



(51) International Patent Classification:

C09K 8/42 (2006.01) C04B 16/06 (2006.01)

C04B 28/02 (2006.01) C04B 20/00 (2006.01)

C04B 24/26 (2006.01) C04B 103/00 (2006.01)

(21) International Application Number:

PCT/US2020/039811

(22) International Filing Date:

26 June 2020 (26.06.2020)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

62/868,024 28 June 2019 (28.06.2019) US

(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: **GAO, Yan**; 5950 North Course Drive, Houston, Texas 77072 (US). **PERRONI, Dominic Vincent**; 110 Schlumberger Drive, MD-3, Sugar Land, Texas 77478 (US). **MEDVEDEV, Anatoly Vladimirovich**; 110 Schlumberger Drive, MD-3, Sugar Land, Texas 77478 (US). **YAKOVLEV, Andrey Vladimirovich**; 110 Schlumberger Drive, MD-3, Sugar Land, Texas 77478 (US).

(74) Agent: **HEWITT, Cathy** 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, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, 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, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ,

(54) Title: CEMENT COMPOSITIONS AND METHODS

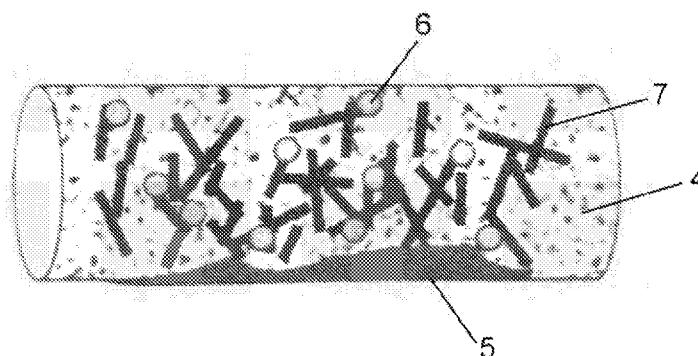


FIG. 3

(57) Abstract: Cement slurries are prepared that comprise water, a hydraulic cement, particles of an oil-absorbent particles and non-swelling hydrophobic particles. The particles are present in an amount sufficient to alter a property of a non-aqueous drilling fluid. The cement slurry is placed in a subterranean well, whereupon the slurry contacts residual drilling fluid on casing and formation surfaces. The oil-absorbent particles and hydrophobic particles in the cement slurry may reduce the mobility of the drilling fluid, thereby improving zonal isolation.



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, 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).

Published:

- *with international search report (Art. 21(3))*
- *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))*

CEMENT COMPOSITIONS AND METHODS

Cross-Reference to Related Applications

[0001] This application claims priority to and the benefit of U.S. Provisional Patent Application Serial No. 62/868024, entitled "Cement Compositions and 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 cement systems. In particular, the disclosure relates to cement systems that contact drilling fluids within a subterranean well.

[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] 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 mud and the preflushes (if any) should be fully removed from the annulus, and the annular space must be completely filled with cement slurry. Once in place, the cement must 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.

[0005] 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 at applied pressure gradient. 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.

[0006] The present disclosure provides well cementing systems that may provide additional zonal isolation by facilitating the removal or dispersion or residual non-aqueous drilling fluids within the wellbore. Such residual non-aqueous drilling fluids may result from drilling the wellbore with non-aqueous drilling fluid prior to cementing. Further, the cement compositions disclosed herein may interact with residual drilling fluids and alter the properties of such drilling fluids. The present disclosure is particularly directed to drilling fluids, such as non-aqueous drilling fluids which range from diesel- or mineral oil-based fluids to synthetic-based systems. Synthetic-based systems may contain synthetic hydrocarbons, ethers, esters or acetals. The synthetic hydrocarbons may include linear paraffins, linear- α -olefins, poly- α -olefins and internal olefins. The synthetic-based systems may be emulsions in which the hydrocarbon is the external phase.

Summary

[0007] In an aspect, embodiments relate to methods for cementing a subterranean well. A cement slurry is prepared comprising water, a hydraulic cement, particles of an oil-absorbing material, and non-swellaable hydrophobic fibers, wherein 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 cement slurry is placed in the subterranean well, causing the oil-absorbent particles and hydrophobic fibers to contact the non-aqueous drilling fluid component, thereby altering the property of the non-aqueous component.

[0008] In a further aspect, embodiments relate to methods for establishing zonal isolation in a subterranean well. A cement slurry is prepared that comprises water, a hydraulic cement, particles of an oil-absorbent particles and non-swellaable hydrophobic fibers, wherein 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 cement slurry is placed in the subterranean well wherein residual drilling fluid is present along casing and formation surfaces, causing the oil-absorbent particles and non-swellaable hydrophobic fibers to contact the residual drilling fluid, thereby altering the property of the non-aqueous component and creating a hydraulic seal in the subterranean well.

Brief Description of the Drawings

[0009] 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.

[0010] Fig. 2 is a cross-sectional diagram showing a drilling fluid channel arising from poor casing centralization in a wellbore.

[0011] 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.

[0012] Fig. 4 compares the rheological properties of diesel-based emulsion drilling fluids after exposure to cement slurries. The yield point of a drilling fluid exposed to a cement slurry containing oil-absorbent particles was higher than that of a drilling fluid exposed to a comparative slurry that did not contain absorbent particles. The crossover points (stress) where the loss modulus was equal to the storage modulus were the fluids' yield points.

[0013] Fig. 5 shows pressure test results for a conventional cement slurry and a cement slurry containing oil-absorbing particles.

[0014] Fig. 6 shows the viscosities of oils containing various oil-absorbent polymers.

[0015] Fig. 7 shows the permeability effects of adding swellable particles and non-swellable hydrophobic fibers to a cement slurry.

Detailed Description

[0016] 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.

[0017] 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 drilling fluids may further contain clays, weighting agents or both.

[0018] 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).

[0019] 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.

[0020] In an embodiment, an oil-absorbing material and hydrophobic particles may be added to the cement slurry. The cement slurry may have a density between about 10 lbm/gal and 24 lbm/gal. 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. The non-swellable hydrophobic fibers may further strengthen the paste-like structure.

[0021] The oil-absorbent particles may comprise rubber, ground rubber, polypropylene, polyethylene, acrylonitrile butadiene, styrene butadiene, styrene isoprene, 2,1 bicycloheptene, alkylstyrene, or crosslinked substituted vinyl acetate copolymer, or combinations thereof. The oil-absorbent particles may be present in the cement slurry at a concentration between 1% and 40% by weight of cement.

[0022] 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** and fibers **7** 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).

[0023] 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.

[0024] 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 1 lbm/bbl and 50 lbm/bbl. Or the block polymer may be present in the cement slurry at a concentration 5 lbm/bbl and 15 lbm/bbl. The particle size of the block polymer particles may be between about 1 μm and 1000 μm , or between 300 μm and 800 μm .

[0025] 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 isoprene, 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.

[0026] The hydrophobic non-swellable fibers may comprise polyethylene, polyolefins, polystyrene, polyvinylchloride, polytetrafluoroethylene, polydimethylsiloxane, epoxies, polyacrylics or polyurethanes or combinations thereof. The fibers may interact and form a interconnected network in the subterranean well, further strengthening the drilling fluid channel. The hydrophobic non-swellable fibers may be present at a concentration between 0.1 wt% and 30 wt%, or between 5.0% and 10 wt%. The hydrophobic non-swellable fibers may have a length between 500 μm and 20 mm, or between 1 μm and 6 mm, and a diameter between 100 nm and 1 mm, or 500 nm and 0.5 mm.

[0027] In addition to the aforementioned particles and fibers, 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, polypropylene, 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.

[0028] 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.

[0029] The particle aspect ratio may be between 1.1 and 2000, or between 10 and 1500, or 15 and 1000 before swelling, or between 2.2 and 3500, or 4 and 1000, or 6 and 350 after swelling.

[0030] Furthermore, the temperature at which the disclosed fluids operate may be between 80°F and 400°F, or between 100°F and 375°F.

[0031] 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. Under these circumstances, the concentration of the oil-absorbent particles may vary between 0% and 40% by weight of cement. This approach may be more economical than scenarios where the oil-absorbent particles are present throughout the cement sheath.

Examples

Example 1 — Drilling Fluid Rheological Properties

[0032] 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.

[0033] 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.

[0034] 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

[0035] 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 Formulacion 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

[0036] 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.

[0037] 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.

[0038] 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.

[0039] 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

[0040] 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.

[0041] 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 Oil-Absorbent Particles with Hydrophobic Fibers

[0042] 5-in steel pipes with 1-in diameter were capped on one end. Two pipes were filled with the base slurry of Table 5 plus 5.0% ground rubber. Two other pipes contained the base slurry plus 4.0% BWOC ground rubber and 1.0% BWOC non-swellable polyethylene fiber (available from MI Swaco, Houston, TX) (Table 5). The fiber diameter was 30–50 μm .

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
Water	5.87 gal/sk

Table 5. Base-slurry composition.

[0043] 3-mm diameter, 7.5-in. length 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).

[0044] 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 approximately 32 psi, which is about 50% higher than the average value observed with the comparative slurries without fibers (Fig. 7).

[0045] 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 cementing a subterranean well, comprising:
placing a cement slurry comprising water, a hydraulic cement, oil-absorbent particles, and non-swellable hydrophobic fibers within the subterranean well, wherein the oil-absorbent particles are present in an amount sufficient to contact a non-aqueous component of a drilling fluid within the subterranean well and alter a property of the non-aqueous component of the drilling fluid.
2. The method of claim 1, wherein the oil-absorbent particles comprise rubber, ground rubber, acrylonitrile butadiene, styrene butadiene, styrene isoprene, 2,1 bicycloheptene, alkylstyrene, or crosslinked substituted vinyl acetate copolymer, or combinations thereof.
3. The method of claim 1, wherein the oil-absorbent particles have a particle size between about 1 μm and about 1000 μm .
4. The method of claim 1, wherein the property of the drilling fluid is flowability, and wherein the oil-absorbent particles decrease the flowability of the drilling fluid.
5. The method of claim 1, wherein the oil-absorbent 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 particles are present at a concentration between about 1% (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 particles varies in the cement slurry, between about 1% BWOC and 40% BWOC, thereby creating a cement sheath in the subterranean well with a variable oil-absorbent particles concentration.
11. The method of claim 1, wherein the non-swellable hydrophobic fibers comprise polyethylene, polyolefins, polystyrene, polyvinylchloride, polytetrafluorethylene, polydimethylsiloxane, epoxies, polyacrylics or polyurethanes or combinations thereof.
12. The method of claim 11, wherein the non-swellable hydrophobic fibers interact in the subterranean well to form an interconnected network.
13. The method of claim 1, wherein the non-swellable hydrophobic fibers are present at a concentration between 0.1 wt% and 30 wt%.
14. The method of claim 1, wherein the non-swellable hydrophobic fibers have a length between 500 μm and 20 mm, and a diameter between 100 nm and 1 mm.
15. A method, comprising:
placing casing within a subterranean well;
providing a cement slurry comprising water, a hydraulic cement, oil-absorbent particles, and non-swellable hydrophobic fibers within the subterranean well,
wherein the oil-absorbent particles are present in an amount sufficient to contact a non-aqueous component of residual drilling fluid on the casing and formation surfaces of the subterranean well to alter a property of the non-aqueous component of the residual drilling fluid.

16. The method of claim 15, wherein the oil-absorbent particles comprise rubber, ground rubber, acrylonitrile butadiene, styrene butadiene, styrene isoprene, 2,1 bicycloheptene, alkylstyrene, or crosslinked substituted vinyl acetate copolymer, or combinations thereof.
17. The method of claim 15, wherein the property of the non-aqueous component of the residual drilling fluid is flowability, and wherein the oil-absorbent particles decrease the flowability of the residual drilling fluid.
18. The method of claim 15, wherein the non-swellable hydrophobic fibers comprise polyethylene, polyolefins, polystyrene, polyvinylchloride, polytetrafluorethylene, polydimethylsiloxane, epoxies, polyacrylics or polyurethanes or combinations thereof.
19. The method of claim 15, wherein the non-swellable hydrophobic fibers are present at a concentration between 0.1 wt% and 30 wt%.

1 / 6

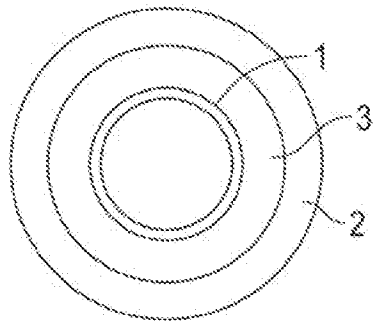


FIG. 1A

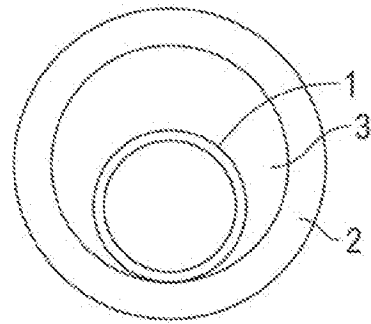


FIG. 1B

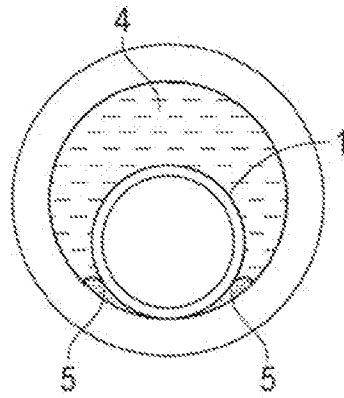


FIG. 2

2 / 6

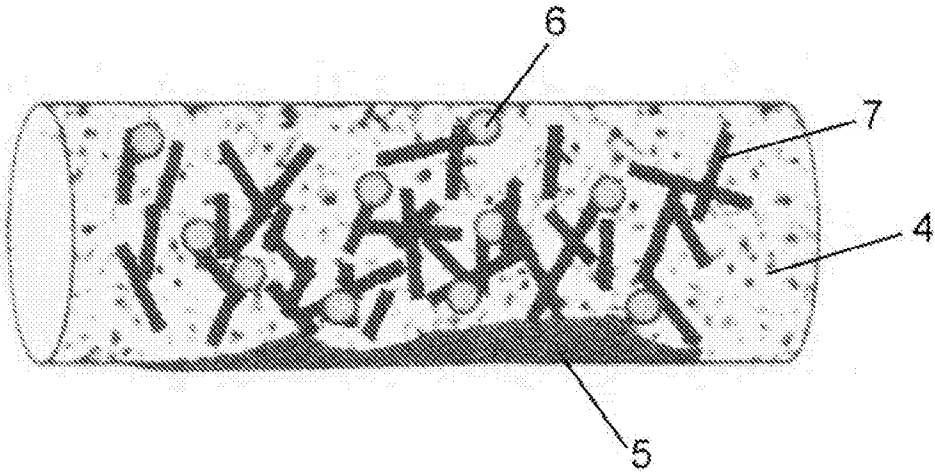


FIG. 3

3 / 6

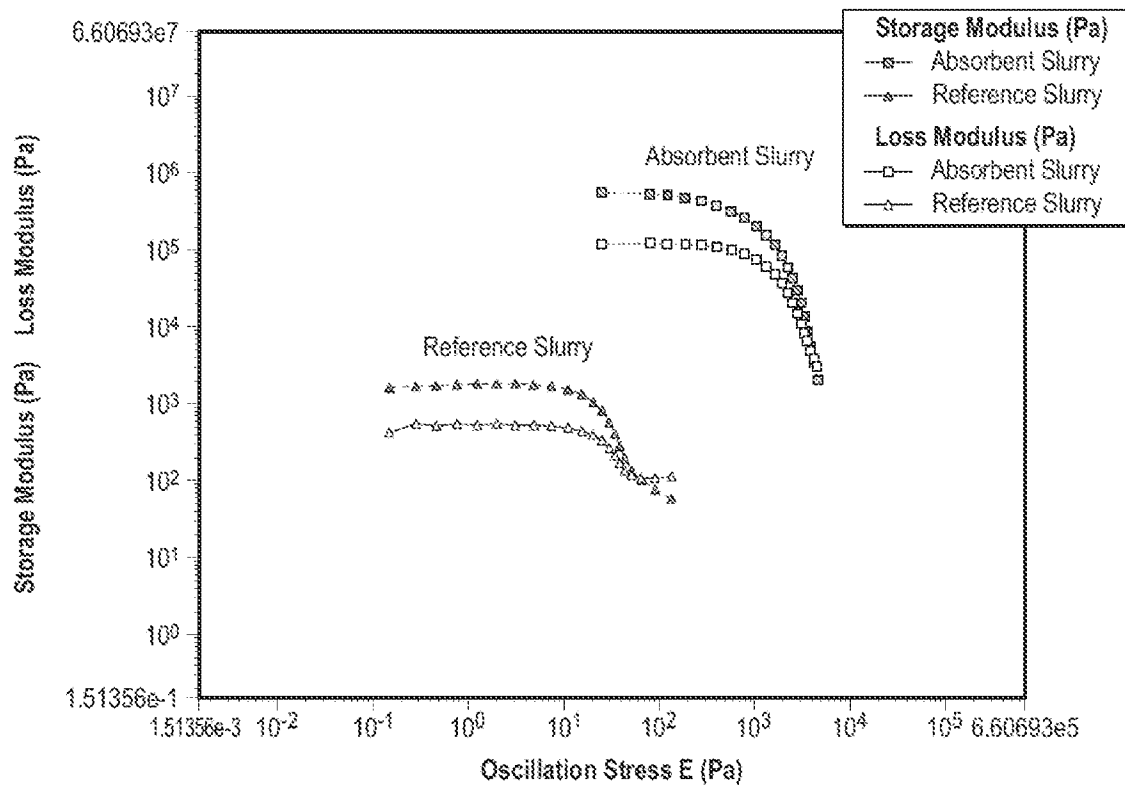


FIG. 4

4 / 6

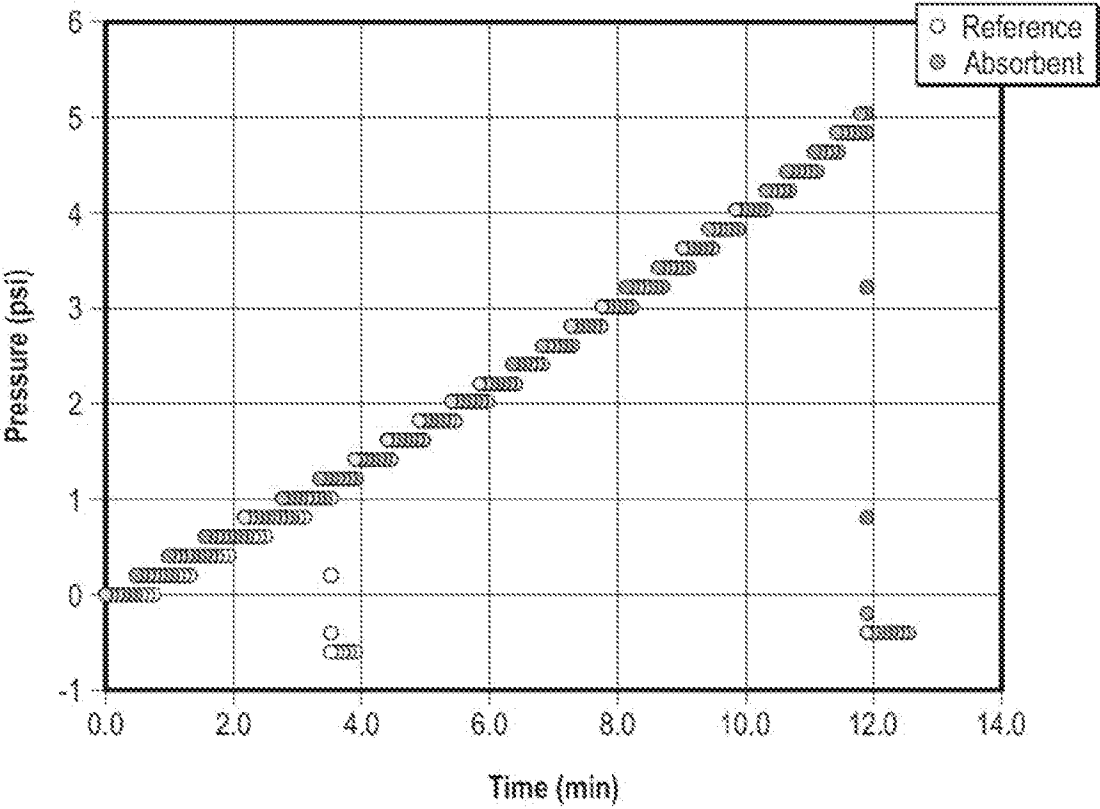


FIG. 5

5 / 6

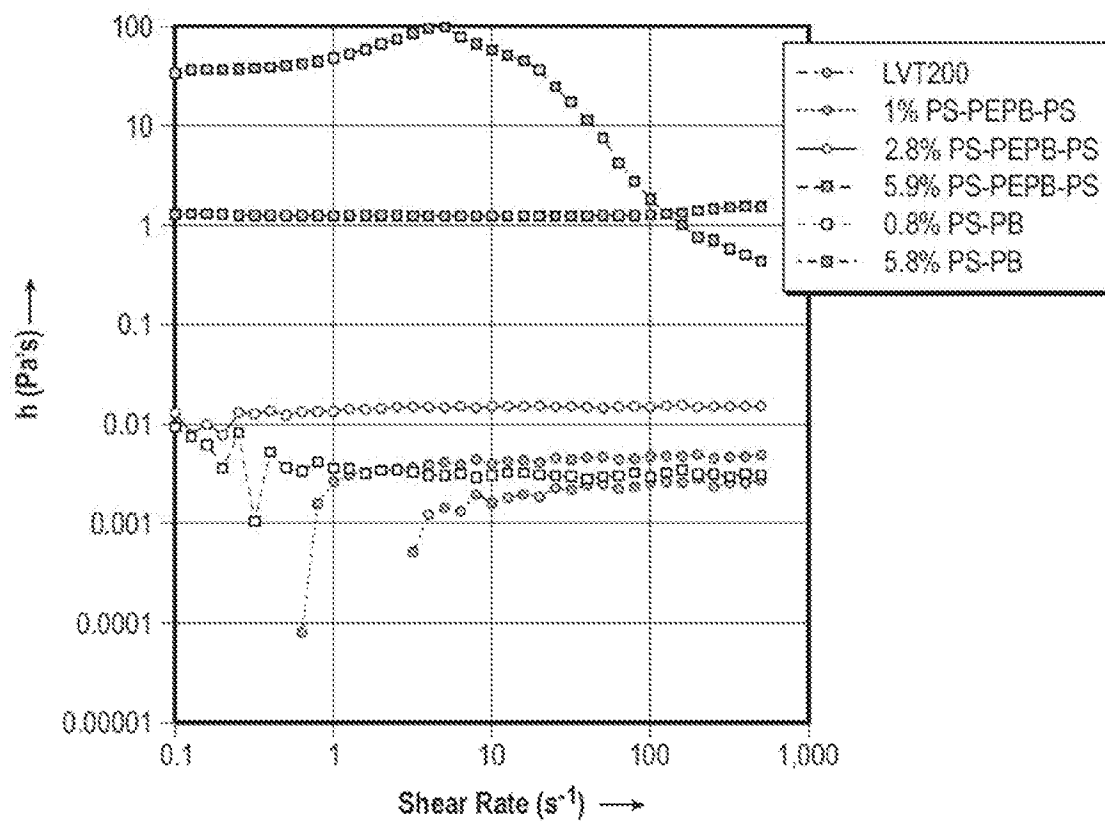


FIG. 6

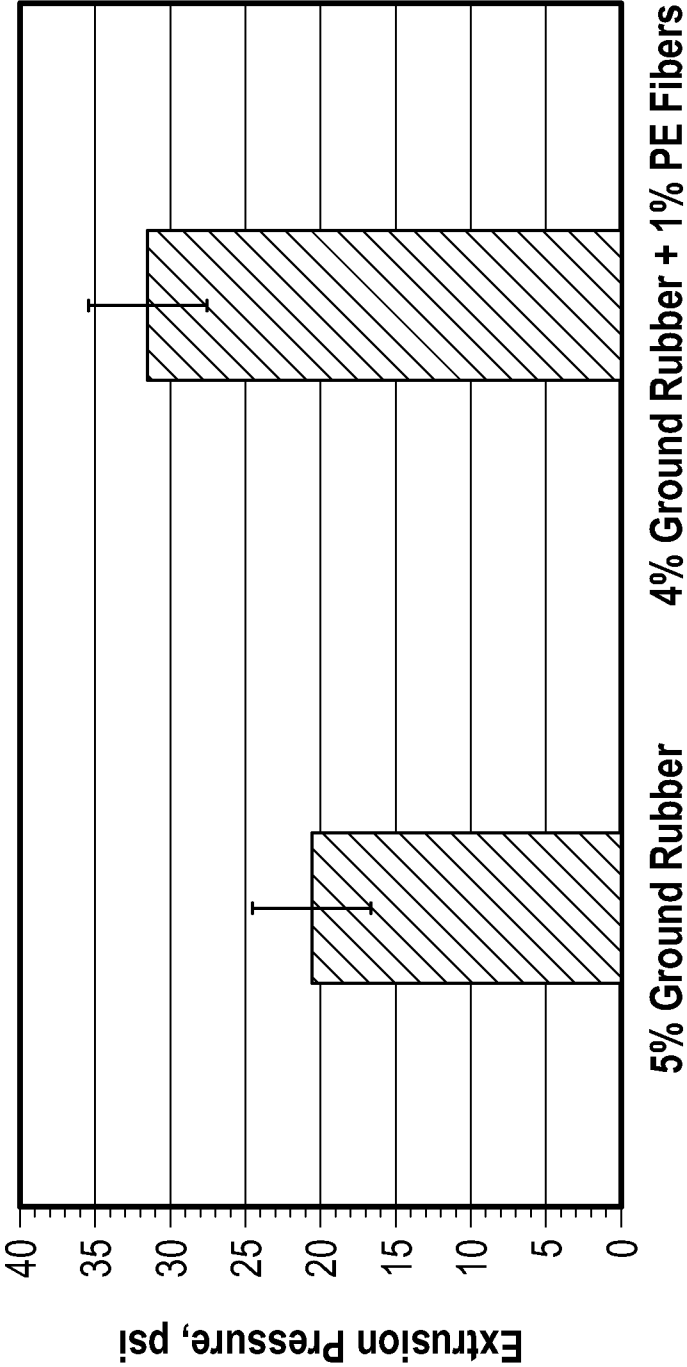


FIG. 7

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2020/039811**A. CLASSIFICATION OF SUBJECT MATTER****C09K 8/42(2006.01)i, C04B 28/02(2006.01)i, C04B 24/26(2006.01)i, C04B 16/06(2006.01)i, C04B 20/00(2006.01)i, C04B 103/00(2006.01)n**

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)

C09K 8/42; C04B 26/00; C09K 8/36; C09K 8/467; C09K 8/52; C09K 8/536; E21B 21/00; E21B 33/13; E21B 33/14; C04B 28/02; C04B 24/26; C04B 16/06; C04B 20/00; C04B 103/00

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 cement, oil-absorbent particles, non-swellable hydrophobic fibers, subterranean well, swell**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2017-023159 A1 (SCHLUMBERGER CANADA LIMITED et al.) 09 February 2017 claims 13-17; paragraphs [0021]-[0040]	1-19
A	US 2017-0267911 A1 (HALLIBURTON ENERGY SERVICES, INC.) 21 September 2017 claim 2	1-19
A	WO 2017-087263 A1 (SCHLUMBERGER TECHNOLOGY CORPORATION et al.) 26 May 2017 the whole document	1-19
A	US 2012-0325476 A1 (BRENNEIS, D. C. et al.) 27 December 2012 the whole document	1-19
A	US 2012-0312535 A1 (MICHAUX, M. et al.) 13 December 2012 the whole document	1-19



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

12 October 2020 (12.10.2020)

Date of mailing of the international search report

19 October 2020 (19.10.2020)

Name and mailing address of the ISA/KR

International Application Division

Korean Intellectual Property Office

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



Facsimile No. +82-42-481-8578

Authorized officer

HAN, Inho

Telephone No. +82-42-481-3362



INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2020/039811

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2017-023159 A1	09/02/2017	US 2018-0230358 A1	16/08/2018
US 2017-0267911 A1	21/09/2017	AU 2013-277767 A1	11/12/2014
		AU 2013-277767 B2	28/01/2016
		BR 112014032173 A2	27/06/2017
		CA 2876395 A1	27/12/2013
		CA 2876395 C	07/03/2017
		EA 030815 B1	31/10/2018
		EA 201590052 A1	31/03/2015
		EP 2864438 A1	29/04/2015
		EP 2864438 B1	21/06/2017
		MX 2014014452 A	06/07/2015
		US 2013-345098 A1	26/12/2013
		US 9701881 B2	11/07/2017
		WO 2013-191776 A1	27/12/2013
WO 2017-087263 A1	26/05/2017	US 10161222 B2	25/12/2018
		US 2016-0122616 A1	05/05/2016
		US 2016-0122620 A1	05/05/2016
		WO 2016-073257 A1	12/05/2016
US 2012-0325476 A1	27/12/2012	CN 101305070 A	12/11/2008
		CN 101305070 C	12/11/2008
		CN 103140562 A	05/06/2013
		CN 103370393 A	23/10/2013
		CN 103370393 B	23/11/2016
		CN 103459348 A	18/12/2013
		CN 104114513 A	22/10/2014
		CN 104812868 A	29/07/2015
		CN 104812868 B	07/05/2019
		CN 104995279 A	21/10/2015
		EP 1928975 A1	11/06/2008
		EP 1928975 B1	04/11/2015
		EP 2158288 A1	03/03/2010
		EP 2245106 A1	03/11/2010
		EP 2245106 B1	06/05/2015
		EP 2350226 A1	03/08/2011
		EP 2362887 A2	07/09/2011
		EP 2362888 A1	07/09/2011
		EP 2387603 A1	23/11/2011
		EP 2417079 A1	15/02/2012
		EP 2421929 A1	29/02/2012
		EP 2435528 A1	04/04/2012
		EP 2465910 A1	20/06/2012
		EP 2465910 B1	11/07/2018
		EP 2480620 A1	01/08/2012
		EP 2480620 B1	08/01/2020
		EP 2480621 A1	01/08/2012
		EP 2493830 A1	05/09/2012

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2020/039811

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
		EP 2493999 A1	05/09/2012
		EP 2521700 A1	14/11/2012
		EP 2521700 B1	16/04/2014
		EP 2585551 A1	01/05/2013
		EP 2585552 A1	01/05/2013
		EP 2585552 B1	03/04/2019
		EP 2622040 A1	07/08/2013
		EP 2651849 A1	23/10/2013
		EP 2655542 A1	30/10/2013
		EP 2743242 A2	18/06/2014
		EP 2814787 A2	24/12/2014
		EP 2814787 B1	26/12/2018
		EP 2841523 A1	04/03/2015
		EP 2848666 A1	18/03/2015
		EP 2855393 A1	08/04/2015
		EP 2867326 A1	06/05/2015
		EP 2867326 B1	02/11/2016
		EP 2888335 A1	01/07/2015
		EP 2888335 A4	06/04/2016
		EP 2890756 A1	08/07/2015
		EP 2890756 A4	13/04/2016
		EP 2907862 A1	19/08/2015
		EP 2912137 A1	02/09/2015
		EP 2912137 A4	20/04/2016
		EP 2935506 A1	28/10/2015
		EP 2935506 A4	26/10/2016
		EP 2989290 A1	02/03/2016
		EP 2989290 A4	14/12/2016
		EP 2989290 B1	20/06/2018
		EP 3002323 A1	06/04/2016
		EP 3118278 A1	18/01/2017
		EP 3121245 A1	25/01/2017
		US 2007-0056475 A1	15/03/2007
		US 2008-0156491 A1	03/07/2008
		US 2009-0114126 A1	07/05/2009
		US 2009-0200029 A1	13/08/2009
		US 2010-0044043 A1	25/02/2010
		US 2010-0258312 A1	14/10/2010
		US 7445669 B2	04/11/2008
		US 7478675 B2	20/01/2009
		US 7631692 B2	15/12/2009
		US 7674332 B2	09/03/2010
		US 7743828 B2	29/06/2010
		US 8307899 B2	13/11/2012
		US 9676989 B2	13/06/2017
US 2012-0312535 A1	13/12/2012	AR 063220 A1	14/01/2009
		CA 2663721 A1	27/03/2008
		CA 2663721 C	29/12/2015
		CN 101541915 A	23/09/2009

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2020/039811Patent document
cited in search reportPublication
datePatent family
member(s)Publication
date

EG 26864 A	09/11/2014
MX 2009002959 A	02/04/2009
US 2010-0081733 A1	01/04/2010
US 8236879 B2	07/08/2012
US 8517101 B2	27/08/2013
WO 2008-034461 A1	27/03/2008