

Brigard & Castr
Abogados

Apartado 3692

Cra. 7 16-56
Bogotá - Colombia S.A.

Tel. Conn. 3802200
Tel./Fax: (57.1) 2827976
(57.1) 3802700

E.Mail:bricas@brigardycastro.com.co

As: 88.884

SUPERINTENDENCIA DE INDUSTRIA Y COM
DIVISION DE NUEVAS CREACIONES
E. S. D.

Radicacion : 02076282 00000004
Fecha (RRD): 2004-07-16 17:36:42
Tramite : 000 PATENTES D 1 REGISTRO/ 538 PETICION
Dependencia: 8128 DIVISION DE NUEVAS CREACIONES

Folios: 2

REF.: Expediente No. 02 076 282 solicitud de Patente a nombre de
INTEVEP, S.A.

Titulada: FLUIDO DE PERFORACION ESPUMABLE MEJORADO DE
POLIMERO

RAMIRO CASTRO DUQUE, vecino de Bogotá, portador de la tarjeta profesional No. 1003 del Consejo Superior de la Judicatura, obrando como apoderado de la Sociedad INTEVEP, S.A., según lo acredita el documento de poder presentado en la Secretaría General, de acuerdo con el Artículo 44 de la Decisión 486 de la Comisión de la Comunidad Andina, me permito solicitar que se examine si la invención contenida en la solicitud en referencia es patentable.

De acuerdo con lo anterior, me permito anexar el recibo oficial de caja No. 04-42,143 por valor de \$353.000.

Señor Superintendente,

RAMIRO CASTRO DUQUE
C.C. No. 170.322 de Bogotá
Código 340
T.P. No.1003 del C.S.J.
Cra 7 No. 16-56 Piso 9

16 de Julio de 2004
CHP/MEV/aac

Por do IQ

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Radicación : 88076282 88888884 Folios: 2
Fecha (AMD): 2004-07-16 17:36:52
Trámite : 002 PATENTES D / REGISTRO/ 538 PETICION
Dependencia: 8888 DIVISION DE NUEVAS CREACIONES

NIT : 800176089-2

RECIBO OFICIAL DE CAJA : 04 - 42,143
FECHA : MAYO 27 DE 2004

***** CONSIGNACION *****

DEPOSITANTE	TIPO PAGO	BANCO	CUENTA	No. PAGO	FECHA PGO	Vr. PAGO
BRIGARD & CASTRO LTDA	CONSIGNACION	BANCO POPULAR	050-00110-6	21734277	27/05/2004	16,673,100.00

***** C O N C E P T O *****

CANT.	RENTISTICO	CONCEPTO	TOTAL CONCEPTO
1	50005-01-01 SOLICITUDES	85 EXAMEN DE PATENTABILIDAD DE INVEN	353,000.00
		TOTAL :	\$ 353,000.00

SOM: TRESCIENTOS CINCUENTA Y TRES MIL PESOS

RESPONSABLE : _____

RECIBO DE CAJA APLICADO AL EXPEDIENTE No. _____

86

87
/

DIVISION DE NUEVAS CREACIONES

RADICACIÓN EXPEDIENTE No. 02- 76282

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

EN LA GACETA DE PROPIEDAD INDUSTRIAL No 540, DE FECHA 31 DE MAYO DE 2004, EL

TERMINO HABIL SEÑALADO POR LA LEY EXPIRA EL 30 DE AGOSTO 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**

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

2020

Bogotá, D. C., 24 de Marzo de 2006

Doctor

RAMIRO CASTRO DUQUE

Representante INTEVEP S.A.

ASUNTO

Radicación No. **02 -76282**
Trámite **002**
Evento **001**
Actuación **430**
Oficio **3759**
Folios **053**

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 5 a 18 de la solicitud en estudio.
- b) Para el presente estudio se tendrán en cuenta los dibujos comprendidos en los folios 23 a 25 de la solicitud en estudio.
- c) Para el presente estudio se tendrá en cuenta el capítulo reivindicatorio que comprende 21 reivindicaciones en los folios 19 a 21 de la solicitud en estudio.
- d) Conforme lo establece los artículos 9, 10 y 11 de la decisión 486 de la Comisión de la Comunidad Andina, la presente solicitud en estudio fue presentada el 28 de agosto de 2002, y en el momento de la radicación SI se reclamo prioridad de la primera solicitud presentada en Estados Unidos US 09/941508

2) Objeto de la Invención

- a) Las reivindicaciones 1 a 21 de la solicitud en estudio se refieren a un fluido de perforación espumable que comprende un solvente acuoso; un tensioactivo; y un polisacárido.
- b) El anterior producto busca proporcionar un mejor fluido de perforación
- c) Según la Clasificación Internacional de Patentes, la codificación para esta solicitud corresponde a C 09 K 7/02

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:

- i) Los dibujos son ilegibles. Además de eso trae los textos en Inglés. Deben anexarse unos nuevos en original, en tinta negra indeleble y con todos los textos en idioma español.
- ii) La redacción de la solicitud es deficiente toda vez que se trata de una mala traducción del documento original. Por ejemplo, el término "espumable" no existe en español. El término "galactomannan" está incorrectamente traducido. La expresión EO no tiene significado técnico válido en español. Etc. En general el documento debe ser revisado por un experto en el arte que haga una correcta traducción del escrito original.
- iii) Muchas de las unidades de medida que se emplean en la presente solicitud, no corresponden a las del sistema Internacional de Unidades, por lo que son inaceptables. Entre ellas se encuentran ppg, cPs, galones, pies y un largo etcétera.

Por lo anterior, la presente solicitud no cumple con el artículo 28 de la Decisión 486. Se deberá enviar un nuevo capítulo completo y correctamente redactado

- 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) Todas las observaciones hechas en el punto de la descripción son también aplicables aquí.
- ii) No se aceptan frases ambiguas como "alrededor de...". Deben eliminarse.

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) Determinación del Estado de la Técnica

El artículo 16 de la Decisión 486 de la Comisión establece:

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

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

Consultadas las bases de datos y los archivos con que cuenta la entidad, especialmente bajo las clasificaciones C 09 K 7/02 y las más cercanas a ellas, se encontró que antes del 28 de agosto 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 fluidos de perforación.

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

Nº	Documento	Título	Fecha de Publicación
D1	WO 95 14066	Method of treating shale and clay in hydrocarbon formation drilling	1995.05.26
D2	WO 00 51922	Transport of solid particles	2000.09.08
D3	US 5 360 558	Slurried polymer foam system and method for the use thereof	1994.11.01

5) Evaluación de los requisitos de patentabilidad

El artículo 14 de la Decisión 486 de la Comisión de la Comunidad Andina establece:

"Los Países Miembros otorgarán patentes para las invenciones, sean de producto o procedimiento, en todos los campos de la tecnología, siempre que sean nuevas tengan nivel inventivo y sean susceptibles de aplicación industrial".

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

a) Evaluación de la novedad y el del Nivel Inventivo

El art. 16 de la Decisión 486 de la Comisión de la Comunidad Andina establece:

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

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

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

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

Los tres documentos enumerados (D1) WO 95 14066, (D2) WO 00 51922 y (D3) US 5 360 558 relacionan composiciones que tienen un solvente acuoso, un tensoactivo y polisacáridos. Como se puede ver es básicamente lo mismo que muestra la actual solicitud. De lo anterior, estos tres documentos afectan directamente la patentabilidad de la presente solicitud.

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	WO 95 14066	1 - 21	Novedad
			Nivel inventivo
D2	WO 00 51922	1 - 21	Novedad
			Nivel inventivo
D3	US 5 360 558	1 - 21	Novedad
			Nivel Inventivo

6) Notificación

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

Notifíquese el presente oficio conforme a lo dispuesto por el numeral 5.2, literal e) del capítulo quinto del título primero de la Circular Única N° 10 de 2001


ALIX CARMENZA CÉSPEDES DE VERGEL
Jefe División de Nuevas Creaciones

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

30-MAR. 2008

Concepto Técnico N°	EXAMINADOR TÉCNICO Código No.	EXAMINADOR JURÍDICO Código No.
469	202003	

2392

PCT

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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6: C09K 7/02, E21B 43/25, C09K 7/08		A1	(11) International Publication Number: WO 95/14066	
			(43) International Publication Date: 26 May 1995 (26.05.95)	
(21) International Application Number: PCT/US94/12820			(81) Designated States: CA, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).	
(22) International Filing Date: 14 November 1994 (14.11.94)				
(30) Priority Data: 08/154,535 19 November 1993 (19.11.93) US				
(71) Applicant: CLEARWATER, INC. (US/US); 5605 Grand Avenue, Pittsburgh, PA 15225 (US).				
(72) Inventors: SMITH, Kevin, W.; 103 Fairway Road, McKersy, PA 15317 (US). THOMAS, Todd, R.; 218 Essex Knoll Drive, Canonsville, PA 15108 (US).				
(74) Agent: KRAYER, William, L.; 241 Merion Drive, Pittsburgh, PA 15228 (US).			Published With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.	
(54) Title: METHOD OF TREATING SHALE AND CLAY IN HYDROCARBON FORMATION DRILLING				
(57) Abstract Swelling and migration of subterranean clay is inhibited during drilling for and stimulation of the production of hydrocarbon fluids, and preparation therefor, by treating said formations with a copolymer of about 5 % to about 50 % of an anionic monomer such as acrylic acid, methacrylic acid, or 2-acrylamido-2-methyl propane sulfonic acid and the balance a cationic monomer selected from dimethyl diallyl ammonium chloride, or acryloxy or methacryloxy ethyl, propyl or 3-methyl butyl trimethyl ammonium chlorides or methosulfates. Permeability damage to the formation is reduced in the presence of the copolymer; it is particularly effective in spite of the presence of a foaming agent.				

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DESCRIPTION**METHOD OF TREATING SHALE AND CLAY IN HYDROCARBON
FORMATION DRILLING****Technical Field**

This invention relates to the drilling of underground formations for the production of oil, gas, and other formation fluids, including water, and particularly to the stabilization of boreholes whether or not to be used for the recovery of formation fluids, as in the case of mining test holes. This invention includes the treatment of subterranean shale and clay to prevent swelling caused by the absorption of water from drilling fluids. It relates particularly to the use of certain polymeric agents for the prevention of swelling of shale and clay in situ by the absorption of water, the consequent adverse effects of the entrance of clay and shale into the drilling system, and the adverse effects of clay and shale sloughing on borehole stability. The polymeric agents we use contain both cationic and anionic monomers. The cationic monomers are typified by dimethyl diallyl ammonium chloride ("DMAAC"), and the anionic monomers are typified by acrylic acid and 2-acrylamido-2-methyl propane sulfonic acid ("AMPS"). The copolymers are shown to be effective for the above described purposes and especially insensitive to shear, while remaining compatible with anionic compounds such as alcohol ether sulfate and alpha olefin sulfonate-based foaming agents.

Background of the Invention

A good description of the problem which this invention addresses in the context of drilling may be found in

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an article by Thomas W. Beihoffer et al in the May 16, 1992 Oil & Gas Journal, page 47 et seq, entitled "Cationic Polymer Drilling Fluid Can Sometimes Replace Oil-based Mud." As stated therein, "(S)hales can become unstable when they react with water in the drilling fluid. These reactive shales contain clays that have been dehydrated over geologic time by overburden pressure. When the formation is exposed, the clays osmotically imbibe water from the drilling fluid. This leads to swelling of the shale, induced stresses, loss of mechanical strength, and shale failure." Shale crumbling into the borehole ("sloughing") can ultimately place a burden on the drill bit which makes it impossible to retrieve.

Salts such as potassium chloride have been widely used in drilling treatments to convert the formation material from the sodium form by ion exchange to, for example, the potassium form which is less vulnerable to swelling; also the use of high concentrations of such potassium salts affects the osmotic balance and tends to inhibit the flow of water away from the high potassium salt concentrations into the shale. However, it is difficult to maintain the required high concentrations of potassium salts in the drilling fluids. In addition, the physical introduction of such salts causes difficulties with the preparation of the viscosifying polymeric materials typically used for drilling. Inorganic salts can also have a harmful effect on the environment if released. While in the above cited Beihoffer et al paper, the use of cationic polymers is suggested as a supplement for the potassium salts in drilling fluids, the authors do not propose the particular polymers we use, which we have found to be especially effective because of their

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resistance to shear and their compatibility with anionic agents, as well as their advantageous charge density.

5 The reader may be interested in "The Separation of Electrolyte Effects From Rheological Effects in Studies of Inhibition of Shales with Natural Moisture Contents" by Baihoffer et al, SPE Paper 18032, which also contains a complete description of the Roll Oven Test referred to below. It is incorporated by reference.

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15 Foaming agents commonly used in air-foam drilling generally tend to be anionic surfactants. Such foaming materials are well known and frequently are ethoxylated and sulfated, such as alcohol ether sulfates. They may be mixed with alpha olefin sulfonates, and commercially may be in solvents, including organic solvents added for freeze resistance. Polymers used in the presence of such surfactants must be compatible with them. Also, the shear forces in air drilling can be particularly high, and any polymeric additive should be able to withstand turbulent flow conditions, i.e. a Reynolds Number of up to about 500,000. Most of the contemporary technology uses acrylamide-based copolymers that shear easily when subjected to such turbulent conditions.

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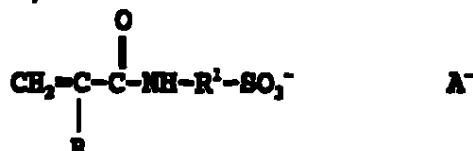
Summary of the Invention

30 We have found that the permeability of subterranean formations may be maintained during drilling, and other contact with aqueous fluids -- that is, shales and clays can be inhibited from swelling, sloughing and retarding the flow of fluids -- by including in

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the drilling or other fluid an effective amount of a polymer including (1) about 50 - 95% of a cationic monomer selected from (A) dimethyl diallyl ammonium chloride having the formula $[\text{CH}_2=\text{CH}-\text{CH}_2]_2\text{N}^+(\text{CH}_3)_2\text{Cl}^-$ ("DMAAC"), (B) an acryloyloxy monomer of the formula $\text{CH}_2=\text{CH}-\text{CO}-\text{R}^1\text{N}^+(\text{CH}_3)_2$, or (C) an acrylamido monomer of the formula $\text{CH}_2=\text{CH}-\text{CONR}^1\text{N}^+(\text{CH}_3)_2$, where R is hydrogen or a methyl group, and R^1 is a connecting linear or branched saturated hydrocarbyl group having from one to about five carbon atoms, such cationic monomers copolymerized with (2) about 5%-50% of acrylic acid, methacrylic acid, or a monomer of a formula



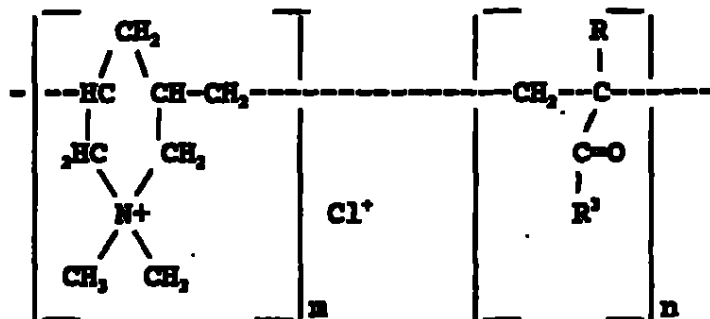
where R and R^1 are as above, and A^- is an anion selected from chloride and methosulfate. Among the anionic comonomers useful in our invention are acrylic acid, 2-acrylamido-2-methyl propyl sulfonic acid ("AMPS"), and methacrylic acid. Useful cationic monomers in addition to DMAAC include methylacryloxy ethyl trimethyl ammonium methosulfate ("METAMS"), acryloxy ethyl trimethyl ammonium methosulfate ("AETAMS"), methylacryloxy ethyl trimethyl ammonium chloride ("METAC"), acryloxy ethyl trimethyl ammonium chloride ("AETAC"), methyl acrylamido propyl trimethyl ammonium chloride ("MAPTAC"), and 3-acrylamido-3-butyl trimethyl ammonium chloride ("AMBTAC"). The copolymers we use are compatible with foaming agents and can withstand highly turbulent flow conditions.

It is known that when DMAAC polymerizes in an aqueous medium such as in the presence of a redox catalyst, it internally cyclizes; thus the DMAAC copolymers we use are randomly copolymerized copolymers having the

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structural formula



where m is the molar equivalent of about 50% to about 95% by weight of the polymer, n is the molar equivalent of about 5% to about 50% by weight of the polymer, and R is selected from hydrogen and methyl, and R' is the remainder of the (meth) acrylamido or (meth)acryloxy group of the anionic monomer described above, such as O^- or $\text{CONHC}(\text{CH}_3)\text{CH}_2\text{SO}_3^-$, with an associated hydrogen or other common cation. These materials can stabilize shales and clays encountered during drilling, and they can do so under the effects of strong shear forces and in the presence of anionic, cationic or nonionic materials such as foaming agents.

As has been documented many times in the literature, shales commonly include clays which may cause difficulties. Examples are clays of the montmorillonite (smectite) group such as saponite, nontronite, hectorite, and sauconite as well as montmorillonite itself; the kaolin group such as kaolinite, nacrite, dickite, and halloysite; the hydrous mica group such as hydrobiotite, glauconite, illite and bramalite; the chlorite group such as chlorite and chamosite, and in addition vermiculite, attapulgite and sepiolite and mixed-layer varieties of the above minerals and groups. The entire specification of Himes and Vinson patent 4,842,073 is

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incorporated herein by reference as it should be understood that the present invention is applicable in all respects to the conditions and environment described in the '073 patent.

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Our copolymers may have average molecular weights from 1000 to about 1,000,000 and preferably in the range of about 20,000 to about 1,000,000. Copolymers of acrylic acid and DMDAAC may be made by the methods described by Boothe et al in US Patent 4,772,462, and particularly as referenced to Butler and Angelo JACS v 29, p 3128 (1957) or the technique suggested in US Patent Re 28,543, and the other copolymers described herein may be made in a similar manner. They may be used in admixture with the stimulation fluid in an amount effective to stabilize the formation against permeability damage at least to some degree as a result of contact with the aqueous fracturing fluid. The copolymer is generally admixed with the aqueous fracturing fluid in an amount of at least about 50 parts (or at least about 0.05%) by weight per million parts by weight of the fracturing fluid. Preferably our copolymer (DMDAAC/acrylic acid copolymer or other copolymer as described herein) is present in an amount of from about 50 to about 50,000 parts per million of the aqueous fracturing fluid; most preferably about 1000 to about 8000 parts per million. In the case of DMDAAC/acrylic acid copolymers, we prefer about 80-95% DMDAAC to about 5-20% acrylic acid. Very small amounts have at least some beneficial effects. An effective amount may be determined by estimates of the amount of clay in the formation using representative core samples in standard core flow testing as is known in the art or by roll over testing as described below.

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The copolymer may be admixed with the drilling fluid at any time prior to contact of the fluid with the subterranean formation. It is readily mixed with the constituents of the aqueous phase of drilling or stimulation fluid both prior to and subsequent to hydration of the gelling agent. The most commonly used gelling agents presently are bentonite clays, polysaccharides and in particular natural guar, hydroxypropyl guar, polyacrylamide, carboxymethylcellulose, hydroxyethylcellulose, and xanthan gum, but our treating agents are compatible with any and all such materials as well as foaming agents and may be used without them. The polysaccharide or other gelling agent may be used in a hydrocarbon solvent to form a "liquid gel concentrate". Our copolymers are also compatible with such concentrates, and also, as is shown below, with commonly used foaming agents. The ratios of polymer to foaming agent may vary widely, but will typically be about 20:1 to about 1:20 by weight.

The drilling or fracturing fluid may thus comprise, for example, a gelling agent, a foaming agent, KCl, and our copolymer.

Detailed Description of the Invention

Table I shows that the polymers we use are stable to shear. Roll over tests were conducted with and without the samples having been subjected to shear. All polymers were at 400 ppm and contained 2000 ppm of a common anionic surfactant. Shearing was accomplished by preparing a 2.5 gallon sample of polymer and passing it through a ceramic choke with a 1000 psi pressure differential at 4 gallons per minute for 30 minutes. The water used was brine water. The

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shale samples were ground to -4 to +10 mesh. Seven grams of sized shale was placed with 50 ml of test fluid in an oven rolling jar. The jars were rolled in the oven for 16 hours at 125° F, then removed and cooled. The granules were collected on a 30 mesh screen, washed gently with distilled water and dried at 95° F until no further change in weight was observed. The percent shale recovery was then calculated as the weight remaining on the 30 mesh screen divided by the original weight.

Table I

	Sample	Shear	% Recovery
	83D/17MAA	NO	87.50
	83D/17MAA	YES	88.78
	90D/10MAA	NO	85.77
	90D/10MAA	YES	88.73
	85D/15K'AA	NO	87.78
	85D/15K'AA	YES	88.35
	85D/15NH,AA	NO	80.85
	85D/15NH,AA	YES	88.65
	95D/5MAA	NO	88.87
	95D/5MAA	YES	88.18
	85D/15NH,AA	NO	94.34
	85D/15NH,AA	YES	84.94
	85D/15NH,AA	NO	88.29
	85D/15NH,AA	YES	85.31
	90D/10NH,AA	NO	80.09
	90D/10NH,AA	YES	84.96

The materials are seen to be little affected by shear. Additional Roll oven tests were performed on other polymers useful in my invention, and the results are reported in Table II:

Table II

	Copolymer	% Recovery
	88DMDAAC/12AMPS	68.1
	74AETAMS/26MAA	26.3
	91AETAC/9AA	70.4
	91METAMS/5AA	84.2

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In Table II, "DMAAC" is, as above, dimethyl diallyl ammonium chloride, "AMPS" is 2-acrylamido-2-methyl propane sulfonic acid, "AETAMS" is acryloxy ethyl trimethyl ammonium chloride, "MAA" is methacrylic acid, "AETAC" is acryloxy ethyl trimethyl ammonium chloride, "AA" is acrylic acid, and "METAMS" is methacryloxy ethyl trimethyl ammonium chloride. The numbers such as 12 and 91 represent the percentages of the monomers by weight in the copolymer.

That the DMAAC/anionic copolymers are compatible with foaming agents is demonstrated in Table III. In Table III, the weight ratio of DMAAC to acrylic acid in a test polymer is written, for example, as 85D/A15, meaning 85% by weight DMAAC and 15% acrylic acid. The weight ratio of polymer to foaming agent is indicated by Poly/Fn; FW/Br means the salinity of the aqueous carrier in the proportion of fresh water to 15% brine. The test was conducted to determine the foam height and its stability in a procedure as follows: 100 cc of the test solution containing 0.32% of the polymer/foam combination was placed in a Waring blender and subjected to a standard agitation for 30 seconds, the material was poured into a 1000 ml cylinder and the foam height immediately measured, and the half-life of the foam was measured in minutes and seconds. The half-life is the amount of time it took for one-half of the original solution to settle out of the foam.

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Table III

	Exmpl	Compos	Foamer	Poly/Pa	FW/Br	FmHt	H21f
5	1	85D/15A*	p	90.9/9.1	100/0	580	4:42
	2	49D/51A	p	90.9/9.1	100/0	580	5:22
	3	85D/15A	p	90.9/9.1	100/0		5:28
	4	85D/15A*	p	90.9/9.1	0/100	230	0:37
	5	85D/15A	p	90.9/9.1	0/100	230	0:42
10	6	85D/15A*	p	90.9/9.1	50/50	400	2:45
	7	85D/15A	p	90.9/9.1	50/50	380	2:25
	8	85D/15A	p	90.9/9.1	100/0	570	4:40
	9	75D/25A	q	10/90	0/100	320	1:55
	10	75D/25A	q	5/95	100/0	510	5:10
15	11	75D/25A	q	10/90	100/0	350	2:12
	12	75D/25A	q	5/95	20/80	360	2:18
	13	75D/25A	q	5/95	40/60	360	2:17
	14	75D/25A	q	5/95	60/40	470	3:18
	15	90D/10A	q	10/90	40/60	400	2:35
20	16	90D/10A	q	10/90	60/40	450	2:47
	17	49D/51A	r	90.9/9.1	100/0	550	5:08
	18	85D/15A	r	90.9/9.1	100/0	550	4:53
	19	85D/15A*	r	90.9/9.1	100/0	580	4:04
	20	49D/51A	q	7.4/92.6	100/0	530	4:44
25	21	49D/51A	q	7.4/92.6	75/25	540	4:40
	22	49D/51A	q	7.4/92.6	50/50	510	4:15

*Very low molecular weight, i.e. about 1000 to about 10,000.

30 Foamers: "p" is a solvent-containing mixture of common anionic surfactants, namely alcohol ether sulfates and alkyl sulfonates, chosen for their ability to foam in fresh water or brine having up to 5% salt; "q" is a commercially available mixture of anionic surfactants chosen for their ability to foam in brine having as much as 23% salt; "r" is "Neodol 91-2.5", a mixture of linear alcohol ethoxylates having 2.5 moles EO per mole of alcohol.

35 Table IV also demonstrates foam heights and lives for four additional copolymers in varied concentrations of brine. In Table IV, the column titled "Fluid" presents the weight ratio of fresh water to 23% brine used in the experiment. In each case, the surfactant was "p" as defined above.

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Table IV

	Control (no polymer)	Fluid	Foam Ht	Half Life	
5			100/0	540	44
			75/25	540	43
			50/50	500	42
			25/75	400	40
			0/100	360	30
10	88DMDAAC/12AMPS		100/0	450	25
			75/25	480	35
			50/50	480	42
			25/75	420	40
			0/100	370	25
15	74AFTAMS/26MAA		100/0	600	48
			75/25	560	42
			50/50	520	40
			25/75	430	40
			0/100	360	35
20	91AFTAC/9AA		100/0	460	22
			75/25	530	52
			50/50	480	42
			25/75	420	35
			0/100	370	32
25	95MFTAMS/5AA		100/0	450	22
			75/25	550	42
			50/50	490	32
			25/75	410	32
			0/100	370	32
30			100/0	450	22
			75/25	550	42
			50/50	490	32
			25/75	410	32
			0/100	370	32

The meanings of AFTAMS, AFTAC, and MFTAMS are as indicated above.

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Claims

1. Method of treating a subterranean formation comprising contacting the subterranean formation with an aqueous solution of a treatment fluid containing a formation control additive including a copolymer comprising (1) about 50% to about 95% by weight of a cationic monomer selected from (a) diallyl ammonium monomers of the formula $(CH_2=CH-CH_2)_2N^+(CH_3)_2 Cl^-$ (b) acryloyloxy monomers of the formula $CH_2=CR-COR^1N^+(CH_3)_2 A^-$ and (c) acrylamido monomers of the formula $CH_2=CR-CONR^1N^+(CH_3)_2$, and (2) about 5% to about 50% of an anionic monomer of the formula $CH_2=CR-COR^2$ where R is hydrogen or CH_3 , R^1 is a connecting linear or branched saturated hydrocarbyl group having from one to about five carbon atoms, and R^2 is OH or $-NHR^3SO_3^-$, whereby permeability damage resulting from contact of the aqueous fluid with the formation is reduced.
2. Method of claim 1 wherein said copolymer is present in an amount of at least about 10 ppm by weight of the treatment fluid.
3. Method of claim 1 wherein said copolymer is present in an amount of about 50 ppm to about 50,000 ppm by weight of the treatment fluid.
4. Method of claim 1 wherein said copolymer is present in an amount of from about 1000 ppm to about 8000 parts per million parts of the treatment fluid.
5. Method of claim 1 wherein the treatment fluid

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includes a gelling agent to viscosify the treatment fluid.

6. Method of claim 1 wherein the copolymer comprises about 80% to about 95% monomer of the formula $(CH_2H-CH_2)_2N^+(CH_3)_2 Cl^-$.

7. Method of claim 1 wherein the treatment fluid includes a foaming agent.

8. Method of claim 7 wherein the foaming agent is present in the treatment fluid in a ratio to the copolymer of about 1:20 to about 20:1.

9. Method of claim 3 wherein the copolymer is a copolymer of dimethyl diallyl ammonium chloride and acrylic acid.

10. Method of claim 1 wherein the average molecular weight of the polymer is about 20,000 to about 1,000,000.

11. The method of stimulating production of hydrocarbons from a clay-containing subterranean formation comprising contacting said formation with an effective amount of an aqueous treatment fluid comprising an aqueous fluid, a foaming agent and a copolymer of acrylic acid and at least about 50% by weight dimethyl diallyl ammonium chloride under conditions such that either a fracture is caused to be created or the fluid contacts said formation whereby the subsequent production of hydrocarbons is facilitated, said formation control additive being present in said treatment fluid in an

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effective amount whereby permeability damage resulting from contact of the clays in the formation with the aqueous fluid in the treatment fluid is reduced.

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12. Method of claim 11 wherein said copolymer is present in an amount in excess of about 0.05% by weight of said aqueous treatment fluid.

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13. Method of claim 11 wherein said copolymer is present in an amount of from about 0.1 to about 5% by weight of said aqueous treatment fluid.

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14. Method of claim 11 wherein said copolymer is a copolymer of about 10% to about 20% by weight acrylic acid and the balance dimethyl diallyl ammonium chloride.

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15. Method of claim 11 wherein said foaming agent is alcohol ether sulfate mixed with alpha olefin sulfonate and solvents.

16. Method of claim 11 wherein the foaming agent is present in amount from about 0.1% to about 5%.

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US006172010B1

(12) **United States Patent**
Argillier et al.

(10) **Patent No.: US 6,172,010 B1**
(45) **Date of Patent: Jan. 9, 2001**

- (54) **WATER-BASED FOAMING COMPOSITION-METHOD FOR MAKING SAME**
- (75) **Inventors:** Jean-François Argillier, Suresnes; Annie Audibert-Hayet, Croissy sur Seine; Sabine Zellinger, Saint Germain en Laye, all of (FR)
- (73) **Assignee:** Institut Français du Pétrole, Rueil (FR)
- (*) **Notice:** Under 35 U.S.C. 154(b), the term of this patent shall be extended for 0 days.
- (21) **Appl. No.:** 09/125,457
- (22) **PCT Filed:** Dec. 3, 1997
- (86) **PCT No.:** PCT/FR97/02186
§ 371 Date: Sep. 22, 1998
§ 102(e) Date: Sep. 22, 1998
- (87) **PCT Pub. No.:** WO98/26864
PCT Pub. Date: Jun. 25, 1998
- (30) **Foreign Application Priority Data**
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- (51) **Int. Cl.⁷** C09K 7/08; B01F 3/04
- (52) **U.S. Cl.** 507/102; 507/202; 507/112; 507/113; 507/120; 507/121; 507/129; 507/135; 507/222; 507/226; 516/10; 516/12; 516/15
- (58) **Field of Search** 507/102, 202, 507/120, 121, 135, 129, 222, 226, 110, 111, 112, 113; 516/10, 12, 15

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- Primary Examiner*—Philip Tucker
- (74) *Attorney, Agent, or Firm*—Millen, White, Zelano & Branigan

- (57) **ABSTRACT**
- The invention concerns a water based foaming composition and the method of making it. The composition is optimized in that it contains a surfactant specifically selected according to the polymer also present in the composition. The surfactant and the polymer are selected so that they are oppositely charged. The invention is very useful in drilling or treating wells.
- 14 Claims, No Drawings**

**WATER-BASED FOAMING
COMPOSITION-METHOD FOR MAKING
SAME**

This invention relates to an aqueous foam composition that consists of an optimized combination of surfactants and polymers that are water-soluble. The applications of such a foam according to this invention vary widely, for example for body care, farming applications, fire-fighting, underground works, such as soil consolidation and operations in wells that are drilled into the subsoil: drilling, treatment of reservoirs, production of hydrocarbons.

The use of an aqueous foam to replace a well fluid that circulates through a pipe lining that goes down into a well which is drilled into the ground is known. In some cases, the density of the aqueous fluid that is used is too high for the type of rock, creating an excessive hydrostatic pressure compared to the fracturing resistance of the rock zones through which the drilling passes. The choice is then made to use aqueous fluids with densities that are reduced by the introduction of gas, and it is attempted to make the thus lightened fluid homogeneous by creating the most stable foam possible so that it will have at least adequate power for clearing the cuttings.

Document US-5513712 describes a drilling process in which a foam that comprises a polymer such as non-cross-linked acrylamide and a surfactant is used, but it does not describe a foaming composition that is stable and optimized by achieving synergy between a specific polymer and a specific surfactant.

Thus, this invention relates to a water-based foaming composition that comprises at least one surfactant and a polymer. The surfactant and the polymer comprise charges of opposite sign.

The applicant has demonstrated that, surprisingly, it was possible to control the production of a stable foam from a composition that is optimized in terms of surfactant concentration if a polymer or a copolymer with a charge that is opposite in sign to that of the charge of the surfactant is combined with said surfactant. A cationic polymer or copolymer is combined with an anionic surfactant; an anionic polymer or copolymer is combined with a cationic surfactant.

The surfactants that can conceivably be used in this invention include all the standard anionic surfactants, such as the anionic group, or:

carboxylates:

soaps of alkaline metals, alkyl or alkyl ether carboxylates,
N-acylemino acids,
N-acylglutamates,
N-acylpolypeptides,

sulfonates:

alkylbenzenesulfonates,
paraffin sulfonates,
 α -olefin sulfonates,
petroleum sulfonates,
lignosulfonates,
sulfosuccinic derivatives,
polynaphthylmethanesulfonates,
alkyl taurides,

sulfates:

alkyl sulfates,
alkyl ether sulfates,

phosphates:

monoalkyl phosphates,
dialkyl phosphates

phosphonates.

As cationic surfactants, it is possible to cite:

alkylamine salts,

quaternary ammonium salts of which nitrogen:

comprises a fatty chain, for example, alkyltrimethyl or trimethylammonium derivatives, alkylidimethyl benzylammonium derivatives,

comprises two fatty chains,

forms part of a heterocycle, for example, the derivatives of pyridinium, imidazolium, quinolinium, piperidinium, morpholinium.

All the standard anionic polymers can be used according to this invention, for example:

synthetic polymers or copolymers that are derived from:

anionic monomers that contain carboxylate or sulfonate or phosphate or phosphonate groups, such as the monomers acrylate, methacrylate, itaconate, 2-acrylamido-2-methyl-propane, sulfonate, 2-methacryloxy ethane sulfonate, 3-acrylamido-3-methyl butanoate, styrene sulfonate, styrene carboxylate, vinyl sulfonate, and maleic acid salts.

synthetic copolymers that are derived from:

an anionic monomer, for example in those that are described above and a neutral monomer, for example, acrylamide, acrylic acid, vinyl pyrrolidone, ethylene oxide, propylene oxide, maleic anhydride, vinyl alcohol, hydroxyethylacrylate, . . .

natural polymers such as:

cellulose derivatives that are modified negatively, such as CMC,
polysaccharides such as xanthanum, alginate,
starches that are modified negatively,
galactomannanes that are modified negatively.

All the standard cationic polymers can be used according to this invention, for example:

synthetic polymers or copolymers that are derived from standard cationic monomers, i.e., of the following general formula:

R1

$\text{O}=\text{CH}_2$

R2 where R1 or R2 comprises at least one N atom,
polyethylene imines,
polyamide amines,
polyamines,

synthetic copolymers that are derived from:

cationic monomers and neutral monomers (described above),

natural polymers:

starches that are modified positively, chitosans,
galactomannanes that are modified positively,
cellulose derivatives that are modified positively.

The surfactant can be cationic at a concentration that is less than about $5 \cdot 10^{-3}$ mol/l, and the polymer can be anionic.

The surfactant can be anionic at a concentration that is less than about $5 \cdot 10^{-3}$ mol/l, and the polymer can be cationic.

The anionic polymer can be a copolymer such as AM/AMPS, of which the level of the charged portion can be between 5 and 40%, and preferably between 10 and 25 . The surfactant can be of the DoTAB type.

The anionic polymer can be a natural polymer that is modified negatively, for example such as CMC.

The cationic polymer can be a copolymer such as AM/MAPTAC, of which the level of the charged portion can

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be between 5 and 40% and preferably between 10 and 25. The surfactant can be of the SDS type.

The invention also relates to a process for producing a foam from water, at least one surfactant, and at least one polymer. In the process, a surfactant and a polymer or a copolymer of opposite charge are combined, and the polymer concentration is determined to obtain a stable foam with as low a surfactant level as possible.

The polymer concentration can be determined based on the charge level of the polymer and the concentration of surfactant that is used. Considering the electrostatic nature of the interactions between polymer and surfactant, their respective concentrations can be a function of the ionic force of the medium.

The foaming solution can, like well fluid (drilling, completion and workover), also contain solids (cuttings, neutral colloids, . . .) or other non-charged water-soluble polymers, anti-corrosion additives, . . .

This invention will be better understood and its advantages will become clearer from reading the tests, by no means limiting, that are described below.

The tests are based mainly on comparing, for different foam compositions, the two following measurements:

the foam volume VM that is formed from a given volume of foaming solution and defined stirring conditions, which makes it possible to characterize the foaming capacity of the solution,

the drainage rate VD, which makes it possible to characterize the stability of the foam that is formed.

Viscosity was measured at the Newtonian level with a low-gradient viscosimeter.

Operating Procedure:

The foaming solution consists of, at least, a mixture of at least one surfactant with variable concentration, at least one water-soluble polymer also of variable concentration, and water. The pH is adjusted to about 9 for all the tests. The foam is obtained from 200 ml of foaming solution by stirring with a whip. The speed of rotation is set at 2000 rpm. As a general rule, the stirring time is about 2 minutes, which is sufficient to obtain a homogeneous foam, as well as a maximum volume.

To measure the drainage rate, which is characteristic of the stability of the foam, the foam that is obtained is poured into a graduated glass funnel, and the volume of drained solution is noted based on time. The drainage rate is defined from the empirical equation that describes the changes in the drainage curves (Bikerman j. j. 1973):

$$V=V_0(1-\exp(-kt))$$

V the drained volume (cm³)

V₀ the volume of the initial solution (cm³)

t time (minute)

From this equation, k, a flow constant, (min⁻¹) is determined.

Drainage rate VD is defined by

$$VD=2V_0/2 \text{ (cm}^3\text{/min.)}$$

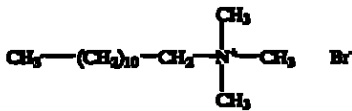
The lower VD is, the more stable the foam.

Tested Systems:

1. Surfactants:

Dodecyltrimethylammonium bromide (DoTAB): cationic surfactant that has the following general formula:

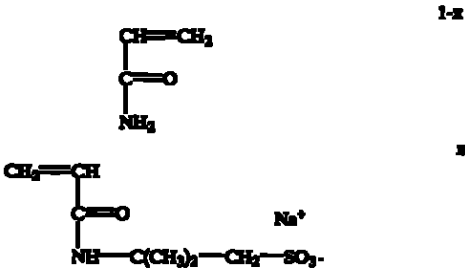
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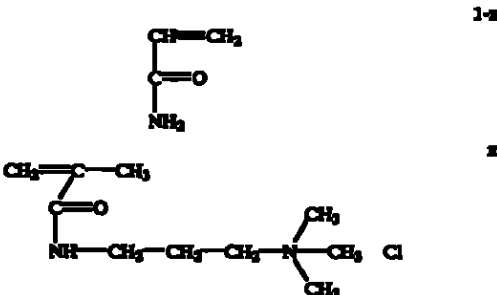
sodium dodecyl sulfate (SDS): anionic surfactant of general formula:



2. Polymers:
Polyacrylamide AM (molecular weight MW about 2.5 10⁶ g/mol).
copolymer acrylamide/acrylamido methyl propane sulfonate AM/AMPS of general formula:



AM/AMPS 75/25 x=25% and Mw=2.8·10⁶ g/mol
AM/AMPS 90/10 x=10% and Mw=3.2·10⁶ g/mol
carboxymethyl cellulose (CMC). The mean degree of substitution of the carboxylic groups by the cellulose cycle of the sample that is studied is close to 1. Its molecular weight is about MW=2·10⁶ g/mol.
copolymer acrylamide/methacrylamido propyltrimethylammonium chloride AM/MAPTAC of general formula:



Copolymers AM/MAPTAC 75/25 (x=25) and AM/MAPTAC 90/10 (x=10%) have molecular weights Mw of about 3·10⁶ g/mol.

Test 1: Single Cationic surfactant (DoTAB)

DoTAB (mol/l)	Polymer (750 ppm)	VM (cm ³)	Viscosity (mPa · s)	VD (cm ³ /min.)
5.10 ⁻³	0	0	0.88	—
5.10 ⁻⁴	0	0	0.86	—

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Test 1: Single Cationic surfactant (DoTAB)				
DoTAB (mol/l)	Polymer (750 ppm)	VM (cm ³)	Viscosity (mPa · s)	VD (cm ³ /min.)
5.10 ⁻³	0	1600	0.85	40
20.10 ⁻³	0	2200	0.83	23

These tests show that an adequate quantity of surfactant is needed in order for the production of a stable foam to take place. At a surfactant concentration of 5.10⁻³ (mol/l), the foam is formed while being stirred, but it is very unstable.

Test 2: Cationic Surfactant and Polymersulfonate AM (non-ionic)				
DoTAB (mol/l)	Polymer (750 ppm)	VM (cm ³)	Viscosity (mPa · s)	VD (cm ³ /min.)
5.10 ⁻³	AM	0	1.43	—
5.10 ⁻⁴	AM	0	1.40	—
5.10 ⁻⁵	AM	1000	1.34	—
20.10 ⁻⁵	AM	1800	1.33	17.2

At a DoTAB concentration of 5.10⁻³ (mol/l), the foam that is formed is destroyed after less than one minute.

This test shows that for DoTAB surfactant concentrations that are less than or equal to about 5.10⁻³ mol/l, it is impossible to form a stable foam even in the presence of a certain polymer concentration of the polyacrylamide type.

Starting at 20.10⁻³ mol/l and up of surfactant, the foam that is formed in the presence of the polyacrylamide-type polymer is more stable than without polymer. This is due mainly to the increase in viscosity of the foaming composition, as the measurements of viscosity confirm.

Test 3: Cationic Surfactant DoTAB and Sulfonated Polyacrylamide				
DoTAB (mol/l)	Polymer (750 ppm)	VM (cm ³)	Viscosity (mPa · s)	VD (cm ³ /min.)
5.10 ⁻³	AM/AMPS-75/25	500	—	—
5.10 ⁻⁴	AM/AMPS-75/25	600	—	—
5.10 ⁻⁵	AM/AMPS-75/25	<400	—	—
20.10 ⁻⁵	AM/AMPS-75/25	precipitated	—	—
5.10 ⁻⁴	AM/AMPS-90/10	500	3.09	5
5.10 ⁻⁵	AM/AMPS-90/10	600	3.05	4.6
5.10 ⁻⁶	AM/AMPS-90/10	1700	1.22	9
20.10 ⁻⁶	AM/AMPS-90/10	precipitated	—	—

With a polymer such as AM/AMPS-75/25, i.e., one that comprises on the order of 25% of a charge with a sign opposite to that of the charge of the surfactant, the foam can form, with between-charge interactions, at concentrations of less than 5.10⁻³ mol/l of surfactant, and in particular at concentrations of 5.10⁻⁵ and 5.10⁻⁴ mol/l of surfactant. Starting at and beyond 5.10⁻³ mol/l of surfactant concentration, foam does not form because there is precipitation, very likely due to excessively strong interactions between the charged polymer and the surfactant. Such a test with a polymer such as AM/AMPS-75/25, however, shows the importance of having opposite charges between surfactant and polymer for forming a foaming composition.

With a less charged polymer, such as AM/AMPS-90/10 (level of charge 10%), it is noted that the foam is produced for concentrations that are less than 5.10⁻³ mol/l of surfactant, as for the polymer with a 25% charge, but for a surfactant concentration of about 5.10⁻³ mol/l, the foaming

composition is greatly optimized since a large and very stable volume of foam is obtained, taking into account the low drainage rate that is measured.

Relative to the foam that is formed from a polyacrylamide polymer (test 2), the foam volume is comparable, but with a quantity of surfactant that is four times smaller and, moreover, with the achievement of greater stability.

Test 4: Cationic Surfactant DoTAB and Carboxymethylcellulose (AQUAPAC produced by the Aquapel Company)				
DoTAB (mol/l)	Polymer (750 ppm)	VM (cm ³)	Viscosity (mPa · s)	VD (cm ³ /min.)
5.10 ⁻³	CMC	450	—	—
5.10 ⁻⁴	CMC	600	—	2.4
5.10 ⁻⁵	CMC	precipitated	—	—
20.10 ⁻⁵	CMC	precipitated	—	22.3

This test shows that the addition of an anionic cellulose natural polymer such as carboxymethylcellulose (CMC) with a cationic surfactant (DoTAB) makes it possible to form foam because of between-charge interactions, with a surfactant concentration of less than 5.10⁻³ mol/l. The foam that is formed with a concentration of 5.10⁻⁴ mol/l of DoTAB and 750 ppm of CMC is very stable. It is verified that an excessive surfactant concentration hampers the formation of a foam, very likely due to the excessively strong interactions between the polymer and the surfactant.

Test 5: Cationic Surfactant DoTAB and Sulfonated Polyacrylamide Influence of the Presence of Salt. 0.5 ml of NaCl is added to the solution.				
DoTAB (mol/l)	Polymer (750 ppm)	VM (cm ³)	Viscosity (mPa · s)	VD (cm ³ /min.)
5.10 ⁻³	0	0	—	—
5.10 ⁻⁴	0	0	—	—
5.10 ⁻⁵	0	1500	—	172 (*)
20.10 ⁻⁵	0	2200	—	20
5.10 ⁻³	AM/AMPS-90/10	450	—	8
5.10 ⁻⁴	AM/AMPS-90/10	700	—	8
5.10 ⁻⁵	AM/AMPS-90/10	1500	—	10
20.10 ⁻⁵	AM/AMPS-90/10	precipitated	—	—

(*) The foam breaks almost instantaneously.

This test confirms that the DoTAB and AM/AMPS-90/10 foaming solution provides excellent results in terms of foam stability, even in the presence of salt.

Test 6: Cationic Surfactant DoTAB and Sulfonated Polyacrylamide Influence of the AM/AMPS-90/10 Comonomer Concentration.				
DoTAB (mol/l)	Polymer (ppm)	VM (cm ³)	Viscosity (mPa · s)	VD (cm ³ /min.)
5.10 ⁻³	100	<150	7.3	—
5.10 ⁻⁴	100	<130	2.5	—
5.10 ⁻⁵	100	1650	0.77	20.6
20.10 ⁻⁵	100	precipitated	—	—
5.10 ⁻³	750	500	3.09	5
5.10 ⁻⁴	750	700	3.05	4.6
5.10 ⁻⁵	750	1700	1.22	9
20.10 ⁻⁵	750	precipitated	—	—
5.10 ⁻⁶	1500	500	46	3

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Test 6: Cationic Surfactant DoTAB and Sulfonated Polyacrylamide Influence of the AM/AMPS-90/10 Copolymer Concentration.				
DoTAB (mol/l)	Polymer (ppm)	VM (cm ³)	Viscosity (mPa · s)	VD (cm ³ /min.)
5.10 ⁻⁴	1500	700	33	3
5.10 ⁻⁵	1500	precipitated	—	—
20.10 ⁻⁵	1500	precipitated	—	—

These results show that even a small polymer concentration (100 ppm) is effective in stabilizing the foam. By increasing the polymer concentration (750 ppm to 1500 ppm), the foam that is formed is also more stable. Taking into account the strong interactions between polymer and surfactant, the surfactant concentration should be adapted to the polymer concentration that is used, or vice versa. In this example, it is possible to determine an optimum surfactant concentration of about 5 · 10⁻³ mol/l and for a polymer concentration of between 100 and 1000 ppm.

This example clearly shows the synergy between the surfactant and the polymer and the way of optimizing the foaming solution.

Test 7: Static SDS Anionic Surfactant				
SDS (mol/l)	Polymer (750 ppm)	VM (cm ³)	Viscosity (mPa · s)	VD (cm ³ /min.)
5.10 ⁻³	0	0	—	—
1.10 ⁻⁴	0	0	0.9	—
5.10 ⁻⁴	0	900	—	22
1.10 ⁻³	0	1700	0.9	21
5.10 ⁻³	0	2000	—	13

This test shows that this solution cannot form foam with a low surfactant concentration and that at a higher concentration, the foam is less stable (VD on the order of 13 cm³/min). It is noted that the measurement that is obtained with this surfactant is a little more stable than that obtained with DoTAB (Test 1).

Test 8: Anionic Surfactant SDS and Cationic Polyacrylamide AM/MAFTAC 90/10				
SDS (mol/l)	Polymer (750 ppm)	VM (cm ³)	Viscosity (mPa · s)	VD (cm ³ /min.)
5.10 ⁻³	AM/MAFTAC 90/10	500	—	2.6
5.10 ⁻⁴	AM/MAFTAC 90/10	600	—	5.4
5.10 ⁻³	AM/MAFTAC 90/10	2200	—	5.1

In this example of foaming composition that comprises an anionic surfactant and a cationic polymer, it is observed that the addition of cationic polymer is very beneficial to the formation and the stability of the foam that is formed, since a stable foam is formed even with only 5 · 10⁻⁵ mol/l of SDS and that with 5.10⁻³ mol/l of SDS, 2200 cm³ of very stable foam (VD close to 5 cm³/min) is formed.

Test 9: Anionic Surfactant SDS and Cationic Polyacrylamide AM/MAFTAC-75/25				
SDS (mol/l)	Polymer (750 ppm)	VM (cm ³)	Viscosity (mPa · s)	VD (cm ³ /min.)
5.10 ⁻³	AM/MAFTAC-75/25	450	—	1.8
5.10 ⁻⁴	AM/MAFTAC-75/25	500	—	2.1
5.10 ⁻⁵	AM/MAFTAC-75/25	precipitated	—	—

This test shows that with a more charged polymer, the combination of a cationic polymer and an anionic surfactant provides very stable foams at a low surfactant concentration. At a higher concentration (in this case greater than or equal to about 5.10⁻³ mol/l), it is noted that the interactions are very strong, which produces precipitation.

In general, it should be noted that adding simple electrolytes to the foaming composition makes it possible to partially screen the interactions of electrostatic origin. In this case, the surfactant concentrations can be higher without there being precipitation.

What is claimed is:

1. A water-based foaming composition that comprises at least one surfactant and a water-soluble polymer, characterized in that said surfactant has charges of a sign that is opposite to those of said polymer, said surfactant being present at a concentration of less than about 5 · 10⁻³ mol/l and said polymer being present in a concentration sufficient to provide a stable foam.
2. A composition according to claim 1, wherein the surfactant is cationic and in which the polymer is anionic.
3. A composition according to claim 1, wherein the surfactant is anionic and wherein the polymer is cationic.
4. A composition according to claim 2, wherein the anionic polymer is an acrylamide/acrylamido methane sulfonate copolymer (AM/AMPS), whose level of the charged portion is between 5 and 40%, and wherein the surfactant is dodecyltrimethylammonium bromide (DoTAB).
5. A composition according to claim 2, wherein the anionic polymer is a natural polymer.
6. A composition according to claim 3, wherein the cationic polymer is AM/MAFTAC, whose level of the charged portion is between 5 and 40%, and wherein the surfactant is SDS.
7. A process for producing a foam from water, at least one surfactant and at least one polymer, wherein a surfactant present in a concentration of less than about 5 · 10⁻³ mol/l and a water-soluble polymer of opposite charge are combined, and the polymer concentration is determined in order to obtain a stable foam with the lowest surfactant level possible.
8. Process according to claim 7, wherein the polymer concentration is determined based mainly on the charge level of the polymer and the surfactant concentration used.
9. In a well that is drilled into the ground, circulating a water-based foaming composition comprising an anionic surfactant and a cationic water-soluble polymer wherein the anionic surfactant is present in a concentration of less than about 5 · 10⁻³ mol/l.
10. A composition according to claim 4, wherein said level is between 10 and 25%.

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11. A composition according to claim 5, wherein the natural polymer is a negatively modified cellulose derivative.

12. A composition according to claim 11, wherein the negatively modified cellulose derivative is CMC.

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13. A composition according to claim 6, wherein said level is between 10 and 25%.

14. In a well that is drilled into the ground, circulating a foaming composition according to claim 12.

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(54) Title: TRANSPORT OF SOLID PARTICULATES			
(57) Abstract A method is provided for incorporating a foaming agent into mixtures of particulates and then forming a foam within the mixture to increase the flowability of the particulates. A method is also provided for excavating solid particulates, incorporating a foaming agent into mixtures of solid particulates, and then forming a foam within the mixture to increase the flowability of the particulates. The particulates can be transported through pipelines or boreholes. Examples of particulates include, but are not limited to, mine tailings, ores, sand, coal, soils, clays, silts, aggregates, and mixtures thereof.			

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FIELD OF THE INVENTION

10 BACKGROUND OF THE INVENTION

20 Ideally, the particulates should remain in suspension while being transported through pipelines or boreholes to their final destination. Particulates such as classified or unclassified mine tailings may be characterized by features that limit the ability to transport the material as a paste. Such characteristics may include: high density or specific gravity, poor or gapped gradation, coarse particle size, highly sorted particle size gradation, or lack of fine particles. These features tend to prevent particulates from being made into a stable paste consistency without the addition of fine materials, such as sands, to enhance the
25 particle size distribution.

Reduction of fluid content may produce a material that approaches the consistency

of a paste, but which would also develop reduced turbulence and shear thickening properties. This makes transport by pumping or by gravity through a transport system less desirable and more problematic than by hydraulic transport.

5 One type of particulate transport is the transport of mine tailings as backfill in mines, or to the surface to remove the tailings from the mine. The backfill mine tailings can be transported alone, or a cement can be added to provide for a set composition. It is desired in the art to transport mine tailings as a paste consistency, rather than by hydraulic transport. However, the particle size distribution needs to be optimized to provide paste
10 consistency transportation. The particle size distribution of a mine tailing may be made to conform to a more idealized particle size distribution by the addition of fine materials or sand. This however increases the handling and treatment costs of the mine tailings and increases costs to the mining operations. The ideal fill exhibits slurry-like properties of ease of transport in pipes (i.e., low pressure losses), but paste-like properties of staying in
15 suspension at relatively low transport velocities with no run off.

Once the slurry of particulates arrives at the desired destination, the transport fluid drains out. The fluid must then be pumped away, which adds additional handling and disposal costs to the operation. Additionally, if a cement is included with the particulates,
20 some cement will be present in the drain water which may then harden in the drain system, and increase the maintenance costs of the operation. In the cases where mine tailings are transported to the surface, a dam must be erected to manage and recover the water. This adds additional cost, potential liability, and is a potential safety hazard.

25 Foam suspends the particulates and reduces the amount of liquid required to transport the material. It is known, as in US Patent No. 5,080,534 to Goodson et al., to generate a foam from a surfactant and then mix the foam with the particulates prior to transport in the pipeline. Also, it has been known, as in US Patent No. 4,451,183 to Lorenz, to inject foam which has been separately prepared into the particulates at various
30 points throughout the pipeline. However, these prior art methods require that the foam be separately prepared before being added to the mixture. The separate preparation requires additional equipment and time to prepare the foam, which adds additional cost to the project.

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Mine backfilling is the process of filling voids in mines left by the underground excavation of ore to provide structural support for the mine or to dispose of mine tailings. Materials used to fill mine voids include waste rock, mine tailings, and sand. Often, sand is mixed in with mine tailings.

5

Mine tailings are the result of grinding the ore or rock fine enough to liberate minerals through a flotation process. Because of the low content of minerals in the ground rock, typically less than 10% by weight, almost all of the rock mined becomes mine tailings. Mine tailings generally have consistencies similar to those of fine clay or silt. 10 Traditionally, large quantities of water must be added to the tailings to make them pumpable. The tailings at final placement then must be thickened to allow the tailings to set in place. There is a very significant cost to the thickening of mine tailings.

Once the mine tailings are pumped from the mill, they are either sent directly to a 15 tailings pond, sent directly to a backfill plant, or processed with a hydro-cyclone to separate the coarse particles from the finer particles. The coarse fraction is sent to the backfill plant, and the fine fraction is sent to the tailings pond. A tailings pond is generally a large area where the tailings are left to settle and the resulting water is drained off to clarification ponds.

20

A method of producing mine backfill from mine tailings is to process the tailings slurry with a bank of hydro-cyclones to remove the coarser portion of the material. The coarser portion (underflow) is fed into a silo and allowed to settle with some of the water overflowing the top of the silo. The denser tailings material is removed from the silo and 25 pumped to a mixer, where cement is added to produce hydraulic backfill.

The backfill, which is a slurry of typically 50% solids by weight, is poured down a vertical hole or pipe to be deposited in the mining voids or stopes left underground. Because it is a slurry, the backfill requires high volumes of cement to consolidate the 30 material, and water that does exude from the backfill must be pumped out of the mine. The cement contents range from about 3% by weight to about 10% by weight. Using a relatively low percentage of cement requires a much longer time for the backfill mass to be considered "load-bearing" or competent.

Another method of backfill is paste backfill. Paste backfill uses a lower cement content, usually about half of that used in the hydraulic backfill method described above. In addition, there is no water exuded from the fill mass to pump to the surface. The consolidation time is reduced to a fraction of the time required to consolidate hydraulic
5 backfill, allowing a faster cycle time. Another advantage of using paste backfill is that it is usually made from total (unclassified) tailings. This reduces the burden of maintaining a large surface impoundment area.

Paste backfill, however, has some drawbacks. It is more difficult to transport paste
10 to the mine or stopes, sometimes requiring a positive displacement pump to transport the paste through the piping. The production of paste is usually accomplished by processing the mill tailing slurry by using large vat thickeners, disc filters, or a combination of both. This requires a large multimillion dollar capital investment.

15 What is needed in the art is a foaming agent which can be incorporated into the solids mixture, then to form the foam within the mixture as a single-stage process, to eliminate the separate stages of preparation, pregeneration, and combination of a foam into the slurry prior to transport of the solids as in a pipe.

20 It is therefore an object of the invention to provide a method of transporting particulates by incorporating a foaming agent in a mixture of particulates and then producing a foam in the mixture prior to transport through pipelines or boreholes as a slurry.

25 SUMMARY OF THE INVENTION

The present invention also provides a method of excavating and transporting solid particulates comprising: removing the solid particulates from an excavation area; mixing a foaming agent with the solid particulates to form a transportable mixture; adding water and
30 a binder to the transportable mixture; mixing the transportable mixture, water, and binder to form a hydraulic composition; and transporting the hydraulic composition to a desired location.

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DETAILED DESCRIPTION OF THE INVENTION

The present invention provides a method of transporting solid materials including providing particulates, adding a foaming agent to form a mixture, and mixing said mixture
5 to form a foam within the mixture.

The benefit of the method of the present invention is that the steps of preparation, pregeneration, and mixing of the foam may be eliminated.

10 The mixing action causes the foaming agent to foam in the mixture. The mixing action may be provided by most commercially-available mixing devices.

The transporting of the mixture may be accomplished by pumping or by gravitational head driven pressure. Another benefit to this method of incorporating a
15 foaming agent into the particulate mixture is that the pressure required to pump the material is reduced. The foaming agent reduces the dilatancy of the particulates in the mixture. The use of the foaming agent therefore allows the pumping of particulates which would have otherwise been unpumpable.

20 The water content of the mixture is less than about 50% based on the mass of the solid material. Preferably, the mixture has a water content of about 5 to 25% to form a paste consistency. The water demand of the material is dictated by the features of the particle size distribution and mineralogy which are unique to each material.

25 Examples of solid materials that which can be transported by the abovementioned method include, but are not limited to, mine tailings, ores, sand, coal, soils, clays, silts, aggregates, and mixtures thereof.

Foaming agents which can be used with the method of the present invention
30 include alkanolamides, alkanolamines, alkylaryl sulfonates, polyethylene oxide-polypropylene oxide block copolymers, alkylphenol ethoxylates, carboxylates of fatty acids, ethoxylates of fatty acids, sulfonates of fatty acids, sulfates of fatty acids, fluorocarbon containing surfactants, silicon containing surfactants, olefin sulfonates, olefin

sulfates, hydrolyzed proteins, and mixtures thereof. A preferred foaming agent is an alpha olefin sulfonate sold under the trademark PS-356 from Master Builders, Inc., Cleveland, Ohio. The foaming agent is added in an amount from about 0.001% to about 0.4% based on the mass of the solid material, preferably about 0.005% to about 0.025%.

5

Preferably, the foaming agent is in the form of a dry powder. This provides ease of handling and improved storability. Liquid foaming agents could solidify in freezing climates, thus necessitating freeze protection or thawing prior to use.

10 Alkanolamide foaming agents according to the present invention include, but are not limited to, those having from about 12 to about 20 carbon atoms

Alkanolamine foaming agents according to the present invention include, but are not limited to, those having from about 12 to about 20 carbon atoms.

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Alkylaryl sulfonate foaming agents according to the present invention include, but are not limited to, those having one aryl group and having alkyl groups with about 12 to about 20 carbon atoms.

20 Polyethylene oxide-polypropylene oxide block copolymer foaming agents according to the present invention include, but are not limited to, those having about 10 to about 20 units of each block.

25 Alkylphenol ethoxylate foaming agents according to the present invention include, but are not limited to, those having an alkyl group of about 12 to about 20 carbon atoms.

Carboxylates of fatty acid foaming agents according to the present invention include, but are not limited to, those in which the fatty acid moiety has about 12 to about 20 carbon atoms.

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Ethoxylates of fatty acid foaming agents according to the present invention include, but are not limited to, those in which the number of ethoxylate groups is about 10 to about 20 and the fatty acid moiety has about 12 to 20 carbon atoms.

Sulfonates of fatty acid foaming agents according to the present invention include, but are not limited to, those in which the fatty acid moiety has about 12 to about 20 carbon atoms.

5 Sulfates of fatty acid foaming agents according to the present invention include, but are not limited to, those in which the fatty acid moiety has about 12 to about 20 carbon atoms.

10 Fluorocarbon containing surfactant foaming agents according to the present invention include, but are not limited to, those having about 12 to about 20 carbon atoms and one or more CH_2 moieties are replaced by CF_2 moieties.

Olefin sulfonate foaming agents according to the present invention include, but are not limited to, those having about 12 to about 20 carbon atoms.

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Olefin sulfate foaming agents according to the present invention include, but are not limited to, those having about 12 to about 20 carbon atoms.

20 Hydrolyzed protein foaming agents according to the present invention include, but are not limited to, the derived products of hydrolysis of proteins. The relative molecular weight of the protein can be any molecular weight that provides for foaming action in a cementitious mixture. Preferably, the relative molecular weight ranges from about 10,000 to about 50,000. Preferred hydrolyzed proteins are hydrolyzed gelatin, hydrolyzed collagen, and hydrolyzed proteins derived from blood. A non-limiting example of
25 hydrolyzed gelatin is TG222 from Milligan & Higgins (Johnstown, New York).

In the method of this invention, the steps of removing the solid particulates from an excavation area and mixing a foaming agent with the particulates to form a transportable mixer preferably occur in a mixing pump.

30

In addition to the foaming agent, there may also be added art-recognized admixtures which have known beneficial effects. These include, but are not limited to: foam-stabilizing agents, water-reducing dispersants, rheology-modifying agents and

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accelerators. One or more of such admixtures may be used, either individually or as mixtures.

A foam stabilizing agent may be added to the mixture to stabilize the foam to
5 provide a longer foam life. Foam stabilizing agents which can be used with the present invention include pre-gelatinized starches, cellulose ethers, polyethylene oxides, very fine clays, natural gums, polyacrylamides, carboxyvinyl polymers, polyvinyl alcohols, a nonpolar hydrophilic material, synthetic polyelectrolytes, silica fume, and mixtures thereof. A foam stabilizer may be needed because the transport time in the pipeline could be long
10 and/or the operating pressure in the pipeline may be high, thus compromising the stability of the foam.

Cellulose ether foam stabilizing agents according to the present invention include, but are not limited to, modified cellulose ether.

15

There are many examples of commercially-available polyethylene oxide foam stabilizing agents according to the present invention, one typical example being POLYOX (registered trade mark) range of Union Carbide. It is preferred that the polyethylene oxides have a weight average molecular weight greater than about 500,000.

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Very fine clay foam stabilizing agents according to the present invention include, but are not limited to, bentonite clay. The definition of very fine clays is meant to include those clays with a particle size less than about 20 microns.

25 Natural gum foam stabilizing agents according to the present invention include, but are not limited to, guar gum, welan gum, and mixtures thereof.

Polyvinyl alcohol foam stabilizing agents according to the present invention include, but are not limited to, those with a weight average molecular weight greater than
30 about 1,000.

Synthetic polyelectrolyte foam stabilizing agents according to the present invention include, but are not limited to, polyvinyl sulfonates with a weight average molecular

weight greater than about 1,000, polyvinyl polymers with a weight average molecular weight greater than about 1,000, and mixtures thereof.

The foam stabilizing agent may be added, either alone or in combination with other
5 foam stabilizing agents, in an amount from about 0.0001% to about 2% based on the mass of the slurry.

Additionally, a water-reducing dispersant may be added to the mixture to disperse the materials and thus allow for a lower water content in the mixture while still maintaining
10 a flowable consistency thus improving the properties of the placed fill material. Water-reducing dispersants which may be used with the present invention include, but are not limited to lignosulfonate salts, beta-naphthalene sulfonate-formaldehyde condensate salts, melamine-containing water reducers, polycarboxylic salts, polycarboxylate copolymers, polycarboxyl amines, polycarboxyl imides, and mixtures thereof. The water-reducing
15 dispersant is added in an amount greater than 0% to about 2% based on the mass of the binder or cementitious system. It should be noted that the dispersant dose rate may also be influenced by the particle size distribution and mineralogy of the solids material being treated, and the chemistry of the admixture.

20 As used herein, the term binder includes those materials which will cause a mixture to set. These include, but are not limited to cements, such as portland or high alumina cements, slags, fly ash, cementitious materials, lime, pozzolans, and mixtures thereof.

Further, any other additives which do not interfere with the properties of the
25 particulate slurry transported by the present invention may be added. These additives may include, but are not limited to, cement, set retarders, set accelerators, lime, fly ash, ground granulated blast furnace slag, and corrosion inhibitors. The amount of binder which may be added is determined by the amount of setting time and compressive strength desired. Typically, the binder or cementitious material is added in an amount greater than 0% to
30 about 30 % based on the mass of the solid material.

An advantage of incorporating a foaming agent into the particulate solids mixture is a reduction in the bleed. Bleeding is the separation of water from the mixture. It is desired

that the water not bleed from the mixture, because that will cause a reduction in the flowability of the mixture. The incorporation of the foaming agent can reduce the bleeding by as much as 100% based on laboratory trials.

5 When the material has been transported to its placement area, the air in the foam may be removed by a variety of methods, if required. These methods include, but are not limited to, mechanical impact as when dropped into a stope underground or when mechanically worked by conventional earth-compacting equipment such as rollers or sheeps-foot rollers. In addition, a chemical additive, such as a defoamer, may be
10 subsequently added to the transported slurry, which will cause the foam to collapse, thus removing most of the air voids from the foamed material.

In another embodiment of the present invention, a method is provided to excavate solid particulates, transform the solid particulates into a paste-like consistency, and then
15 transport the solid particulates to a placement area. First the solid particulates are removed from the excavation area by a pump and the foaming agent is mixed in. Some water may be necessary to break up the solid particulates to allow initial pumping; however, the amount of water needed does not generally exceed an amount that would lower the total solids below paste consistency.

20

The foaming agent may be added to the solid particulates in a mixer separate from the pump, or a mixing pump can be used. An example of a mixing pump is the Toyo DP/DL wet end pump. This type of pump is a submersible, bottom suction pump with an agitator and water supply at the bottom. In this pump, water is fed to the agitator to break
25 up thick materials or sludge and convert it to a paste to allow initial pumping. The pump is fitted with a nozzle to inject the foaming agent, or any other desired admixture, in the agitator portion of the mixer pump. The foaming agent is injected by use of a carrier, which can be water, compressed air, or any other gas. If the foaming agent is a dry powder, it can be dissolved in a water stream, or it can be blown in with the gas.
30 Alternatively, a pre-generated foam can be used in place of the in-situ foaming agent embodiment. The foam provides the pumpability of the transportable mine tailing mixture slurry.

The pump is moved about the excavation area to remove the solid particulates. Any suitable method of moving the pump is satisfactory. The pump may be suspended from a barge or a crane. Alternatively, the pump may be suspended from a two-dimensional cable pulley system which covers the excavation area. Such a cable pulley
5 system typically includes parallel opposed pulleys with a pulley mounted transversely between the parallel pulleys. The pump can move side to side on the transverse pulley and end to end on the parallel pulleys.

From the excavation area, the foamed solid particulates are transported to a backfill
10 plant. At the backfill plant, binder is added to the foamed solid particulates. The water content of the incoming foamed solid particulates is measured with a moisture analyzer. If necessary to achieve the desired total solids level in the final solid particulates binder mixture, water can be added to the mixture. The amount of water is calculated based on the total solids of the incoming foamed solid particulates.

15

Traditionally, a pug mixer with two counter-rotating mixer screws, variable speed drive, and adjustable pitch blades is used to mix binder and optional water into the solid particulates to form a hydraulic solid particulate composition. After being mixed, the hydraulic solid particulate composition is transported to the placement area by gravity feed
20 or by pumping.

In the above embodiment, the excavation area can be a mine tailings pond, the solid particulates can be mine tailings, and the placement area can be a mine or a stope.

25 When referring to a mine throughout this specification, it is also meant to include a stope.

EXAMPLES

The invention can be described by the following non-limiting examples. In the examples set forth below, slump is measured by ASTM C143 and C143M. Density is
30 measured by placing the mixture into a 400ml cup. The tare weight of the cup is 749g.

Mix A

40kg wet mine tailings

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1.2kg cement-Portland Cement from Lafarge

4kg water

Total weight of mixture and cup 1738.5g.

Density=989.5g/400ml

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The water content is varied to determine the slump.

Total water at 5.4kg: slump: large cone 11.3 cm

Total water at 6kg: slump: large cone 17.8 cm

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Mix B

40kg mine tailings

1.2kg cement-Portland Cement from Lafarge

3.9kg water

8.96ml of a polyoxyalkylene derivatized methacrylate polymer*

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5.0ml of a polyoxyalkylene derivatized methacrylate polymer*

Total weight of mixture and cup 1741.8g.

Density=992.8g/400ml

* - Polymer is FC-900 from Master Builders, Inc., Cleveland, Ohio

20

Next, a pre-generated foam is added to the mixture.

Slump of the mixture with foam large cone 14 cm small cone 4.4 cm

Total weight of mixture and cup 1510.3g.

Density=761.3g/400ml

25

Next, mixtures are prepared and tested as a plain reference and then with foaming agents added. The slump and density of the mixtures are tested, then test cylinders are prepared to test bleeding and compressive strength. There are prepared 4 7.6 cm x 15.2 cm cylinders, with 1 cylinder to measure bleedwater, and 3 for compressive strength determination.

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Set 1

45kg mine tailings @10.9% moisture

1.335kg cement-Portland Cement from Lafarge

6.6kg water is added to bring the pulp density to 72% solids.

1A

Slump large cone 19 cm

5 Total weight of mixture and cup 1571.9g.

Density=822.1g/400ml

Note: The material segregates and bleeds rapidly.

1B

10 To the Set 1A mixture, 9ml of a 15% solution of a modified cellulose ether is added.

Slump large cone 19 cm

Total weight of mixture and cup 1549.1g.

Density=800.1g/400ml

15 Note: The material segregates and bleeds.

1C

To the Set 1B mixture, 10g PS-356 is added as a foaming agent.

Slump large cone 17.8 cm

20 Total weight of mixture and cup 1469.6g.

Density=720.6g/400ml

Note: The mixture is stable and does not segregate.

Set 2

25 The mixture is prepared as per Set 1, but with 5.4 kg additional water to produce a pulp density of 74%.

2A

To the Set 2 mixture, a modified cellulose ether @8.87% or 1.88 g/kg of cement; and

30 a water reducing foam stabilizer @8.87% or 1.88 g/kg of cement; and 10g PS-356 are added.

Slump large cone 7.6 cm

Total weight of mixture and cup 1427.5g

Density=678.5g/400ml.

2B

To Mixture 2A, 1.2kg of water is added to yield a pulp density of 72%.

- 5 Slump large cone 15.9 cm
Total weight of mixture and cup 1421.2g.
Density=672.2g/400ml
Note: Slight bleeding is observed

- 10 The results of compressive strength and bleed testing for the above examples are listed below in Table 1.

TABLE 1

Sample	Bleed Test (ml of water) (cumulative)		Compressive Strength (MPa)	
	@4-5 hours	3 days	3 day	28 day
1A	22.5	50.5	0.26	2.39
1B	15	38	0.23	2.61
1C	3	12		1.69
2A	0	0	0.15	1.97
2B	3	3	0.12	1.76

- 15 Mix 1A shows the typical characteristics of an untreated slurry. Table 1 shows a high amount of bleeding in that Mix 1C a nearly 90% and 80% reduction in bleeding with the addition of the foaming agent and foam stabilizer at 4 to 5 hours and 3 days, respectfully. Mix 2A shows a combination of water reducer, several foam stabilizers, and foaming agent that produced a mix that did not bleed. Also, Table 1, shows that all of the
- 20 mixtures achieved an acceptable compressive strengths.

EXAMPLE 2

Three tests of mine tailings are made with PS-356 foaming agent supplied by Master Builders, Inc., Cleveland, Ohio.

- 25 The moisture of the mine tailings is approximately 14% by mass of the solids with a consistency of a loose, moist sand which has a "packing" consistency and will not flow as a liquid.

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In Test #1, 1000 grams of the mine tailings is mixed with 0.25g of PS-356 in a Hobart mixer. After approximately one minute of mixing, the material produces a mud-like quality which allowed the material to flow and could be pumped. With continued mixing, the density of the mix is reduced with further mixing as shown in Table 2 below.

5

In test #2, 1000 grams of the mine tailings is mixed with 0.1g of PS-356 in the Hobart mixer. After approximately one minute of mixing, the material produces a mud-like consistency which flowed and is pumpable. With continued mixing, the density of the mix is reduced as shown in Table 2 below.

10

In test #3, 1000 grams of the mine tailings were mixed with 0.05g of PS-356 in the Hobart mixer. After approximately one minute of mixing, the material produced a mud-like consistency that flowed and was pumpable. With continued mixing, the density of the mix was reduced as shown in Table 2 below.

15

TABLE 2

Mix Time (min)	PS-356 0.25g dose		PS-356 0.1g dose		PS-356 0.05g dose	
	Mass/400ml	Mass/ml	Mass/400ml	Mass/ml	Mass/400ml	Mass/ml
0	856	2.14	856	2.14	856	2.14
1	427.6	1.818	560.5	1.4	637.1	1.59
2	407.8	1.019	508.4	1.27	645.9	1.61
3	358.7	0.896	502.6	1.25	665.4	1.66
4	323.1	0.807	503.8	1.26	not tested	not tested

The tests results in Table 2 show that the addition of the foaming admixture can convert a tailing material with little free moisture into a material that has fluid properties when converted to a foamed mixture. The resulting material has lower density and better flow characteristics than the original moist tailings starting material.

It should be appreciated that the present invention is not limited to the specific embodiments described above, but includes variations, modifications and equivalent embodiments defined by the following claims.

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+32
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CLAIMS

1. A method of transporting particulates comprising,
providing particulates;
5 adding a foaming agent to form a mixture; and
mixing said mixture to form a foam within the mixture.
2. A method according to claim 1, wherein the mixture has a water content of less
than about 50% based on the mass of the particulates.
3. A method according to claim 1 or claim 2, wherein the foaming agent is in the form
10 of a dry powder.
4. A method according to any one of claims 1-3, further comprising adding a foam
stabilizing agent and mixing said mixture.
5. A method according to any one of claims 1-4, further comprising adding a water
reducing dispersant to the mixture and mixing the mixture.
- 15 6. A method according to any one of claims 1-5, further comprising adding a binder to
the mixture.
7. A method according to claim 6, wherein the binder is added at least one of prior to
the mixing step and after the transportation step.
8. A method of excavating and transporting solid particulates comprising:
20 a. removing the solid particulates from an excavation area;
b. mixing a foaming agent with the solid particulates to form a transportable
mixture;
c. adding water and a binder to the transportable mixture;
d. mixing the transportable mixture, water, and binder to form a hydraulic
25 composition; and
e. transporting the hydraulic composition to a desired location.
9. A method according to claim 8, wherein adding further comprises adding an
admixture.

10. A method according to claim 9, wherein the admixture is selected from the group consisting of foam stabilizing agent, water reducing dispersants, rheological modifying agents, accelerators, set retarders, corrosion inhibitors and mixtures thereof.



US005360558A

United States Patent [19]
Pakulski et al.

[11] **Patent Number:** **5,360,558**
[45] **Date of Patent:** **Nov. 1, 1994**

[54] **SLURRIED POLYMER FOAM SYSTEM AND METHOD FOR THE USE THEREOF**
[75] **Inventors:** Marek Pakulski, The Woodlands; Barry T. Hildek, Shenandoah, Tex.
[73] **Assignee:** The Western Company of North America, Houston, Tex.
[21] **Appl. No.:** 981,946
[22] **Filed:** Sep. 28, 1992

Related U.S. Application Data

[63] **Continuation of Ser. No. 660,298, Feb. 22, 1991, abandoned.**
[31] **Int. Cl.³** E21B 43/26
[32] **U.S. Cl.** 252/8.551; 166/308
[38] **Field of Search** 166/308; 252/8.551

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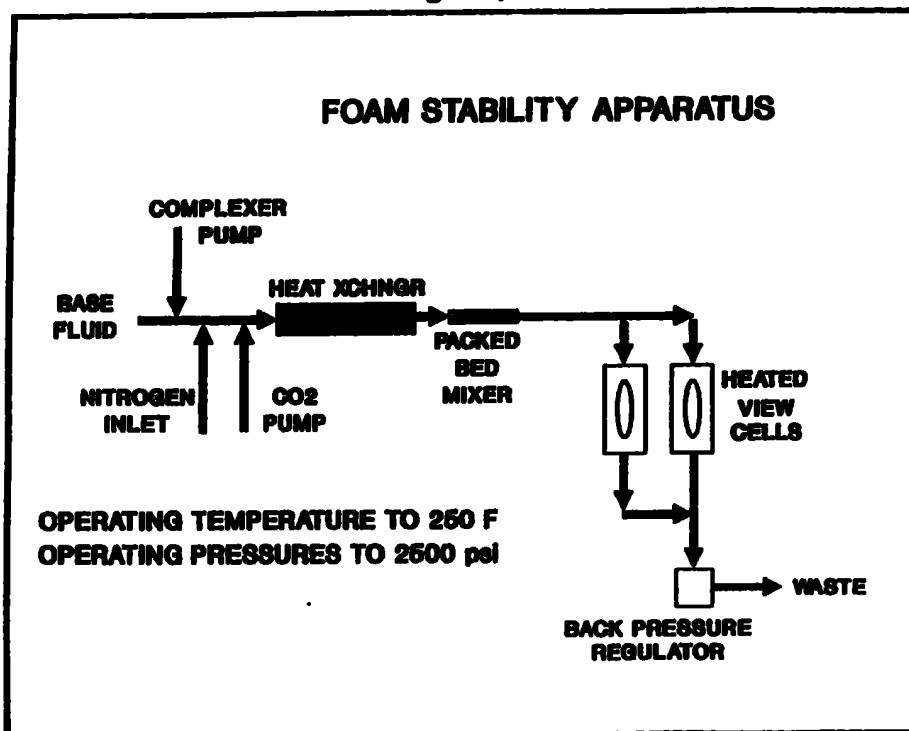
[57] **ABSTRACT**

This invention record describes a method for fracturing subterranean formations utilizing a foam comprising a water-based fracturing fluid comprised of water or brine or water and brine or brine and alcohol and a polymer slurry in diesel oil. Preferably, the polymer is comprised of a guar polymer and diesel oil in equal amounts. The foamer component preferably is comprised of cocobetaine, a solvent, an alpha-olefin sulfonate and water. The energizing phase component is comprised of carbon dioxide, nitrogen or a mixture of carbon dioxide and nitrogen.

34 Claims, 1 Drawing Sheet

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Figure 1



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**SLURRIED POLYMER FOAM SYSTEM AND
METHOD FOR THE USE THEREOF**

This is a continuation of U.S. patent application Ser. No. 07/660,298 filed Feb. 22, 1991 now abandoned.

TECHNICAL FIELD OF THE INVENTION

The present invention provides a method for fracturing subterranean formations utilizing a foam comprised of a fracturing gel component containing a polymer and liquid hydrocarbon mixed with water, brine, or water and brine, a foamer component which is compatible with the fracturing gel component, and an energizing phase component.

BACKGROUND OF THE INVENTION

The use of fluids to treat subterranean formations penetrated by a well bore containing hydrocarbons to increase the permeability, conductivity and production from these formations is well known in the art. The process of treating the formations to increase conductivity through the use of these fluids is known as "fracturing" the formation. Generally, in a fracturing process, a fluid of sufficient viscosity is pumped and/or injected into the formation at sufficient pressure and rate to fracture the formation. The fracturing fluid is of sufficient viscosity to carry proppant into the formation and of sufficient viscosity to obtain fracturing of the formation at high pressure, shear and temperature. The proppant consists of such materials as sand, glass beads, sintered bauxite, fine gravel and the like. The proppant is carried into the fracture and helps keep the formed fractures open after fluid recovery. The newly formed fracture is held open by proppant which provides increased routes or channels through which hydrocarbons can flow increasing production. Various fracturing fluids and processes for their use are known in the art. The art discloses the use of slurries, emulsions and gels. More recently, it was discovered that foams could be used in place of the known slurries, emulsions and gels. See U.S. Pat. No. 3,937,283 to Blauer.

As described in Blauer, various gases and liquids can be used to compose the fracturing foam. Generally, the foams include nitrogen, carbon dioxide and water with a suitable surfactant. The foam, as with the slurries, gels and emulsions in the art, containing proppant is pumped into the formation at such a pressure that it causes the fracture of the formation. However, unlike the previous fracturing systems, the use of foams increases well clean up due to the fact that the foam is easily removed from the well because when the pressure is released or reduced, the foam expands. Various foam fracturing systems are known in the art.

Generally, in making a foam, a fracturing gel is first made from water or brine, a gelling agent, i.e., a polymer and a suitable surfactant. The water or brine may contain up to about 20% alcohol, for instance, methanol. In addition, the fracturing gel may be crosslinked by use of known crosslinkers. After the gel is made, a foamer is added and the gel with the foamer is added to an energizing phase such as carbon dioxide or nitrogen or a combination of carbon dioxide and nitrogen to create a foam. Various systems for the addition of the energizing phase to the gel phase have been described in the art. Indeed, various systems have been devised wherein the carbon dioxide is added as the gel is

pumped down hole into the well bore and subsequently into the formation.

Various foamers are known in the prior art. For example, see U.S. Pat. Nos. 4,480,696, and RE 32,302. Betaines are known foamers. Betaines are multipurpose foaming agents or foamers primarily used in foam fracturing applications. Betaines are used to foam aqueous fluids while offering excellent detergency and interfacial tension-reducing properties. Betaines are particularly applicable to any reservoir which is generally classified as "water sensitive," that is, a reservoir which is slow to return water-based treatment fluids. Such reservoirs are often characterized by low permeability, and moderate amounts of clay or shale. Betaines offer superior performance in high temperature wells, where other foamers degrade.

Originally, fracturing foams were made utilizing a dry polymer which was mixed with water and the foamer before addition of the energizing phase. However, the use of a dry polymer, i.e., gelling agent was not conducive to fracturing systems wherein the water was gelled as it was pumped, that is, dry polymer was more limited to first mixing the polymer with water until a gel was formed and then pumping the gel for addition with the energizing phase and subsequent introduction into the formation. This method required more energy to be supplied by the surface pumps due to the increased viscosity of the gel. Further, if the fracturing job using the dry polymer system had to be abandoned or terminated permanently, the disposal of the pre-mixed gel created a problem.

In response to the above problems, a slurried polymer system was introduced into the market by The Western Company of North America. Western's slurried polymer system utilizes 50% diesel oil and 50% of a guar or guar-based polymer. The slurried polymer system of Western can include other liquid hydrocarbons besides diesel oil; for example, kerosene, naphtha, light mineral oil, and the like. Further, the fracturing gel made utilizing the slurried polymer system can be crosslinked. This system provides the advantage of being able to supply the gelling agent polymer in liquid form to the aqueous fluid as the aqueous fluid is pumped into the formation. If the fracturing job has to be discontinued, then the supply of polymer is simply stopped, thus, the user does not have to face disposal problems of unused gel. Further, there is provided a system which increases in viscosity while being pumped, decreasing surface pump horsepower needed. However, it was discovered that the slurried polymer system was not compatible with fracturing gels utilizing an alkylbetaine, i.e., cocobetaine, as the foamer. It was specifically discovered that diesel oil and other liquid hydrocarbons used in the system are very efficient defoamers and made the use of the slurried polymer system with the betaine foamer undesirable due to the lack of stability of the foam produced.

Therefore, a need exists for a foamer which is compatible with the slurried polymer system utilizing a liquid hydrocarbon like diesel oil and demulsifiers as components. The present invention provides foamers which are compatible with a slurried polymer system and provides a foam which has the desired rheological properties under high temperature, shear and pressure.

SUMMARY OF THE INVENTION

The present invention provides a foamer which is compatible with a fracturing gel comprising polymer

slurried in diesel oil which is injected into brine to be used to fracture a subterranean formation. Preferably, the foamer is comprised of alkylbetaine, an alkali metal or ammonium alpha-olefin sulfonate, a hydrophilic solvent and water.

The present invention also provides a method for fracturing a subterranean formation utilizing a first fracturing gel component comprised of diesel oil and a polymer mixed with brine. The fracturing gel may be crosslinked if desired with crosslinkers known in the art. Simultaneously, while injecting the first fracturing gel component into a well bore adding a second foamer component comprised of solvent, betaine, an alpha-olefin sulfonate and water. After the addition of the first and second components and while injecting the first and second components into the well bore adding a third energizing phase component of carbon dioxide or nitrogen or a mixture of carbon dioxide and nitrogen. Further, after injecting the first, second and third components into the well bore, maintaining a pressure on the formation for a period of time sufficient to fracture the formation and subsequently releasing the pressure on the formation.

The present invention also provides a foam for fracturing subterranean formations comprised of a first fracturing gel component comprised of a polymer and diesel oil mixed with water, brine, or water and brine, a second foamer component comprised of a solvent, a betaine, an alpha-olefin sulfonate and water, and a third energizing phase component comprised of carbon dioxide or nitrogen or carbon dioxide and nitrogen.

The present invention further provides a foamer which is compatible with and to be used with fracturing gels containing diesel oil and demulsifiers which produces a 70% quality foam having a half life of at least one hour at 1,000 psi and 225° F.

The present invention further provides a fracturing foam composition comprised of (1) from about 0.2% to about 3% by volume slurry comprised of from about 50% to about 70% by volume polymer and from about 30% to about 50% by volume diesel oil, (2) from about 0.1% to about 2% by volume foamer component compatible with the slurry, (3) from about 10% to about 40% by volume water or brine or a mixture of water and brine or a mixture of brine and alcohol, and (4) from about 50% to about 90% by volume energizing phase component.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a diagram of the foam generation equipment used to test foamers of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

The fracturing foam composition of the present invention comprises a slurried polymer component, brine or water or brine and alcohol, a foamer component, and an energizing phase component.

The invention is directed to slurried polymer components comprised of a mixture of a liquid hydrocarbon and a polymer. For example, liquid hydrocarbons such as kerosene, naphtha, light mineral oil, diesel oil and the like and mixtures thereof are useful in the present invention. Preferably, the liquid hydrocarbon utilized is diesel oil. Preferably, the diesel oil and polymer are present in equal amounts by weight percent of the slurried polymer component.

The polymer useful in the preparation of the slurried polymer component of the present invention includes solvatable polysaccharides having molecular weights of at least 100,000. Examples of polysaccharides useful in the present invention include the galactomannan gums, glucomannan gums, and their derivatives. Solvatable galactomannan and glucomannan gums are naturally occurring. The galactomannan gums and glucomannan gums can also be reacted with hydrophilic constituents to thereby produce derivatized polymers useful in the present invention. Solvatable polysaccharides having molecular weights of greater than about 200,000 are preferred in the practice of the present invention. The most preferred solvatable polysaccharides useful herein have molecular weights in the range of from about 200,000 to about 3 million. Examples of such polysaccharides include guar gum, locust bean gum, carra gum, xanthan gum, and guar derivatives such as sodium carboxymethyl guar, hydroxyethyl guar, sodium carboxymethylhydroxyethyl guar, hydroxypropyl guar, sodium carboxymethylhydroxypropyl guar. Cellulose derivatives such as hydroxypropylcellulose, carboxymethylcellulose, and carboxymethylhydroxypropylcellulose are also useful in the present invention. The preferred polymers are guar gum, hydroxypropyl guar and sodium carboxymethylhydroxypropyl guar; the most preferred gelling agent is sodium carboxymethylhydroxypropyl guar.

The foamer component of the present invention shows excellent nitrogen, carbon dioxide or binary foam stability in the presence of liquid hydrocarbons and/or demulsifiers (emulsion breakers). It has been found that the use of some of these foamers singularly do not produce a foam of good stability in the presence of liquid hydrocarbon solvents and/or demulsifiers. One embodiment of the foamer component of the present invention is comprised of a water miscible solvent, an alkylbetaine, an alpha-olefin sulfonate and water.

The solvent of the foamer component can be any of the lower molecular weight alcohols having molecular weights of 120 or less, like methanol, ethanol, propanol, isopropanol, isobutanol and the like. Further, the solvent can be any glycol, polyglycol, glycol ether, polyglycol ether, glycol ester, polyglycol ester, glycol ether ester, polyglycol ether ester, or a mixture of any of the above solvents. The preferred solvents of the foamer component are ethanol, methanol and propanol, and preferably are present in an amount of about 5% to about 20% by weight of the total foamer component composition.

The betaines of the foamer component of the present invention are of the general formula $RN+(CH_2)_nCH_2COO^-$ where R is a saturated or unsaturated hydrocarbon chain having from 6 to 22 carbon atoms derived from natural or synthetic sources. The betaines are present in an amount of about 10% to about 40% by weight of the total foamer component composition. The preferred betaine is dodecyl betaine (lauryl betaine) or cocobetaine (mixture of saturated and unsaturated betaines having from 8 to 18 carbon atoms) derived from natural coconut oil. Preferably, the cocobetaine is present in an amount of about 10% to about 30% by weight of the total foamer component composition.

The alpha-olefin sulfonate useful in the present invention is derived from an alpha-olefin having from 3 to 40 carbon atoms and preferably, having from 10 to 22 carbon atoms present in amount of about 1% to about 20% by weight of the total foamer component composition.

tion. The alpha-olefin sulfonate useful in the practice of the present invention may be ammonium, sodium or potassium alpha-olefin sulfonate and the like. An example of an alpha-olefin sulfonate useful in the practice of the present invention is sodium alpha-olefin sulfonate. A solution and is available and marketed by Witco Company, Organics Division, under the tradename of Witconate AOS. Several other examples of known alpha-olefin sulfonates available and suitable for use in the practice of the present invention are sold under the tradenames as follows: Bio-Terge, Polystep, and Stepan marketed by the Stepan Company; Calsoft AOS marketed by the Pilot Chemical Company.

Another embodiment of the foamer component of the present invention is comprised of an ammonium salt of an alkylether sulfate and lauramide diethanolamine (DEA). An example of a salt of an alkylether sulfate suitable for use in the present invention is sold under the tradename of Maxon 41 produced and sold by the PPG/Masur Inc. of Chicago or produced by the Stepan Company of Chicago under the tradenames of Steel CA-460 and Steel CS-460. Lauramide DEA is also produced by the Stepan Company and is sold under the tradenames of Ninol 30-LL and Ninol 40CO. Preferably, the alkylether sulfate is present in an amount of about 304 to about 404 by weight of the total foamer composition. Preferably, lauramide DEA is present in an amount of about 154 to about 254 by weight of the total foamer component composition.

The energizing phase component of the present invention is comprised of carbon dioxide, nitrogen, or a mixture of carbon dioxide and nitrogen. Preferably, if only carbon dioxide is used as the energizing phase component, a carbon dioxide flow rate to maintain about a 60% to about 90% foam quality is utilized in the practice of the present invention. Preferably, a flow rate sufficient to maintain a 70% foam quality is utilized. Foam quality, as used in the art, refers to the ratio of gaseous phase to sum of gaseous and liquid phases. If nitrogen is used as the energizing phase component, then a flow rate to maintain from about a 60% to about a 90% foam quality is utilized. Preferably, the nitrogen flow rate is such to maintain a 70% quality foam. If a mixture of carbon dioxide and nitrogen is utilized, then preferably a ratio of about 5:2 carbon dioxide to nitrogen is utilized with the total flow rate sufficient to maintain about 70% foam quality.

In the practice of the present invention, various proppant materials can be used. For example, sand, glass beads, sintered bauxite, fine gravel and the like can be used. The proppant is mixed with the gel before or after the foamer is added and prior to the introduction of the energizing phase component. The amount of proppant utilized in the practice of the present invention can be varied to provide the desired amount of proppant for introduction into the formation as is known in the art.

The method of fracturing a subterranean formation utilizing the present invention comprises: (1) mixing diesel oil or other liquid hydrocarbons with a polymer or a mixture of polymers in a batch mixer in a 1:1 ratio to form a slurry; (2) pumping water or brine (or a mixture of water and brine or brine and alcohol) to the well head; (3) while pumping the water or brine to the well head, adding the diesel oil/polymer slurry to the brine or water, thus generating a fracturing gel component; (4) while pumping the fracturing gel component to the well head, adding a foamer component of the present invention to the fracturing gel; (5) after the addition of

the foamer component to the gel, adding an energizing phase component of carbon dioxide, nitrogen or carbon dioxide and nitrogen to the mixture of the fracturing gel and the foamer component; (6) after the addition of the energizing phase component, injecting the mixture of the fracturing gel component, the foamer component, and energizing phase component into the well bore and subsequently into the formation; (7) maintaining a sufficient pressure on the well head until fracture of the formation is achieved and subsequently releasing the pressure to recover the mixture injected. If desired, the fracturing gel may be crosslinked with crosslinkers known in the art. Further, and if desired, a proppant material can be added to the mixture of the fracturing gel component with the foamer component before the addition of the energizing phase.

Foam generation equipment, as shown in FIG. 1, was used to test foamers of the present invention at conditions up to 1000 psi and 225° F. to see if the foamers were compatible with fracturing gels containing liquid hydrocarbons or demulsifiers. The equipment consisted of a conduit containing base fluid comprised of the fracturing gel component of polymer slurried in diesel and/or demulsifier mixed with foamer and with a 2% potassium chloride aqueous solution. To the fracturing gel component, there was added a complexer, i.e., crosslinker by the complexer pump if desired. After the addition of the crosslinker, nitrogen and then carbon dioxide was added. The mixture of the fracturing gel component and the energizing phase was run through a heat exchanger where the mixture was heated to the desired temperature. Subsequently, the mixture was directed to a packed bed mixer where the mixture was mixed to form a foam. After the mixer, the foam was directed to one of the two heated view cells through which the mixture was passed until the pressure, temperature and flow rates reached precalculated values and the system was equilibrated. After this, the other heated view cell was loaded with the foam and the view cell was subsequently closed. The view cells are conduits with valves at either end which may be opened and closed. The view cells were constructed to withstand the temperature of at least 250° F. and pressure up to 2500 psi. The view cells were also constructed such that a portion of a side of the view cell conduit is an observation window to allow observation of the stability of the foam contained in the view cell conduit. The foam destabilization was observed and the volume of liquids drained from the foam was recorded. Tests were performed at (1) 160° F. and 700 psi on guar polymer 40 pounds/1000 gallons in 2% potassium chloride (KCl) aqueous solution, pumping rate 40 milliliters per minute (ml/min), the carbon dioxide flow rate was 0.017 lb/min, nitrogen flow rate was 2.96 standard cubic feet per minute (SCF/min), and (2) at 225° F./1000 psi on guar polymer 40 pounds/1000 gallons in 2% KCl aqueous solution, pumping rate was 40 ml/min, carbon dioxide flow rate was 0.018 lb/min, nitrogen flow rate was 3.05 SCF/min. The flow rates were calculated to assure a 70% foam quality, 90% CO₂, 20% N₂, 30% liquid.

The polymer component used was (1) a dry, diesel oil free product (see Experiment 1 of Table 1 below) or (2) was a 1:1 mixture with diesel oil (see Experiments 2-16 of Table 1 below). As stated, in a typical experiment, all foam components were pumped through one view cell until temperature, pressure, and flow rates reached precalculated values and the system equilibrated. At this point, the other view cell was loaded with foam.

Next, the cell was closed and foam destabilization was observed. The volume of liquids drained from the foam was recorded at five minute intervals. Foam quality and

one solution (artificial brine) slurried polymer component with the foamer component of the present invention.

TABLE 1

Half-Life Time of 70% Quality Heavy Foams Generated from Different Foamer Compositions					
Experiment #	Gel	Foam Composition (loading concentration vol %)		T _{1/2}	
				700 psi 160° F.	1000 psi 225° F.
1	No Diesel	Cocobetaine (0.7%)	Den (0.1%)	3:00 hr	20 min
2	Diesel Present	Cocobetaine (0.7%)	Cocobetaine (0.7%)	33 min	
3	Diesel Present	Cocobetaine (0.7%)	Den (0.1%)	5 min	0
4	Diesel Present	Cocobetaine (1.0%)	Den (0.1%)		0
5	Diesel Present	Cocobetaine (1.5%)	Den (0.1%)	>2:00 hr	1:10 hr
6	Diesel Present	AOS (0.1%)	Den (0.1%)	33 min	
7	Diesel Present	AOS (0.7%)		3:10 hr	
8	Diesel Present	AOS (0.7%)	Den (0.1%)	2:20 hr	30 min
9	Diesel Present	Manna 41 (0.7%)	Den (0.1%)	>3:00 hr	1:30 hr
10	Diesel Present	Steel CA-480 (0.56%)	Den (0.1%)	3:30 hr	1:50 hr
		Minal 30-LL (0.14%)			
11	Diesel Present	Cocobetaine (0.5%)	Den (0.1%)		1:50 hr
		AOS-12 (0.2%)			
12	Diesel Present	Cocobetaine (0.5%)	Den (0.1%)	>3:00 hr	2:00 hr
		AOS (0.2%)			
13	Diesel Present	Cocobetaine (0.58%)	Den (0.1%)		2:15 hr
		AOS (0.12%)			
14	Diesel Present	Cocobetaine (0.3%)	Den (0.1%)		1:05 hr
		AOS (0.1%)			
15	Diesel Present	Cocobetaine (0.54%)	Den (0.1%)		2:00 hr
		AOS (0.16%)			
16	Diesel Present	Cocobetaine (0.62%)	Den (0.1%)	3:20 hr	2:20 hr
		AOS (0.18%)			

AOS = C-14-C-14, alpha-olefin sulfonate (40% sol).
Manna 41 = alpha-phenylpolythiophene sulfonate (40% sol).
Minal 30-LL = lauryl dimethylsulfonate (40% sol).
AOS-12 = C-12, alpha-olefin sulfonate (40% sol).
Steel CA-480 = ammonium lauryl sulfate (40% sol).
Den = Random copolymer sulfonate (40% sol).

half-life time (T_{1/2}) were measured. Foam quality was calculated as follows:

35

$$\text{Foam Quality} = \frac{\text{View Cell Volume} - \text{Liquids in Cell After Total Foam Collapse}}{\text{View Cell Volume}} \times 100\%$$

Foam half-life time was recorded when half of liquid drained to the bottom of a view cell containing the foam.

Various foamers were tested on a binary foam generator under the above conditions (See Table 1 for results). Analysis of the results indicate that diesel oil severely, and demulsifiers to a lesser extent, inhibit the performance of foamers. Results of single foamer experiments (Nos. 1-9) compared to results obtained from a mixture of various foamers (Nos. 10-16) clearly indicate the superiority of the mixtures versus the same foamer components applied singularly and separately. For example, in experiment 5, a 1.5% concentration of cocobetaine had to be applied to achieve the same foam stability (T_{1/2}:05 = 1:10 hr/1000 psi 225° F.) as when 0.4% of a mixture (0.3% cocobetaine, 0.1% AOS) was used in experiment no. 14.

The foam generated with the foamers of the present invention exhibits little temperature and pressure dependency, that is, temperature and pressure have small destabilization effects on the foam. Table 1 illustrates that eight foamer component compositions of the present invention are not diesel oil or demulsifier sensitive and are compatible therewith, i.e., they have a half-life of at least one hour at 1000 psi and 225° F. in the presence of diesel oil and/or demulsifiers. The tests in Table 1 illustrate that very stable foams were generated using a 50% diesel and 50% guar in 2potassium chloride aque-

What is claimed is:

1. A fracturing gel comprised of polymer, diesel oil and a foamer, said foamer comprised of (a) from about 5% to 20% by weight solvent, said solvent comprised of an alcohol having a molecular weight of 120 or less, a glycol, or mixtures thereof; (b) from about 10% to about 30% by weight betaine; and (c) from about 1% to about 20% by weight alpha-olefin sulfonate.

2. The fracturing gel of claim 1 wherein the polymer is crosslinked.

3. The fracturing gel of claim 1 wherein the betaine Of the foamer is selected from the group comprised of betaines having from 6 to 22 carbon atoms.

4. The fracturing gel of claim 1 wherein the alpha-olefin sulfonate of the foamer is sodium or ammonium alpha-olefin sulfonate.

5. The fracturing gel of claim 1 wherein the alpha-olefin sulfonate of the foamer is potassium alpha-olefin sulfonate.

6. The fracturing gel of claim 1 wherein the alpha-olefin sulfonate of the foamer has from about 10 to about 22 carbons atoms.

7. The fracturing gel of claim 1 wherein the diesel oil and polymer are present in equal amounts by weight percent.

8. The fracturing gel of claim 1 additionally including brine or brine and alcohol.

9. A fracturing foam composition comprised of: from about 0.2% to about 3% by volume slurry polymer component comprised of from about 30% to 50% by volume liquid hydrocarbon and from 50% to 70% volume polymer;

from about 10% to 40% by volume water, brine or a mixture of brine and alcohol;
from 0.1% to about 2% by volume foamer component comprised of a betaine; an olefin sulfonate, and a solvent; and
from about 50% to 90% by volume energizing phase component comprised of nitrogen, carbon dioxide or nitrogen and carbon dioxide.

10. The fracturing foam composition of claim 9 wherein the polymer is comprised of galactomannan gum, glucomannan gum, or cellulose and mixtures thereof.

11. The fracturing foam composition of claim 9 wherein the foamer component is comprised of a betaine, a hydrophilic solvent comprised of an alcohol, a glycol, or mixtures thereof, and an alpha-olefin sulfonate.

12. The fracturing foam composition of claim 11 wherein the alpha-olefin sulfonate of the foamer component is an alkali metal or ammonium alpha-olefin sulfonate derived from an alpha-olefin having from about 10 to about 22 carbon atoms.

13. The fracturing foam composition of claim 9 wherein the foamer component is comprised of from about 10% to about 30% betaine by weight; from about 5% to about 20% solvent by weight; and from about 1% to about 20% alpha-olefin sulfonate by weight.

14. The fracturing foam composition of claim 9 wherein the mixture of brine and alcohol is comprised of from about 1% to about 20% methanol.

15. A foam comprising a polymer, diesel oil, carbon dioxide or nitrogen or carbon dioxide and nitrogen, and a foamer, said foamer comprising about 12% by weight of the foamer methanol, about 23% by weight of the foamer cocobetaine, about 8% by weight of the foamer sodium alpha-olefin sulfonate, and water.

16. The foam of claim 15 wherein the foamer comprises from about 0.1% by volume to about 3% by volume of the foam.

17. A foam comprised of diesel oil, polymer, and a foamer, said foam being 70% quality with a half-life of at least one hour at 1,000 psi and 225° F., said foamer comprised of ammonium salt of an alkylether sulfate and lauramide diethanolamine.

18. The foam of claim 17 wherein the foamer is comprised of about 30% to about 40% by weight ammonium salt of alkylether sulfate and about 15% to 25% by weight lauramide diethanolamine.

19. A foam used for fracturing subterranean formations comprised of:

- (a) a fracturing gel component comprised of a polymer, diesel oil, water or brine,
- (b) a foamer component comprised of solvent, betaine, and an olefin sulfonate, and

(c) an energizing phase component comprised of carbon dioxide or nitrogen or carbon dioxide and nitrogen.

20. The foam of claim 19 wherein the polymer of the fracturing gel component is comprised of guar or cellulose.

21. The foam of claim 19 wherein the alpha-olefin sulfonate of the second foamer component is an alkali or ammonium alpha-olefin sulfonate derived from an alpha-olefin having from about 10 to about 22 carbon atoms.

22. The foam of claim 19 wherein the polymer and diesel oil of the first fracturing gel component are present in equal amounts by weight percent.

23. The foamer component of claim 19 wherein the solvent is methanol.

24. The foam of claim 19 wherein the fracturing gel component is comprised of about 20% alcohol or less.

25. The foam of claim 19 wherein the polymer of the fracturing gel component is crosslinked.

26. A foamer comprised of a mixture of an alkylether sulfate and lauramide diethanolamine or a mixture of a betaine and an alpha-olefin sulfonate for fracturing gels containing diesel oil and demulsifiers, said foamer and gels producing a 70% quality foam having a half-life of at least one hour at 1,000 psi and 250° F.

27. The foamer of claim 26 wherein the foamer is additionally comprised of a solvent comprised of an alcohol having a molecular weight of 120 or less or a glycol, or mixtures thereof.

28. The foamer of claim 27 wherein the foamer is comprised from about 10% to about 30% by weight betaine, about 5% to about 20% by weight solvent, and about 1% to about 20% alpha-olefin sulfonate.

29. The foamer of claim 27 wherein the solvent of the foamer is comprised of an alcohol having a molecular weight of the 120 or less.

30. The foamer of claim 27 wherein the alpha-olefin sulfonate is an alkali metal or ammonium alpha-olefin sulfonate having from about 10 to about 22 carbon atoms.

31. A fracturing foam comprising a polymer, diesel oil, carbon dioxide or nitrogen or a mixture thereof, and a foamer, said foamer comprised of: a hydrophilic solvent comprised of an alcohol, a glycol, or mixtures thereof; a betaine; and an alpha-olefin sulfonate.

32. A fracturing foam comprising a polymer, diesel oil, carbon dioxide or nitrogen or a mixture thereof, and a foamer comprised of an ammonium salt of an alkylether sulfate and lauramide diethanolamine.

33. The fracturing foam composition of claim 32 wherein the foamer is comprised of an ammonium salt of an alkylether sulfate and lauramide diethanolamine.

34. The fracturing foam of claim 33 wherein the foamer is comprised of about 30% to about 40% by weight ammonium salt of alkylether sulfate and from about 15% to about 25% by weight lauramide diethanolamine.

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