



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

<b>(51) International Patent Classification <sup>6</sup> :</b>  <b>E21B 43/26</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 99/63199</b>  <b>(43) International Publication Date:</b> 9 December 1999 (09.12.99)
<b>(21) International Application Number:</b> PCT/US99/10362  <b>(22) International Filing Date:</b> 11 May 1999 (11.05.99)  <b>(30) Priority Data:</b> 09/087,282      29 May 1998 (29.05.98)      US  <b>(71) Applicant:</b> 3M INNOVATIVE PROPERTIES COMPANY [US/US]; 3M Center, P.O. Box 33427, Saint Paul, MN 55133-3427 (US).  <b>(72) Inventors:</b> IRWIN, Michael, J.; P.O. Box 33427, Saint Paul, MN 55133-3427 (US). MUIR, David, J.; P.O. Box 33427, Saint Paul, MN 55133-3427 (US).  <b>(74) Agents:</b> BJORKMAN, Dale, A. et al.; 3M Innovative Properties Company, Office of Intellectual Property Counsel, P.O. Box 33427, Saint Paul, MN 55133-3427 (US).		<b>(81) Designated States:</b> AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> ENCAPSULATED BREAKER SLURRY COMPOSITIONS AND METHODS OF USE		
<b>(57) Abstract</b>  <p>An encapsulated breaker slurry composition for reducing the viscosity of a fracturing fluid. The slurry has a flashpoint above 93 °C, and the liquid of the slurry does not facilitate release of the breaker from the coating. Methods of using the slurry composition are also described.</p>		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

ENCAPSULATED BREAKER SLURRY COMPOSITIONS  
AND METHODS OF USE

FIELD OF INVENTION

- 5           This invention relates to encapsulated breakers. More specifically, this invention relates to slurries of encapsulated breakers.

BACKGROUND OF THE INVENTION

- 10           Hydraulic fracturing of oil subterranean formations is a well known technique for increasing the permeability of subterranean formations. In this technique, a viscous fluid ("fracturing fluid," commonly an aqueous fracturing fluid, most commonly guar) is introduced to the wellbore, pressure is applied to induce fracture, and proppants in the fluid (most commonly sand) maintain the fractures in an open state. The viscous fluid must then be removed, and oil is
- 15           harvested from the thus opened subterranean formation. In order to facilitate the quick removal of the fracturing fluid, chemicals are used to reduce or "break" the viscosity of the fracturing fluid; these chemicals (most commonly oxidizers, and in particular persulfates) are known as "breakers." The chemical reaction of the breaker with the fracturing fluid is undesirable prior to completion of the fracturing
- 20           operation. Therefore, it is advantageous to encapsulate or coat the particles with a polymer to delay the release of the breaker, and hence to delay the breaking of the fracturing fluid.

- Many materials have been used in the art to encapsulate breakers for fracturing fluids. For example, US Patent 4,506,734 (Nolte) describes a breaker
- 25           within a crushable glass or ceramic coat that ruptures upon closure of the induced fractures. US Patent 4,741,401 (Walles, et.al.) teaches that a polymer can be applied to a solid breaker chemical, most preferably by air suspension coating. The polymers of Walles are most typically homopolymers and copolymers of polyolefin and ethylene oxides. This patent describes the release of the breaker by

rupture of the membrane, either by the force of closure of the fractures within the subterranean formation or by the osmotic pressure of water diffusing into the shell. In US Patent 5,164,099 (Gupta, et.al.), a polymer is applied to a solid particle of a breaker chemical by interfacial polymerization. Typically, this polymer is a  
5 polyamide or a crosslinked cellulosic material. This patent states that breaker is released from the capsules described therein by diffusion through the membrane of the encapsulation.

U.S. Pat. No. 5,591,700 (Harris, et.al.) relates to encapsulated breakers that are coated by surfactants that are solid at ambient surface conditions and which  
10 dissolve at elevated temperatures in the subterranean formation. The surfactants are mixed in from the dry state.

Alkyl-2-cyanoacrylate monomers polymerize immediately in the presence of a weak base, and as such have been widely used for encapsulation and particle coating in the pharmaceutical industry, primarily for the purpose of drug delivery.  
15 For example, Kante *et al.* (Int. J. Pharm., 1980, 7, 45.) have described a method for preparing actinomycin D nanoparticles using poly(butylcyanoacrylate).

US Patent 4,452,861 (to RCA Corporation) describes a method for coating luminescent, inorganic phosphors using polymeric cyanoacrylates. The procedure outlined involves a five stage process which requires complete evaporation of the  
20 nonaqueous solvent during each of the coating stages and a final step which calls for washing of the coated particles.

#### SUMMARY OF THE INVENTION

An encapsulated breaker slurry composition is provided for reducing the  
25 viscosity of a fracturing fluid. The breaker is enclosed within a coating and is provided as a slurry, together with a liquid that is selected such that the overall slurry has a flashpoint above 93°C. The liquid is also selected such that it does not facilitate release of the breaker from the coating. The slurry also contains a suspension aid in an amount sufficient to maintain the suspension of the

encapsulated breaker in the liquid. Methods of use of these encapsulated breaker slurry compositions are also provided.

#### DETAILED DESCRIPTION OF THE INVENTION

5           While certain encapsulated breakers have been utilized before in the prior art, a new format for delivery of encapsulated breakers has been discovered, which format provides surprising advantages over previous formats. It has been found that providing encapsulated breakers in a slurry format has distinct advantages, because these compositions are easier to ship, mix and pump than prior art  
10 compositions. Because the slurry composition preferably contains surfactant, the fracturing fluid will readily flow from the fractured formation after breaking, and thereby provides easier cleanup of the subterranean formation.

          The slurry compositions of the present invention are easy to handle at the pumping site because there is no need to use solid metering devices. Time is  
15 thereby saved at the work site because liquids mix faster, more completely and easier than solids with liquids. Because the breaker in a slurry composition may be more readily and completely mixed with the fracturing fluid, the breaker will be more uniformly distributed in the fluid pumped downhole, and will thereby also be more effective in completely breaking the fracturing fluid in even the remotest  
20 parts of the subterranean formation.

          As an additional advantage, the slurry format allows the user to greatly simplify their logistics in maintaining work supplies. Because the materials may now be provided in a simple to use, stable, premixed format, the number of components that must be ordered and kept in inventory and or supply at the drilling  
25 site by the user may be substantially reduced. Further, the likelihood of error on the part of workers at the site in mismeasuring or improperly mixing components is substantially reduced as well.

          Providing the encapsulated breaker in a slurry format allows the optional surfactant to be present in an available liquid phase at time of mixing with the

fracturing fluid. This format aids in providing easy and complete mixing of the breaker throughout the fracturing fluid.

Additionally, because the encapsulated breaker is provided as a slurry for mixing with the fracturing fluid, the material to be pumped downhole is more homogeneous in distribution of both the breaker and any surfactant in the composition. Use of the present invention therefore may result in fewer agglomeration problems, especially downhole, while removing the fracturing fluid from the formation, because the breaker is available throughout the fracturing fluid and the surfactant is available at the site of the breaker to assist in removal of agglomerates in the broken fracturing fluid from the formation.

The preferred breaker material for aqueous-based fracturing fluids can comprise, for example, enzymes such as hemicellulase, oxidizers such as sodium or ammonium persulfate, organic acids or salts, such as citric acid or a citrate, fumaric acid, liquids adsorbed on a solid substrate, solid perborates, solid peroxides or other oxidizers, mixtures of two or more materials and the like. Most preferably, the breaker material is potassium persulfate. For gelled hydrocarbon fracturing fluids, preferred breakers include calcium oxide, calcium hydroxide, *p*-nitrobenzoic acid, triethanolamine, sodium acetate, sodium bicarbonate, and the like.

The coating of the encapsulated breaker is any coating suitable for protecting the breaker from premature reaction with the fracturing fluid, while providing an appropriate release mechanism to allow the breaker to reduce the viscosity of the fracturing fluid in the desired time frame, thereby allowing removal of material from the subterranean formation. Examples of suitable coating materials include glass coatings, ceramic coatings, homopolymers and copolymers of polyolefin and ethylene oxides, polyamides, crosslinked cellulosic materials, polyureas, polyurethanes, dehydrated gums (such as guar), surfactant coatings, and the like.

The encapsulated breaker of the present invention is preferably enclosed within a hydrolytically degradable polymer coating. By "hydrolytically degrade"

is meant that the polymer coating will react with water to chemically break down the polymer coating to predominantly non-solid components in a time and temperature range appropriate for the intended use. Preferably, the coating will hydrolytically degrade within four hours at 70°C. An encapsulated breaker having  
5 a coating that hydrolytically degrades is superior to prior art systems, because it allows better control of release time and ease of handling not previously afforded by prior art systems. Because the breaker is encapsulated in a material that reacts with water, rather than simply dissolves or dissipates in water, the release can be controlled by reaction rate of the coating with water. Preferred encapsulated  
10 breakers of this type are disclosed in an application entitled ENCAPSULATED BREAKERS, COMPOSITIONS AND METHODS OF USE (docket no. 54239USA5A) filed on even date with this application, which is hereby incorporated by reference.

The preferred polymer shell material of the present invention is primarily a  
15 poly(alkyl-2-cyanoacrylate), which is present in an amount sufficient to allow the coating to hydrolytically degrade at temperatures of use above room temperature. Preferably, the poly(alkyl-2-cyanoacrylate) is at least about 50% by weight of the total content of the coating, more preferably at least about 70% and most preferably at least about 90%. Other materials that may be incorporated into the  
20 coating of the present material include comonomers that are copolymerizable with alkyl-2-cyanoacrylate.

The liquid of the present slurry compositions is selected such that the overall slurry has a flashpoint above 93°C for transport safety considerations as measured according to ASTM D 93-90 (the standard test method for flashpoint by  
25 Pensky-Martens, closed tester.) In the case of solvents that have flashpoints that are too low, the effective flashpoint of the slurry composition may be adjusted by mixing solvents. The slurry therefore will be considered to be safe for transport from a flammability and combustibility perspective.

The liquid is further selected such that it does not facilitate release of the  
30 breaker from the coating. Thus, the liquid will not cause diffusion of the breaker

out of the encapsulation shell; diffusion of the liquid into the capsule, thereby causing rupture and release of the breaker prematurely; dissolution of the encapsulating shell; degradation of the encapsulation shell; or initiate any other release mechanism.

- 5            Optionally, the liquid of the slurry composition may comprise an oily or waxy material to further control the time for release of the breaker in embodiments where release of the breaker is effected by contact of the coating with water or other liquid. Access of water or other liquid to the capsule wall to initiate release of the the breaker may be retarded because of the coating of oil or wax.
- 10          Optionally, the polymer that coats the breaker material may be chemically modified by selection of pendant functionality or surface treatment of the coated breaker, so that the coated breaker has an enhanced affinity to wet out an oily or waxy solvent. This further affinity serves to provide additional short term
- 15          solvents is particularly contemplated in this embodiment, whereby a hydrophobic solvent that will have an affinity to the coated breaker may be provided together with a solvent that is more hydrophilic. The presence of the more hydrophilic solvent will serve to render the slurry more readily mixable with an aqueous fracturing fluid.
- 20           As a specific example, mineral oil has surprisingly been found to be an extremely suitable liquid for use in slurries of encapsulated breaker for most coating materials. Thus, polyurethane, polyurea, polyamides, poly(alkyl-2-cyanoacrylates) coating materials, and the like have all been found to be stable with respect to mineral oil. Other liquids, such as hydrofluoroethers have also been
- 25          found to be good liquids for use in formation of stable slurries of the present invention.

                Particularly preferred solvents are non-hygroscopic solvents that provide a pumpable slurry under conditions of use. Examples of preferred solvents include mineral oil (such as drill mud oil), vegetable oil, canola oil, siloxanes,

30          hydrofluoroethers and the like. Materials are preferably selected such that the

material is pumpable even at freezing temperatures. Aliphatic solvents may additionally be used, such as alkanes or aliphatic mixtures including kerosene. In the case of solvents that have flash points that are too low, the effective flashpoint of the slurry composition may be adjusted by mixing of solvents.

5                   Suspension aids suitable for use in the present invention include surfactants, and the like. Thickeners may additionally be incorporated into the slurry. A preferred class of suspension aids are thickeners, which include natural extracts such as gum arabic, gum ghatti, khaya gum, agar, pectin, carrageenin and alginates; modified natural extracts; various gums including guar gum, rhamosan  
10 gum, xanthan gums; modified cellulose, such as sodium carboxymethyl cellulose, methyl cellulose, and hydroxyalkylcelluloses; and synthetic polymers such as ultra high molecular carboxy vinyl (carbomers) and acrylic polymers; inorganic thixotropes such as fumed silica, thixotropic clays, and titanates; polysaccharides (e.g., celluloses, starches, alginates); and the like.

15                   Preferably, the slurry composition will maintain a uniform suspension at room temperature for at least two weeks. More preferably, the slurry composition will maintain a uniform suspension at room temperature for at least one month.

                  The breaker slurry composition preferably contains a surfactant. Surfactants provide enhanced stability of the slurry and even distribution of the  
20 particles suspended in the slurry, although the surfactant alone may not be sufficient to properly suspend the encapsulated breaker. Preferred surfactants include oxyalkylated phenolic resin surfactants, resin ester surfactants, polyol surfactants, alkylaryl sulfonate surfactants, polymeric amine surfactants, alcohol ether sulfonates, imidazoline cationic surfactants, complex phosphate esters, amine  
25 alkylaryl sulfonates, alkyl amidoamine surfactants, polyamido imidazoline surfactants, fatty imidazoline surfactants, dimer trimer acid surfactants, polyoxyethylated rosin amines, polyoxyethylated rosin amines, polyoxyethylene glycol surfactants, alcohol ether sulfonate surfactants, alcohol ether sulfate  
30 ether sulfates, calcium alkylaryl sulfonates, amine dodecylbenzene sulfonates, fatty

acid amides, alkanolamides, and mixtures thereof. Such surfactants are generally known as petroleum surfactants, generally commercially available from Witco Company. Other surfactants include fluorinated surfactants, such as the Fluorad™ surfactants from 3M.

- 5           Clays may be used in the slurry compositions of present invention, including smectic clays including modified montmorillonites, hectorites, and bentonites.

- Proppants additionally may be provided in the slurry composition to assist in holding the fractured subterranean formation open after breaking and removal of  
10   the fracturing fluid. Proppants may be selected from any material appropriate for introduction downhole, including sand and sintered bauxite.

- The slurry composition comprising the encapsulated breaker may additionally comprise adjuvants suitable for incorporation in breaker compositions, such as colorants, fragrances, preservatives, anti-settling agents, pH controlling  
15   buffers, and viscosity modifiers.

- Typically, the fracturing fluid is a hydrated polymer such as guar, hydroxyalkylguar, hydroxyalkylcellulose, carboxyalkylhydroxyguar, carboxyalkylhydroxyalkylguar, cellulose or other derivatized cellulose, xanthan and the like in an aqueous fluid to which is added a suitable crosslinking agent.  
20   Suitable crosslinking agents include compounds such as borates, zirconates, titanates, pyroantimonates, aluminates and the like.

- The encapsulated breaker of the present invention is preferably added to the fracturing fluid before the fluid is pumped downhole. In the preferred aspect of the present invention, the encapsulated breaker is extremely stable even in the  
25   presence of water at ambient conditions above ground, so the mixing with the fracturing fluid can be taken with due time and care without concern as to premature viscosity breakdown. Because the encapsulated breaker is provided as a slurry, it may be easily mixed with the fracturing fluid without the need to resort to solid metering devices. Most preferably, the slurry composition of the present  
30   invention is pumped simultaneously with the fracturing fluid downhole using

liquid metering devices. Optional liquid mixing equipment to ensure even mixing of the two liquid streams may additionally be utilized.

The following examples are provided for purposes of illustrating the present invention, and are not intended to be limiting of the broadest concepts of the present invention. Unless otherwise indicated, all parts and percentages are by weight.

#### Example

##### 10 Example 1:

A 1 L polymerization flask fitted with stainless steel baffles was charged with 300 mL of IPAR 3 drill mud oil (commercially available from Petro-Canada) and 80 g of industrial grade potassium persulfate (60 - 100 mesh). Over a period of about 20 minutes, 15 g ethyl-2-cyanoacrylate was added to the mixture. The persulfate salt was dispersed by stirring at 1500 RPM with a 6-blade turbine agitator. After stirring for about 10 minutes, 0.1 g of triethanolamine was added to the suspension. Stirring continued at room temperature for a further twenty minutes to ensure complete reaction of the cyanoacrylate. With continued stirring, 17 g of "Cab-O-Sil M-5" Silicon Dioxide was added to the mixture in order to provide a stable slurry of the coated persulfate particles.

##### Example 2

25 A 1 L tripore vessel fitted with stainless steel baffles was charged with 300 mL of hexanes and 80 g of industrial grade potassium persulfate (60 - 100 mesh). The persulfate salt was dispersed by stirring at 1500 RPM with a 6-blade turbine agitator. Over a period of about 20 minutes, 15 g Loc-tite™ 411 (85-90% ethyl cyanoacrylate, 10-15% poly (methyl methacrylate), 1-3% fumed amorphous silica (crystalline free), 0.1-1% phthalic anhydride, 0.1-0.5% hydroquinone, batch number 7KP023A) was added to the mixture, and after stirring for about 10

minutes, 0.1 g of triethanolamine was added to the suspension. Stirring continued at room temperature for a further twenty minutes to ensure complete reaction of the cyanoacrylate. The white powder was collected by filtration and re-dispersed in 350 mL of IPAR 3 drill mud oil along with 3 g of Fluorad™ FC-760

5 fluorochemical surfactant (available from 3M) at a mixing rate of 1430 RPM. A clay pre-gel comprised of 120 mL of IPAR 3 drill mud oil, 7.5 g of Tixogel™ MP150 clay and 3 g of a 95/5 propylene carbonate/water mixed under high shear (Omni-Mixer, Omni International, Waterbury, Connecticut) for 20 minutes was added to the slurry of coated breaker and the mixture was stirred for a further 30

10 minutes to ensure a stable, uniform suspension.

## CLAIMS:

1. An encapsulated breaker slurry composition comprising
  - 5 a) a breaker capable of reducing the viscosity of a fracturing fluid enclosed within a coating,
  - b) a liquid selected such that the overall slurry has a flashpoint above 93°C, wherein the liquid does not facilitate release of the breaker from the coating, and
  - 10 c) a suspension aid in an amount sufficient to maintain the suspension of the encapsulated breaker in the liquid.
2. The encapsulated breaker slurry composition of claim 1,  
15 additionally comprising a proppant.
3. The encapsulated breaker slurry composition of claim 1, wherein  
said suspension aid comprises a surfactant.
4. The encapsulated breaker slurry composition of claim 1, wherein  
20 said suspension aid comprises clay.
5. The encapsulated breaker slurry composition of claim 1, wherein  
said coating is hydrolytically degradable.
- 25 6. The encapsulated breaker slurry composition of claim 1, wherein  
said coating is made from poly(alkyl-2-cyanoacrylate).
7. The encapsulated breaker slurry composition of claim 1, wherein  
said coating is selected from the group consisting of glass coatings, ceramic  
30 coatings, homopolymers and copolymers of polyolefin and ethylene oxides,

polyamides, crosslinked cellulosic materials, polyureas, polyurethanes, dehydrated gums, and surfactant coatings.

8. The encapsulated breaker slurry composition of claim 1, wherein  
5 said liquid is an organic solvent.

9. The encapsulated breaker slurry composition of claim 8, wherein  
said organic solvent is predominantly aliphatic.

10 10. The slurry composition of claim 8, wherein said organic solvent is  
mineral oil.

11. The slurry composition of claim 8, wherein said organic solvent  
comprises a blend of one or more hydrocarbons.

15

12. The slurry composition of claim 3, wherein said surfactant is  
selected from the group consisting of oxyalkylated phenolic resin surfactants, resin  
ester surfactants, polyol surfactants, alkylaryl sulfonate surfactants, polymeric  
amine surfactants, alcohol ether sulfonates, imidazoline cationic surfactants,  
20 complex phosphate esters, amine alkylaryl sulfonates, alkyl amidoamine  
surfactants, polyamido imidazoline surfactants, fatty imidazoline surfactants, dimer  
trimer acid surfactants, polyoxyethylated rosin amines, polyoxyethylated rosin  
amines, polyoxyethylene glycol surfactants, alcohol ether sulfonate surfactants,  
alcohol ether sulfate surfactants, sulfonate surfactants, sodium alpha olefin  
25 sulfonates, sodium alcohol ether sulfates, calcium alkylaryl sulfonates, amine  
dodecylbenzene sulfonates, fatty acid amides, alkanolamides, fluorinated  
surfactants, and mixtures thereof.

13. A method of breaking a fracturing fluid comprising

- a) mixing an encapsulated breaker slurry composition of claim 1  
with a fracturing fluid,
- b) pumping said mixture into a subterranean formation and  
fracturing said formation, and
- 5 c) allowing said fracturing fluid to break.
14. A method of breaking a fracturing fluid comprising
- a) mixing proppant at site with a slurry composition of claim 1,
- 10 b) mixing the composition formed in step a) with a fracturing fluid
- c) pumping the composition formed in step b) into a subterranean  
formation and fracturing said formation, and
- d) allowing said fracturing fluid to break.
15. A method of breaking a fracturing fluid comprising
- a) mixing proppant with a fracturing fluid
- b) mixing the composition formed in step a) with a slurry  
composition of claim 1,
- c) pumping the composition formed in step b) into a subterranean
- 20 formation and fracturing said formation, and
- d) allowing said fracturing fluid to break.

# INTERNATIONAL SEARCH REPORT

Internat	Application No
PCT/US 99/10362	

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 6 E21B43/26

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

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 E21B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X A	US 5 187 011 A (GEIGER ALBERT J ET AL) 16 February 1993 (1993-02-16) column 3, line 20 - line 45  column 11, line 3 - line 27 ---	1-4, 7, 8, 10, 13-15 5, 6, 9, 11, 12
X	EP 0 379 236 A (PUMPTech NV ;SCHLUMBERGER CIE DOWELL (FR)) 25 July 1990 (1990-07-25) column 3, line 36 - column 5, line 55; claims 1,20 ---	1, 3, 5, 7, 8, 10-13
X	EP 0 275 624 A (PETROLITE CORP) 27 July 1988 (1988-07-27) column 3, line 51 - column 6, line 49; examples 2,3 column 1, line 6 - line 51 ---	1, 2, 5, 7, 13-15
	-/--	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

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

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

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

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

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

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

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

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

"&" document member of the same patent family

Date of the actual completion of the international search

16 August 1999

Date of mailing of the international search report

25/08/1999

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Assogna, R

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 99/10362

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 164 099 A (COONEY AIDAN P ET AL) 17 November 1992 (1992-11-17) cited in the application column 3, line 58 - column 7, line 7 ----	1-3,7, 13-15
X	US 4 506 734 A (NOLTE KENNETH G) 26 March 1985 (1985-03-26) cited in the application column 1, line 15 - line 63 column 2, line 51 - column 4, line 56 -----	1,2,7,8, 10,11, 13-15

# INTERNATIONAL SEARCH REPORT

Information on patent family members

Internati Application No

PCT/US 99/10362

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5187011 A		US 5102559 A	07-04-1992
		US 5102558 A	07-04-1992
		US 5110486 A	05-05-1992
		US 5192615 A	09-03-1993
		US 5204183 A	20-04-1993
		CA 2098620 A	05-07-1992
		EP 0585228 A	09-03-1994
		WO 9212328 A	23-07-1992
		CA 2098619 A	05-07-1992
		EP 0639241 A	22-02-1995
		WO 9212327 A	23-07-1992
		CA 2104691 A	29-09-1992
		EP 0586383 A	16-03-1994
		WO 9217683 A	15-10-1992
EP 0379236 A	25-07-1990	US 4919209 A	24-04-1990
		AU 661952 B	10-08-1995
		AU 3716493 A	01-07-1993
		AU 4799290 A	26-07-1990
		CA 1302870 A	09-06-1992
		NO 300858 B	04-08-1997
EP 0275624 A	27-07-1988	US 4770796 A	13-09-1988
		AU 593923 B	22-02-1990
		AU 7569287 A	14-07-1988
		CA 1291867 A	12-11-1991
		JP 63176587 A	20-07-1988
US 5164099 A	17-11-1992	AT 152500 T	15-05-1997
		DE 69125945 D	05-06-1997
		DK 559783 T	03-11-1997
		EP 0559783 A	15-09-1993
		NO 303650 B	10-08-1998
		WO 9210640 A	25-06-1992
US 4506734 A	26-03-1985	CA 1221822 A	19-05-1987