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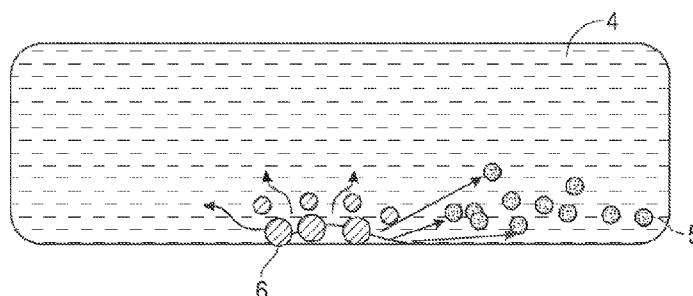


FIG. 3

(57) Abstract: A cement slurry is prepared that comprises water, a hydraulic cement and particles of an oil-absorbent material. The particles are present in an amount sufficient to interact with a non-aqueous component of a drilling fluid and alter a property of the drilling fluid within the subterranean well. The drilling fluid contains calcium hydroxide. The cement slurry is placed in the subterranean well. The oil-absorbent particles contact the non-aqueous drilling fluid component, thereby altering the property of the non-aqueous component. A hydraulic fracturing operation is performed, wherein a pad fluid comprises nanosize silica particles. The nanosize silica particles contact the residual drilling fluid, thereby further altering the property of the drilling fluid and creating a hydraulic seal in the subterranean well.



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WELL TREATMENT METHODS

Cross-Reference to Related Application

[0001] This application claims priority to and the benefit of U.S. Provisional Patent Application Serial No. 62/867993, entitled “Well Treatment Methods,” filed June 28, 2019, which is hereby incorporated by reference in its entirety for all purposes.

Background

[0002] The present disclosure relates generally to well cementing and stimulation. In particular, the disclosure relates to improving zonal isolation by incorporating nanosize silica in fracturing fluids.

[0003] During the construction of a subterranean well it is common, during and after drilling, to place a tubular body (e.g., liner or casing) in the well, secured by cement pumped into the annulus around the outside of the liner. The cement supports the tubular body and provides hydraulic isolation of the various fluid-producing zones through which the well passes. This latter function is important because it prevents fluids from different layers contaminating each other. For example, the cement prevents formation fluids from entering the water table and polluting drinking water, or prevents water production instead of oil or gas. A complete discussion of cementing techniques may be found in the following publication. Nelson EB and Guillot D (eds.): *Well Cementing – 2nd Edition*, Houston, Schlumberger (2006).

[0004] After the construction of a subterranean well it is common to perform stimulation operations to improve well productivity. Such operations include matrix acidizing and hydraulic fracturing. Hydraulic fracturing operations are those during which fluids are pumped into the well at rates such that the applied fluid pressure exceeds the fracturing pressure of the formation being treated. The fracturing fluids are usually pumped through perforations in casing that are adjacent to the formation to be stimulated.

[0005] Most fracturing operations involve pumping two fluids. The first fluid, known as a pad fluid, usually contains little or no particulates and is responsible for creating

the fracture and propagating the fracture beyond the wellbore. The fracture may propagate along the pathway of least stress, forming "wings" that extend in two opposing directions away from the wellbore. After the pad fluid has created and propagated the fracture, a second fluid known as a proppant slurry may be pumped through the perforations. Proppant is a particulate material that is deposited inside the fracture, forming a proppant pack. When pumping pressure is released, the fracture closes upon the proppant pack. The proppant pack is sufficiently permeable to allow efficient fluid flow from the formation to the wellbore, enabling the production of hydrocarbons. A complete discussion of fracturing techniques may be found in the following publication. Economides MJ and Nolte KG (eds.): *Reservoir Stimulation – 3rd Edition*, Chichester, John Wiley & Sons Ltd. (2000).

[0006] Drilling fluid removal has been a subject of interest in the well-cementing community for many years because of its effect on cement quality and zonal isolation. The principal objective of a primary cement job is to provide complete and permanent isolation of the formations behind the casing. To meet this objective, the drilling fluid and the preflushes (if any) should be fully removed from the annulus, and the annular space should be completely filled with cement slurry. Once in place, the cement should harden and develop the necessary mechanical properties to maintain a hydraulic seal throughout the life of the well. Therefore, efficient mud removal and proper slurry placement promote well isolation.

[0007] Incomplete removal of drilling fluids within a wellbore may affect the quality of hydraulic cement placement in the wellbore annulus resulting in incomplete zonal isolation. This may occur particularly in horizontal wellbores where poorly centralized casing may increase the likelihood that gelled mud channels may form. Compromised zonal isolation may increase the potential for fluid flow along the casing. Later in the life of the well, such mud channels that have formed may serve as non-productive communication pathways between stages during a stimulation treatment.

Summary of the Disclosure

[0008] In an aspect, embodiments relate to methods for stimulating a subterranean well. A cement slurry is prepared that comprises water, a hydraulic cement and particles of an oil-absorbent material. The particles are present in an

amount sufficient to interact with a non-aqueous component of a drilling fluid and alter a property of the drilling fluid within the subterranean well. The drilling fluid contains calcium hydroxide. The cement slurry is placed in the subterranean well. The oil-absorbent particles contact the non-aqueous drilling fluid component, thereby altering the property of the non-aqueous component. A hydraulic fracturing operation is performed, wherein a pad fluid comprises nanosize silica particles.

[0009] In a further aspect, embodiments relate to methods for establishing zonal isolation in a subterranean well. A subterranean well is drilled with a drilling fluid that contains calcium hydroxide. A cement slurry is prepared that comprises water and a hydraulic cement. The cement slurry is placed in the subterranean well wherein residual drilling fluid is present along casing and formation surfaces. A hydraulic fracturing operation is performed, wherein a pad fluid comprises nanosize silica particles. The nanosize silica particles contact the residual drilling fluid, thereby altering the property of the drilling fluid and creating a hydraulic seal in the subterranean well.

Brief Description of the Drawings

[0010] Fig. 1a is a cross-sectional diagram showing 100% casing centralization in a wellbore. Fig. 1b is a cross-sectional diagram showing eccentric casing centralization, which may occur in deviated or horizontal well sections.

[0011] Fig. 2 is a cross-sectional diagram showing a drilling fluid channel arising from poor casing centralization in a wellbore.

[0012] Fig. 3 is a diagram showing a drilling fluid channel that has been deposited in the narrow region of an eccentric annulus and affected by the cement slurry according to the present disclosure.

[0013] Fig. 4 compares the rheological properties of diesel-based emulsion drilling fluids after exposure to cement slurries. The amplitude dependent storage and loss moduli of drilling fluid exposed to a cement slurry containing oil-absorbent particles are higher than those of a drilling fluid exposed to a comparative slurry that did not contain absorbent particles.

[0014] Fig. 5 shows pressure test results for a conventional cement slurry and a cement slurry containing oil-absorbing particles.

[0015] Fig. 6 shows the viscosities of oils containing various oil-absorbent polymers.

[0016] Fig. 7 shows rheological data comparing the performance of a drilling fluid containing nanosilica compared to a control system without nanosilica.

Detailed Description

[0017] At the outset, it should be noted that in the development of any such actual embodiment, numerous implementations—specific decisions must be made to achieve the developer's specific goals, such as compliance with system related and business related constraints, which will vary from one implementation to another. Moreover, it will be appreciated that such a development effort might be complex and time consuming but would nevertheless be a routine undertaking for those of ordinary skill in the art having the benefit of this disclosure. In addition, the composition used/disclosed herein can also comprise some components other than those cited. In the summary of the disclosure and this detailed description, each numerical value should be read once as modified by the term "about" (unless already expressly so modified), and then read again as not so modified unless otherwise indicated in context. Also, in the summary of the disclosure and this detailed description, it should be understood that a concentration range listed or described as being useful, suitable, or the like, is intended that any and every concentration within the range, including the end points, is to be considered as having been stated. For example, "a range of from 1 to 10" is to be read as indicating each and every possible number along the continuum between about 1 and about 10. Thus, even if specific data points within the range, or even no data points within the range, are explicitly identified or refer to only a few specific points, it is to be understood that inventors appreciate and understand that any and all data points within the range are to be considered to have been specified, and that inventors possessed knowledge of the entire range and all points within the range.

[0018] As discussed earlier, one indication of successful cement placement is complete drilling fluid removal. Complete removal of non-aqueous drilling fluids may be challenging because they may leave casing and formation surfaces oil wet, which may negatively affect cement sheath bond quality. It is known in the art that such non-aqueous drilling fluids may further contain clays, weighting agents or both.

[0019] During most cementing operations, casing **1** is present inside a wellbore having a wall **2**. An annulus **3** is therefore present between the casing and the wellbore wall. Optimal drilling-fluid removal may occur when the casing is fully centralized in the wellbore (Fig. 1a). 100% casing centralization maximizes circulation efficiency because there are no narrow regions that may be resistant to fluid flow. However, achieving 100% casing centralization may not be achievable in deviated or horizontal well sections (Fig. 1b). Due to gravity, the casing has a tendency to migrate toward a borehole wall. As a result, during the cement placement process, when cement slurry **4** is pumped to fill the annulus, the eccentric casing position may lead to poor drilling-fluid displacement in the narrow portion of the casing/wellbore annulus, leaving a drilling-fluid channel **5** (Fig. 2).

[0020] The present disclosure presents methods for altering drilling-fluid properties as well as achieving zonal isolation. Embodiments may combat drilling fluid channels by interacting with the drilling fluid channels and altering properties of the drilling fluid channels. The present disclosure further presents methods for achieving zonal isolation by performing fracturing operations that employ pad fluids that contain nanosize silica.

[0021] In an aspect, embodiments relate to methods for stimulating a subterranean well. A cement slurry is prepared that comprises water, a hydraulic cement and particles of an oil-absorbent material. The particles are present in an amount sufficient to interact with a non-aqueous component of a drilling fluid and alter a property of the drilling fluid within the subterranean well. The drilling fluid contains calcium hydroxide. The cement slurry is placed in the subterranean well. The oil-absorbent particles contact the non-aqueous drilling fluid component, thereby altering the property of the non-aqueous component. A hydraulic fracturing operation is performed, wherein a pad fluid comprises nanosize silica particles. The nanosize

silica particles contact the residual drilling fluid, thereby further altering the property of the drilling fluid and creating a hydraulic seal in the subterranean well.

[0022] In a further aspect, embodiments relate to methods for establishing zonal isolation in a subterranean well. A subterranean well is drilled with a drilling fluid that contains calcium hydroxide. A cement slurry is prepared that comprises water and a hydraulic cement. The cement slurry is placed in the subterranean well wherein residual drilling fluid is present along casing and formation surfaces. A hydraulic fracturing operation is performed, wherein a pad fluid comprises nanosize silica particles. The nanosize silica particles contact the residual drilling fluid, thereby altering the property of the drilling fluid and creating a hydraulic seal in the subterranean well.

[0023] In an embodiment, an oil-absorbing material may be added to the cement slurry. The oil-absorbing material may begin interacting with drilling fluid first at the interface between the drilling fluid and cement. Not being bound to any theory, the oil absorbing material may promote oil diffusion into the set cement material. Once oil from oil-based drilling fluid is absorbed or diffused into the cement, the rheological properties of the drilling fluid may change. Consequently, the drilling fluid may be converted from a fluid-like material to a paste-like structure. Such conversion inside the drilling-fluid channel may prevent fluid flow inside the channel and serve to provide zonal isolation. In addition, oil-absorbing particles in the cement sheath may increase in size, physically blocking small channels or compressing a paste-like mud structure.

[0024] In an embodiment, a process contributing to achieving zonal isolation may include dynamic removal of the mud channel during cement slurry displacement. The oil-absorbing particles **6** flowing near the drilling fluid channel may physically remove a portion of the drilling fluid **5** and transport the portion away from the drilling fluid channel. Thus, the particles may significantly reduce the size of the drilling fluid channel or even remove it (Fig. 3).

[0025] In an embodiment, a material that viscosifies oil may be added to the cement slurry. Oil-viscosifying particles may interact and diffuse into oil-based drilling fluid during placement or after the cement setting process, and viscosify the residual

oil-based mud to an extent that zonal isolation is achieved. Such cement compositions may contain a sufficient concentration of oil-viscosifying particles to increase the yield point (Ty) to a level higher than that of cement compositions that do not contain the oil-viscosifying particles. The yield point increase may take place within three days of exposure, and the ultimate yield point measured by oscillatory rheometry may be at least 100 Pa. In some cases, the yield point may rise to 4600 Pa (see Example 3). Or the yield point may be between 500 Pa and 3000 Pa. Or the yield point may be between 1000 Pa and 2000 Pa. The higher the yield point, the better the zonal isolation may be.

[0026] For all embodiments, the nanosize particles in the pad fluid may be present at a concentration between 5.0 lbm/bbl and 50 lbm/bbl, or 5.0 lbm/bbl and 10 lbm/bbl. The abbreviation "bbl" refers to a barrel, which is equivalent to 42 U.S. gallons. The nanosize particles may have a particle size between 1 nm and 100 nm. The nanosize particles may be added to the pad fluid in solid form or as a liquid slurry or suspension.

[0027] During the fracturing operation the pad fluid may commingle with the mud channel, thereby exposing the nanosize silica particles to calcium hydroxide. Without relying on any particular theory, it is possible that the silica and calcium hydroxide react to form a calcium silicate hydrate, thereby increasing the strength of the mixture and improving zonal isolation.

[0028] For all embodiments, the cement slurry may comprise portland cement, high alumina cement, fly ash, blast furnace slag, microcement, geopolymers, chemically bonded phosphate ceramics, plaster or resins or combinations thereof. The cement slurry further comprises polymers, random copolymers and block polymers comprising alternating sections of one chemical compound separated by sections of a different chemical compound, or a coupling group of low molecular weight. For example, block polymers may have the structure (A-b-B-b-A), wherein A represents a block that is glassy or semi-crystalline and B is a block that is elastomeric. In principle, A can be any polymer that is normally regarded as thermoplastic (e.g., polystyrene, polymethylmethacrylate, isotactic polypropylene, polyurethane, etc.), and B can be any polymer that is normally regarded as elastomeric (e.g., polyisoprene, polybutadiene, polyethers, polyesters, etc.).

Example thermoplastic block polymers include styrene-isoprene-styrene (SIS), styrene-butadiene-styrene (SBS) and mixtures thereof. The block-polymer-additive may be in one or more shapes, including (but not limited to) spherical, ovoid, fibrous, ribbon-like and in the form of a mesh. The tensile strength of the block polymer may vary between, but not be limited to, about 1.5 MPa and 40 MPa, or between 3.4 to 34 MPa, or between 2MPa and 3.45 MPa or between 28 MPa and 34 MPa. The thermoplastic block polymers may be present in the cement slurry at a concentration between about 5 lbm/bbl and 50 lbm/bbl. Or the block polymer may be present in the cement slurry at a concentration 8 lbm/bbl and 15 lbm/bbl. The particle size of the block polymer particles may be between about 1 μm and 850 μm , or between 300 μm and 800 μm .

[0029] The thermoplastic block-particles may be further associated with one or more compounds from the list comprising an emulsion of polymer comprising a betaine group, poly-2, 2, 1-bicyclo heptene (polynorbornene), alkylstyrene, crosslinked substituted vinyl acrylate copolymers, diatomaceous earth, natural rubber, vulcanized rubber, polyisoprene rubber, vinyl acetate rubber, polychloroprene rubber, acrylonitrile butadiene rubber, hydrogenated acrylonitrile butadiene rubber, ethylene propylene diene monomer, ethylene propylene monomer rubber, styrene-butadiene rubber, styrene/propylene/diene monomer, brominated poly(isobutylene-co-4-methylstyrene), butyl rubber, chlorosulfonated polyethylenes, polyacrylate rubber, polyurethane, silicone rubber, brominated butyl rubber, chlorinated butyl rubber, chlorinated polyethylene, epichlorohydrin ethylene oxide copolymer, ethylene acrylate rubber, ethylene propylene diene terpolymer rubber, sulfonated polyethylene, fluoro silicone rubbers, fluoroelastomers, substituted styrene acrylate copolymers and bivalent cationic compounds.

[0030] In addition to the aforementioned particles, the cement slurries may also comprise customary additives such as retarders, accelerators, extenders, fluid-loss-control additives, lost-circulation additives, gas-migration additives, gas-generating additives, expansion additives and antifoam agents. Furthermore, the cement slurries may contain additives that enhance the flexibility and/or toughness of the set cement. Such additives include, but are not limited to, flexible particles having a Young's

modulus below about 5000 MPa and a Poisson's ratio above about 0.3. Such particles may have a Young's modulus below about 2000 MPa. Examples include, but are not limited to, nonswellable polypropylene, nonswellable polyethylene, acrylonitrile butadiene, styrene butadiene and polyamide. Such additives may also include fibers selected from the list comprising polyamide, polyethylene and polyvinyl alcohol. Metallic microribbons may also be included.

[0031] In an embodiment, the oil-absorbent particles may be elongated, fibrous, cylindrical or asymmetrical. Such particles with an aspect ratio higher than about 1 may interact and form a network inside the cement slurry. The elongated shape may also improve the absorbing ability of the particles. The higher aspect ratio increases the probability that the particles will contact each other throughout the cement slurry, allowing more efficient oil absorption and lower absorbent-particle concentrations to achieve a given result.

[0032] The particle aspect ratio may be between 1.1 and 2000, or 10 and 1500, or 15 and 1000 before swelling, and between 2.2 and 3500, or 4 and 1000, or 6 and 350 after swelling. Furthermore, the temperature at which the disclosed fluids operate may be between 80°F and 400°F, or between 100°F and 375°F.

[0033] For all embodiments, the concentration of oil-absorbent particles may vary in the cement sheath. This may be accomplished by varying the rate at which the oil-absorbent particles are added to the cement slurry during mixing and pumping. Certain portions of the cement sheath may not contain oil-absorbent particles. As long as there are regions along the cement sheath providing zonal isolation, the well as a whole may have a hydraulic seal. For example, sections containing the oil-absorbent particles may be located above and below producing zones. This approach may be more economical than scenarios where the oil-absorbent particles are present throughout the cement sheath.

[0034] For all embodiments, the disclosed methods may also be performed during perforating operations. When perforating is performed in the presence of a completion fluid containing the nanosized silica particles, the completion fluid may achieve the same objective as the previously described pad fluid for hydraulic fracturing that contains the nanosized silica particles.

[0035] The completion fluids may comprise any fluid of proper density and flow characteristics. The density may be chosen such that the completion fluid, plus other fluids in the wellbore, exerts sufficient hydrostatic pressure to maintain well control. The flow characteristics may be chosen such that the completion fluid enters perforation tunnels to an extent sufficient to allow flushing out debris from explosive charges or loose formation material. The completion fluids may comprise aqueous brines containing chloride, bromate or formate salts.

Examples

Example 1 — Drilling Fluid Rheological Properties

[0036] Two 600-mL cement slurries were prepared in a Waring blender according to a mixing procedure published by the American Petroleum Institute (RP-10B). The density of both slurries was 15 lbm/gal (1800 kg/m³). Both slurries were prepared with Texas Lehigh Class H cement.

[0037] A comparative slurry composition is given in Table 1.

Additive	Concentration
AMPS/Acrylamide copolymer	0.3% BWOC
Sodium Polynaphthalene Sulfonate	0.1% BWOC
Polysaccharide Biopolymer	0.3% BWOC
Polypropylene Glycol	0.050 gal/sk
Water	6.02 gal/sk

Table 1. Comparative cement slurry composition. BWOC = by weight of cement; sk = 94-lb sack of portland cement. AMPS = 2-acrylamido-2-methylpropane sulfonic acid.

[0038] A cement composition according to the disclosure is given in Table 2. The cement slurry contained absorbing particles composed of ground rubber particles. The particle size of the rubber varied between 100 μm and 800 μm.

Additive	Concentration
Ground Rubber	31.0% BVOB
Barium Sulfate	8.4% BVOB
Crystalline Silica	15% BVOB
AMPS/Acrylamide copolymer	0.3% BWOC
Sodium Polynaphthalene Sulfonate	0.4% BWOC
Polysaccharide Biopolymer	0.8% BWOC
sodium glucoheptonate/crystalline silica/hematite	0.5% BWOC
Polypropylene Glycol	0.1 gal/sk
SIS Copolymer	1% BWOB
Water	4.27 gal/sk

Table 2. Cement slurry composition according to the disclosure. BWOB = by weight of blend; BVOB = by volume of blend; SIS = styrene-isoprene-styrene

[0039] Both slurries were conditioned for 35 min at 168°F in an atmospheric consistometer. A representative 13 lbm/gal (1620 kg/m³) inverse emulsion drilling fluid was chosen that contained diesel as the continuous phase (MegaDril™, available from Schlumberger). 15 mL of the conditioned slurry were placed at the bottom of a glass vial. 5 mL of the drilling fluid was carefully added to the top of the conditioned slurry. The glass vials were placed in a Turbiscan AGS instrument (available from Formulaction Inc., Worthington, OH) that was preheated to 140°F (60°C) and allowed to cure for 8 days. During this time the slurry developed compressive strength, and the drilling fluid in contact with the slurry containing the absorbent particles increased its yield strength compared to that in contact with the comparative cement system. To quantify this rheological change, the drilling fluids were extracted from the vials. The yield strength was analyzed on a TA-DHR3

rheometer (available from TA Instruments, New Castle, DE) in a parallel plate configuration. An oscillatory amplitude sweep was conducted at 68°F (20°C) with an angular frequency of 10 rad/s and a logarithmic strain percent sweep from 0.01% to 100%. The drilling fluid that was exposed to the absorbent slurry exhibited a yield strength in some cases approximately 65 times higher than that of the drilling fluid exposed to the comparative slurry under the same conditions (Fig. 4)

Example 2 — Channel Flow Reduction

[0040] Applicant developed a laboratory method to investigate the ability of absorbent containing cement slurry to reduce fluid flow in a drilling-fluid filled channel. Two 600-mL cement slurries were prepared in a Waring blender. The cement was Class H portland cement. The density of both slurries was 14.5 lbm/gal (1740 kg/m³). Both slurries were extended with fly ash.

[0041] A comparative slurry composition is given in Table 3.

Additive	Concentration
Fly ash	40 lb/sk
AMPS/Acrylamide copolymer	0.3% BWOC
Sodium Polynaphthalene Sulfonate	0.3% BWOC
Polysaccharide Biopolymer	0.3% BWOC
Silica Fume	8.0% BWOB
Sodium Lignosulfonate	0.3% BWOB
Polypropylene Glycol	0.050 gal/sk
Water	5.91 gal/sk

Table 3. Comparative Cement Slurry Composition.

A slurry composition according to the disclosure is given in Table 4.

Additive	Concentration
Fly ash	40 lb/sk
AMPS/Acrylamide copolymer	0.3% BWOC
Sodium Polynaphthalene Sulfonate	0.1% BWOC
Polysaccharide Biopolymer	0.3% BWOC
Polypropylene Glycol	0.050 gal/sk
Sodium Lignosulfonate	0.3% BWOB
Silica Fume	8.0% BWOB
Ground Rubber	5.0% BWOC
SIS Copolymer	1% BWOB
Water	5.87 gal/sk

Table 4. Cement slurry composition according to the disclosure.

[0042] A 3-in. long by 1-in. wide steel pipe was capped on one end and filled with slurry and then capped on the other end. Small vent holes were added to the caps to equalize the pressure during high pressure curing. The pipes containing slurry were loaded into a curing chamber and were exposed to 170°F (77°F) and 3000 psi (21 MPa). After the slurry had set, a hole was drilled in the cement leaving a channel of about 1/8-in. (0.3-cm) diameter. The bottom of the hole was plugged, the channel was filled with 13-lbm/gal (1620-kg/m³) MegaDril drilling fluid, and was allowed to set for 6 days at atmospheric conditions. The permeability of the resulting mud channel was probed by the flow of water through the channel. The flow rate was set at 1 mL/min and resulting pressure were measured using a Teledyne ISCO D-series syringe pump.

[0043] The results, presented in Fig. 5, show that the cement prepared according to the present disclosure was 5 times more pressure resistant compared to the comparative cement. The absorbent additive concentration could be adjusted to increase pressure even higher, up 14 psi, if needed. In order to scale the laboratory results to a real application, it could be calculated that 5 psi in a 3-in. tube corresponds to 3000 psi at a 50-ft distance.

Example 3 — Oil Viscosification

[0044] The ability of an absorbent particle to viscosify oil was investigated. The absorbent particles were made of polystyrene-block-poly(ethylene-ran-butylene)-block-polystyrene and polystyrene-block-polybutadiene-block-polystyrene polymers (manufactured by Sigma-Aldrich Chemie GmbH, Steinheim, Germany). The oil was LVT200 oil, a hydrotreated light distillate manufactured by Deep South Chemical, Inc., Broussard, LA.

[0045] The following samples were investigated: 0.8 wt% and 5.8 wt% solutions of polystyrene-block-polybutadiene-block-polystyrene polymer (PS-PB) in LVT200 oil and 1 wt%, 2.8 wt%, 5.9 wt% solutions of polystyrene-block-poly(ethylene-ran-butylene)-block-polystyrene polymer (PS-PEPB-PS) in LVT200. The viscosities of samples were measured by MCR300 rheometer from Anton Paar in parallel plate CC17 geometry (Fig. 6). The results show that the oil viscosities increase with polymer concentration.

Example 4 — Elongated Absorbent Particles

[0046] Two 5-in steel pipes with 1-in diameter were capped on one end. One pipe was filled by a 14.5-lbm/gal (1740-kg/m³) comparative cement slurry containing 0.8% BWOC polyethylene fiber (Sytholix, available from EP Minerals, Reno, NV) The fiber length was 30–50 µm. The slurry also contained 4.2% BWOC ground rubber. The reference slurry was identical to the comparative slurry, except that the ground rubber concentration was 5.0% BWOC and no fibers were present.

[0047] 3-mm channels were created by inserting wooden dowels into the cement slurries and removing the dowels after 24 hours when the cement slurries had developed sufficient gel strength to maintain the channel structure. Then the

channels were filled with 13.0 lbm/gal (1560 kg/m³) MegaDril mud (available from MI-Swaco).

[0048] After 72 hours of interaction time between the set cement and the mud channel, permeabilities of the channels were measured using the same apparatus described in Example 2. The pressure necessary to initiate flow through the test channel was 6.4 psi/in, 1.8 times higher than that observed with the comparative slurry.

Example 5 — Mud Channel Strengthening

[0049] 10 g of a 13 lbm/gal (1560 kg/m³) MegaDril drilling fluid were mixed with 5 g of an aqueous nanosilica dispersion. A control system was prepared that contained 10 g of a 13 lbm/gal (1560 kg/m³) MegaDril drilling fluid, mixed with 5 g of water. After mixing, the two systems were left undisturbed at ambient temperature and pressure for 3 days.

[0050] Solidification and strength development of the systems were measured by subjecting them to parallel plate oscillatory rheometry. A frequency sweep was performed with 0.15% strain and an angular frequency between 0.1 and 100 rad/s at 68°F. The results are presented in Fig. 7. Drilling fluid exposed to the nanosilica had a higher storage modulus, indicating it had become more solid-like than the control system.

[0051] The preceding description has been presented with reference to present embodiments. Persons skilled in the art and technology to which this disclosure pertains will appreciate that alterations and changes in the described structures and methods of operation can be practiced without meaningfully departing from the principle, and scope of this present disclosure. Accordingly, the foregoing description should not be read as pertaining only to the precise structures described and shown in the accompanying drawings, but rather should be read as consistent with and as support for the following claims, which are to have their fullest and fairest scope.

Claims

1. A method for stimulating a subterranean well, comprising:
preparing a cement slurry comprising water, a hydraulic cement, and particles of an oil-absorbent material, wherein the particles are present in an amount sufficient to interact with a non-aqueous component of a drilling fluid to alter a property of the drilling fluid within the subterranean well, wherein the drilling fluid contains calcium hydroxide;
placing the cement slurry in the subterranean well;
allowing the oil-absorbent material particles to contact the non-aqueous drilling fluid component to alter the property of the non-aqueous component; and
performing a hydraulic fracturing operation, wherein a pad fluid comprises nanosize silica particles.
2. The method of claim 1, wherein the oil-absorbent material comprises rubber, ground rubber, polypropylene, polyethylene, acrylonitrile butadiene, styrene butadiene, 2,1 bicycloheptene, alkylstyrene, or crosslinked substituted vinyl acetate copolymer, or combinations thereof.
3. The method of claim 1, wherein the oil-absorbent material particles have a particle size between about 1 μm and about 850 μm .
4. The method of claim 1, wherein the property of the non-aqueous component of the drilling fluid is flowability, and wherein the oil-absorbent material decreases the flowability of the non-aqueous component.
5. The method of claim 1, wherein the oil-absorbent material particles are elongated, having an aspect ratio between 15 and 1000 before swelling, and between 5 and 350 after swelling.
6. The method of claim 5, wherein the elongated particles interact in the subterranean well to form an interconnected network.

7. The method of claim 1, wherein the oil-absorbent material particles are present at a concentration between about 1% by weight of cement (BWOC) and about 40% BWOC.
8. The method of claim 1, wherein the cement slurry has a density between about 10 lbm/gal and about 24 lbm/gal.
9. The method of claim 1, wherein the non-aqueous component comprises diesel, mineral oil, olefins, esters, synthetic paraffins, or refined paraffins, or combinations thereof.
10. The method of claim 1, wherein a concentration of the oil-absorbent material particles varies in the cement slurry, between about 0% BWOC and 40% BWOC, thereby creating a cement sheath in the subterranean well with a variable oil-absorbent material concentration.
11. The method of claim 1, wherein the nanosize particles are present in the pad fluid at a concentration between 5.0 lbm/bbl and 50 lbm/bbl.
12. The method of claim 1, wherein the nanosize particles have a particle size between 1 nm and 100 nm.
13. A method for establishing zonal isolation in a subterranean well, comprising:
 - drilling the well with a drilling fluid that contains calcium hydroxide;
 - preparing a cement slurry that comprises water and a hydraulic cement;
 - placing the cement slurry in the subterranean well wherein residual drilling fluid is present along casing and formation surfaces;
 - performing a hydraulic fracturing operation, wherein a pad fluid comprises nanosize silica particles; and

causing the nanosize silica particles to contact the residual drilling fluid, thereby altering the property of the drilling fluid to create a hydraulic seal in the subterranean well.

14. The method of claim 13, wherein the nanosize silica particles react with the calcium hydroxide, forming a calcium silicate hydrate that strengthens the residual drilling fluid.

15. The method of claim 13, wherein the cement slurry has a density between about 10 lbm/gal and about 24 lbm/gal.

16. The method of claim 13, wherein the non-aqueous component comprises diesel, mineral oil, olefins, esters, synthetic paraffins, or refined paraffins, or combinations thereof.

17. The method of claim 13, wherein the nanosize particles are present in the pad fluid at a concentration between 5.0 lbm/bbl and 50 lbm/bbl.

18. The method of claim 13, wherein the nanosize particles have a particle size between 1 nm and 100 nm.

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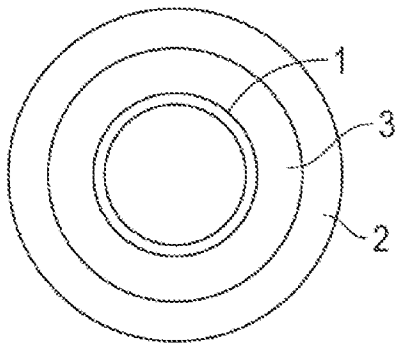


FIG. 1A

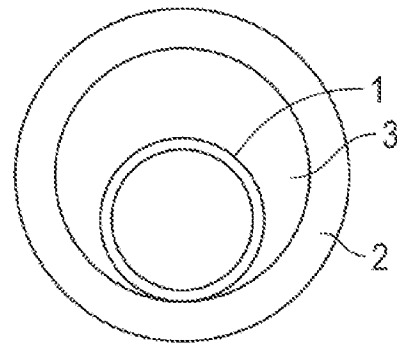


FIG. 1B

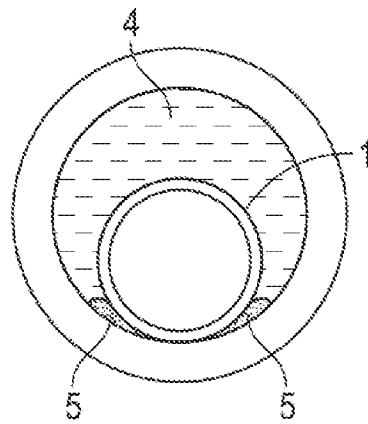


FIG. 2

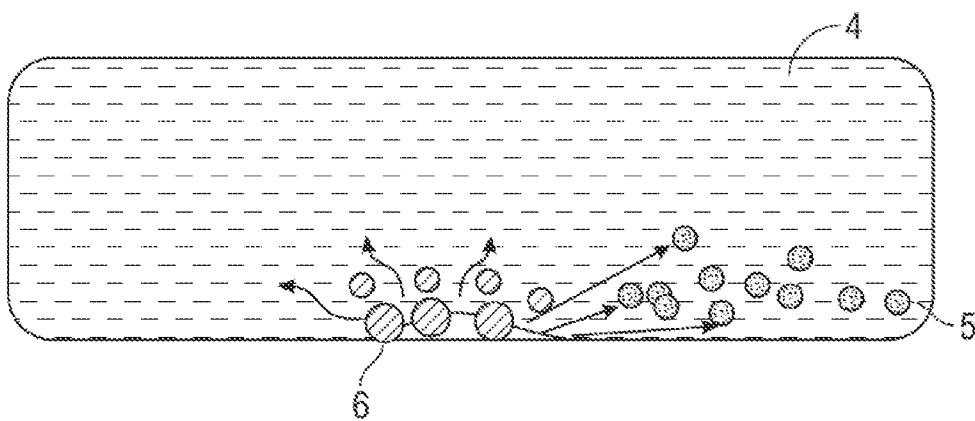


FIG. 3

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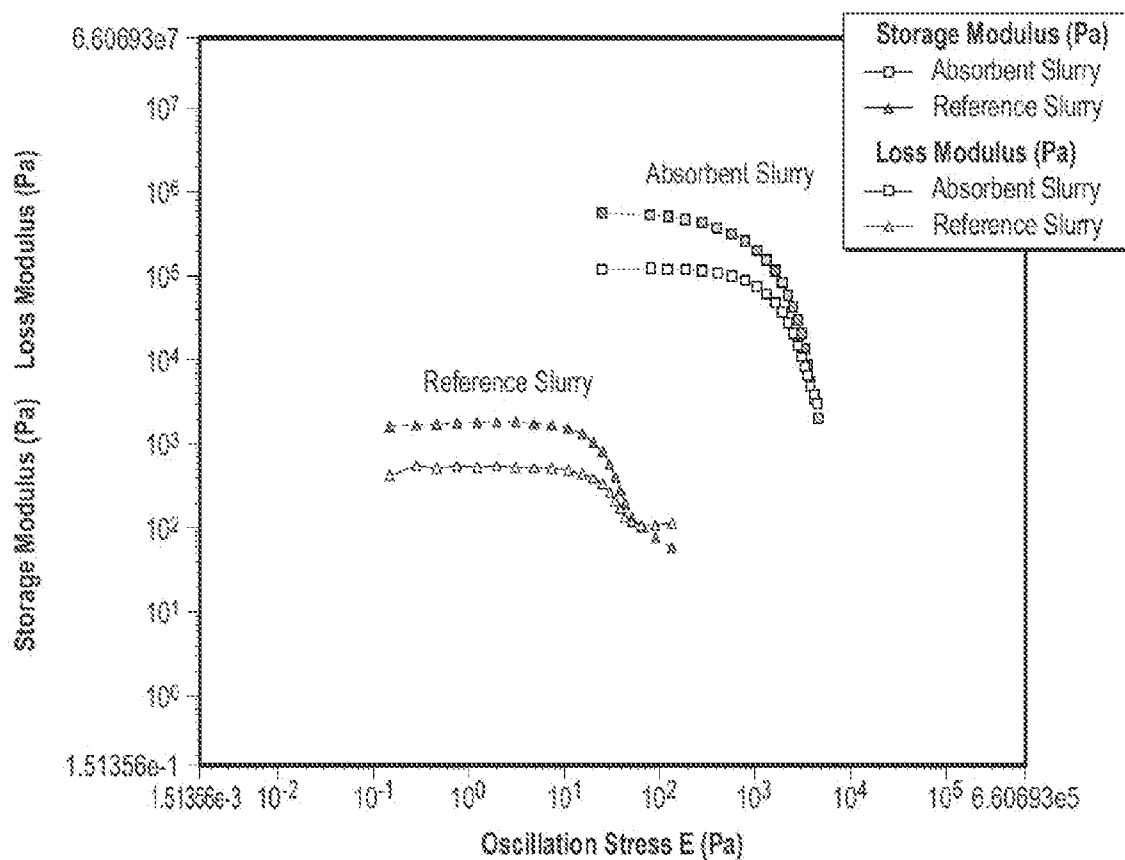


FIG. 4

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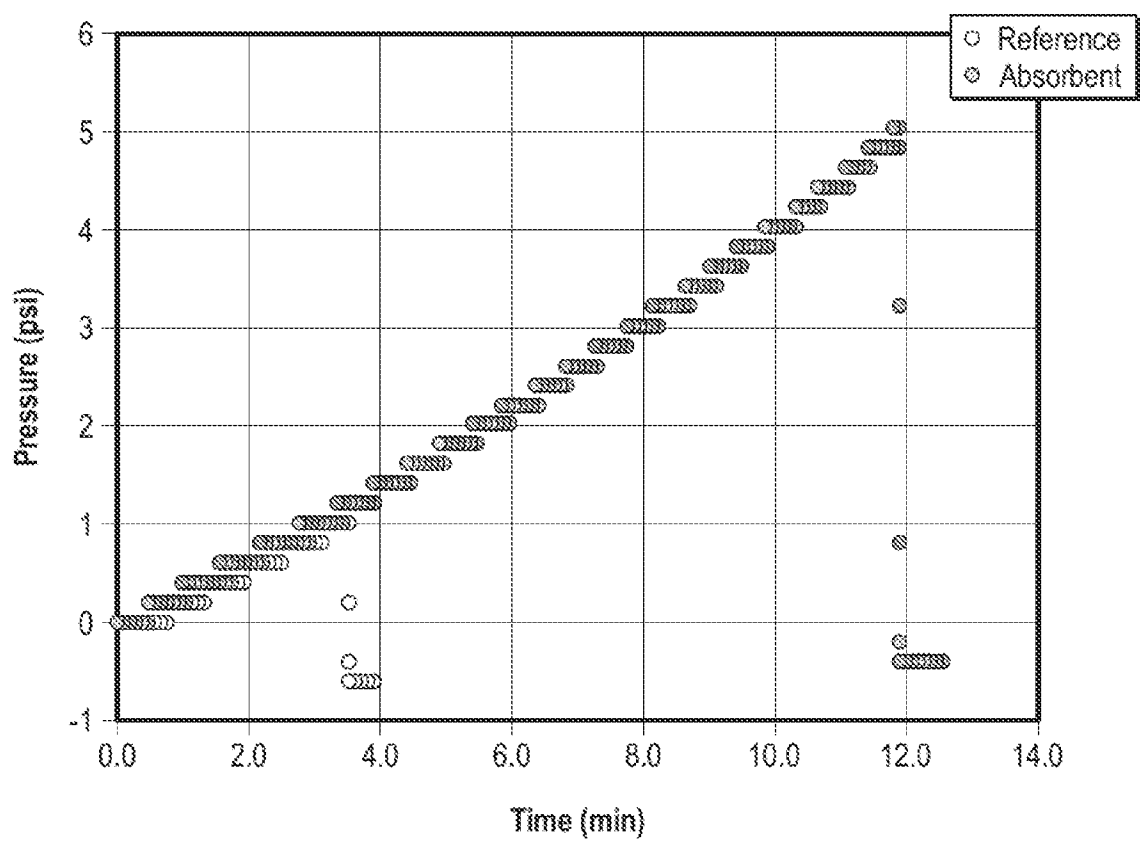


FIG. 5

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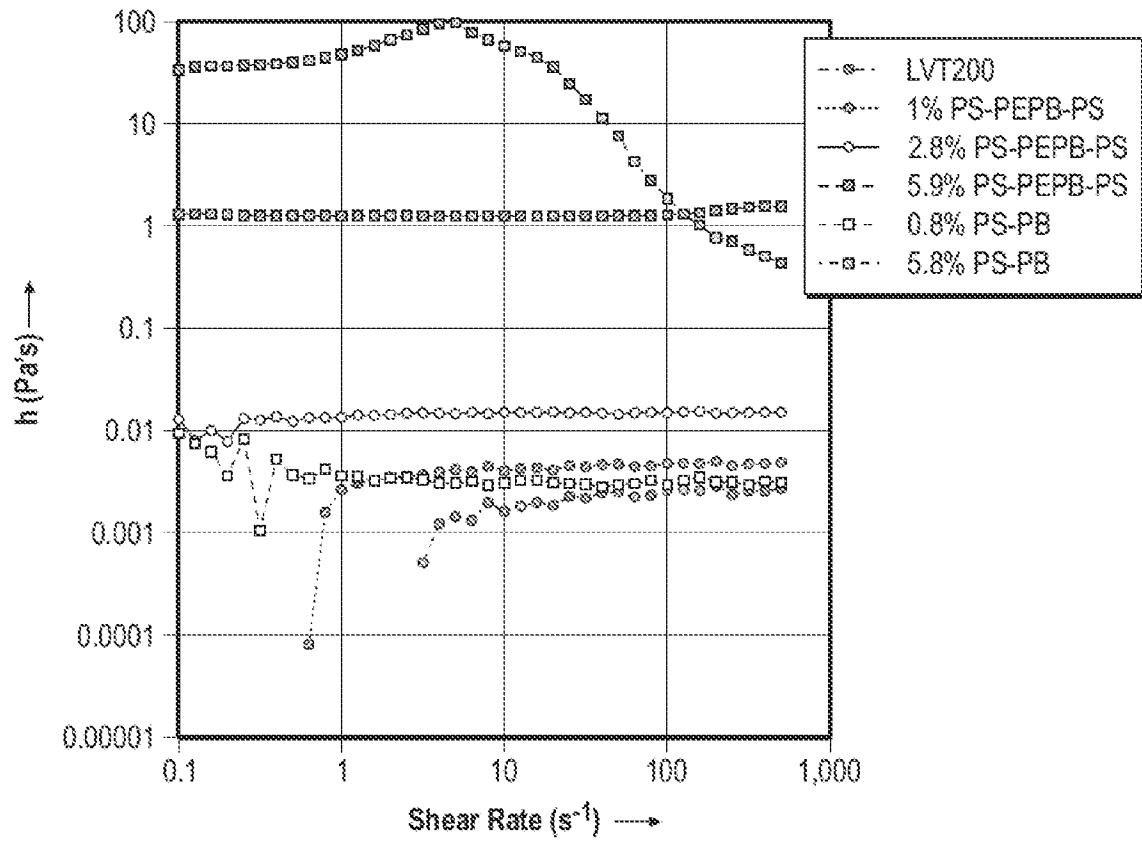


FIG. 6

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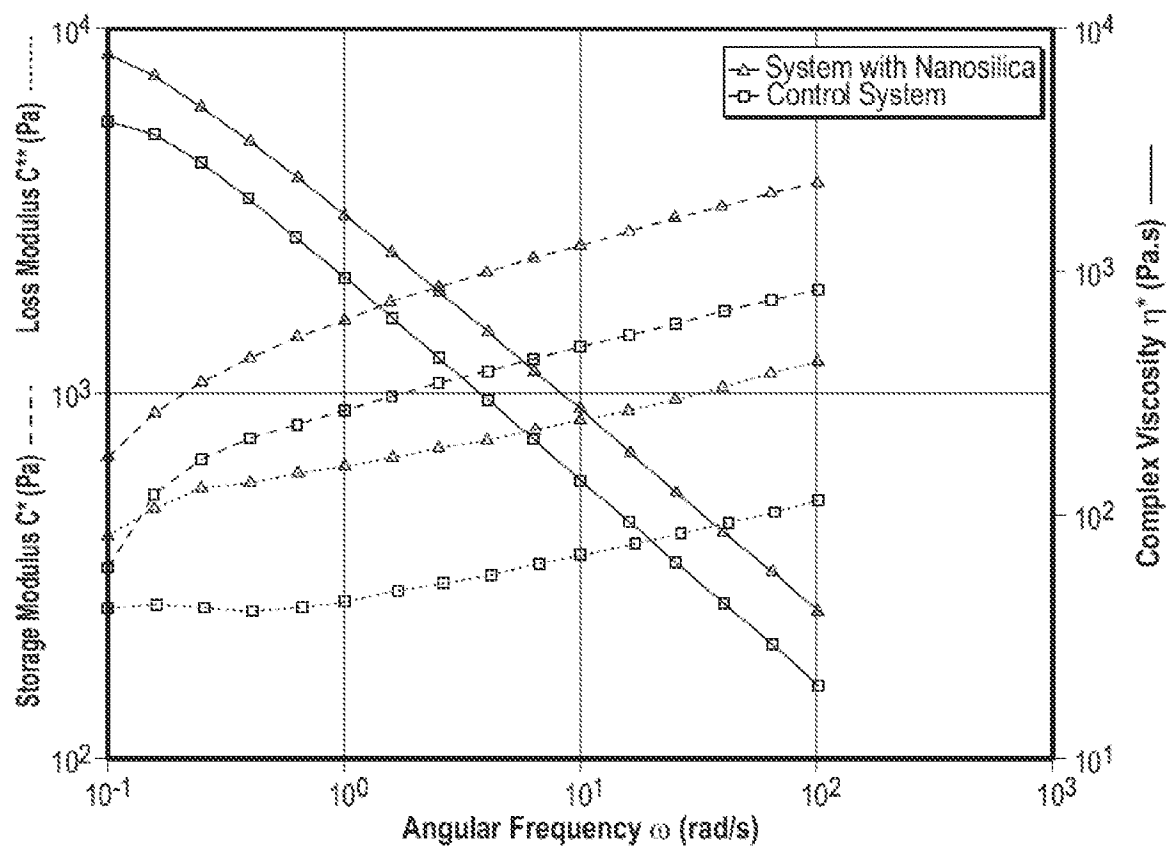


FIG. 7

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2020/039812**A. CLASSIFICATION OF SUBJECT MATTER****E21B 43/26(2006.01)i, E21B 43/267(2006.01)i, C09K 8/84(2006.01)i, C09K 8/92(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; C04B 18/14; C04B 18/16; C09K 7/02; C09K 8/00; C09K 8/508; C09K 8/58; E21B 33/13; E21B 33/14; E21B 43/22; E21B 43/267; C09K 8/84; C09K 8/92

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: cement, oil-absorbent material, drilling fluid, calcium hydroxide, fracturing fluid, silica

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2016-0264842 A1 (HALLIBURTON ENERGY SERVICES, INC.) 15 September 2016 paragraphs [0001]–[0010], [0039]	1–18
Y	WO 2015-069293 A1 (HALLIBURTON ENERGY SERVICES, INC.) 14 May 2015 paragraphs [0065]–[0068] and claims 1, 46, 56, 60	1–18
A	EP 2004569 B1 (HALLIBURTON ENERGY SERVICES, INC.) 01 May 2013 claims 1, 6, 15	1–18
A	EP 0605113 B1 (HALLIBURTON COMPANY) 04 June 1997 claims 1–2	1–18
A	WO 2005-123871 A2 (SCHLUMBERGER CANADA LIMITED et al.) 29 December 2005 paragraphs [0018]–[0024] and claim 1	1–18



Further documents are listed in the continuation of Box C.



See patent family annex.

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"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

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Date of mailing of the international search report

22 October 2020 (22.10.2020)

Name and mailing address of the ISA/KR

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189 Cheongsa-ro, Seo-gu, Daejeon, 35208, Republic of Korea



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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2020/039812

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26/09/2006

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