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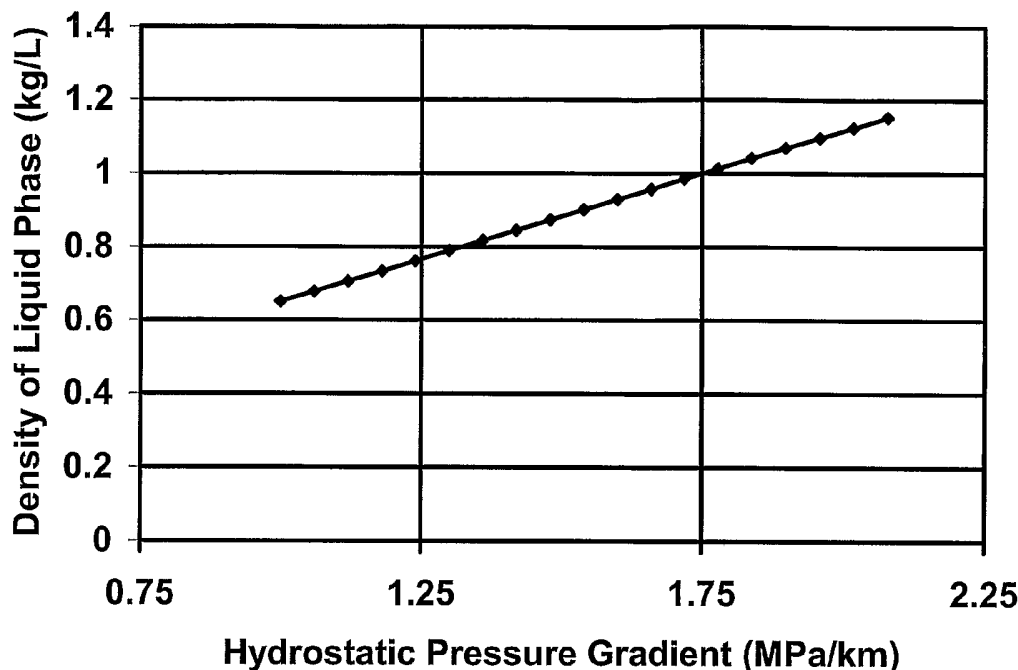
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(54) Title: HYDRAULIC FRACTURING METHOD



(57) Abstract: The invention relates to a method of fracturing a subterranean formation at reduced surface pressure including injecting into a wellbore an energized fracturing fluid based on a liquid medium having a density higher than 1.2 g/cm<sup>3</sup>.

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## Hydraulic Fracturing Method

### Technical Field of the Invention

[0001] This invention relates generally to the art of hydraulic fracturing in subterranean formations and more particularly to a method and means for optimizing fracture treatment.

### Background of the Invention

[0002] Hydrocarbons (oil, natural gas, etc.) are obtained from a subterranean geological formation (i.e., a "reservoir") by drilling a well that penetrates the hydrocarbon-bearing formation. This provides a partial flowpath for the hydrocarbon to reach the surface. In order for the hydrocarbon to be "produced," that is travel from the formation to the wellbore (and ultimately to the surface), there must be a sufficiently unimpeded flowpath from the formation to the wellbore.

[0003] Hydraulic fracturing is a primary tool for improving well productivity by placing or extending channels from the wellbore to the reservoir. This operation is essentially performed by hydraulically injecting a fracturing fluid into a wellbore penetrating a subterranean formation and forcing the fracturing fluid against the formation strata by pressure. The formation strata or rock is forced to crack and fracture. Proppant is placed in the fracture to prevent the fracture from closing and thus, provide improved flow of the recoverable fluid, i.e., oil, gas or water.

[0004] Hydraulic fracturing for well stimulation relies on the ability to pump the fracturing fluid at a bottomhole pressure sufficient to overcome the formation in-situ stresses so that the rock can be cracked. Once a fracture is initiated, enough bottomhole pressure must be maintained to propagate the fracture further away from the wellbore and generate the necessary fracture width for it to be filled with the propping material that will keep the fracture open once the pumping has stopped. The initial breakdown pressure is usually higher than the minimum pressure needed to re-open the same fracture. This is due to the tectonic stress in the rock that has to be initially overcome. The minimum pressure needed to re-open the fracture after breakdown is called the fracture opening

pressure. This pressure is usually slightly higher than the fracture closure pressure due to poroelastic effects and other factors due to the geologic setting. The fracture closure pressure is the pressure at which the fracture will close. Therefore, after the fracture is reopened, the bottomhole pressure or BHP needs to be above the fracture closure pressure to successfully perform the fracturing treatment.

[0005] The effective bottomhole pressure is the sum of the surface pressure provided by the pumping equipment and the hydrostatic pressure, minus the pressure losses due to friction forces while the fluid passes through the surface and subterranean equipments such as pipes. The required bottomhole pressure is governed by the mechanical properties of the formation and is therefore an intangible parameter. To match the required and effective bottomhole pressure, the focus shall be on either increasing the surface pressure and/or the hydrostatic pressure or lowering the friction pressures.

[0006] The maximum surface pressure may be the limitation of the service company pumping equipment and may be increased by either using different pumps with a higher pressure capacity. Increasing the numbers of pumps, or utilization of pumps with a higher hydraulic horsepower (HHP) rating, is needed if the limitation is the amount of HHP needed to pump the fracturing treatment. Obviously, this results in increased cost, not only equipment but also logistic and personal costs. Moreover, this option may simply not be available for instance on an offshore rigs. Regardless of the cost and availability of the equipment, an increased of the surface pressure may be also ruled out by the surface and/or subterranean equipment. This is because the surface pressure is also limited based on the “weakest point” in the completion of the well, consisting of surface equipment for instance such as blowout preventers, valves, tree-savers; casing and tubing properties (size, weight and grade), packers, etc.

[0007] Lowering the friction pressure is a main focus of the well services industry and also involves early planning during the well construction by increasing the size (internal diameter) of the tubing or casing. Other fracturing designs options include pumping the fracturing fluid down the annulus instead of the smaller tubing, using lower pumping rates or maximizing the drag reduction properties of the fluid by adding friction reducer or delaying the crosslink time for polymer-based fluids for instance. Though dramatic

progresses have been done in that area in recent years, there is a limit to the reduction that can be achieved that way since the friction pressure cannot be annihilated.

[0008] As mentioned above, the required bottomhole pressure is governed by the mechanical properties of the formation. In general, but not always, the deeper the well, the higher the needed bottomhole pressure. As a rule of thumb, a bottomhole pressure of 0.75 psi is required by foot of depth (or in other words, about 17 kPa/m). With a focus towards deeper wells for low permeability gas field development, and towards wells in deep water where friction pressure accounts for a larger part of the surface treating pressure, there is therefore a remaining need for fracturing processes that will allow achieving higher bottomhole pressure while keeping relatively low surface pressure.

[0009] Particularly high pumping pressures may be required for foamed systems where the hydrostatic pressure is low due to the presence of gas. Foamed systems include foam or and energized fluids and are stable mixture of gas and liquid, which are mainly used in fracturing low pressure or water sensitive formations. Foam and energized fracturing fluids are generally described by their foam quality, i.e. the ratio of gas volume to the foam volume. If the foam quality is between 52% and 95%, the fluid is usually called foam. Above 95%, a foam is generally changed to mist. Stable dispersion of gas in liquid with foam quality less than 52% is called energized fluid. In the present patent application, the term "foamed system" will be used however to describe any stable mixture of gas and liquid, whatever the foam quality is. The foam half-life is another important parameter to evaluate the stability of foam or energized fluids. The half life of a foam or energized fluids is the time necessary for one-half of the liquid used to generate the foam to break out of the foam under atmospheric conditions.

[0010] Foam systems however present numerous advantages. They expand when they flow back from the well and therefore force the fluid out of the fracture, consequently ensuring a superior clean-up. They typically require less viscosifying agent while presenting good fluid loss control and fluid efficiency. As a result, foamed systems are often cheaper than conventional systems unless the cost benefit due to the use of lower quantities of chemicals is overturned by the need of higher horse power, and consequently of specific pumping equipment.

**Summary of the Invention**

[0011] According to a first aspect of the present invention, a method of fracturing a subterranean formation is proposed that includes injecting into a wellbore a foamed fracturing fluid based on a liquid medium having a density higher than  $1.2 \text{ g/cm}^3$ , thereby allowing the use of a surface pressure at least 10% smaller than the surface pressure required with a foamed fracturing fluid based on a liquid medium having a density of about  $1 \text{ g/cm}^3$ .

[0012] The method of the invention is particularly useful for fracturing wells that require high bottomhole pressure at least during part of the treatment and makes possible the stimulation of wells previously eliminated as candidates due to surface pressure restrictions. In particular, the invention allows the use of standard equipment, that have an upper limit of typically about 103 MPa or even of standard coiled tubing pumping unit that have an upper limit of typically about 48.3 MPa.

[0013] Such a high density is obtained for instance by preparing the liquid phase of the foam fluids with a viscoelastic surfactant compatible with high concentrations and or densities of salts, preferably such as a zwitterionic surfactant. The surfactant is not only used to viscosify the liquid phase of the foam fluids, but also used as a foaming agent to create and stabilize the foam.

[0014] Zwitterionic surfactants suitable for carrying out the method of the present invention include mixture of amphoteric/zwitterionic surfactants and an organic acid, salt and/or inorganic salt as it is known from International Patent Publication WO 98/56497. The surfactants are for instance dihydroxyl alkyl glycinate, alkyl ampho acetate or propionate, alkyl betaine, alkyl amidopropyl betaine and alkylamino mono- or di-propionates derived from certain waxes, fats and oils. The surfactants are used in conjunction with an inorganic water-soluble salt or organic additives such as phthalic acid, salicylic acid or their salts. Amphoteric/ zwitterionic surfactants, in particular those comprising a betaine moiety are useful at temperature up to about  $150 \text{ }^\circ\text{C}$  and are therefore of particular interest for medium to high temperature wells.

[0015] According to one embodiment of the invention, the method of fracturing involves the use of a betaine that contains an oleyl acid amide group (including a  $C_{17}H_{33}$  alkene tail group).

[0016] Yet a preferred embodiment of the present invention is a method of fracturing subterranean formation while maintaining lower surface pressure involving the use of a betaine that contains an erucic acid amide group (including a  $C_{21}H_{41}$  alkene tail group). The surfactant may be further stabilized by the addition of an alcohol, and preferably methanol.

[0017] To be noted that to alleviate the inconvenient of low hydrostatic pressure, it is often proposed to use carbon dioxide as gas phase. However, carbon dioxide leads to the formation of calcium carbonate that may precipitate. Moreover, carbon dioxide is more expansive than nitrogen, raises security issues and is not compatible with highly basic systems. The invention expands the range of use of nitrogen, while being compatible with the use of carbon dioxide when further increase of the hydrostatic pressure is suitable.

#### **Brief description of the drawings**

[0018] The above and further objects, features and advantages of the present invention will be better understood by reference to the appended detailed description, and to the drawings wherein:

[0019] Figure 1 is the plot of overall hydrostatic pressure gradient versus liquid phase density of a typical foam fracturing fluid;

#### **Detailed description and preferred embodiments**

[0020] In most cases, a hydraulic fracturing treatment consists in pumping a proppant-free viscous fluid, or pad, usually water with some high viscosity fluid additives, into a well faster than the fluid can escape into the formation so that the pressure rises and the rock breaks, creating artificial fracture and/or enlarging existing fracture. Then, a propping agent such as sand is added to the fluid to form a slurry that is pumped into the fracture to prevent it from closing when the pumping pressure is released. The proppant transport ability of a base fluid depends on the type of viscosifying additives added to the

water base, on the density difference between the proppant and the water base carrier fluid and on the velocity of the slurry in the hydraulic fracture.

[0021] The downhole pressure required to crack the subterranean formation is function of the surface pressure, the weight of the hydraulic column (the hydrostatic pressure) and is reduced by the pressure losses due in particular to the tubing and other downhole equipment frictions and to the perforation friction pressure. In the key initial stage of fracturing, the pumped fracturing fluid is proppant-free, and therefore the hydrostatic pressure is not enhanced by the weight of the proppant, typically consisting of sand or ceramic particles.

For foam fracturing treatment, the overall hydrostatic pressure is contributed by hydrostatic pressure from both liquid and gas phases. An increase of the liquid phase density results in an increase of liquid hydrostatic pressure and further results in an increase of the overall hydrostatic pressure and downhole pressure available for fracturing the formation without the need to increase the surface pressure. For a typical case listed in table 1, figure 1 shows us the relationship between overall hydrostatic pressure and the density of the foam liquid phase.

Table 1

Parameter	Unit	Value
Frac Gradient	MPa/m	0.00226
Vertical Depth	m	4572
Liquid Ratio	decimal	0.5
Gas Ratio	decimal	0.5
Geothermal Gradient	degree°C/100m	0.169
Bottomhole Pressure	MPa	77.5
Wellhead Pressure	MPa	59

[0022] Nature of high density of foamed fluids invented provides high hydrostatic head for the fracturing operation. Horsepower will be accordingly saved by this property compared to other polymeric or VES foamed fracturing fluids. Table 2 shows that the present invention allows horsepower savings of more than 10%. Meanwhile, 1.0kg/L



fluid cannot be used in this example case due to the high friction from tubing and perforation, resulting in high standard of surface pumping pressure. The use of 1.5kg/L foamed fluid according to this invention reduces the surface pressure by 11%, making it possible to successfully fracture the well.

Table 2

Liquid Phase Density	kg/L	1.0	1.48	1.96
Frac Gradient	MPa/m	0.00226	0.00226	0.00226
Vertical Depth	m	4572	4572	4572
Liquid Ratio	decimal	0.5	0.5	0.5
Gas Ratio	decimal	0.5	0.5	0.5
Geothermal Gradient	degree°C/100m	0.169	0.169	0.169
Bottomhole Pressure	MPa	77.5	77.5	77.5
Wellhead Pressure	MPa	59	59	59
Friction pressure (tubing+perf)	MPa	62	62	62
Overall Hydrostatic Pressure	MPa	32	43	54
Surface Pumping Pressure	MPa	107.6	96.6	85.7
Pump Rate	m <sup>3</sup> /min	3.97	3.97	3.97
Surface HHP	HHP	9691	8702	7715
HHP Savings	%		11%	20%

[0023] Since the first foam fracturing application in the mid-1970's, water soluble polymers, such as guar gums, high-molecular weight polysaccharides composed of mannose and galactose sugars, or guar derivatives such as hydroxypropyl guar (HPG), carboxymethylhydroxypropyl guar (CMHPG), are mainly used to prepare the liquid phase of the foam fluids. Crosslinking agents based on boron, titanium, zirconium or aluminum complexes are typically used to increase the effective molecular weight of the polymer and make them better suited for use in high-temperature wells.

[0024] Xanthan gum has been shown to have excellent proppant-suspension ability as well as foam stabilizing capacity even though they are more expensive than guar derivatives and therefore used less frequently.

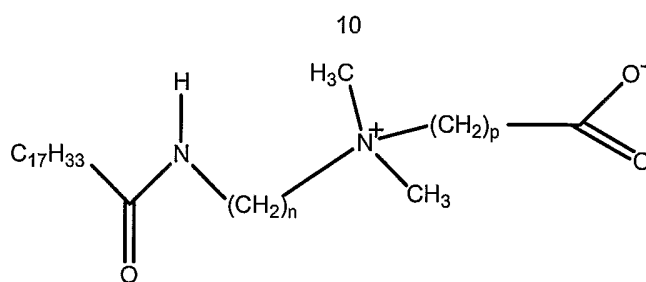
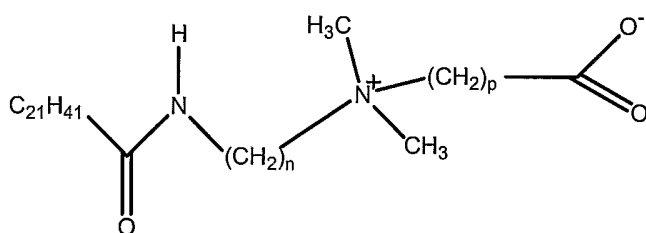
[0025] Though some attempts have been made in the past (see for instance U.S. Patents 5,785,747 and 6,100,222), high-density brines comprising above water-soluble polymers, which could be potentially used for the preparation of foam fluid liquid phase, are typically not practicable due to adverse effect of brines on polymer hydration and foam stability.

[0026] Polymer-free, liquid phase of foam fluids can be obtained using viscoelastic surfactants. These fluids are normally prepared by mixing in appropriate amounts suitable surfactants such as anionic, cationic, nonionic and zwitterionic surfactants in aqueous solutions. The viscosity of viscoelastic surfactant fluids is attributed to the three dimensional structure formed by the components in the fluids. When the concentration of surfactants in a viscoelastic fluid significantly exceeds a critical concentration, and in most cases in the presence of an electrolyte, surfactant molecules aggregate into species such as micelles, which can interact to form a network exhibiting viscosity and elastic behavior to further stabilize the foamed systems. Meanwhile, the surfactant also acts as foaming agent to create the stable dispersion of gas in viscous liquid

[0027] Cationic viscoelastic surfactants - typically consisting of long-chain quaternary ammonium salts such as cetyltrimethylammonium bromide (CTAB) - have been so far of primarily commercial interest in above applications. Common reagents that generate viscoelasticity in the surfactant solutions are salts such as ammonium chloride, potassium chloride, sodium chloride, sodium salicylate and sodium isocyanate and non-ionic organic molecules such as chloroform. The electrolyte content of surfactant solutions is also an important control on their viscoelastic behavior. Reference is made for example to U.S. patents No. 4,695,389, No. 4,725,372, No. 5,551,516, No. 5,964,295, and No. 5,979,557. However, fluids comprising this type of cationic viscoelastic surfactants usually tend to lose viscosity at high brine concentration (1.2 kg/L or more) and may be unstable in presence of divalent salts such as calcium bromide or calcium chloride. Therefore, these fluids have seen limited use as high density liquid phase of the foam fracturing fluids or in other applications requiring heavy fluids to balance well pressure or to minimize surface treating pressure.

[0028] It is also known from International Patent Publication WO 98/56497, to impart viscoelastic properties using amphoteric/zwitterionic surfactants and an organic acid, salt and/or inorganic salt. The surfactants are for instance dihydroxyl alkyl glycinate, alkyl ampho acetate or propionate, alkyl betaine, alkyl amidopropyl betaine and alkylamino mono- or di-propionates derived from certain waxes, fats and oils. The surfactants are used in conjunction with an inorganic water-soluble salt or organic additives such as phthalic acid, salicylic acid or their salts. Amphoteric/ zwitterionic surfactants, in particular those comprising a betaine moiety are useful at temperature up to about 175°C and are therefore of particular interest for medium to high temperature wells. However, like the cationic viscoelastic surfactants mentioned above, in absence of co-additive, they are usually not compatible with high brine concentration.

[0029] Some betaine surfactants are particularly useful in forming aqueous gels of exceptional thermal stability in any electrolyte concentration as well as in forming a stable foams with no added salt or even in heavy brines. Their compatibility with heavy brines at unexpectedly high temperatures is an important feature of the present invention. Two preferred examples are betaines called, respectively, BET-O and BET-E. The surfactant BET-O-30 is shown below and may be obtained from Rhodia, Inc. Cranbury, New Jersey, U. S. A. The O indicates that it contains an oleyl acid amide group (including a C<sub>17</sub>H<sub>33</sub> alkene tail group) and the 30 indicia refers to a concentration of active surfactant of about 30%; the remainder being substantially water, sodium chloride, and propylene glycol. An analogous material, BET-E-40, is also available from Rhodia, contains a erucic acid amide group (including a C<sub>21</sub>H<sub>41</sub> alkene tail group) and is 40% active ingredient, with the remainder substantially water, sodium chloride, and isopropanol. The surfactant in BET-E-40 is also shown below. BET surfactants, and others, are described in U. S. Patent No. 6,258,859. According to that patent, cosurfactants may be useful in extending the brine tolerance, and to increase the gel strength and to reduce the shear sensitivity of the VES-fluid, especially for BET-O. An example given in U. S. Patent No. 6,258,859 is sodium dodecylbenzene sulfonate (SDBS). Other suitable cosurfactants for BET-O-30 are certain chelating agents such as trisodium hydroxyethylethylenediamine-triacetate.

Surfactant in BET-O-30 (when  $n = 3$  and  $p = 1$ )Surfactant in BET-E-40 (when  $n = 3$  and  $p = 1$ )

[0030] As shown in figures 2 to 4, with BET-E, high-density brine can be made from metal halide (KCl, CaBr<sub>2</sub>, CaCl<sub>2</sub>, ZnBr<sub>2</sub>...etc), chelants (EDTA, EDTA metal salts...etc), sequesters (phosphates, polyphosphates...etc), other inorganic metal salts like K<sub>2</sub>CO<sub>3</sub>, K<sub>2</sub>SO<sub>4</sub>...and organic salts such as formates and acetates.

[0031] Proppant carrying capacity of foam fluids is contributed by both liquid phase and foam structures. An increase of the density of the liquid phase leads to better proppant suspension since the proppant settling velocity in liquid phase of the foam fluids is generally proportional to the density difference of the proppant and liquid phase. As described by Novotny equation, proppant settling in a power-law fluid is

$$U_{sol} = (1-f_v)^\beta [(\rho_{sol}-\rho_f)gd^{n+1}/(3^{n-1}18K')]^{1/n}$$

Where:  $\beta$  = proppant settling velocity

$f_v$  = volume fraction of proppant

$\rho_{sol}$  = proppant density

$\rho_f$  = fluid density

n, K' = power law parameters

d = proppant particle diameter

[0032] Assuming same parameters of  $\beta$ ,  $f_v$ , n, K' and d, we will have  $U_{sol} \propto (\rho_{sol} - \rho_f)^{1/n}$ . For a case of 3.0SG proppant and n=0.5 fluid, relationship of proppant settling velocity in fluids with different densities is calculated in table 3.

**Table 3**

Proppant Density	3.0 g/cc
Fluid density	1 kg/L and 1.67 kg/L
n	0.5
Settling velocity in 1.67 kg/L settling velocity in 1 kg/L	0.4324

[0033] From above calculation, proppant settling velocity in high density foam fracturing fluid of this invention is much lower than that in traditional polymeric foamed fracturing fluids.

[0034] An additional requirement for foam fluids is their ability to be stable and not to segregate into different phases or layers. From that point of view, foamed fracturing fluids whose liquid phase and foaming agent prepared with BET-E are particularly interesting. Table 4 below lists the rheology comparison between different energized fluids at 26°C.

26C.

**Table 4**

Base fluid	Foam quality	Viscosity (cp)		
		40sec-1	170sec-1	511sec-1
Linear Guar in 2% KCl water at 2.4 g/L	52%	85	48	---
Crosslinked guar in 2% KCl water at 2.4 g/L	52%	---	68	34
1.5% Cationic surfactant in 3% NH <sub>4</sub> Cl water	52%	---	120	---
10% BET-E in 40% CaCl <sub>2</sub> brine	52%	---	144	91

[0035] Table 5 shows the viscosity at 100 sec<sup>-1</sup> (in cP) of the foam fluid with 10% BET-E in 40% calcium chloride brine at 3.10 MPa pressure and different temperatures.

**Table 5**

Temperature	n'	k'	Viscosity at 100sec <sup>-1</sup> (cp)
26.7 °C	0.4467	0.0753	282
37.7 °C	0.1779	0.4700	511
51.7 °C	0.1422	0.7123	656
65.5 °C	0.1254	1.1230	958
79.4 °C	0.2299	0.8379	1156
93.3 °C	0.5274	0.2077	1128
107.2 °C	0.1029	0.6077	467
121.1 °C	0.2281	0.3903	534
135 °C	0.6598	0.0465	465
148.9 °C	0.9503	0.0070	268
162.8 °C	1.1219	0.0014	115
176.7 °C	1.2467	0.0002	34

[0036] Above rheology data listed in tables 4 and 5 indicate that foamed fracturing fluids prepared in heavy brines of this invention have much better viscosity than normal polymeric or other surfactant foamed fluids regarding to the foam stability, fluid loss control and proppant suspension capacities.

[0037] Table 6 compares the foam half-life of different foam fluids, all measurements were performed at 93.3 °C.

**Table 6**

Fluids	Foam quality	Formula	Half Life
Linear Guar	70%	0.5% foaming agent and 2.4 g/L guar in 2% KCl water	6 minutes
Cationic surfactant	70%	4% cationic surfactant in 3% NH <sub>4</sub> Cl	10 minutes
BET-E in CaCl <sub>2</sub> brine	60%	5% BET-E in 20% CaCl <sub>2</sub>	270 minutes

BET-E in CaCl <sub>2</sub> brine	60%	5% BET-E in 16% CaCl <sub>2</sub>	>240 minutes
BET-E in CaCl <sub>2</sub> brine	60%	5% BET-E in 32% CaCl <sub>2</sub>	>280 minutes
BET-E in CaCl <sub>2</sub> brine	60%	5% BET-E in 4% CaCl <sub>2</sub>	<100 minutes
BET-E in CaCl <sub>2</sub> brine	60%	5% BET-E in 8% CaCl <sub>2</sub>	<120 minutes

[0038] After 4 hours at 93.3°C, a foam comprising 5% BET-E and 16% calcium chloride is still stable. Increasing the amount of calcium chloride to 32% provides even better stability. Initial weight and final weight was measured after static aging, No weight change was observed. However, samples prepared with only 4% or 8% of calcium chloride show the formation of a water layer under the foam after 2 hours.

[0039] Table 7 lists fluid properties of two energized fracturing fluids particularly suitable for carrying out the present invention. The systems are stable for longer than 90 minutes even at temperatures above 135°C and about 0.69 MPa pressure.

**Table 7**

Fluids	I	II
Formula	5% BET-E + 36% CaCl <sub>2</sub>	10% BET-E + 36% CaCl <sub>2</sub>
Foam Quality	50%	40%
Temperature (C)	135	149
Half Life at temperature	150 minutes	85 minutes

[0040] Data listed in tables 6 and 7 indicate that foamed fluids of this invention have much better foam stability in heavy brines than traditional polymeric or cationic surfactant foamed fluids.

**Having described, I claim:**

1. A method of fracturing a subterranean formation at reduced surface pressure including injecting into a wellbore an energized fracturing fluid based on a liquid medium having a density higher than  $1.2 \text{ g/cm}^3$ .
2. The method of claim 1, wherein the liquid medium has a density greater than  $1.5 \text{ g/cm}^3$ .
3. The method of claim 1, wherein the energizing gas is selected from the group consisting of nitrogen, carbon dioxide, air and mixtures thereof.
4. The method of claim 1, wherein the energized fracturing fluid has a foam quality of at least 25%.
5. The method of claim 1, wherein the energized fracturing fluid has a foam quality of at least 50%.
6. The method of claim 1, wherein the liquid medium comprises an aqueous solution, a zwitterionic surfactant as gelling agent and salts.
7. The method of claim 6, wherein said zwitterionic surfactant is a betaine containing an erucic acid amide group.
8. The method of claim 6, wherein said zwitterionic surfactant is a betaine containing a oleyl acid amide group.
9. The method of claim 1, wherein the fluid comprises at least a density-enhancer selected from the group consisting of salts, sugar, chloroform, carbon tetrachloride and glycerol and mixtures thereof.
10. The method of claim 9, wherein said density enhancer is a salt selected from the group consisting of calcium chloride, calcium bromide, potassium bromide, sodium bromide and mixtures thereof.



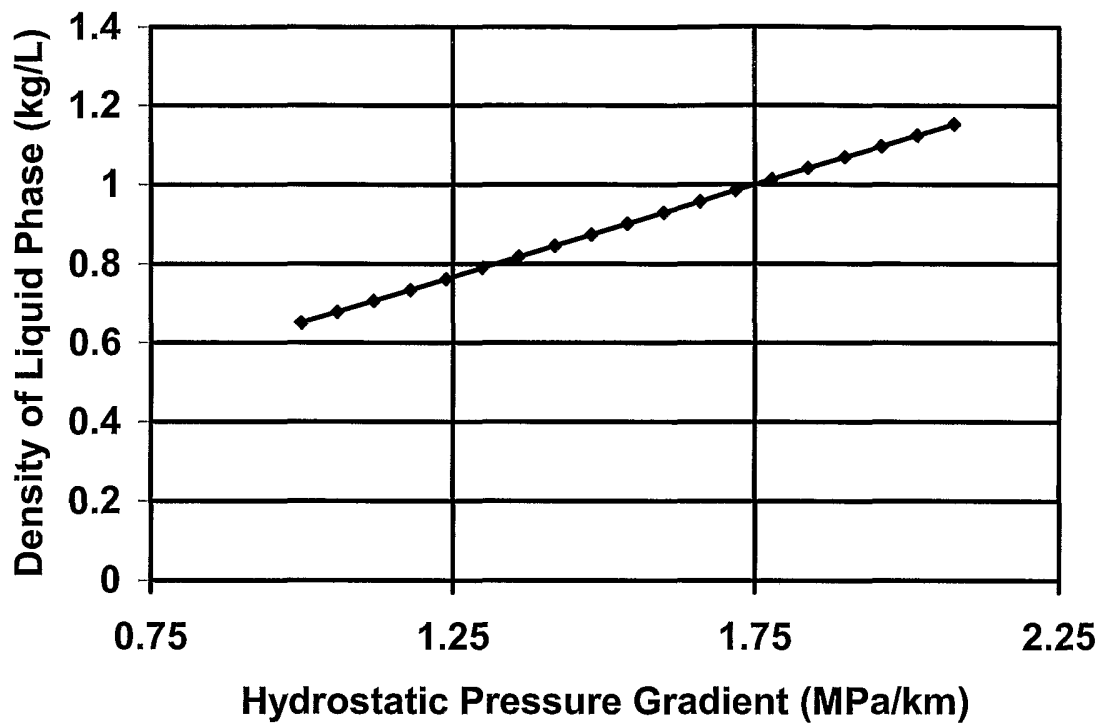


Figure 1

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/IB2004/050924

<b>A. CLASSIFICATION OF SUBJECT MATTER</b> IPC 7 E21B43/26				
According to International Patent Classification (IPC) or to both national classification and IPC				
<b>B. FIELDS SEARCHED</b>				
Minimum documentation searched (classification system followed by classification symbols) IPC 7 C09K				
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) EPO-Internal, WPI Data, PAJ				
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>				
Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.		
X	WO 03/048267 A (SOFITECH NV ; SCHLUMBERGER CA LTD (CA); SCHLUMBERGER SERVICES PETROL ) 12 June 2003 (2003-06-12) claims paragraphs '0014! - '0031! -----	1-3,6-10		
X	WO 98/56497 A (RHODIA) 17 December 1998 (1998-12-17) cited in the application claims page 3, line 5 - line 9 page 12, line 15 - line 35 page 13, line 24 - line 36 page 15, line 1 - line 3 example 6 ----- -/--	1-3,6, 8-10		
<table style="width: 100%; border: none;"> <tr> <td style="width: 50%; border: none;"><input checked="" type="checkbox"/> Further documents are listed in the continuation of box C.</td> <td style="width: 50%; border: none;"><input checked="" type="checkbox"/> Patent family members are listed in annex.</td> </tr> </table>			<input checked="" type="checkbox"/> Further documents are listed in the continuation of box C.	<input checked="" type="checkbox"/> Patent family members are listed in annex.
<input checked="" type="checkbox"/> Further documents are listed in the continuation of box C.	<input checked="" type="checkbox"/> Patent family members are listed in annex.			
° Special categories of cited documents :				
<table style="width: 100%; border: none;"> <tr> <td style="width: 50%; border: none; vertical-align: top;">                     *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                 </td> <td style="width: 50%; border: none; vertical-align: top;">                     *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.                      *&amp;* document member of the same patent family                 </td> </tr> </table>			*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
*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	Date of mailing of the international search report			
17 November 2004	25/11/2004			
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  <b>RODRIGUEZ FONTAO, M</b>			

INTERNATIONAL SEARCH REPORT

International Application No

1/IB2004/050924

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>US 2002/033260 A1 (MORRIS ELIZABETH ET AL) 21 March 2002 (2002-03-21)                      claims                      paragraphs '0010! - '0026!                      paragraphs '0043! - '0046!                      paragraph '0050!</p> <p style="text-align: center;">-----</p>	<p>1-3,6, 8-10</p>
X	<p>US 2002/169085 A1 (SAMUEL MATHEW ET AL) 14 November 2002 (2002-11-14)                      claims                      paragraphs '0009!, '0010!, '0021!,                      '0029!, '0034!</p> <p style="text-align: center;">-----</p>	<p>1-3,6-10</p>

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/IB2004/050924

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 03048267      A	12-06-2003	WO 03048267 A1	12-06-2003
		US 2003236174 A1	25-12-2003
		US 2003166471 A1	04-09-2003
WO 9856497      A	17-12-1998	AT 246957 T	15-08-2003
		AU 753011 B2	03-10-2002
		AU 8066298 A	30-12-1998
		BR 9810023 A	15-01-2002
		CA 2297185 A1	17-12-1998
		CA 2380311 A1	17-12-1998
		CN 1389538 A	08-01-2003
		CN 1263481 T	16-08-2000
		DE 69817182 D1	18-09-2003
		DE 69817182 T2	17-06-2004
		DK 993334 T3	08-12-2003
		EP 1323888 A1	02-07-2003
		EP 0993334 A1	19-04-2000
		ID 27732 A	26-04-2001
		NO 996089 A	08-02-2000
		NO 20030096 A	08-02-2000
		RU 2198906 C2	20-02-2003
		RU 2217585 C1	27-11-2003
		US 6258859 B1	10-07-2001
		WO 9856497 A1	17-12-1998
		US 2003040546 A1	27-02-2003
US 6482866 B1	19-11-2002		
US 2004082484 A1	29-04-2004		
US 2004176478 A1	09-09-2004		
US 2002033260      A1	21-03-2002	AU 2355202 A	02-04-2002
		WO 0224831 A2	28-03-2002
		GB 2383813 A ,B	09-07-2003
		NO 20031290 A	20-05-2003
		US 2004023812 A1	05-02-2004
US 2002169085      A1	14-11-2002	CA 2439364 A1	12-09-2002
		EA 4614 B1	24-06-2004
		WO 02070862 A1	12-09-2002