Di Lullo Arias et al.

[11] Patent Number: 5,529,125

[45] Date of Patent: Jun. 25, 1996

[54] ACID TREATMENT METHOD FOR SILICEOUS FORMATIONS

[75] Inventors: Gino F. Di Lullo Arias; Atikah J. Ahmad, both of Singapore, Singapore

[73] Assignee: B. J. Services Company, Houston, Tex.

[21] Appl. No.: 367,487

[22] Filed: Dec. 30, 1994

[51] Int. Cl.⁶ E21B 43/27

[52] U.S. Cl. 166/307; 507/237; 507/923; 507/933

[58] Field of Search 166/307, 308; 507/237, 923, 933

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Primary Examiner—George A. Suchfield
Attorney, Agent, or Firm—Arnold, White & Durkee

[57] ABSTRACT

A method of stimulating production in sandstone formations of oil and gas wells is achieved by using an acid system which slowly dissolves the silicate and clay formations of the sandstone to increase its permeability. The acid system uses phosphonate compounds, including phosphonate acids and the salts and esters thereof, in combination with hydrofluoric acid. The hydrofluoric acid may be provided by hydrolyzing ammonium bifluoride or hydrofluoric acid itself. The phosphonate compounds of the acid systems retard the rate at which the hydrofluoric acid reacts with the clays while enhancing the reaction rate with silica, which comprises the bulk of sandstone formations. This allows more penetration of the formation immediately adjacent to the wellbore. The phosphonate materials also improve the dispersion and suspension properties of the treating solution with silts and fines and improves the complexing capacity of the acids with silicate and alumina complexes.

42 Claims, 7 Drawing Sheets

Solubility of various acid systems (3% HF) with quartz

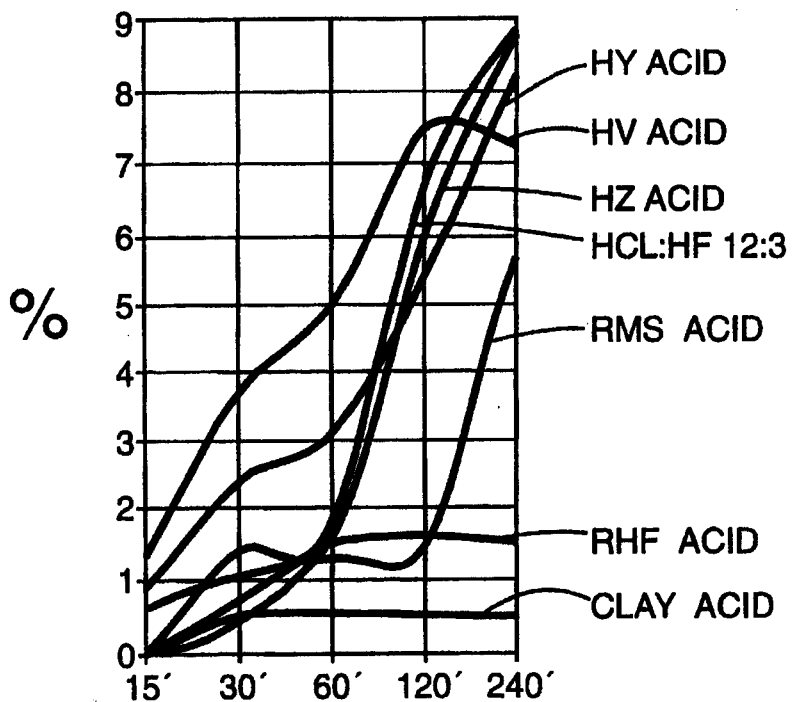


FIG. 1

Solubility of various acid systems (3% HF) with clay

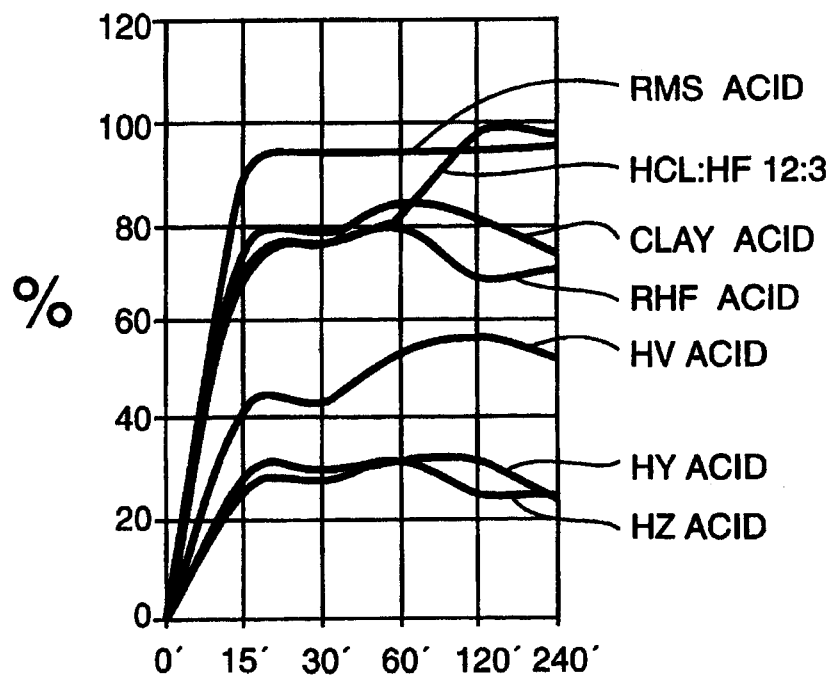


FIG. 2

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Solubility of various acid systems (3% HF) with 80:20 Quartz:Clay mixture

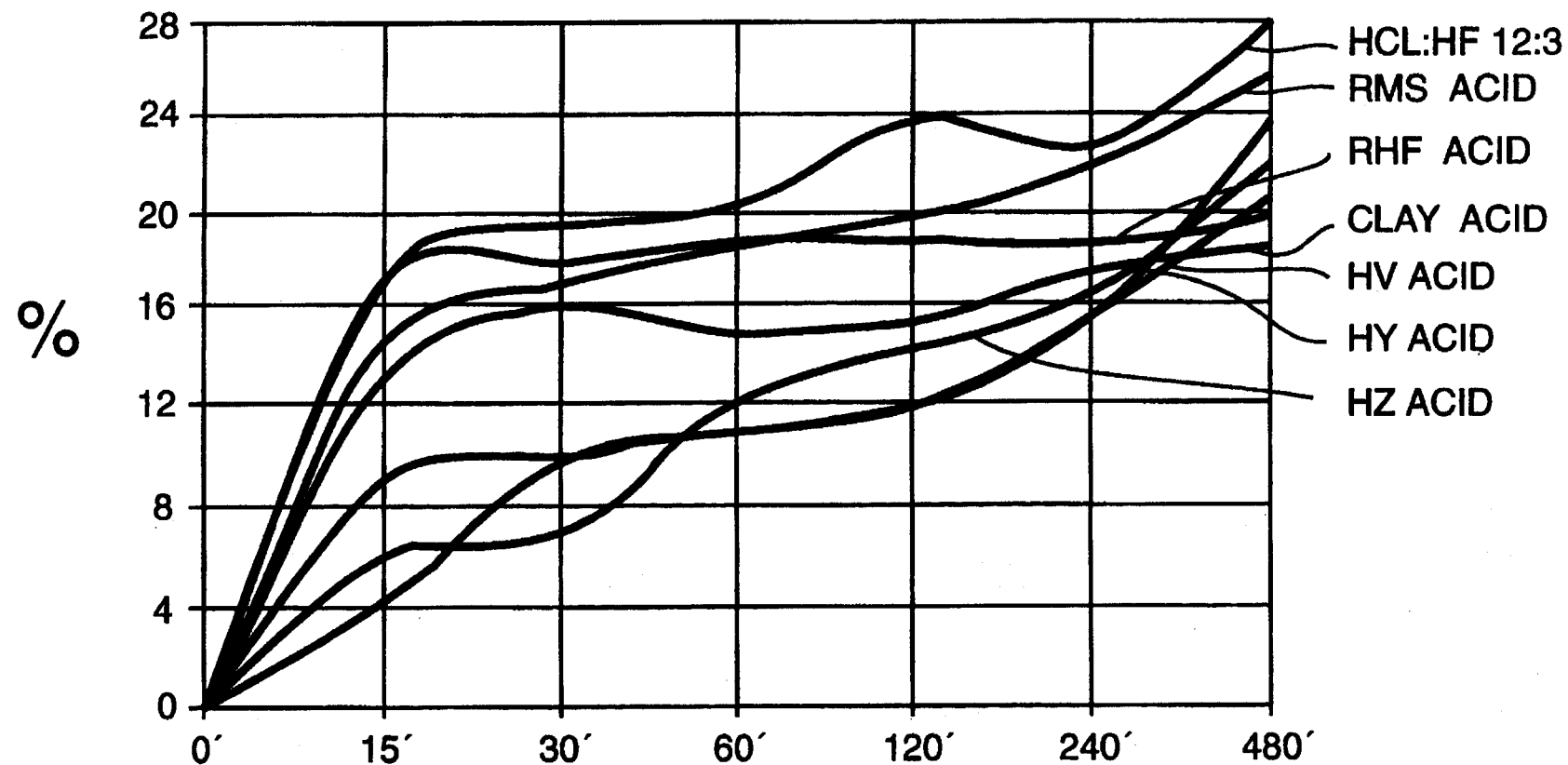


FIG. 3

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Solubility of various acid systems (3% HF) with Quartz

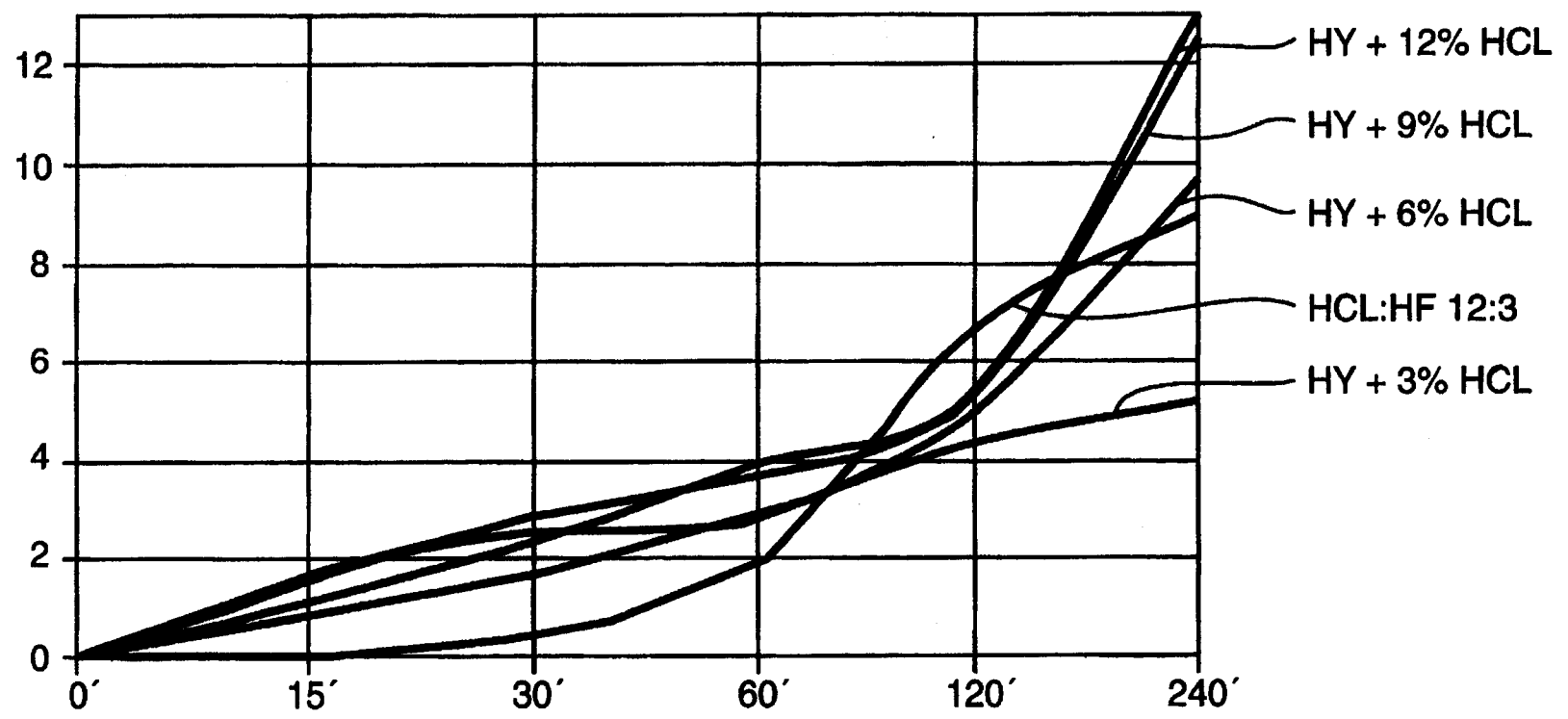


FIG. 4

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Solubility of various acid systems (3% HF) with Clays

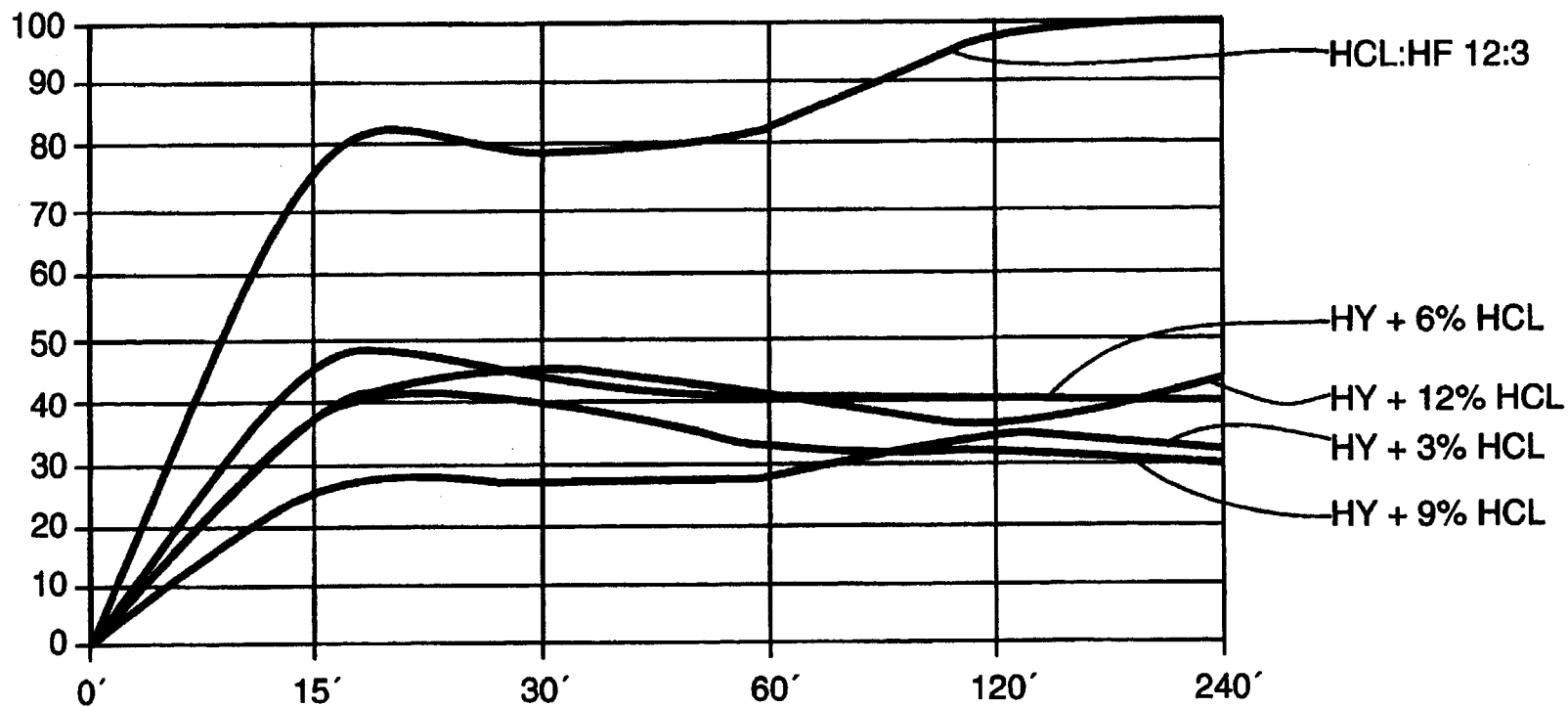


FIG. 5

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Solubility of Clays using L.HF+HCL:S Acid Blends

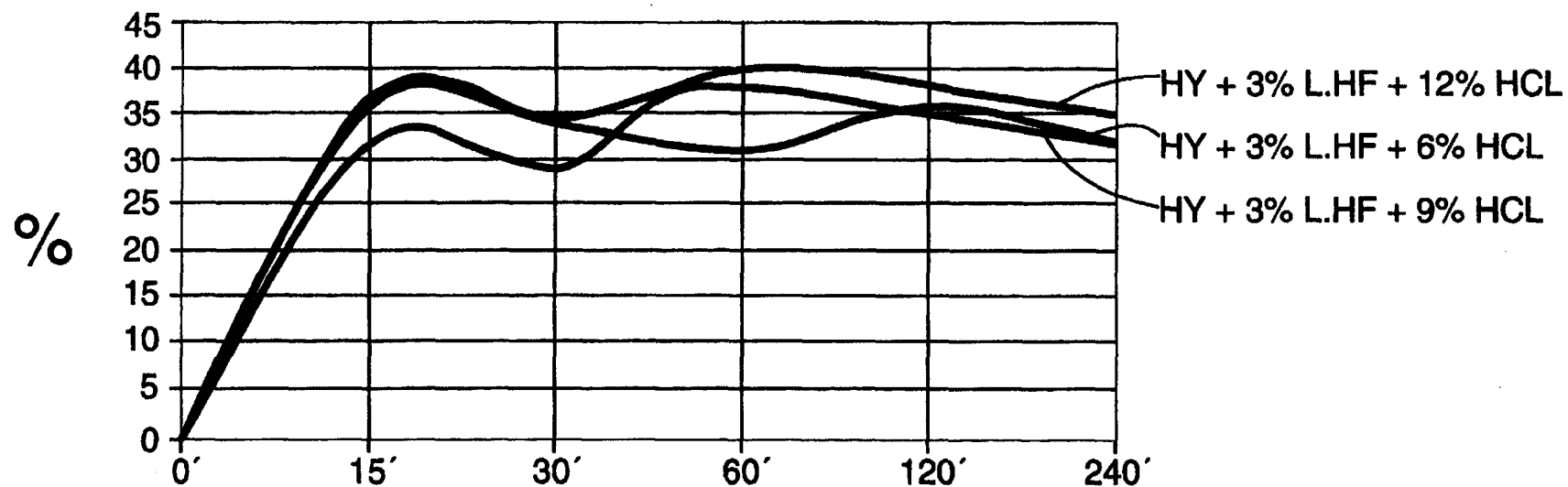
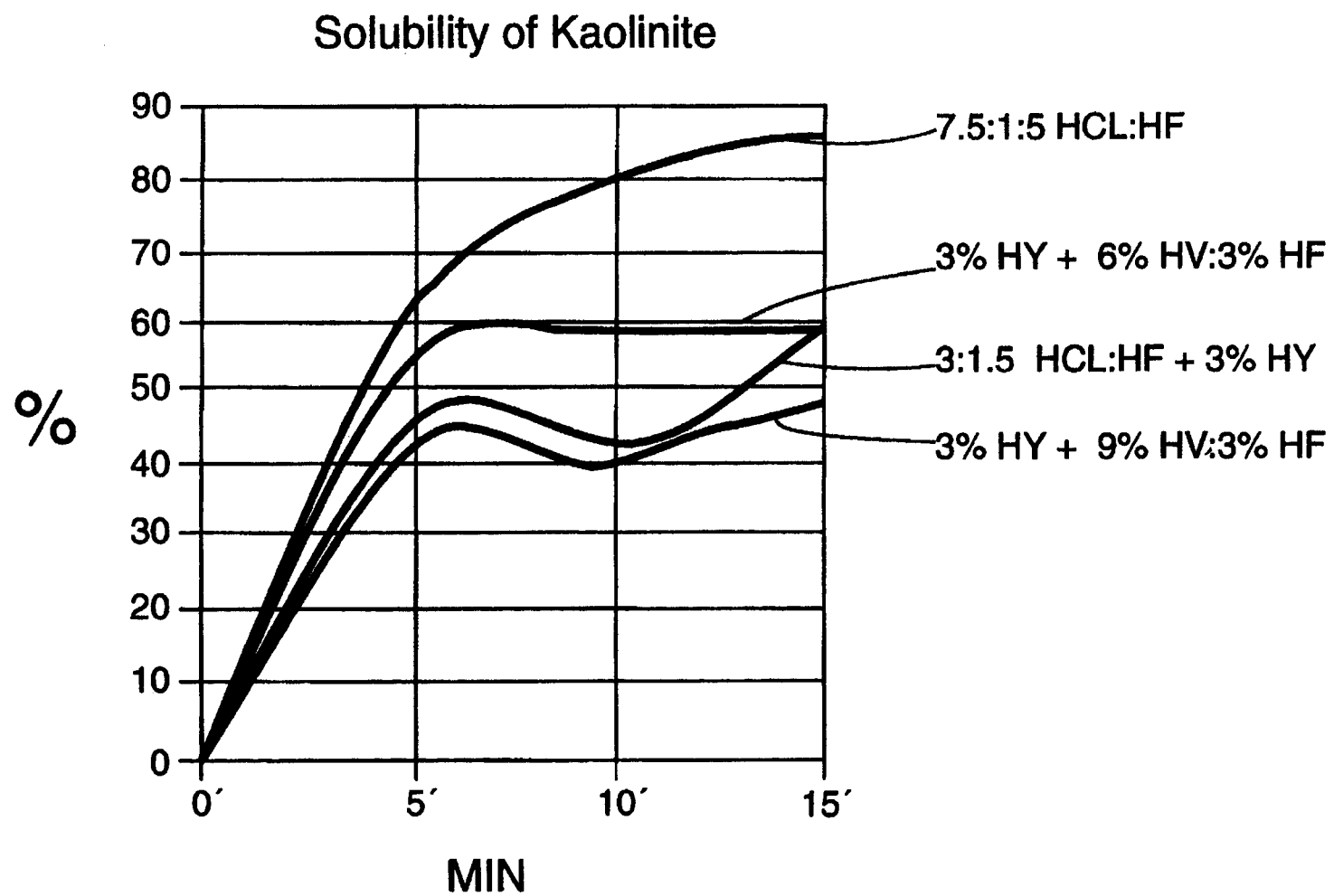


FIG. 6

**FIG. 7**

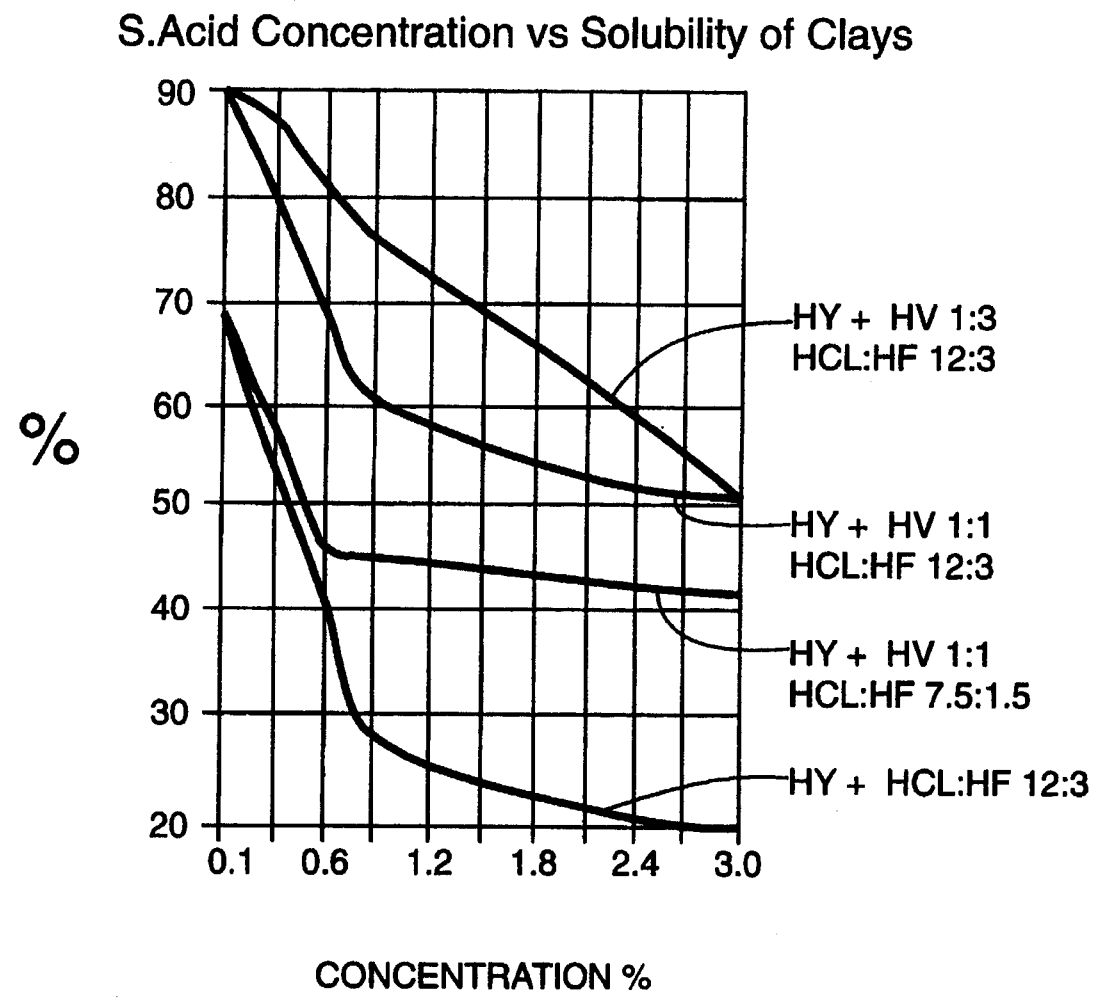


FIG. 8

ACID TREATMENT METHOD FOR SILICEOUS FORMATIONS

BACKGROUND OF THE INVENTION

1. Field of the Inventions

This invention relates to a method of treating siliceous formations to increase the permeability of the formations.

2. Description of the Prior Arts

Subterranean sandstone or siliceous formations in oil and gas wells have been treated in the past with acid treatments to increase their permeability thus increasing or improving production from the formation. As used herein the term "siliceous" refers to the characteristic of having silica and/or silicate. Most sandstone formations are composed of over 70% sand quartz particles, i.e. silica (SiO_2), bonded together by various amounts of cementing material including carbonate (calcite or CaCO_3) and silicates. The acid treatment of siliceous formations should be distinguished from the acid treatment of carbonate formations. Carbonate formations can be treated with a variety of acid systems, including hydrochloric, acetic and formic acids, with usually equal success. The treatment of siliceous formations with these acids, however, has little or no effect because they do not react appreciably with the silica and silicates which characterizes the sandstone formations.

By far the most common method of treating sandstone formations involves introducing hydrofluoric acid into the wellbore and allowing the hydrofluoric acid to react with the surrounding formation. Hydrofluoric acid is preferred almost uniformly because of its reactivity with silica and silicates. The silicates include such things as clays and feldspars. Hydrofluoric acid tends to react very quickly with authigenic clays, such as smectite, kaolinite, illite and chlorite, especially at temperatures above 150°F . Because of this, the hydrofluoric acid penetrates only a few inches of the formation before it is spent. Simultaneously, precipitation of various alumni and/or silicate complexes occur as a result of the reaction of the hydrofluoric acid with the clays and silts. The precipitation products plug pore spaces and reduce the porosity and permeability of the formation, thus impairing flow potential. Because clays are normally a part of the cementitious material that holds the sandgrains of sandstone formations together, the dissolution of clay also weakens and unconsolidates the sandstone matrix in the vicinity of the wellbore, thus causing damage to the formation. The damaging effects due to both the unconsolidation of the matrix and the precipitation of complexes which clog the pore spaces of the formation can eliminate or even revert the stimulation effect of the acid treatment.

One of the most common prior art methods of reducing the reaction rate of hydrofluoric acid with the area of the formation immediately surrounding the wellbore, is accomplished by the slow hydrolysis of ammonium bifluoride to convert it to hydrofluoric acid, either at the surface or within the well. While this method allows the acid to penetrate slightly further into the formation, it does not eliminate precipitates from forming and clogging the matrix. Other methods such as retarding the acid reaction by introducing an oil wetting surfactant into the well to prevent and reduce contact of the acid with the formation have also been used with limited success. Oil wetting surfactants create problems

What is therefore needed is a method of treating siliceous or sandstone formations using hydrofluoric acid which reduces the amount of precipitates produced and which inhibits the reactivity of the hydrofluoric acid with the clay or silicate elements of the formation.

SUMMARY OF THE INVENTION

A method of treating siliceous formations which reduces the amount of precipitates produced and which inhibits the reactivity of the hydrofluoric acid with clay or silicate elements of the formation is achieved by preparing a treatment solution containing a phosphonate compound and a source of hydrofluoric acid. The formation is then contacted with the solution so that siliceous materials of the formation are dissolved.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a graphical representation of the solubility of quartz with various acid systems over time.

FIG. 2 is a graphical representation of solubility of clays with various acid systems.

FIG. 3 is a graphical representation of the solubility of an 80:20 Quartz:Clay mixture in a variety of acid systems.

FIG. 4 is a graphical representation of the solubility of quartz with various acid systems containing varying amounts of hydrochloric acid.

FIG. 5 is a graphical representation of the solubility of clays with various acid systems with varying amounts of hydrochloric acid.

FIG. 6 is a graphical representation of the solubility of clays using a phosphonate acid with liquid hydrofluoric acid and hydrochloric acid in varying concentrations.

FIG. 7 is a graphical representation of the solubility of kaolinite using various acid systems.

FIG. 8 is a graphical representation of the solubility of clays in relation to different acid concentrations of various acid systems.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

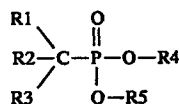
The precipitation of silicates when acidizing siliceous formations is difficult to efficiently prevent due to the multicomponent nature of the deposits formed. In order to overcome the shortcomings of the hydrofluoric acid systems which are commonly employed today, various materials were evaluated based upon their ability to complex with aluminum and silicate compounds in acidic environments. Of the materials evaluated, the phosphonate materials used in the prevention and inhibition of silicate scale were selected for use with hydrofluoric acid systems. Specifically, these acid systems included conventional hydrochloric/hydrofluoric acid systems and organic/hydrofluoric acid systems which include formic/hydrofluoric acid mixtures. Unless otherwise indicated, all concentrations or compositions are based on weight percent.

The phosphonate materials used for acid treatment of sandstone formations include the phosphonic acids and the phosphonate salts of the phosphonic acids. The general formula

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Where R1, R2 and R3 may be hydrogen, alkyl, aryl, phosphonates, phosphates, acyl, amine, hydroxy and carboxyl groups, and R4 and R5 may consist of hydrogen, sodium, potassium, ammonium or an organic radical. Examples of these materials include aminotri (methylene phosphonic acid) and its pentasodium salt, 1-hydroxyethylidene-1,1-diphosphonic acid and its tetrasodium salt, hexamethylenediaminetetra (methylene phosphonic acid) and its hexapotasassium salt, and diethylenetriaminepenta (methylene phosphonic acid) and its hexasodium salt.

Among the phosphonate materials evaluated, emphasis was concentrated on aminotri (methylene phosphonic acid), herein referred to as "HZ acid," available in 50% strength as "DEQUEST 2000" from Monsanto Co.; 1-hydroxyethylidene-1,1-diphosphonic acid, herein referred to as "HV acid," available in 60% strength as "DEQUEST 2010" from Monsanto Co.; and diethylene triamine penta (methylene phosphonic acid), herein referred to as "HY acid," available in 50% strength as "DEQUEST 2060" from Monsanto Co. Table 1 shows the inhibition of calcium and magnesium silicate scale buildup using these different phosphonate compounds and mixtures thereof.

TABLE 1

INHIBITOR 100 PPM	24 HOURS @ 50° C. INHIBITION
HZ Acid	N/A
HV Acid	22
HY Acid	12.2
HV + HY (1:1)	14.2

The phosphonate materials were also evaluated because of their potential for retarding the acid reaction with clays and their ability to slowly hydrolyze ammonium bifluoride or ammonium fluoride to produce hydrofluoric acid. By titrating various phosphonate acids with tetra methyl ammonium chloride, the acidity constants of the different acids was determined. These are set forth in Table 2.

TABLE 2

ACID	N° ACIDITY CONSTANTS	pK ₁	pK ₂	pK ₃	pK ₄	pK ₅
HY	10	<2.0	<2.0	<2.8	4.5	<5.5
HZ	6	<2.0	<2.0	<4.3	<5.4	<6.7
HV	5	<1.0	<2.5	<7.0	<11.4	—

It is known that under downhole conditions, the acid's pH remains between 1 and 3. This implies that not all of the hydrogen ions (H⁺) are used so that their utilization is dependent on the spending of the solution. From Table 2, it can be seen that the HY acid should produce the slowest hydrolysis rate. These materials are hydrolytically and thermally stable, with some materials being stable up to temperatures as high 400° F.

Overall, the HY, HV, and HZ acids are weak acids, however when evaluated for the first and second hydrogen (i.e. pK₁, pK₂) they behave as moderately strong acids. Table 3 shows a comparison of the phosphonate acids used to standard mineral and organic acids used in oil field related

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TABLE 3

ACID	pK ₁ (STRONGEST HYDROGEN)
HYDROCHLORIC ACID	<1
HV ACID	<1
HY ACID	<2
CITRIC ACID	<3.1
HYDROFLUORIC ACID	<3.5
FORMIC ACID	<3.8
ACETIC ACID	<4.8
BORIC ACID	<8.7

A pK value below 2 is regarded as a strong acid, while a pK value between 2 and 3 is regarded as a moderately strong acid, a pK value of between 4 and 7 is a weak acid, and a pK value above 7 is characterized as a very weak acid.

In order to evaluate the effect of phosphonates on the solubility of quartz and clays, several mixtures of the phosphonate acids were prepared using ammonium bifluoride as the source of hydrofluoric acid. The phosphonate acid mixtures were then tested along with standard hydrofluoric acid systems and other commercially available retarded acid systems using static and dynamic solubility tests. The commercially available retarded acid systems used consisted of "CLAY ACID", "RMS ACID" and "RHF ACID". "CLAY ACID" is a fluoroboric acid solution available from Dowell Schlumberger. "RMS ACID" is available from BJ Services and consists primarily of a hydrochloric acid and hexafluorophosphoric acid mixture. The "RHF ACID" is a retarded hydrofluoric acid system consisting of 12% hydrochloric acid and 3% hydrofluoric acid using ammonium bifluoride as the source of hydrofluoric acid and an aluminum salt as a retarder. "RHF ACID" is available from Halliburton Company.

To simulate quartz, 20-40 mesh sand was used instead of formation quartz, and bentonite and kaolin clay were used to simulate formation clays. Tests were also conducted using a mixture of sand and clay in an 80:20 ratio to simulate a typical sandstone formation. All the solubility tests were performed at 180° F. which appeared to be the critical temperature to effectively retard acid reaction rate with clays. For FIGS. 1-3, the concentration of the HY acid was 3% by volume of the total solution (4.1% by weight). For HV acid the concentration was 3% by volume (3.0% by weight). For HZ acid the concentration was 3% by volume (3.1% by weight). The results of these solubility tests are presented in FIGS. 1-3. The initial reaction rates with quartz for the HY and HV acid, as shown in FIG. 1, are much higher than that of standard hydrofluoric acid. From FIG. 2, it can be seen that the phosphonate acids retard the reaction rate with clays during the initial 15 minutes. After this initial 15 minute period, the clay's solubility is limited as shown by the flattened portion of the curve of FIG. 2. FIG. 3 shows the same trends with a much lower solubility at all times for the three phosphonate acids used compared to the other acid systems.

Normally, during matrix acidizing of sandstone formations, extra hydrochloric acid is used to prepare the hydrofluoric acid solutions. Keeping the pH low during the treatment prevents precipitation of fluorides, i.e. Ca, Mg, etc. . . , and favors precipitation of the more soluble fluorosilicates. To determine how the phosphonate acid/hydrofluoric acid systems work using various concentrations of hydrochloric acid, tests were conducted to determine the reaction rate of these acids with quartz and clays. The results are presented in FIGS. 4 and 5. The concentration of the HY

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weight). As shown in FIG. 4, when the hydrochloric acid concentration increases, the reaction rate and the solubility of quartz increases. However, with clays, as seen in FIG. 5, only in the first 15 minutes did the solubility increase proportionately to the hydrochloric acid strength. The solubility then stabilized with low amplitude oscillations similar to those of FIG. 2 without using hydrochloric acid. As shown in FIG. 6, the same results were obtained using liquid hydrofluoric acid instead of ammonium bifluoride. The concentration of the HY acid used was 3% by volume (3.8-4.0% by weight) of the total solution.

As a result of these tests, it was concluded that the main mechanism for retarding the reaction rate and limiting the solubility of clays was either physical and/or chemical adsorption. Phosphonates adsorb to the rock disregarding the electrostatic charge of the rock surface. Up to ten gallons of the phosphonate acids can be adsorbed and fully coated on one cubic meter of rock. Physical adsorption depends mainly on the surface area of the rock. Therefore, in a sandstone formation, phosphonate will adsorb preferentially to the clays. Table 4 gives some idea of the relative surface area of various mineral materials. As can be seen, clays have a much higher surface area, therefore more of the phosphonates will adsorb to the clay materials.

TABLE 4

Material	Formula	Charge @ pH <1	Surface Area
Sand	SiO ₂	+	183 sq. cm/g
Silica Flour	SiO ₂	+	3770 sq. cm/g
Montmorillonite	Al ₄ (OH) ₄ Si ₈ O ₂₀	-	750 sq. m/g
Kaolinite	Al ₄ (OH) ₄ Si ₄ O ₁₀	+	22 sq. m/g
Feldspar	KAl Si ₃ O ₈	+	29 sq. m/g
Illite	KAl ₂ (AlSi ₃ O ₁₀)(OH) ₂	+	113 sq. m/g
Chlorite	(Fe,Mg) ₂ Al ₂ (AlSi ₃ O ₁₀)(OH) ₂	+	29 sq. m/g
Oligoclase	90% NaAlSi ₃ O ₈ + 10% CaAlSi ₂ O ₈	+	29 sq. m/g

Besides physical adsorption, chemical adsorption is also possible with clays or silts that have a higher content of calcium, iron or aluminum. Because reactivity increases proportionately to the surface area/volume ratios, solubility tests were performed using kaolinite instead of bentonite. The objective was to verify if phosphonates could adsorb faster than the acid could dissolve the clays. These test results are presented in FIG. 7 which show lower reaction rates and solubility for the phosphonate/hydrofluoric acid mixtures. Two more tests were also conducted using carbonate chips instead of kaolinite with equivalent results, indicating that retardation and solubility limitations are possible even with fast dissolving minerals. The slow reac-

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Similar solubility results were obtained when presoaking the clays in either hydrochloric acid and 0.6% HY acid by volume (0.8% by weight of solution) or plain 1% HY acid by volume (1.4% by weight) and then treating the clays with conventional hydrofluoric acid systems. This procedure is not recommended by itself, however, for two reasons. First, it cannot be guaranteed that the preflush and the main acid will flow through the same channels within the formation. Second, the system loses some of the suspending and dispersing properties provided by the phosphonate in the acid systems.

Dynamic solubility tests were performed to determine the optimum concentration of each phosphonate acid system. The results are shown in FIG. 8. It can be seen from FIG. 8, that to achieve a 50% reduction in solubility, concentrations between 0.25 to 0.6% HY acid by volume of the total solution (0.3%-0.8% by weight) are required, without regard to the hydrochloric acid concentration and the source of the hydrofluoric acid used. Moreover, the concentration of the phosphonate is directly proportional to the concentration of hydrofluoric acid to obtain the same solubility performance. In other words, for a 50% solubility of clay using 3% hydrofluoric acid by weight, around 0.6% by volume (0.8% by weight) of the HY acid is required (i.e. 12 gals/1000 gals

of a 50% strength HY acid). For 1.5% hydrofluoric acid by weight, only 0.3% HY acid by volume (0.4% by weight) is required.

Slightly higher concentrations are required when HZ acid is used and even higher concentrations when HV acids or mixtures thereof are used. Depending on the concentration of the HY acid, the HY acid could limit smectite or equivalent size clay solubility to a range within 20 to 70%. This is shown by the curve using only HY acid in combination with hydrochloric and hydrofluoric acid. However, to achieve equivalent solubility limitations with finer clays, such as kaolinite, higher concentrations are required. Table 5 shows the solubility of kaolinite after 10 minutes using various concentrations of HY acid and hydrochloric/hydrofluoric acid mixtures.

TABLE 5*

Acid	10 MINUTES SOLUBILITY %						
	0	HY 4 GPT	HY 8 GPT	HY 12 GPT	HY 24 GPT	HY 40 GPT	HY 60 GPT
7.5:1.5 HCl:HF	82	66	64	63	61	55	49
12:3 HCl:HF	96	89	88	87	86	85	54

*GPT indicates gal/1000 gals using 50% strength HY acid.

tion rate with carbonates is very important because calcium ions readily form insoluble precipitates with silicates and

Because these tests do not exactly replicate matrix solubility in formation cores where there is much less material available for surface reaction, it was concluded that consid-

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by volume of HY acid (0.4%–5.8% by weight) is all that is required. However, if the amount of small clays is higher than 10%, HY acid can be added to a hydrochloric acid preflush as well.

The prior art methods of using cationic surfactants to retard the acid reaction rate oftentimes results in damage to the formation. This is due to the surfactant's oil wetting properties which are hard to revert, thus affecting future production rates of oil and gas from the well. It was found that clay samples which were treated with a hydrochloric/hydrofluoric and HY acid mixture agglomerated in toluene while they dispersed readily in methanol. This indicated that the phosphonate acid mixtures made a water wet surface for the clay formations so that the production of oil and gas would not be detrimentally affected.

Another major benefit of the phosphonates used in the acid systems is their ability to deflocculate and disperse colloidal particles. Phosphonates are able to suspend these particles over extended periods of time. This is due to their negative charge and surface adsorption. Kaolin clay slurries are completely deflocculated by phosphonates.

Phosphonates also keep large amounts of scalant in solution at very low concentrations. This phenomenon is known as "threshold effect." This threshold inhibition caused by the

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4) A visual examination was conducted and pH was determined for each acid mixture.

5) An additional equivalent concentration of 1000 pounds Na_2CO_3 per 1000 gallons of available acid was added to each mixture and allowed to react.

6) The procedure of step 4 was repeated.

7) The precipitate and undissolved solids were then filtered, washed with distilled water, dried and weighed.

The results of these tests are presented in Table 6. As can be seen, no precipitate was formed when using the HY and HV acids without hydrochloric acid. When using HY and HV acid in this way, a minimum amount of 1% HY acid by volume (1.4% by weight) must be used, with the amount of HV acid being 2 or 3 times the amount of HY acid used. For example, a suitable formulation would be 2% by volume (2.6% by weight) HY acid+6% by volume (7.8% by weight) HV acid+3% by weight hydrofluoric acid. In the examples of Table 6, the concentration of HY acid was 3% by volume (3.8–3.9% by weight). The concentrations of HV and HZ acid were 9% and 9% by volume (13.5% and 10.9% by weight), respectively.

TABLE 6

	Clay Acid	RHF ACID	12:3 HCl:HF	3% HY + 3% HF + 9% HCl	3% HY + 3HF + 9% HV	3% HY + 3HF + 9% HZ
Step 1						
pH	0.5	0.5	1.1	1.9	2.6	2.6
ppt	NONE	NONE	NONE	NONE	NONE	YES
Step 3						
pH	5.0	0.9	1.4	2.2	4.4	N/A
ppt	YES	NONE	CLOUDY	NONE	NONE	N/A
Step 5						
pH	7.8	7.4	2.1	3.5	7.6	N/A
ppt	YES	YES	YES	YES	NONE	N/A

phosphonates depends on conditions such as the type of scalant, fluid composition, saturation level, temperature, pH and the type of phosphonate used. Brine tests were conducted to evaluate the possible formation of precipitates under acidizing conditions found in the oil field. To conduct these tests, various brines were prepared using 2% KCl, 2% NaCl, 2% CaCl_2 and 2% MgCl_2 by weight in distilled water. A reaction test was then conducted with various acids using the following procedure.

- 1) Each acid mixture was placed into a plastic container and mixed with an equal volume of the above-described brine.
- 2) A visual examination was conducted and pH was determined on each sample after 1 hour at 75° F.
- 3) An equivalent concentration of Na_2CO_3 (1000 pounds per 1000 gallons of available acid) was added to each acid mixture and allowed to react.

Because the above test did not include aluminum or silicates, which are substances reclaimed from clay and quartz dissolution processes, the following tests were performed to evaluate solubility and precipitate inhibition of various acid systems. A brine was prepared with 100 ppm Ca, 100 ppm HCO_3 , 40 ppm Mg and 40 ppm Al in tap water. A reaction was then conducted with various acids using the following procedure.

- 1) Each acid mixture was placed in a plastic container mixed with an equal volume of the above described brine (50 ml+50 ml) and stirred for 5 minutes.
- 2) A visual examination was conducted.
- 3) One ml of sodium silicate solution (2900 ppm of SiO_2) was added in gradual steps after an elapsed time of one hour.

The results of these tests are presented in Table 7. From these results it can be seen that under a low pH environment, the phosphonates do inhibit the precipitation of silicates.

TABLE 7*

ACID SYSTEM	1 ML S. SILICATE SOLUTION	2 ML S. SILICATE SOLUTION	3 ML S. SILICATE SOLUTION
12:3 HCl:HF	NO PRECIPITATE	NO PRECIPITATE	PRECIPITATE

TABLE 7*-continued

ACID SYSTEM	1 ML S. SILICATE SOLUTION	2 ML S. SILICATE SOLUTION	3 ML S. SILICATE SOLUTION
12:3 HCL:HF + 12 GPT HY	NO PRECIPITATE	NO PRECIPITATE	SLIGHTLY CLOUDY
RHF ACID	SLIGHT PRECIPITATE	PRECIPITATE	PRECIPITATE
CLAY ACID	SLIGHTLY CLOUDY	PRECIPITATE	PRECIPITATE
RMS ACID	PRECIPITATE	PRECIPITATE	PRECIPITATE

*GPT indicates gal/1000 gals using 50% strength HY acid.

When using the phosphonate compounds in sandstone acidizing, the source of hydrofluoric acid could be either liquid hydrofluoric acid, ammonium bifluoride or ammonium fluoride. When ammonium bifluoride or ammonium fluoride are used as a source of hydrofluoric acid, enough acid should be present to completely hydrolyze the ammonium bifluoride or ammonium fluoride. For example, for a 3% by weight hydrofluoric acid solution prepared by hydrolyzing ammonium bifluoride, 3% by volume (3.8% by weight) HY acid+9% by volume (13.5% by weight) HV acid with no hydrochloric acid should be used.

The concentration of phosphonates or their mixtures should be kept just to the optimum point as established by solubility tests, such as those performed and shown in FIG. 8. From FIG. 8, the optimum point would be just to the left of the point where the curve begins to level out. Additional phosphonate beyond this amount could jeopardize the threshold effect discussed previously, with possible precipitation of insoluble salts. The threshold effect is unpredictable and may be caused by one or a combination of the phosphonate concentration, concentration in excess of 40,000 ppm Ca ions, increases in concentrations of other cations, and by neutralization or increase of the pH of the solution.

Phosphonates are strongly anionic materials with each RPO_3H_2 linkage inhibiting precipitation of up to 10,000 molecules of scalant. Their affinity with alkaline metal is very strong so that Ca, Na and NH_4 ions complex with the phosphonate leaving very little to form as precipitates with fluorides or fluorosilicates at the initial stages of the acid's reaction. Although the use of ammonium bifluoride is preferred in prior art acidizing treatments, ammonium bifluoride adds cations that combine with the phosphonates, inhibiting to a minor extent the beneficial effect of the phosphonate material in complexing with the formation ions. Therefore, liquid hydrofluoric acid is preferably used in forming the acidizing solutions.

Because the phosphonate acid systems of the invention do not react completely with clays, swelling of smectite may be a potential problem. Therefore, all phosphonate acid mixtures discussed were checked for compatibility with clay stabilizing agents, such as dimethyldiallyl ammonium chloride and polymethyldiallyl ammonium chloride. The use of clay stabilizing agents is only important when smectite is present in the formation. Preferably the clay stabilizers are added as a preflush and with the main acid. Suitable clay stabilizing agents are available from BJ Services, Inc., and marketed under the name "CLAYTROL". During tests con-

ducted, concentrations of the clay stabilizing agent were used from 1-5 gallons per thousand gallons of treatment solution with no visual deterioration or detrimental performance with regard to the precipitation, clay swelling and acid retardation. The test procedure was as follows. Ten grams of bentonite were soaked for 5 minutes at room temperature in 40 ml of various acid solutions. The clays were then filtered and dropped in 30 ml of water. Initial and final clay volumes were visually measured. The results are presented in Table 8.

TABLE 8*

TREATING FLUID	CLAYTROL INTERNATIONAL	VOLUME CHANGE
WATER	0	2.5
WATER	2	1.8
12:3 HCL:HF	0	0.6
12:3 HCL:HF	2	0.3
12:3 HCL:HF + 12 GPT HY	0	0.8
12:3 HCL:HF + 12 GPT HY	2	0.3

*GPT indicates gal/1000 gals using 50% strength HY acid.

The phosphonate acids were also tested with iron sequestering agents to see if there were any compatibility problems. Specifically, citric acid, nitrilotriacetic acid (NTA), ethylenediaminetetraacetic acid (EDTA), acetic acid, lactic acid, isoascorbic acid and their ammonium salts were used as the iron control additives with no observed compatibility problems. When treating formations, the concentration of the iron sequestering agent should be enough to sequester 3000 ppm iron, preferably as both a pre-flush and with the main acid. Without the iron sequestering agent, impermeant permeability of the formation may result due to iron phosphonate precipitates.

The acids of the invention were also tested with different corrosion inhibitors. Although some corrosion inhibitors produced small amounts of sludge due to their cationic charge, the corrosion inhibitor "CI-9" available from BJ Services, Inc., produced adequate protection without sludge formation. After several additives and various mixtures were tried to boost inhibition performance, a mixture of 75% of CI-9 and 25% HZ acid by volume, herein referred to as "CI-9/HZ" was found to produce the best results. Corrosion inhibition of the CI-9/HZ is shown in Table 9 using various acid systems. The results are not surprising due to the fact that phosphonates are normally used to boost metal protection in various corrosion inhibitor formulations.

TABLE 9*

ACID SYSTEM	TEMP °F.	CI-9/HZ GPT	PROTECTION TIME (HR.)	Weight Lost (LB./sq ft)
15% HCl	180	2	8	0.028

TABLE 9*-continued

ACID SYSTEM	TEMP °F.	CL-9/HZ GPT	PROTECTION TIME (HR.)	Weight Lost (L.B./sq ft)
12:3 HCl:HF	180	5	16	0.055
7.5:1.5 HCl:HF + 6 GPT HY	180	3	16	0.048
12:3 HCl:HF + 12 GPT HY	140	3	16	0.030
12:3 HCl:HF + 12 GPT HY	160	4	16	0.047
12:3 HCl:HF + 12 GPT HY	180	6	16	0.040

*GPT indicates gal/1000 gals using 50% strength HY acid.

Compatibility and emulsion tests were performed with the phosphonate materials with diesel, light oils and heavy crude. The de-emulsifiers "NE-10", "NE-32" and "NE-18", available from BJ Services, Inc., produced good results. In addition other formulations were checked for compatibility with ethylene glycol monobutyl ether, "INFLO-100", "S-400" and "PARAVAN", also available from BJ Services, Inc., without any problems. Table 10 gives the results of emulsion tests carried out using the emulsion breaker and preventer NE-10. The tests were conducted in the following manner.

- 1) The acids to be tested were prepared with or without the non-emulsifier.
- 2) The acids and the oil were then mixed in a blender in equal volumes at high speed to create an emulsion.
- 3) The emulsion was quickly poured into a graduated cylinder and timing was commenced simultaneously.
- 4) The separation of oil and/or aqueous phases from the emulsion were observed at different time intervals and the results were recorded as percentage breakout.

should be used to maintain the pH of the solution and to hydrolyze any ammonium fluoride or bifluoride if it is used.

An example where other acids may be used besides the standard hydrochloric/hydrofluoric combination is where high temperatures are encountered and when it is difficult to protect the well casing from the corrosive effects of the hydrochloric acid. Here the organic acids, such as acetic and formic acids, can be used in place of the hydrochloric acid. Formulations containing 5%-10% by weight acetic acid and 1.5-3% by weight hydrofluoric acid were used to treat quartz with a mixture of HY and HV acids in a ratio of 1:2 by weight, respectively. The concentration of HY acid ranged between about 1-2% by weight with the amount of HV acid ranging between about 2-4% by weight. These formulations showed improved quartz solubility over conventional hydrochloric/hydrofluoric acid systems.

In treating most siliceous or sandstone formations, where possible, hydrochloric acid should be used as a preflush prior to the acid treatment. The concentration of the hydrochloric acid should be between 3-8% by weight of the preflush solution. Where high proportions of kaolinite and feldspar

TABLE 10*

ACID SYSTEM	1 min.*	2 min.*	4 min.*	6 min.*	8 min.*	10 min.*	15 min.*	30 min.*	Surface Tension Dyne/cm
12:3 HCl:HF W/O NE-10	0	0	0	0	0	0	0	0	65
12:3 HCl:HF 2 GPT NE-10	53	55	55	57	57	59	62	81	36
Clay acid W/O NE-10	13	13	14	14	16	16	20	69	37
Clay acid 2 GPT NE-10	69	72	74	75	77	79	83	90	33
RMS acid W/O NE-10	55	56	57	60	63	65	67	79	67
RMS acid 2 GPT NE-10	59	63	64	65	67	67	69	85	33
12:3 + 12 GPT HY*	32	35	37	38	40	41	49	59	48
12:3 + 12 GPT HY*	47	49	53	58	62	64	75	90	33

*GPT indicates gal/1000 gal.

* Percentage breakout measured as the volume broken out per total volume used to make the emulsion multiplied by 100%.

* HY acid at 50% strength.

From Table 10 it is seen that better results are achieved with HY acid than when using conventional hydrochloric/hydrofluoric acid systems and that HY acid is equivalent to other retarded acid systems.

Depending on the particular application, other mineral and organic acids or mixtures thereof can also be used with the phosphonate compounds with or without hydrofluoric acid. These acids include hydrochloric, chloroacetic, sulfuric, sulfamic, nitric, acetic, lactic, fumaric and formic acid. Final concentrations may vary but will typically range

are present, i.e. greater than 20%, the use of HY acid is recommended in the preflush in an amount of about 0.2-0.6% by volume (0.2-0.8% by weight) of the preflush solution, with about 0.25% by volume (0.3% by weight) being preferred. The amount of preflush should be around 7 pore volumes for the first foot of formation.

The main phosphonate acid systems used in treating the formation may be formulated merely by adding the phosphonate compounds of the invention to standard hydrofluoric acid mixtures used in the treatment of sandstone. The optimal concentration of the phosphonate used should be

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samples of the formation to be treated. The amount of phosphonate used could vary from about 0.1% by weight of the total solution up to as much as 15% by weight, depending on whether hydrochloric acid is also used. However, concentrations will normally be between about 0.3-2.0% by weight of the solution when using hydrochloric/hydrofluoric acid. Stronger hydrochloric/hydrofluoric acid mixtures can also be used with the phosphonate acid systems than was used previously with conventional acidizing treatments. Between 0.25-15% by weight of the hydrofluoric acid can be used in the phosphonate acid systems. However, the ratio of hydrochloric acid to hydrofluoric acid should be kept between 3:1 to 4:1 at these higher concentrations.

Once the phosphonate acid has been introduced into the formation, it is preferable not to flow the wells immediately after treatment. Better results are obtained with soaking times of between 1 and 6 hours. A hydrochloric or ammonium chloride afterflush may then be used. The afterflush should be between 7 to 15 pore volumes for the first foot of formation.

To illustrate the effectiveness of the phosphonate acid systems, core flow tests were conducted using various acid treatments. Due to equipment limitations, cores were not saturated using vacuum, but nitrogen was used to push the fluids, causing fluctuation in the liquids rate due to the presence of the gas. Field cores and Berea cores varying in length from 2 to 14 inches and from 1 to 2 inches in diameter were used having permeabilities ranging between 0.5 to 3 md. From all core flow tests carried out using phosphonate acids, the ones with 4 to 6 hours shut in time produced better results. Considering that clay solubility is limited in these acids, the permeability improvement could only be derived from slow dissolution of the quartz portion of the matrix. The normal volume of acid used in the core flow test was around 10 to 20 pore volumes. Compressive strength was measured in a few tests before and after acid flow to check the matrix integrity. An average reduction in the compressive strength of between 5 to 10% was observed. Table 11 shows results obtained in 5 core flow tests performed on 14 inch long Berea Sandstone cores of 2 inches in diameter of various acid systems.

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There are several advantages to the acid systems of the invention. Because the acids retard the reaction of hydrofluoric acid with silicates, it is not necessary to hydrolyze ammonium bifluoride in order to slow down the reaction. Thus, liquid hydrofluoric acid can be used in preparing the main acid. The retarded reaction rate with the silicates also allows the hydrofluoric acid to react more readily with quartz or silica while leaving the cementitious or clay components of the formation intact so that the integrity of the formation is not compromised. The phosphonates also have the ability to maintain alumini and silicate complexes in suspension which would otherwise precipitate out and clog the pore spaces of the formation. The phosphonate acids of the invention also leave the formation water wet so that production is not adversely affected after being treated.

The phosphonate acid systems also have a variety of applications in addition to normal matrix acidizing. Although they are of particular use in sandstone formations, they could also be used in the acidizing of carbonate formations. They can be used for remedial workovers of oil and gas wells to remove sand deposits and keep silicates in suspension. The presence of the phosphonate compounds within the well also aid in reducing scale buildup. The phosphonate acids can be gelled using viscosifiers, such as xanthan gum, for either friction reduction or to gel the acid to improve acid diversion or distribution into the rock's matrix. It is also within the scope of the present invention to incorporate phosphonate acids into acid fracturing treatments, especially in low permeability (short frac) sandstone formations. In such applications the phosphonate acid systems would be injected into the well at a high enough pressure to form fractures or open existing fractures. Channels are formed by the dissolving of material within the fractured formation with the channels remaining open after the pressure is reduced.

Although the invention has been described with reference to a specific embodiment, this description is not meant to be construed in a limiting sense. Various modifications of the disclosed embodiment as well as alternative embodiments of the invention will become apparent to persons skilled in the art upon reference to the description of the invention. It is

TABLE 11*

Pre Flush	Main Acid	After Flush	Overall Pre-Job Perm To Diesel	Overall Post-Job Perm to diesel	Last 2" Pre-Job Perm To Diesel	Last 2" Post-Job Perm To Dicsel	Overall Flow Ratio	Last 2" Flow Ratio
7.5% HCl	7.5:1.5HCl:HF	3% Am. Cl	35.4	65.0	64	93	1.83	1.45
7.5% HCl	RHF ACID	3% Am. Cl	17.5	7.2	19.6	8.2	0.41	0.41
7.5% HCl	CLAY ACID	3% Am. Cl	30.5	30.4	26.5	22.6	1.0	0.85
7.5% HCl	7.5:1.5 HCl:HF + 6 GPT HY	3% Am. Cl	42.0	144.0	17.9	25.22	3.42	1.46
7.5% HCl	7.5:1.5 HCl:HF + 6 GPT HY	3% Am. Cl	5.5	8.8	7.0	7.0	1.60	1.0
7.5% HCl	24:6 HCl:HF + 18 GPT HY	3% Am. Cl	8.8	58.0	7.0	84.0	6.60	12.0
7.5% HCl	12:3 HCl:HF + 12 GPT HY no Claytrol	3% Am. Cl	33	61.5	36	55	1.86	1.52

*GPT indicates gal/1000 gals using 50% strength HY acid.

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any such modifications or embodiments that fall within the true scope of the invention.

We claim:

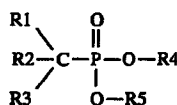
1. A method of treating a siliceous formation to increase the formation's permeability, comprising the steps of:

preparing a treatment solution containing an amount of a phosphonate compound and a compound capable of dissolving siliceous materials of the formation; and then

contacting the siliceous formation with the solution so that siliceous materials within the formation are dissolved, the phosphonate compound adsorbing to non-silica materials of the formation so that the rate of reaction of the non-silica materials with said compound capable of dissolving siliceous materials is effectively reduced and silica materials of the formation are more readily dissolved, thereby increasing the formation's permeability.

2. The method of claim 1, wherein:

the phosphonate compound has the formula:



where R1, R2, and R3 are each selected from a group consisting of hydrogen, alkyl, aryl, phosphonates, phosphates, acyl, amine, hydroxy and carboxyl groups; and R4 and R5 are each selected from a group consisting of hydrogen, sodium, potassium, ammonium and organic radicals.

3. The method of claim 1, wherein:

the phosphonate compound is selected from a group consisting of 1-hydroxyethylidene-1,1-diphosphonic acid, diethylene triamine penta (methylene phosphonic acid), and aminotri (methylene phosphonic acid).

4. The method of claim 1, wherein:

the compound capable of dissolving siliceous materials is hydrofluoric acid.

5. The method of claim 4, wherein:

the hydrofluoric acid is provided by hydrolyzing a fluoride salt in the treatment solution.

6. The method of claim 1, wherein:

the amount of the phosphonate compound is between about 0.1-15% by weight of the total solution.

7. The method of claim 4, wherein:

the treatment solution further contains hydrochloric acid.

8. The method of claim 4, wherein:

the amount of hydrofluoric acid is between about 0.25-15% by weight of the treatment solution.

9. The method of claim 7, wherein:

the ratio of hydrochloric acid to hydrofluoric acid is between about 3:1-5:1 by weight.

10. The method of claim 1, further comprising the step of:

contacting the siliceous formation with a hydrochloric acid solution prior to contacting the formation with the treatment solution.

11. The method of claim 10, wherein:

the hydrochloric acid solution has a hydrochloric acid concentration of between about 3-8% by weight of the total hydrochloric acid solution.

12. The method of claim 10, wherein:

the hydrochloric acid solution also contains a phosphonic acid in an amount of between about 0.2-0.8% by

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13. The method of claim 1, wherein:

the treatment solution contains a one or two carbon organic acid.

14. The method of claim 1, wherein:

the treatment solution contains an acid selected from the group consisting of hydrochloric, chloroacetic, sulfuric, sulfamic, nitric, acetic, lactic, fumaric and formic acid.

15. A method of stimulating production in a siliceous subterranean formation of an oil or gas well comprising the steps of:

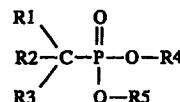
preparing a treatment solution containing an effective amount of a phosphonate compound capable of adsorbing to silicate materials of the formation and a source of hydrofluoric acid;

introducing the solution into the well; and

contacting the formation with the treatment solution so that siliceous materials of the formation are dissolved, the phosphonate compound adsorbing to silicate materials of the formation so that the rate of reaction of the silicate materials with the hydrofluoric acid is effectively reduced and silica materials of the formation are more readily dissolved, thereby increasing the permeability of the formation.

16. The method of claim 15, wherein:

the phosphonate compound has the formula:



where R1, R2, and R3 are each selected from a group consisting of hydrogen, alkyl, aryl, phosphonates, phosphates, acyl, amine, hydroxy and carboxyl; and R4 and R5 are each selected from a group consisting of hydrogen, sodium, potassium, ammonium and organic radicals.

17. The method of claim 15, wherein:

the phosphonate compound is selected from a group consisting of 1-hydroxyethylidene-1,1-diphosphonic acid, diethylene triamine penta (methylene phosphonic acid), and aminotri (methylene phosphonic acid).

18. The method of claim 15, wherein:

the treatment solution is introduced into the well at high pressure to cause fractures within the formation.

19. The method of claim 15, wherein:

the hydrofluoric acid is provided by hydrolyzing a fluoride salt in the treatment solution.

20. The method of claim 15, wherein:

the amount of the phosphonate compound is between about 0.1-15% by weight of the total solution.

21. The method of claim 15, wherein:

the solution further contains hydrochloric acid.

22. The method of claim 15, wherein:

the amount of hydrofluoric acid is between about 0.25-15% by weight of the treatment solution.

23. The method of claim 21, wherein:

the ratio of hydrochloric acid to hydrofluoric acid is between about 3:1-5:1 by weight.

24. The method of claim 15, further comprising:

contacting the siliceous formation with a hydrochloric acid solution prior to contacting the formation with the treatment solution.

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the hydrochloric acid solution has a concentration of hydrochloric acid between about 3–8% by weight of the total hydrochloric acid solution.

26. The method of claim 24, wherein:

the hydrochloric acid solution also contains a phosphonic acid in an amount of between about 0.2–0.8% by weight of the hydrochloric acid.

27. A method of treating a siliceous formation of an oil or gas well at temperatures in excess of 150° F. to increase the production of oil or gas from the formation, the method comprising the steps of:

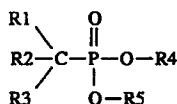
preparing an aqueous treatment solution containing about 0.1–15% by weight of the treatment solution of a phosphonate compound and about 0.25–15% by weight of the treatment solution of hydrofluoric acid;

introducing the treatment solution into the well; and

contacting the siliceous formation with the treatment solution so that siliceous materials within the formation are dissolved, the phosphonate compound adsorbing to silicate materials of the formation so that the rate of reaction of the silicate materials with the hydrofluoric acid is effectively reduced and silica materials of the formation are more readily dissolved, thereby increasing the permeability of the formation.

28. The method of claim 27, wherein:

the phosphonate compound has the formula:



where R1, R2, and R3 are each selected from a group consisting of hydrogen, alkyl, aryl, phosphonates, phosphates, acyl, amine, hydroxy and carboxyl groups; and R4 and R5 are each selected from a group consisting of hydrogen, sodium, potassium, ammonium and organic radicals.

29. The method of claim 27, wherein:

the phosphonate compound is selected from a group consisting of 1-hydroxethylidene-1,1-diphosphonic acid, diethylene triamine penta (methylene phosphonic acid), and aminotri (methylene phosphonic acid).

30. The method of claim 27, wherein:

the treatment solution is introduced into the well at high pressure to cause fractures within the formation.

31. The method of claim 27, wherein:

the hydrofluoric acid is provided by hydrolyzing a fluoride salt in the treatment solution.

32. The method of claim 27, wherein:

the treatment solution further contains hydrochloric acid.

33. The method of claim 27, wherein:

the treatment solution further contains a one or two carbon organic acid.

34. The method of claim 27, wherein:

the treatment solution further contains an acid selected from the group consisting of hydrochloric, chloroacetic, sulfuric, sulfamic, nitric, acetic, lactic, fumaric and formic acid.

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35. The method of claim 32, wherein:

the ratio of hydrochloric acid to hydrofluoric acid is between about 3:1–5:1 by weight.

36. The method of claim 27, further comprising:

contacting the siliceous formation with a hydrochloric acid solution prior to contacting the formation with the treatment solution.

37. The method of claim 36, wherein:

the hydrochloric acid solution has a hydrochloric acid concentration of between about 3–8% by weight of the total hydrochloric acid solution.

38. The method of claim 36, wherein:

the hydrochloric acid solution also contains a phosphonic acid in an amount of between about 0.2–0.8% by weight of the hydrochloric acid.

39. A composition for treating a siliceous formation to increase the permeability of the formation, the composition comprising:

a solution containing an effective amount of a phosphonate compound and hydrofluoric acid, the phosphonate compound being capable of adsorbing to silicate materials of the formation so that the rate of reaction of the silicate materials with the hydrofluoric acid is effectively reduced to allow silica material of the formation to be more readily dissolved, thereby increasing the permeability of the formation.

40. A method of treating a siliceous formation to increase the formation's permeability, comprising the steps of:

preparing a treatment solution containing an amount of a phosphonate compound and a compound capable of dissolving siliceous materials of the formation; and then

contacting the siliceous formation with the solution so that siliceous materials within the formation are dissolved, thereby increasing the formation's permeability; and wherein

the phosphonate compound is selected from a group consisting of 1-hydroxethylidene-1,1-diphosphonic acid, diethylene triamine penta (methylene phosphonic acid), and aminotri (methylene phosphonic acid).

41. A method of treating a siliceous formation to increase the formation's permeability, comprising the steps of:

preparing a treatment solution containing an amount of a phosphonate compound, hydrofluoric acid and hydrochloric acid; and then

contacting the siliceous formation with the solution so that siliceous materials within the formation are dissolved, thereby increasing the formation's permeability.

42. The method of claim 41, wherein:

the ratio of hydrochloric acid to hydrofluoric acid is between about 3:1–5:1 by weight.