



(51) International Patent Classification:

E21B 43/26 (2006.01)

(21) International Application Number:

PCT/US2024/029521

(22) International Filing Date:

15 May 2024 (15.05.2024)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

2023112555

15 May 2023 (15.05.2023)

RU

(71) Applicant (for US only): **SCHLUMBERGER TECHNOLOGY CORPORATION** [US/US]; 300 Schlumberger Drive, Sugar Land, Texas 77478 (US).

(71) Applicant (for CA only): **SCHLUMBERGER CANADA LIMITED** [CA/CA]; 125 – 9 Avenue SE, Calgary, Alberta T2G 0P6 (CA).

(71) Applicant (for FR only): **SERVICES PETROLIERS SCHLUMBERGER** [FR/FR]; 42 rue Saint Dominique, 75007 Paris (FR).

(71) Applicant (for all designated States except CA, FR, US): **SCHLUMBERGER TECHNOLOGY B.V.** [NL/NL]; Parkstraat 83, 2514 JG The Hague (NL).

(72) Inventors: **FEDOROV, Andrey Vladimirovich**; 1/7 Zelenaya Gorka St., Novosibirsk, 630060 (RU). **LASHKHIDZE, Galina Valeryevna**; 1/7 Zelenaya Gor-

ka St., Novosibirsk, 630060 (RU). **SEMIN, Leonid Georgievich**; 1/10 Zelenaya Gorka St., Novosibirsk, 630060 (RU). **DEMIDOV, Demid Valeryevich**; 1/10 Zelenaya Gorka St., Novosibirsk, 630060 (RU).

(74) Agent: **FLYNN, Michael L.** et al.; Schlumberger, 10001 Richmond Avenue, Room 4720, Houston, Texas 77042 (US).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CV, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IQ, IR, IS, IT, JM, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, MG, MK, MN, MU, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, WS, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, CV, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SC, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, ME, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

(54) Title: THE METHOD OF HYDRAULIC FRACTURING WITH LOW VISCOSITY FLUID CONTAINING PROPPANT AGGREGATES WITH POLYELECTROLYTE COMPLEXES

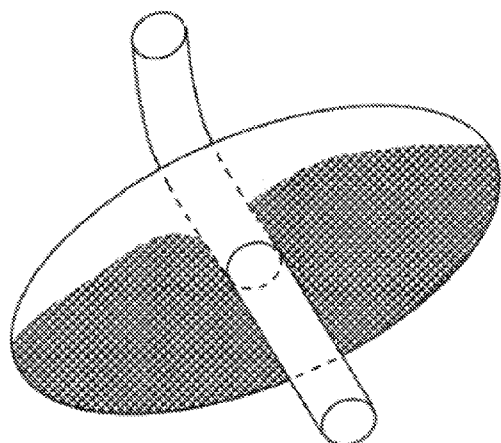


Fig. 2

(57) Abstract: The provided solution relates to well systems for producing various fluids, in particular for producing fluid from the hydrocarbon-bearing formation using hydraulic fracturing. The solution provides a method for hydraulic fracturing that comprises injecting a proppant-free fluid through a well into a formation to create and propagate a fracture; preparing a fracturing fluid by mixing at least water, proppant and at least the first polymer additive and the second polymer additive to produce flocculated proppant particles; injecting the fracturing fluid containing prepared flocculated proppant particles into the formation; and injecting a displacement fluid into the well. The provided method ensures placing a proppant in sufficient concentrations at a distance from the wellbore and achieving high vertical propagation of proppant across the complex fracture network.

Published:

— *with international search report (Art. 21(3))*

**THE METHOD OF HYDRAULIC FRACTURING WITH LOW VISCOSITY
FLUID CONTAINING PROPPANT AGGREGATES WITH
POLYELECTROLYTE COMPLEXES**

5

CROSS REFERENCE PARAGRAPH

This application claims the benefit of Russian Federation Application No. 2023112555, entitled "THE METHOD OF HYDRAULIC FRACTURING WITH LOW VISCOSITY FLUID CONTAINING PROPPANT AGGREGATES WITH POLYELECTROLYTE COMPLEXES" filed May 15, 2023, the disclosure of which is
10 hereby incorporated herein by reference.

TECHNICAL FIELD

The present invention relates to hydrocarbon production, in particular, to a method for hydraulic fracturing using a low-viscosity fluid containing polyelectrolyte complex-based proppant aggregates.

15

INTRODUCTION

Hydraulic fracturing is widely used for stimulating the inflow of oil, gas, and water into a well and involves fracturing a subterranean formation by injecting fluid with a pressure higher than the fracturing pressure of the formation. Along with the fluid, a proppant is also placed in the fracture to prevent it from closing once the pressure is
20 relieved at the end of the stimulation treatment. Different carrier fluids can be used to transport proppant from the surface to the fracture depth.

Hereinafter, the terms "sand" and "proppant" are intended to mean any type of

propping agents placed inside a fracture to keep it from closing when the pressure is relieved.

Tight formations, such as shale or tight sandstone, are usually treated with low-viscosity fluids (e.g., slickwater). Low-viscosity fluids are believed to create a complex fracture network inside tight formations, thus improving a flow rate of reservoir fluids, such as oil, gas, or water. However, using low-viscosity fluids for hydraulic fracturing entails issues related to prevention of sand/proppant settling, especially when dealing with long fracture shut-in time. To overcome these problems, high volumetric flow rate fluid injection and proppant with small particle size (100 and 40/70 mesh) are commonly used. Despite all these additional restrictions, it is still challenging to place proppant in sufficient concentrations in a fracture at a distance from the wellbore and ensure adequate vertical coverage. The secondary and tertiary fractures are often left unpropped resulting in not fully maximized well production rate.

A propping agent maintains a gap between the fracture walls to create conductive channels within a formation. Heterogeneous placement of proppant further increases conductivity of a formation and fluid yield.

Tight formations, such as shale or tight sandstone, can be treated with low-viscosity fluids, such as slickwater. "Slickwater", also called "slick water", is a water-based hydraulic fracturing fluid supplemented with a friction reducer which is usually a high-molecular chemical or a polymer. In practice, polyacrylamide is often used to make slickwater by adding to water to reduce friction and increase the velocity of fluid injection into a well for hydraulic fracturing of tight formations. During treatment with low-viscosity hydraulic fracturing fluid, sedimentation of the propping agent normally occurs

at an intense rate, especially when dealing with long fracture closure time, which reduces the reservoir fluid production. Additionally, it is still challenging to place propping agent in deep fractures and ensure high vertical coverage within the formation when handling tight formations.

5

PRIOR ART

There are solutions known in the art that are based on making use of low-viscosity fluids for hydraulic fracturing.

For example, solution WO2017078560A1 provides a method for hydraulic fracturing that includes a sequence of steps: injecting a slug of a proppant-free fluid
10 through a well, into a formation, to create and propagate a fracture; injecting a slug of proppant-laden slurry into the formation to form a proppant pack in the fracture; injecting a slug of slurry comprising a fluid and polyelectrolyte complex-based proppant aggregates into the formation to form permeable channels in the near wellbore zone of the fracture; and injecting a slug of a displacement fluid into the well. This workflow
15 allows avoiding the proppant slurry overdisplacement deep into the hydraulic fracture, maintaining high fracture conductivity, and increasing the well productivity. However, this solution is not focused on placing proppant in sufficient concentrations in a fracture at a distance from the wellbore and ensuring high vertical propagation of proppant across a complex fracture network. This solution is focused on placing proppant pack in the near
20 wellbore zone to prevent overdisplacement of proppant from the near wellbore zone after clean-up.

Also, solution US10961832B2 provides methods for treatment of subterranean formation with polymeric structures generated inside the formation. This document

discloses the methods for subterranean formation treatment that include placing a treatment fluid in the subterranean formation, wherein the treatment fluid contains one or more polymers capable of consolidating to form a polymeric structure in the bottom hole or in the near wellbore zone. It also discloses treatment fluids that comprise a polymeric structure optimized for subterranean formation treatment. However, this solution is not focused on placing proppant in sufficient concentrations in a fracture at a distance from the wellbore and ensuring high vertical propagation of proppant across a complex fracture network. This solution involves formation of agglomerates in the bottom hole by activating the component in situ under the effect of high shear stress created in the course of injection.

Solution US20150060072A1 also discloses the methods for subterranean formation treatment that include placing a treatment fluid in the subterranean formation, wherein the treatment fluid contains a solid agent and one or more polymers capable of consolidating to form a polymeric structure in the bottom hole or in the near wellbore zone. However, this solution is not focused on placing proppant in sufficient concentrations in a fracture at a distance from the wellbore and ensuring high vertical propagation of proppant across a complex fracture network. Additionally, this solution involves formation of agglomerates in the bottom hole area after completion of perforation.

Solution US20160040059A1 provides a method for heterogeneous placement of proppant in fractures by aggregation of fine particles of proppant or other materials, such as fibers, in subterranean formation fractures. A polymer is injected into the subterranean formation, following which it undergoes a chemical reaction, such as hydrolysis, under

downhole conditions, which leads to formation of either cationic or anionic polyelectrolytes. In an alternative embodiment, the polyelectrolyte is formed directly inside the well, e.g., as a product of the Hofmann degradation or the Mannich reaction. The polyelectrolyte acts as a flocculant and facilitates aggregation of solid particles, such as sand, mica, silica flour, ceramic particles, and the like, which leads to formation of microaggregates containing proppant particles deep in the fracture. Methods for aggregation of fibers to enhance bridging and other applications of controlled flocculation are also provided.

However, this solution is not focused on placing proppant in sufficient concentrations in a fracture at a distance from the wellbore and ensuring high vertical propagation of proppant across a complex fracture network.

Therefore, the prior art requires the creation of a mechanism for application of low-viscosity fluids for placement of proppant in sufficient concentrations in a fracture at a distance from the wellbore and ensuring high vertical propagation of proppant across the complex fracture network.

SUMMARY OF THE INVENTION

The claimed invention provides a method for hydraulic fracturing that involves injecting a proppant-free fluid through a well, into a formation, to create and propagate a fracture; preparing a fracturing fluid by mixing at least water, proppant and at least the first polymer additive, and the second polymer additive to obtain flocculated proppant particles; injecting the fracturing fluid containing the flocculated proppant particles into the formation; and injecting a displacement fluid into the well.

BRIEF DESCRIPTION OF DRAWINGS

Further, embodiments of the claimed invention are described in more details by means of drawings, wherein:

Fig. 1 shows proppant distribution in a fracture during conventional hydraulic
5 fracturing operation using slickwater.

Fig. 2 shows proppant distribution in a fracture during hydraulic fracturing operation using proppant aggregates based on polyelectrolyte complex disclosed in the present invention.

Fig. 3 shows PEC that binds the proppant particles together. PEC is formed from
10 oppositely charged polymers.

Fig. 4 shows proppant aggregates between the walls of a fracture.

Fig. 5 shows laboratory setup for conducting the experiment.

Fig. 6a and Fig. 6b show schematic representation of the experiment results (increased height of the proppant bank). Fig. 6. Height of the proppant bank with regular
15 slickwater (Fig. 6a) and with PEC agglomerates (Fig. 6b).

Figs. 7a and 7b show schematic representation of results of the experiment conducted using regular slickwater (Fig. 7a) and PEC agglomerates in salt water (Fig. 7b).

Fig. 8a and Fig. 8b show that enhanced vertical fracture coverage with
20 polyelectrolyte complex-based proppant aggregates remains stable for several hours.

Fig. 9a and Fig. 9b show simulation of proppant pack distribution in a fracture for a fluid based on conventional slickwater and for polyelectrolyte complex-based proppant aggregates.

Fig. 10a and Fig. 10b show comparison of regular proppant and “loose”
5 flocculated particles in a proppant aggregate pack based on the polyelectrolyte complex.

DESCRIPTION OF EMBODIMENTS

The claimed invention provides a method for hydraulic fracturing that involves injecting a proppant-free fluid through a well, into a formation, to create and propagate a fracture; preparing a fracturing fluid by mixing at least water, proppant and at least the
10 first polymer additive, and the second polymer additive to obtain flocculated proppant particles; injecting the fracturing fluid containing the flocculated proppant particles into the formation; and injecting a displacement fluid into the well.

Hydraulic fracturing is widely used for well stimulation. This technology involves injecting a fluid into the subterranean formation under a high pressure, which exceeds the
15 rock fracturing pressure, in order to form fractures. To prevent fractures from closing when the pressure is relieved after completion of the well treatment, proppant is injected into the subterranean formation.

In many cases, operators perform multistage hydraulic fracturing (a well-known practice for inclined and horizontal wells) which considerably increases the permeability
20 of the zone around the well. Each stage of this process is a complete hydraulic fracturing job. Hydraulic fracturing comprises creating and propagating a formation fracture and injecting proppant (propping agent) to create a highly conductive proppant pack through

which production fluids flow into the well. In so-called multistage hydraulic fracturing, fracture intervals are separated by mechanical isolation devices (such as isolation packer plugs) or chemical diverters.

Hydraulic fracturing is a standard practice for increasing the productivity of oil
5 and gas wells. In low-permeability formations, such technologies as hydraulic fracturing using slickwater or hybrid hydraulic fracturing are commonly used. Low-viscosity fluids make it possible to create more narrow and long fractures forming a complex fracture network, which is more economically effective for the well productivity. However, due to low viscosity of the carrier fluid, premature settling of proppant tends to occur, which
10 may cause poor vertical placement of proppant and possible plugging during treatment. Poor vertical placement of proppant leads to healing of unpropped part of the fracture after closure, thus reducing its productivity.

The present invention relates to hydraulic fracturing of any type of formation using slickwater and focuses on improving the consolidation of proppant particles inside
15 a fracture and enhancing the vertical coverage. Fig. 1 illustrates distribution of proppant in a fracture during conventional hydraulic fracturing operation using slickwater. Fig. 2 shows proppant distribution in a fracture during hydraulic fracturing operation using proppant aggregates based on polyelectrolyte complex disclosed in the present invention.

Proppant aggregates disclosed in the present invention are characterized by
20 enhanced transport performance and minimum settling, which contributes to improved vertical proppant placement and increased productivity compared to hydraulic fracturing methods where conventional low-viscosity fluids are used.

Methods for use of proppant aggregates (or proppant agglomerates) are described

in information sources published before the date of this application submission.

More specifically, previously published Application US2012068584 (Hydrocarbon-based fluid composition and method of using same) discloses the formation of agglomerates in the fracturing fluid which is based on hydrocarbons (e.g.,
5 oil or diesel) and includes a small (up to 5%) amount of water. Water has a “physical glue” effect on the proppant particles, binding them together. This reduces the proppant flowback in its bound form. However, in actual practice, hydraulic fracturing with a hydrophobic (oily) liquid as a carrier fluid is rarely used in the oil production industry. In addition, such agglomerates have low mechanical strength, which hinders the transport
10 of the required amount of proppant.

Application WO2015/076693 (Controlled inhomogeneous proppant aggregate formation, published on May 25, 2015) discloses a method for improving the fluid flow into the fracture that comprises making a slurry from a proppant, light particles, and a carrier fluid. The carrier fluid can act as a binding medium that facilitates the formation
15 of agglomerates from proppant particles and light particles. The slurry is injected into a formation, and agglomeration of the proppant and/or light particles is induced. More specifically, the binding fluid is formed when a cationic polyelectrolyte (or its precursor) reacts with an anionic polyelectrolyte (or its precursor), which leads to the formation of solid particle aggregates (from proppant and light particles) due to the formation of the
20 polyelectrolyte complex (PEC). Formed PEC clusters retain proppant particles and other particles within their volumes. Consolidation of proppant structures reduces proppant flowback from a treated formation. Due to low specific weight of the formed PEC-based aggregates (compared to the specific weight of the proppant), the proppant settling in the

course of hydraulic fracturing is reduced, and enhanced rate of proppant transport into the fracture is provided.

The composition and the methods for production of polymer composites containing particles of a solid agent (proppant or fibers) are disclosed in Patent
5 Application US20150060072 (published on March 5, 2015). In an embodiment of the disclosure, a solid agent (proppant) is coated with a layer of polyanions, and then the polymer-coated proppant is added to the solution of an oppositely charged polyelectrolyte (e.g., hydrated carboxymethyl cellulose (CMC) gel). Active mixing of two polymers leads to formation of elongated polymeric structures due to formation of PEC around the
10 proppant particles. Such approach is used for production of polymeric fluid-based “fibrous composites” inside a formation by the consolidation of the dissolved polymers which is initiated by the shear stress applied to the polymeric fluid. Such fibrous composite polymer structures are used as fibrous additives in formation treatment fluids used in the oil and gas industry (the list of options comprises additives for reducing water
15 loss, water isolation compositions, fracturing fluids, drilling fluids, bridging compositions, etc.).

The key terms “polyelectrolyte”, “polyelectrolyte complex (PEC)”, and “polyelectrolyte complex-based aggregate” hereinafter have the meanings as defined in patent document WO2015/076693. “Polyelectrolyte” is a polymer consisting of
20 macromolecules, in which a considerable part of their repeating units includes ionized or ionizable groups. “Polyelectrolyte complex” is substantially neutral or near-neutral polymer-polymer complex composed of macromolecules carrying opposite charges causing the macromolecules to be bound together by electrostatic interactions, as defined

in the International Union of Pure and Applied Chemistry (IUPAC) Recommendations [Pure Appl. Chem., Vol. 78, No. 11, pp. 2067–2074, 2006. IUPAC Recommendations 2006]. Cationic polyelectrolytes are also called “polybases”, and anionic polyelectrolytes are called “polyacids”. The fact that after cross-linking the polymeric gel forms one phase, and consolidation of polymers in a polyelectrolyte complex forms two separate phases, i.e. dense polymer-polymer complex clusters and low-viscosity fluid with a residual concentration of initial polyelectrolytes, is one of the external features that distinguish polyelectrolyte complexes from polyelectrolyte-based cross-linked gel. Aggregates (clusters) of polyelectrolyte complexes also tend to adhere to solid particles. In other words, a polymer-polymer complex can serve as an “consolidating agent” or a “binding agent” for solid particles in formation treatment fluids.

In the literature, the products of interactions between a water-soluble charged polyelectrolyte (polycationic or polyanionic) and an oppositely charged surface active compound (surfactant) are also classified as polyelectrolyte complexes. When interacting with a macromolecule, charged surfactant groups neutralize the oppositely charged groups of the polyelectrolyte macromolecule (a neutralizing surfactant coat forms around the charged polymer molecule), which leads to the formation of a neutral complex (PEC). Examples of such compositions in the polymer-surfactant form can be found in Patent Application US2015060072.

In the present invention, the method for production of the “proppant agglomerate” is based on the flocculation mechanism which enables the capture of solid proppant particles by a polyelectrolyte complex that consists of a mixture of polyelectrolytes, resulting in the formation of loose aggregates of flocculated proppant particles. In the

literature, the term “flocculation” refers to a process in which fine particles suspended in liquid or gas medium form loose flake-like agglomerations, i.e. flocs. Flocculation can occur using both individual flocculation agents and, for example, mixtures of oppositely charged polyelectrolytes that form polyelectrolyte complexes when
5 interacting. N. Smirnova, M. Savelyeva. Using polyelectrolyte complexes for removal of suspended particles in water treatment and water purification processes. Russian ecology and industry. 2020, vol. 24(5), pp. 46–50. Formation of flocculated proppant particles is accomplished by preparing a proppant slurry in aqueous solution of one of the polyelectrolytes, followed by adding the second polyelectrolyte or its aqueous solution,
10 while mixing vigorously. Typically, the reaction of interaction between the two oppositely charged polyelectrolytes runs at a fast rate, and mixing is required to ensure uniform distribution of components in the mixture and to prevent local interaction between polyelectrolytes without the capture of the proppant. Moreover, mixing can contribute to breaking initially formed large formations with weak polymer-polymer
15 bonds into smaller (normally 2–3 mm) formations with the subsequent increase in density of bonds between oppositely charged polyelectrolytes due to restructuring and reconfiguration of polymer chains caused by mechanical impact. Eventually, stable formations are formed, consisting of proppant flocculated by the polyelectrolyte complex—flocculated proppant particles with the maximum size of up to 5 mm, in
20 particular case of 2–3 mm. Fig. 3 shows PEC that binds the proppant particles together. PEC is formed from oppositely charged polymers.

In the present invention, a water-soluble cationic polyelectrolyte and a water-soluble cationic surfactant are used as positively charged polymers. In this case, the water-soluble cationic polyelectrolyte comprises, but is not limited to, cationic copolymers of

polyacrylamide, poly(diallyldimethylammonium)chloride (DADMAC), polyethyleneimine (PEI), branched polyethyleneimine (PEI), poly(4-vinyl-1-methylpyridinium)bromide, P(BrVMP), poly(diallyldimethylammonium)chloride, P(CIDDA), or a combination thereof.

5 A water-soluble anionic polyelectrolyte and a water-soluble anionic surfactant are used as negatively charged polymers. In this case, the water-soluble anionic polyelectrolyte comprises, but is not limited to, polyacrylamides, polyacrylates, poly(methacrylic acid), sodium polystyrene sulfonate, carboxymethyl cellulose (CMC), or a combination thereof.

10 In an embodiment, in order to produce flocculated proppant particles, a mixture of proppant and a water-soluble cationic polyelectrolyte is prepared first, followed by adding a water-soluble anionic polyelectrolyte into the mixture.

 In another embodiment, in order to produce flocculated proppant particles, a mixture of proppant and a water-soluble anionic polyelectrolyte is prepared first, followed
15 by adding a water-soluble cationic polyelectrolyte into the mixture.

 In another embodiment, in order to produce flocculated proppant particles, a mixture of proppant and a water-soluble cationic polyelectrolyte is prepared first, followed by adding a water-soluble anionic surfactant into the mixture.

 In another embodiment, in order to produce flocculated proppant particles, a
20 mixture of proppant and a water-soluble anionic surfactant is prepared first, followed by adding a water-soluble cationic polyelectrolyte into the mixture.

 In another embodiment, in order to produce flocculated proppant particles, a

mixture of proppant and a water-soluble anionic polyelectrolyte is prepared first, followed by adding a water-soluble cationic surfactant into the mixture.

In another embodiment, in order to produce flocculated proppant particles, a mixture of proppant and a water-soluble cationic surfactant is prepared first, followed by
5 adding a water-soluble anionic polyelectrolyte into the mixture.

In an embodiment of the method disclosed, the fluid containing the proppant aggregates may further comprise some additives known in the art (and/or combinations thereof) which are used as components of fracturing fluids, for example, an oxidizing agent acting as a breaker, a microbiocide, a clay stabilizer, a scale inhibitor, fibers, a
10 corrosion inhibitor, a pH control agent, etc.

To achieve the technical effect of the present invention, it is essential to select optimum concentrations for both polyelectrolytes, as excessive amounts of the chemical agents will cause strong agglomeration in the form of large, high-viscous, poorly injectable formations of proppant with polyelectrolyte complex. At the same time, it is
15 essential to ensure adequate viscosity of the fluid carrying the flocculated proppant into the fracture. In an embodiment of the present invention, one of the polyelectrolytes also acts as the gelling agent that ensures the desired viscosity of the fracturing fluid; it is added in stoichiometric excess to the second polyelectrolyte. Therefore, after formation of the flocculated proppant based on the polyelectrolyte complex, the first polymer is still
20 not completely consumed, and the fracturing fluid still remains sufficiently viscous to keep on carrying the flocculated proppant.

Thus, no large, high-viscous, poorly injectable formations of proppant with polyelectrolyte complex are formed, and flocculated proppant particles with the

maximum size of up to 5 mm, in particular case of 2–3 mm, are formed alone. As a result, once the fracturing fluid that contains such flocculated proppant particles is injected, a loose proppant pack is formed in the fracture. Fig. 10a and Fig. 10b show the comparison of regular proppant (Fig. 10b) and “loose” flocculated particles in a proppant aggregate
5 pack based on the polyelectrolyte complex (Fig. 10a). In this non-limiting example, 0.4 g/l of the base polymer + 0.1 g/l of the second polymer are used (i.e. the ratio is 4:1), therefore, the fracturing fluid remains viscous and capable of carrying proppant agglomerates/flocculated proppant particles.

The goal of this approach is to place the formed proppant aggregates deep inside
10 the complex fracture network and keep them there either due to interaction with fracture walls (mechanical impact, adhesion, etc.) or due to stress created in the formation that would keep the proppant between the fracture walls, as schematically shown in Fig. 4. The placement of consolidated packs/pillars inside the fracture network is believed to allow the fracture conductivity and well productivity to be considerably improved. PEC-
15 based proppant aggregates also feature higher transport performance and minimum settling, which ensures enhanced vertical placement in a complex fracture network, increased size of the propped region and higher well productivity.

Then, a slug of displacement fluid is injected into the well to wash the residual proppant out of the wellbore. When the bottomhole pressure becomes lower than the
20 fracture pressure, the fracture closes (closure step). As the settling rate of the formed proppant aggregates is minimum, it ensures better vertical coverage even if the closing time is long.

Another embodiment of the method involves hydraulic fracturing followed by

isolating the fracture using a mechanical packer or a chemical diverter. The next hydraulic fracturing job is then performed in the next interval.

Increased size of the propped fracture region provides higher fluid conductivity via permeable channels between the proppant aggregates and high strength of the proppant aggregates (pillars) to keep the walls of the fracture open after completion of the hydraulic fracturing job. Displacement fluid is used to remove (wash out) the proppant from the wellbore.

EXAMPLES

Example 1

This example describes the use of proppant aggregates that involves placing them in the fracture and forming a proppant pack with improved vertical coverage in this region. Fig. 5 shows the laboratory setup used to conduct the experiment.

Figs. 6a and 6b show schematic representation of the experiment results (increased height of the proppant bank for regular slickwater (Fig. 6a) and PEC agglomerates (Fig. 6b)). The fluid containing a polyelectrolyte complex (PEC) and a proppant is injected through the laboratory unit (schematically shown in Fig. 5). A 2 mm wide slot between two acrylic glass panels is used for the test (the slot imitates an open fracture).

First, aqueous solutions of two polyelectrolyte types are prepared for injection. These aqueous solutions have a neutral pH or are slightly alkaline. For example, the first polyelectrolyte (polyelectrolyte 1) is a cationic charged polymer, while the second polyelectrolyte in aqueous solution (polyelectrolyte 2) is an anionic charged polymer

(prepared with the same pH level as the aqueous solution). A sufficient amount of proppant is added to one of the polyelectrolyte flows. Since the proppant (sand) is a neutral material, it can be added to any of the polyelectrolyte flows. Thus, one of the flows into the mixer is a proppant slurry in the aqueous polyelectrolyte solution, and the
5 other flow is the aqueous solution of the oppositely charged electrolyte.

Two oppositely charged polyelectrolytes (charged polymers) and proppant (sand (50/140 mesh)) are mixed before being fed into the slot, which causes very quick formation of polyelectrolyte complex-based clusters which are called “proppant aggregates” or “proppant agglomerates”. The fluid containing formed polyelectrolyte
10 complex-based proppant aggregates was fed into the slot (which imitated an open hydraulic fracture).

In Example 1 (Fig. 6a and Fig. 6b), a polymer fluid of the following composition was tested: 1) 0.24 kg/l of water-sand slurry (50/140 mesh), 0.4 g/l of anionic polyacrylamide (APAM); and 2) 0.24 kg/l of water-sand slurry (50/140 mesh), 0.4 g/l of
15 anionic polyacrylamide (APAM), and 0.1 g/l of branched polyethyleneimine (b-PEI), or 0.1 g/l of anionic polyacrylamide (APAM) and 0.4 g/l of branched polyethyleneimine (b-PEI). Aqueous polymer solutions had the pH = 8.5. Tests in the test unit (shown in Fig. 5) were performed at the room temperature (+20°C).

The experiments also included testing different concentrations of the first
20 polyelectrolyte and the second polyelectrolyte with various concentration ratios, not only 4:1, but with ratios ranging from 2:1 to 8:1 as well, which also demonstrated satisfactory performance.

This example shows that polyelectrolyte complex-based proppant aggregates

(anionic polymer and cationic surfactant aggregation in Fig. 6b) provide forming a proppant pack with a vertical coverage increased by at least 75% compared to regular slickwater (Fig. 6a).

Example 2

5 This example demonstrates the application performance of polyelectrolyte complex-based proppant aggregates in salt water.

Two oppositely charged polyelectrolytes (charged polymers) and sand (50/140 mesh) are mixed in salt water before being fed into the slot, which causes very quick formation of polyelectrolyte complex-based clusters. The fluid containing formed
10 polyelectrolyte complex-based proppant aggregates was fed into the slot.

Figs. 7a and 7b show schematic representation of results of the experiment conducted using regular slickwater (Fig. 7a) and PEC agglomerates in salt water (Fig. 7b). Similarly to the process described in Example 1, in the course of the experiment the proppant aggregates were produced and transported into a 2 mm wide slot. This
15 example shows that polyelectrolyte complex-based proppant aggregates (Fig. 7b) provide forming a proppant pack with a vertical slot coverage increased by at least 150% compared to regular slickwater (Fig. 7a).

In the example shown in Fig. 7b, a polymer fluid of the following composition was tested: 1) 0.24 kg/l of water-sand slurry (50/140 mesh), 0.4 g/l of anionic polyacrylamide (APAM), 0.5 g/l of NaCl; 3 g/l of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$; 3 g/l of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$; and 2) 0.24 kg/l of water-sand slurry (50/140 mesh), 0.4 g/l of anionic polyacrylamide (APAM), 0.1 g/l of branched polyethyleneimine (b-PEI), and 0.5 g/l of NaCl; 3 g/l of
20

$\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$; 3 g/l of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$. Aqueous polymer solutions had the pH = 8.5. Tests in the test unit (shown in Fig. 5) were performed at the room temperature (+20°C).

Example 3. Bank settling after 12 h

In the following example, Fig. 8a and Fig. 8b show that the enhanced vertical slot coverage with polyelectrolyte complex-based proppant aggregates remains stable for several hours. Fig. 8a shows the aggregate immediately after injection into the fracture. Then the aggregates from Example 2 were left in the slot for 12 h to test their stability. It can be noted that after settling the vertical coverage remains practically unchanged over the 12-hour period. It confirms that the polyelectrolyte complex-based proppant aggregates remain stable against settling even if a fracture takes a long time to close.

Example 4

The placement of polyelectrolyte complex-based proppant aggregates inside a fracture was modeled using a hydraulic fracturing simulator, in comparison with proppant placement when conventional slickwater was used. Simulation outputs in Fig. 9a and Fig. 9b show that using polyelectrolyte complex-based proppant aggregates disclosed in the present invention ensures enhanced vertical fracture coverage and a less compact proppant pack. Simulation of proppant pack distribution in a fracture for a fluid based on conventional slickwater is shown in Fig. 9a, and for polyelectrolyte complex-based proppant aggregates, in Fig. 9b. These facts confirm that a fracture with enhanced vertical coverage and a less compact proppant pack are certain to improve permeability for better production of reservoir fluids.

Although the above disclosure relates to methods for oil production, it can as well be applied for production and injection of other fluids (liquids or gases).

Apparently the above embodiments shall not be regarded as a limitation of the scope of the patent claims. One skilled in the art will appreciate that it is possible to make multiple changes to the technique described above without departing from the principles of the claimed invention.

CLAIMS

The method of hydraulic fracturing comprising:

- 5 (i) injecting a proppant-free fluid through the well into the formation to create and propagate a fracture;
- (ii) preparing a fracturing fluid by mixing at least water, proppant and at least the first polymer additive and the second polymer additive to produce flocculated proppant particles;
- 10 (iii) injecting the fracturing fluid containing prepared flocculated proppant particles into the formation;
- (iv) injecting a displacement fluid into the well.

2. The method of claim 1, wherein the first polymer additive is a water-soluble cationic polyelectrolyte, and the second polymer additive is a water-soluble anionic
15 polyelectrolyte.

3. The method of claim 1, wherein the first polymer additive is a water-soluble cationic polyelectrolyte, and the second polymer additive is a water-soluble anionic
20 surfactant.

4. The method of claim 1, wherein the first polymer additive is a water-soluble cationic surfactant, and the second polymer additive is a water-soluble anionic
polyelectrolyte.

25 5. The method of claim 1, wherein the production of flocculated proppant particles

at stage (ii) comprises first preparing a mixture of proppant and a water-soluble cationic polyelectrolyte, followed by adding a water-soluble anionic polyelectrolyte into the mixture.

5 6. The method of claim 1, wherein the production of flocculated proppant particles at stage (ii) comprises first preparing a mixture of proppant and a water-soluble anionic polyelectrolyte, followed by adding a water-soluble cationic polyelectrolyte into the mixture.

10 7. The method of claim 1, wherein the production of flocculated proppant particles at stage (ii) comprises first preparing a mixture of proppant and a water-soluble cationic polyelectrolyte, followed by adding a water-soluble anionic surfactant into the mixture.

15 8. The method of claim 1, wherein the production of flocculated proppant particles at stage (ii) comprises first preparing a mixture of proppant and a water-soluble anionic surfactant, followed by adding a water-soluble cationic polyelectrolyte into the mixture.

20 9. The method of claim 1, wherein the production of flocculated proppant particles at stage (ii) comprises first preparing a mixture of proppant and a water-soluble anionic polyelectrolyte, followed by adding a water-soluble cationic surfactant into the mixture.

10. The method of claim 1, wherein the production of flocculated proppant particles at stage (ii) comprises first preparing a mixture of proppant and a water-soluble cationic surfactant, followed by adding a water-soluble anionic polyelectrolyte into the

mixture.

11. The method of claim 2, wherein the water-soluble anionic polyelectrolyte comprises polyacrylamides, polyacrylates, poly(methacrylic acid), sodium polystyrene
5 sulfonate, carboxymethyl cellulose (CMC), or a combination thereof.

12. The method of claim 2, wherein the water-soluble cationic polyelectrolyte comprises cationic copolymers of polyacrylamide, poly(diallyldimethylammonium)chloride (DADMAC), polyethyleneimine (PEI),
10 branched polyethyleneimine (PEI), poly(4-vinyl-1-methylpyridinium)bromide, P(BrVMP), poly(diallyldimethylammonium)chloride, P(CIDDA), or a combination thereof.

13. The method of claim 1, wherein the first polymer additive is added in
15 stoichiometric excess to the second polymer additive.

14. The method of claim 1, wherein the second polymer additive is added in stoichiometric excess to the first polymer additive.

20

15. The method of claim 1, wherein the first polymer additive acts as a gelling agent for the fracturing fluid.

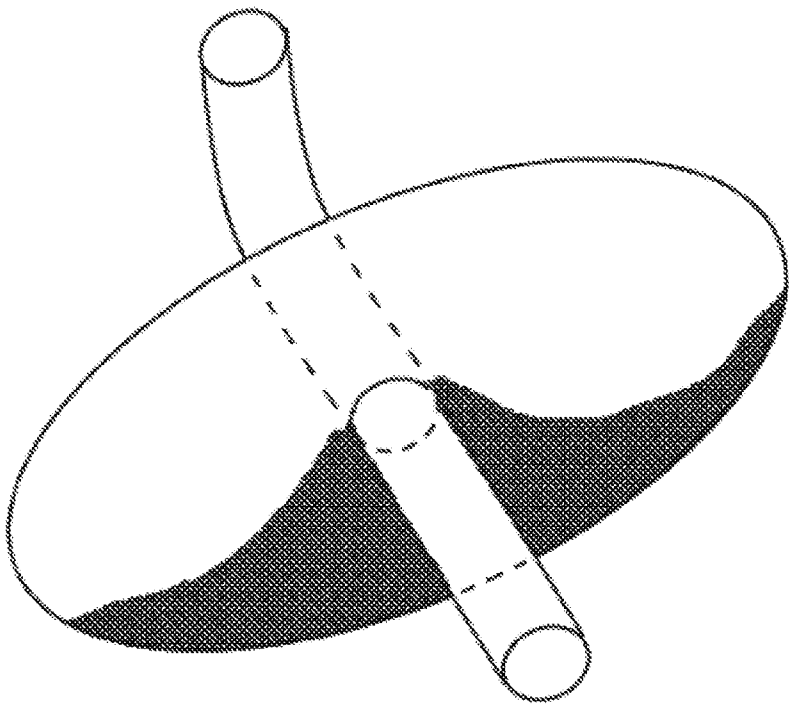


Fig. 1

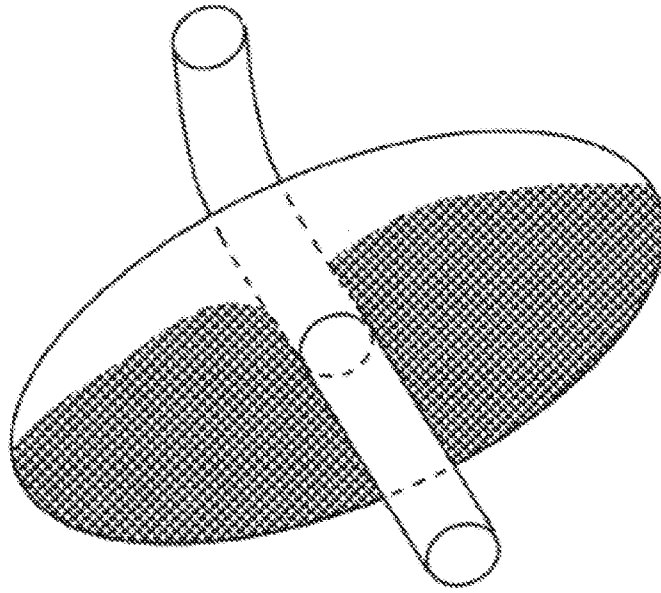


Fig. 2

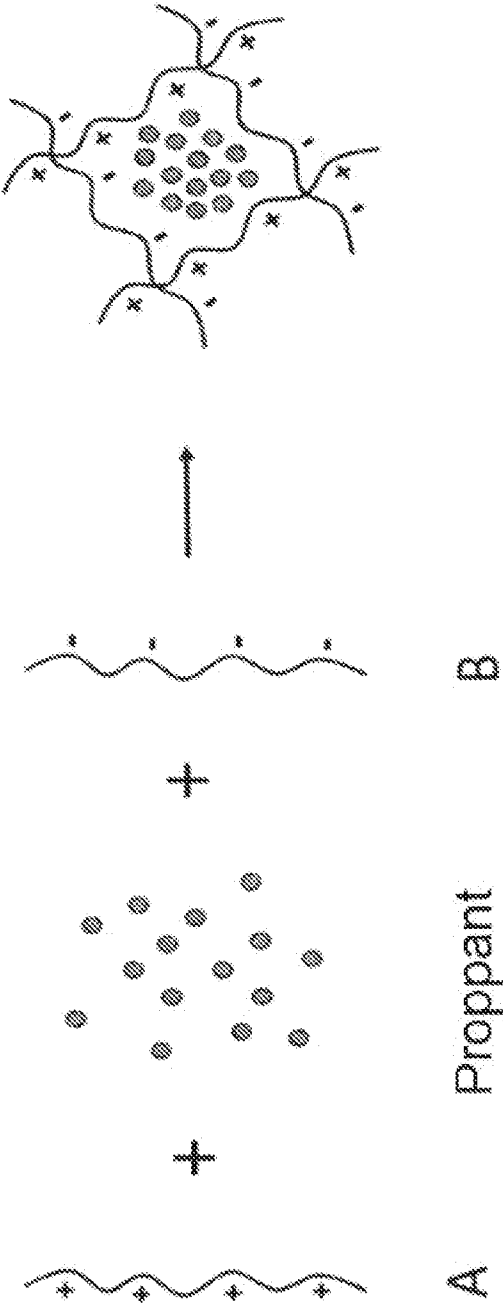


Fig. 3

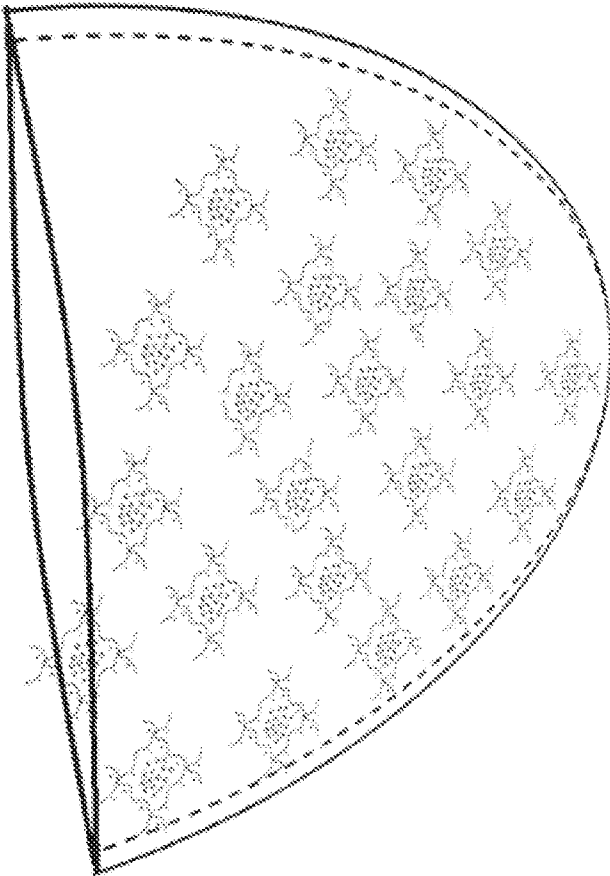


Fig. 4

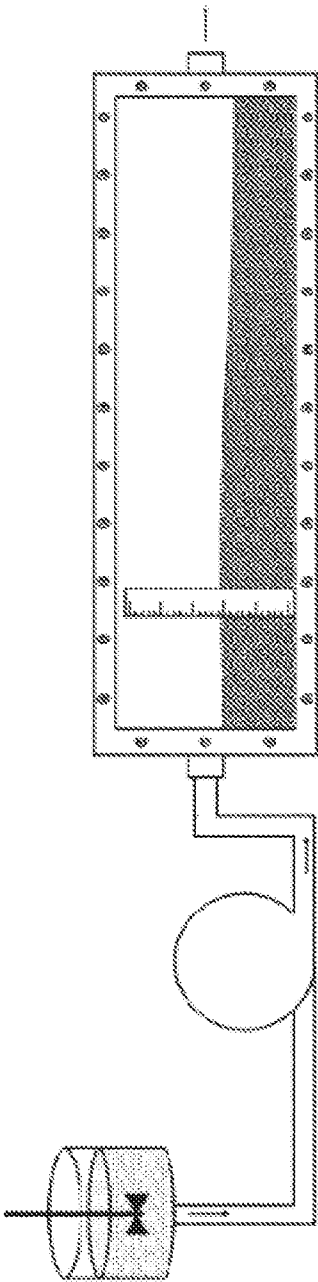


Fig. 5

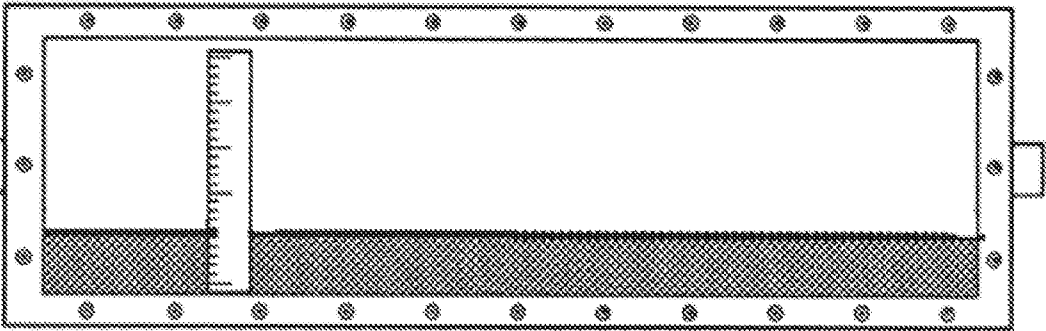


Fig. 6a

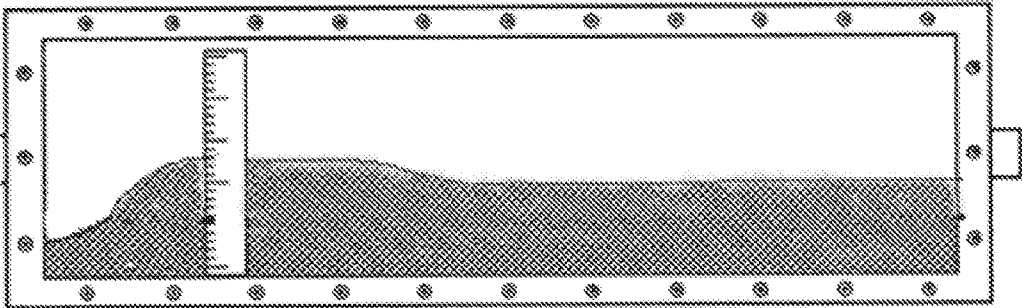


Fig. 6b

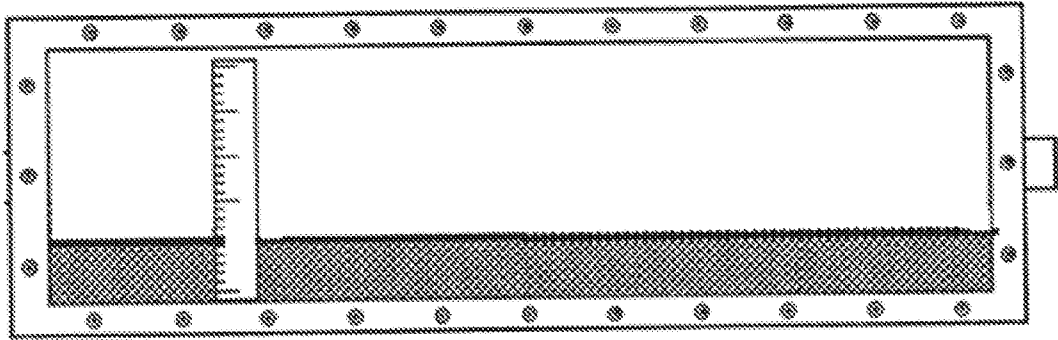


Fig. 7a

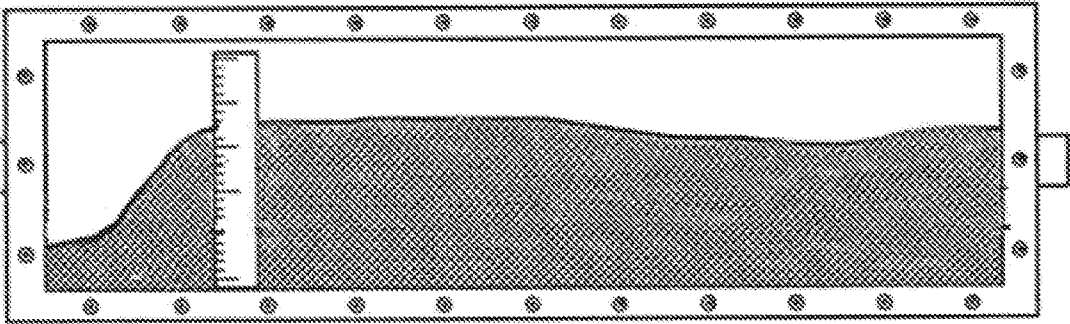


Fig. 7b

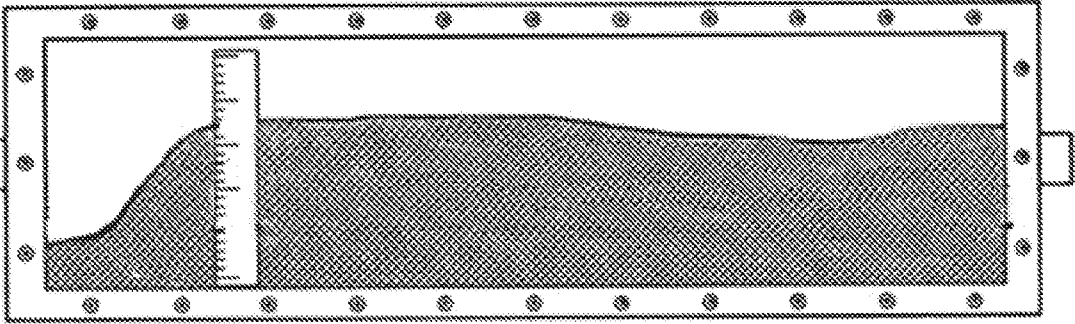


Fig. 8a

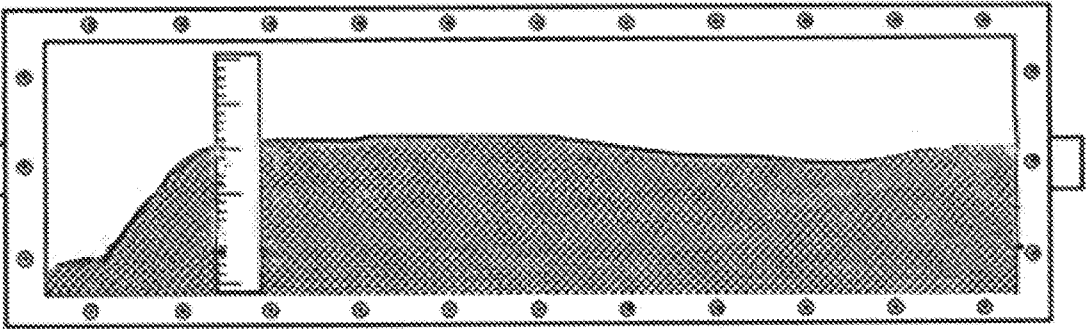


Fig. 8b

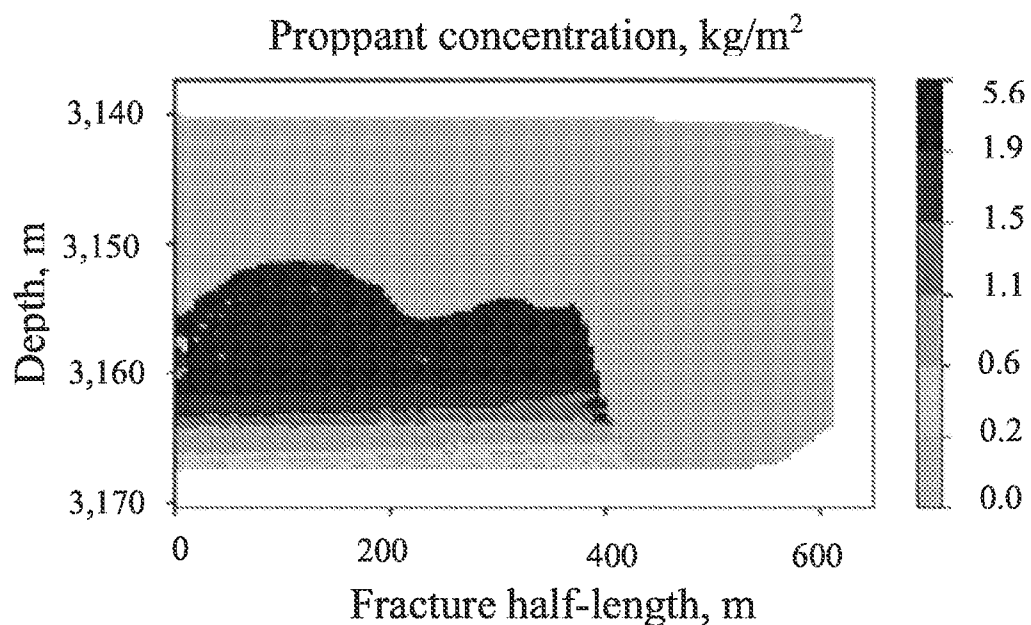


Fig. 9a

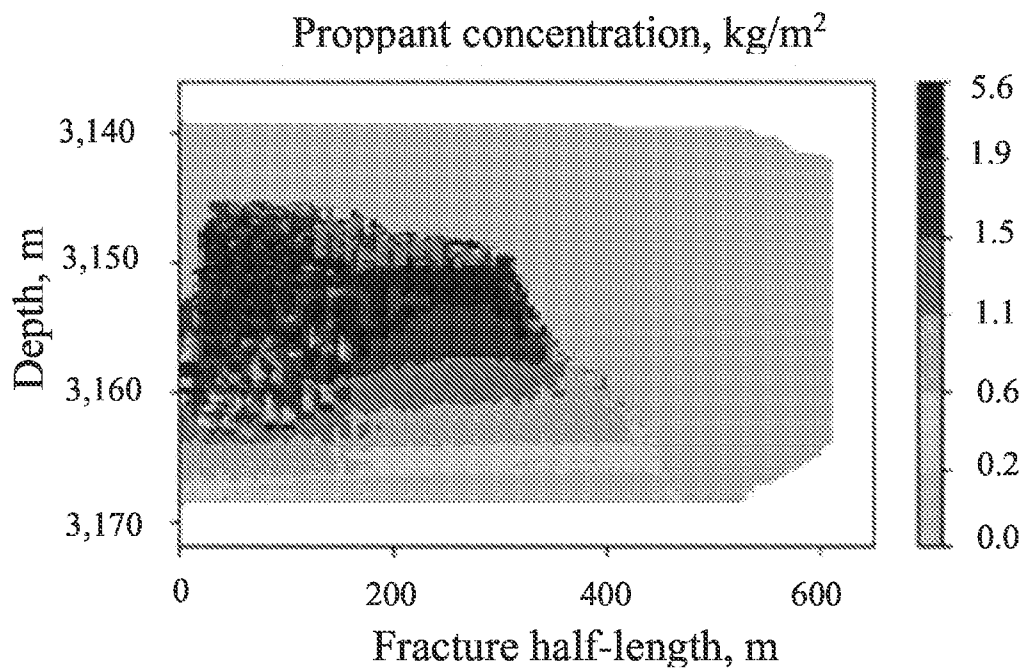


Fig. 9b

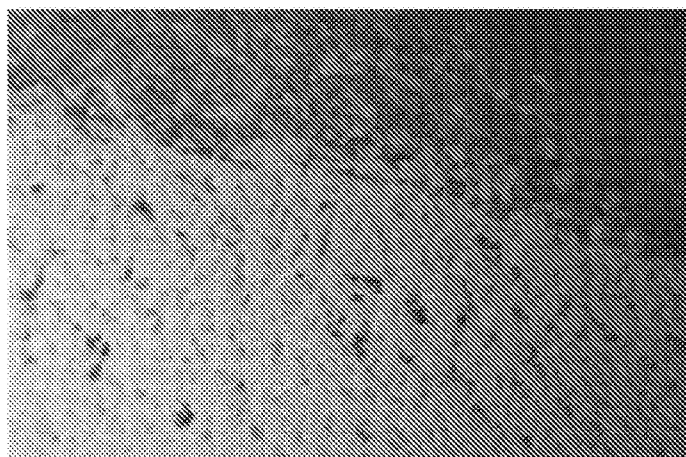


Fig. 10a

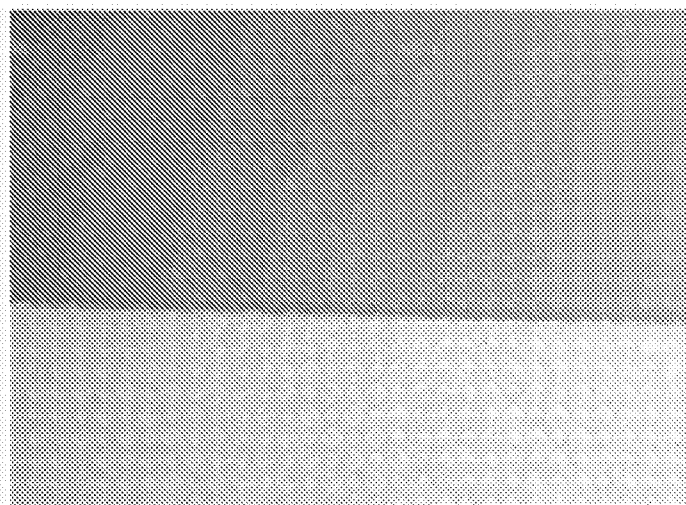


Fig. 10b

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2024/029521

A. CLASSIFICATION OF SUBJECT MATTER**E21B 43/26(2006.01)i**

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)

E21B 43/26(2006.01); C09K 8/42(2006.01); C09K 8/487(2006.01); C09K 8/516(2006.01); C09K 8/80(2006.01);
E21B 21/00(2006.01); E21B 43/267(2006.01)

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

Korean utility models and applications for utility models
Japanese utility models and applications for utility models

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

eKOMPASS(KIPO internal) & Keywords: hydraulic fracturing, proppant-free fluid, fracturing fluid, proppant, polymer additive, displacement fluid, polyelectrolyte, surfactant, cationic, anionic

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
DY	US 11008844 B2 (SCHLUMBERGER TECHNOLOGY CORPORATION) 18 May 2021 (2021-05-18) column 7, line 9 - column 10, line 62 and claims 1-5, 11-13	1-15
Y	US 2015-0144339 A1 (SCHLUMBERGER TECHNOLOGY CORPORATION) 28 May 2015 (2015-05-28) paragraphs [0004], [0006]-[0007] and claims 1, 9	1-15
A	US 2015-0083423 A1 (BAKER HUGHES INCORPORATED) 26 March 2015 (2015-03-26) paragraphs [0012], [0017], [0026]-[0032], claim 11, and figures 1-2	1-15
A	WO 2022-093059 A1 (SCHLUMBERGER CANADA LIMITED et al.) 05 May 2022 (2022-05-05) claims 1, 5 and figure 4	1-15
A	US 2013-0056213 A1 (MEDVEDEV et al.) 07 March 2013 (2013-03-07) paragraphs [0001], [0008]-[0010], [0028]-[0030], [0042], [0053] and claim 16	1-15



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:

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

“D” document cited by the applicant in the international application

“E” earlier application or patent 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

04 September 2024

Date of mailing of the international search report

04 September 2024

Name and mailing address of the ISA/KR

**Korean Intellectual Property Office
189 Cheongsa-ro, Seo-gu, Daejeon
35208, Republic of Korea**

Facsimile No. +82-42-481-8578

Authorized officer

PARK, Tae Wook

Telephone No. +82-42-481-3405

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

PCT/US2024/029521

Patent document cited in search report			Publication date (day/month/year)	Patent family member(s)			Publication date (day/month/year)
US	11008844	B2	18 May 2021	AR	106409	A1	10 January 2018
				US	2018-0238161	A1	23 August 2018
				WO	2017-078560	A1	11 May 2017
US	2015-0144339	A1	28 May 2015	AR	098521	A1	01 June 2016
				CA	2872284	A1	25 May 2015
				CN	104653165	A	27 May 2015
				MX	2014014293	A	01 October 2015
				RU	2014147149	A	10 June 2016
				RU	2014147149	A3	24 July 2018
				WO	2015-076693	A1	28 May 2015
US	2015-0083423	A1	26 March 2015	AR	091580	A1	11 February 2015
				AU	2013-280404	A1	22 January 2015
				AU	2013-280404	B2	02 February 2017
				AU	2013-280418	A1	22 January 2015
				AU	2013-280418	B2	02 March 2017
				AU	2015-301423	A1	06 April 2017
				AU	2015-301423	B2	17 January 2019
				BR	112014032573	A2	27 June 2017
				BR	112014032657	A2	27 June 2017
				BR	112014032657	A8	06 April 2021
				BR	112019000843	A2	30 April 2019
				CA	2877708	A1	03 January 2014
				CA	2877708	C	22 May 2018
				CA	2877830	A1	03 January 2014
				CA	2877830	C	20 March 2018
				CA	2961350	A1	18 February 2016
				CA	3031541	A1	25 January 2018
				CA	3031541	C	09 November 2021
				CN	104508079	A	08 April 2015
				CN	106795750	A	31 May 2017
				CN	109689836	A	26 April 2019
				CO	7160106	A2	15 January 2015
				EP	2864441	A2	29 April 2015
				EP	2864442	A2	29 April 2015
				EP	2864442	B1	31 October 2018
				EP	3180494	A1	21 June 2017
				EP	3180494	A4	03 January 2018
				EP	3487951	A1	29 May 2019
				HU	E040215	T2	28 February 2019
				MX	2014016037	A	26 September 2016
				MX	2014016040	A	06 July 2015
				MX	356996	B	22 June 2018
				MX	366098	B	27 June 2019
				MY	180172	A	24 November 2020
				NO	20170388	A1	15 March 2017
				NZ	730072	A	23 February 2018
PL	2864442	T3	29 March 2019				
RU	2017108449	A	17 September 2018				
RU	2017108449	A3	17 September 2018				
RU	2681011	C2	01 March 2019				

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

PCT/US2024/029521

Patent document cited in search report			Publication date (day/month/year)	Patent family member(s)		Publication date (day/month/year)					
				SA	519400940	B1	07 July 2022				
				US	10041327	B2	07 August 2018				
				US	10988678	B2	27 April 2021				
				US	11111766	B2	07 September 2021				
				US	11486241	B2	01 November 2022				
				US	2013-0126177	A1	23 May 2013				
				US	2013-0341025	A1	26 December 2013				
				US	2013-0341030	A1	26 December 2013				
				US	2014-0352959	A1	04 December 2014				
				US	2015-0041132	A1	12 February 2015				
				US	2017-0051599	A1	23 February 2017				
				US	2018-0201827	A1	19 July 2018				
				US	2018-0202276	A1	19 July 2018				
				US	2018-0202278	A1	19 July 2018				
				US	2018-0347332	A1	06 December 2018				
				US	8899332	B2	02 December 2014				
				US	9580642	B2	28 February 2017				
				US	9919966	B2	20 March 2018				
				US	9920607	B2	20 March 2018				
				US	9920610	B2	20 March 2018				
				US	9938811	B2	10 April 2018				
				WO	2014-004611	A2	03 January 2014				
				WO	2014-004611	A3	19 June 2014				
				WO	2014-004689	A2	03 January 2014				
				WO	2014-004689	A3	19 June 2014				
				WO	2016-025936	A1	18 February 2016				
				WO	2018-017482	A1	25 January 2018				
				WO	2022-093059	A1	05 May 2022	EP	4237654	A1	06 September 2023
								MX	2023005155	A	16 June 2023
								US	12043791	B2	23 July 2024
US	2023-0407162	A1	21 December 2023								
US	2013-0056213	A1	07 March 2013	AR	102843	A1	29 March 2017				
				CA	2797294	A1	03 November 2011				
				MX	2012012330	A	29 January 2013				
				RU	2012150663	A	10 June 2014				
				RU	2544943	C2	20 March 2015				
				US	2015-0152321	A1	04 June 2015				
				WO	2011-136678	A1	03 November 2011				
				WO	2016-130298	A1	18 August 2016				