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

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
17 August 2017 (17.08.2017)

WIPO | PCT

(10) International Publication Number
WO 2017/137791 A1

(51) International Patent Classification:
C04B 28/02 (2006.01) *C09K 8/473* (2006.01)
C04B 20/10 (2006.01)

(21) International Application Number:
PCT/IB2016/000272

(22) International Filing Date:
11 February 2016 (11.02.2016)

(25) Filing Language: English

(26) Publication Language: English

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(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, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, 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, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, 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, 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))*

(54) Title: PH SENSITIVE ENCAPSULATED EXPANSION AGENT FOR WELL CEMENTING

(57) Abstract: Low-pH mix water has dispersed capsules of expanding agent and a pH activated shell that becomes permeable at a higher cement slurry pH. Cement slurries and systems contain water, hydraulic cement, and the capsules. Cement slurry preparation methods involve forming a first mixture by dispersing the capsules in an aqueous medium, where the first mixture has a pH less than the activating pH, and mixing the first mixture with hydraulic cement to form the cement slurry having a pH greater than the activating pH. Pre-stressed cementing methods involve preparing the cement slurry, placing the slurry in an annulus in the well, hardening the cement, and delaying expansion of the set cement.

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PH SENSITIVE ENCAPSULATED EXPANSION AGENT FOR WELL CEMENTING

BACKGROUND

The statements in this section merely provide background information related to the present disclosure and may not constitute prior art.

The present disclosure broadly relates to cement and cementing operations.

Hydraulic cement is any substance provided (at least at one time in the manufacturing process) in a powdered or granular form, that when mixed with a suitable amount of water, can form a paste that can be poured or molded to set as a solid mass. In the oil and gas industry, good bonding between set cement and casing, and also between set cement and the formation, are essential for effective zonal isolation. Poor bonding limits production and reduces the effectiveness of stimulation treatments. Communication between zones can be caused by inadequate mud removal, poor cement/formation bonding, expansion and contraction of the casing resulting from internal pressure variations or thermal stresses, and cement contamination by drilling or formation fluids. Under such circumstances a small gap or microannulus may form at the cement/casing interface, the cement/formation interface, or both.

Representative examples of shrinkage-compensating cement are found in US7988782, US20150107493 and US4419136.

Expansive cement has also been used in the oil and gas industry to cement wells. Representative examples of this technology are found in US2465278, US3884710, US4002483, US4797159, US5942031, US6966376, and US14/307430. Use of expanding agents to cement wells is problematic since the expanding agents known in the art begin hydrating and thus begin to expand as soon as they contact water. Accordingly, if the expanding agent is going to expand the cement after the cement slurry is positioned within the well, the expanding agent cannot be added to the cement slurry mix water. Also, when the expansion agent is added to the slurry, the viscosity and/or yield stress of the slurry may increase before the slurry can be placed and set. This is especially problematic when the cement slurry is exposed to increased temperature conditions such as are frequently encountered downhole in a well. Incorporation of expanding agents thus leads to difficulties in pumping and placement of the slurry, along with complicating job design.

Moreover, since the cement slurry is readily flowable, any hydration of the expanding agent that occurs before the cement begins to set does not contribute to producing a compressive force within the annulus of the well due to the expansion of the set cement.

Various efforts to delay expansion have been suggested. Coating of metal oxide particles with non-hydratable or previously hydrated minerals such as metal carbonates, hydroxides and hydrates was suggested in US4332619, US5741357, EP2169027A1, EP2246408, US7494544, US20020037306, US7670627, but these materials are not activated by pH to begin a delay process which allows for placement in the annulus of the well prior to allowing expansion of the cement. These formulations are also difficult to prepare and have had only limited success. Other general examples of encapsulated materials for delivery include US20130065755, US20050123596, US20040234597, US20040109894, WO2005030174, US7722954, and US6209646.

Portland cement manufacturers have employed shrinkage-compensating cements that include an offsetting "expansive cement", which is a cement that when mixed with water forms a paste. This paste then sets to form a hardened cement. After setting, the cement increases in volume to significantly greater degree than Portland cement paste to form an expanded set cement as defined in the American Concrete Institute 223R-10 Guide for the Use of Shrinkage-Compensating Concrete (2010). Representative examples of shrinkage-compensating cement are found in US7988782, US20150107493 and US4419136.

The cement industry in general, is in need of ways to improve the preparation, handling and design of hydraulic cements with hydratable expanding agents that address these problems and shortcomings; and the oil and gas industry is in need of ways to better and more controllably delay expansion of the expanding agents, and to improve the bonding between the set cement and the casing within the well annulus.

SUMMARY

Some embodiments of the present disclosure are directed to expanding cement formulations, along with methods and systems for placing the cement. In some embodiments, the formulations include a delayed action encapsulated expanding agent activated by the basic pH of the cement, which expands as the cement sets to form a radially pre-stressed cement sheath within an annulus between the well casing and a surrounding barrier, such that the expanded set cement is transversely compressed between, and bonded to, the well casing and the borehole wall or another tubular body concentric with the well casing.

In one aspect, embodiments are directed to capsules comprising an expanding agent at least partially surrounded by a shell, wherein the shell is essentially impermeable to water at a pH in the range of 6 to 9 below an activating pH of the shell, and wherein the shell becomes water permeable from exposure to at least one pH in the range of 10 to 14 greater than the activating pH of the shell.

In another aspect, embodiments are directed to the capsules in an aqueous medium at a pH below the activation pH.

In another aspect, embodiments are directed to the capsules in a cement slurry comprising hydraulic cement and water at a pH above the activation pH. In some embodiments, the expanding agent is present in the cement slurry at a concentration between 0.1 weight percent and 30 weight percent, based on the total weight of the hydraulic cement present.

In another aspect, embodiments are directed to the capsules in a dry blend with hydraulic cement.

In another aspect, embodiments are directed to a method to cement a subterranean well having a borehole disposed through a formation, comprising: (i) preparing a cement slurry comprising water, hydraulic cement, the capsules according to any one of claims 1 to 11, and a pH above the activating pH; (ii) placing the slurry in an annular region of the well between a first tubular body and a borehole wall, or between the first tubular body and a second tubular body; (iii) hardening the slurry to form an at least partially set cement; and (iv) hydrating and expanding the expanding agent to form an expanded set cement within the annular region.

In another aspect, embodiments are directed to a system for cementing a subterranean well in an annulus between a casing disposed within a borehole and a formation, comprising the capsules in a cement slurry comprising hydraulic cement and water at a pH above the activation pH; and a pumping system to place the cement slurry in the annulus.

In another aspect, embodiments are directed to a method to produce a cement slurry, comprising: combining water and the capsules to form a first mixture of the capsules in aqueous medium at a pH below the activation pH; combining the first mixture with hydraulic cement to produce the cement slurry having a pH greater than the activating pH; and delaying the infiltration.

In another aspect, embodiments are directed to a cement slurry comprising water, a hydraulic cement and capsules comprising an expanding agent comprising calcium oxide, magnesium oxide, calcium sulfate hemihydrate, or a combination thereof, at least partially surrounded by a shell which becomes water permeable at the pH of the cement slurry, e.g., a pH greater than about 10, and which allows less than 50% relative expansion of the cement, based on a total percent expansion of the expanded set cement determined according to API-10B-5, prior to an initial set time for the cement slurry, and greater than 50% relative expansion of the cement, based on the total percent expansion of the expanded set cement after the initial set time for the cement slurry, determined according to ASTM C191-04a.

In still another aspect, a system for cementing a subterranean well in an annulus between a casing disposed within a borehole and a formation, comprises: a cement slurry comprising water, hydraulic cement and capsules comprising an expanding agent at least partially surrounded by a shell which becomes water permeable at a pH greater than about 8 to allow infiltration of a portion of the water into the capsules hydrating the expanding agent thereby expanding the expanding agent to form an expanded set cement; and a pumping system suitable to place a stage of the slurry in the annulus.

In another aspect, embodiments are directed to methods to cement a subterranean well having a borehole disposed through a formation, comprising: (i) preparing a cement slurry comprising water, hydraulic cement and capsules comprising an expanding agent at least partially surrounded by a shell which becomes water permeable from exposure to a pH greater than an activating pH, e.g., at a pH of the cement slurry that is greater than about 10; (ii) placing the slurry in an annular region of the well between a first tubular body and a borehole wall, or between the first tubular body and a second tubular body; (iii) hardening the slurry to form an at least partially set cement; and (iv) hydrating and expanding the expanding agent to form an expanded set cement within the annular region.

In another aspect, embodiments are directed to mix water useful to prepare a cement slurry, comprising an aqueous medium and capsules dispersed in the aqueous medium, the capsules comprising an expanding agent at least partially surrounded by a shell essentially impermeable to water, wherein the shell becomes water permeable from exposure to at least one pH in the range of 10 to 14 greater than an activating pH of the shell, and wherein the aqueous medium comprises a pH in the range of 6 to 9 below the activating pH.

In another aspect, embodiments are directed to a cement slurry comprising water, a hydraulic cement, a pH in the range of 10 to 14, and capsules comprising an expanding agent at least partially surrounded by a shell, wherein the shell is essentially impermeable to water at a pH in the range of 6 to 9, wherein the shell becomes water permeable from exposure to the pH of the cement slurry, and wherein the shell allows less than 50% relative expansion, based on a total percent expansion of the expanded set cement determined according to API-10B-5, to occur prior to an initial set time for the cement slurry determined according to ASTM C191-04a, and greater than 50% relative expansion determined according to API-10B-5, based on the total percent expansion of the expanded set cement, to occur after the initial set time for the cement slurry, determined according to ASTM C191-04a.

In another aspect, embodiments are directed to a mixture comprising capsules in an aqueous medium, wherein the capsules comprise an expanding agent at least partially surrounded by a shell, wherein the shell is essentially impermeable to water at a pH in the range of 6 to 9 below an activating pH of the shell, wherein the shell becomes water permeable from exposure to at least one pH in the range of 10 to 14 greater than the activating pH of the shell, and wherein the aqueous medium comprises a pH below the activation pH.

In another aspect, embodiments are directed to a method to produce a cement slurry, comprising: combining water and capsules comprising an expanding agent at least partially surrounded by a shell, which becomes water permeable at a pH greater than an activating pH, to form a first mixture having a pH less than the activating pH; combining the first mixture with a hydraulic cement to produce the cement slurry having a pH greater than the activating pH to allow hydration of the expanding agent; and expanding the expanding agent to form an expanded set cement in which less than 50% relative expansion, based on a total percent expansion of the expanded set cement determined according to API-10B-5, occurs prior to an initial set time for the cement slurry determined according to ASTM C191-04a, and greater than 50% relative expansion of the cement occurs after the initial set time for the cement slurry.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1A is a schematic diagram showing an essentially impermeable capsule according to embodiments of the disclosure;

FIG. 1B is a schematic diagram showing the capsule of FIG. 1A after becoming permeable according to embodiments of the disclosure;

FIG. 1C is a schematic diagram showing the capsule of FIG. 1A and or FIG. 1B after removal of shell material according to further embodiments of the disclosure;

FIG. 2 shows a diagram of a well cemented according to embodiments of the disclosure;

FIG. 3 shows a diagram of an annulus between two tubular members cemented according to embodiments of the disclosure;

FIG 4 shows a capsule having a matrix island arrangement according to embodiments of the disclosure;

FIG. 5 shows a diagram of an apparatus for measuring cement expansion and pre-stress development;

FIG. 6A qualitatively shows the expected results of confined cement expansion experiments with expanding agent capsules according to embodiments of the disclosure; and

FIG. 6B qualitatively show the expected results of confined cement expansion experiments with expanding agent capsules according to embodiments of the disclosure;

FIG. 7 is a graph of shear stress vs. shear rate for cement slurries containing dry expanding agent and expanding agent exposed to wet conditions;

FIG. 8 is a graph showing mass loss of Nylon 6 upon aging at neutral pH and 130°C; and

FIG. 9 is a graph showing mass loss of Nylon 6 upon aging at pH=12.6 and 130°C.

DETAILED DESCRIPTION

The present disclosure will be described in terms of treatment of vertical wells, but is equally applicable to wells of any orientation. As used herein, "transverse" is intended to refer to a direction transverse to the axis of the well, e.g., the horizontal direction in a vertical well and vice versa. The disclosure will be described for hydrocarbon-production wells, but it is to be understood that the disclosed methods can be used for wells for the production or injection of other fluids, such as water or carbon dioxide, for example. It should also be understood that throughout this specification, when a concentration or amount range is described as being useful, or suitable, or the like, it is intended that any and every concentration or amount within the range, including the end points, is to be considered as having been stated. Furthermore, each numerical value should be read once as modified by the term "about" (unless already expressly so modified) and then read again as not to be so modified unless otherwise stated in context. 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. In other words, when a certain range is expressed, even if only a few specific data points are explicitly identified or referred to within the range, or even when no data points are referred to within the range, it is to be understood that applicant appreciates and understands that any and all data points within the range are to be considered to have been specified, and that the applicant has possession of the entire range and all points within the range.

As used in the specification and claims, "near" is inclusive of "at." The term "and/or" refers to both the inclusive "and" case and the exclusive "or" case, whereas the term "and or" refers to the inclusive "and" case only and such terms are used herein for brevity. For example, a component comprising "A and/or B" may comprise A alone, B alone, or both A and B; and a component comprising "A and or B" may comprise A alone, or both A and B.

In this disclosure, the tubular body may be any string of tubulars that may be run into the wellbore and at least partially cemented in place. Examples include casing, liner, solid expandable tubular, production tubing, drill pipe, and the like. As used herein, a "set cement" refers to a cement which has set (e.g., been allowed to cure, allowed to harden, and the like) for a time greater than or equal to the "initial time of setting", also referred to herein simply as the "initial set time" as determined according to ASTM C191-04a, "Time of Setting of a Hydraulic Cement by Vicat Needle", or an equivalent thereof. This same method is also used to determine the "final set time" of the cement slurry.

As used herein, a "bond" between a body within the wellbore and the expanded set cement refers to acoustically coupled contact between the body and the cement. Likewise, a bond between the expanded set cement and the borehole or formation wall refers to contact between the two such that the two are acoustically coupled and/or form a fluid-tight seal. For purposes herein, a well casing, e.g., a tubular body, also referred to herein as a tubular member, is acoustically coupled to the expanded set cement when the cement is shown to exist behind the well casing by acoustic logging techniques known in the art. Accordingly, for purposes herein, a bond does not exist between a well casing and a cement sheath when a micro annulus or airspace is present between the two as shown by acoustic logging techniques. Likewise, as used herein, "compression" in the annular region refers to compression in the transverse direction against or between the first tubular member and the borehole wall or second tubular member due to expansion of the cement.

As used herein, a shell which becomes water permeable at an "activation pH" comprises one or more components or features which allow for water infiltration into the core through all or part of the shell upon exposure, or following a period of delay after the exposure, of the shell to an alkaline pH above the activation pH, such as when the cement slurry has a pH substantially above the activation pH, e.g., 1 or more pH units. For purposes herein, unless stated otherwise, it is to be understood that the "pH activated shell" (i.e., a shell which becomes water permeable at a particular pH above 7) is essentially impermeable to water when present in an aqueous solution having a pH substantially less than the pH needed to activate the shell, e.g., 1 or more pH units below the activation pH. It is to be further understood that for purposes herein, a pH activated shell exposed to pH conditions below the activation pH may allow a trivial amount of water infiltration.

As used herein, "essentially impermeable" means that the pH activated shell is sufficiently resistant to water infiltration such that there is substantially no hydration of the encapsulated material in the particular slurry, system or method and/or conditions thereof, prior to increasing the pH above the activation pH, e.g., less than 5% relative expansion of the core material in a 48-hour period of exposure at the actual conditions, or less than 1 wt% liquid infiltration into the capsule in a 48-hour period of exposure to the particular slurry or fluid at atmospheric pressure and 25°C, based on the total weight of the capsule. In all embodiments herein, the shell may be essentially impermeable to water at a pH of 10 or less, or a pH of 9.5 or less, or a pH of 9 or less, or a pH of 8.5 or less, or at a pH otherwise below the activation pH.

For purposes herein, it is considered that evaluating whether a particular pH is above or below the activation pH does not necessarily require knowledge of a precise or even an approximate activation pH; this determination can be made simply by observing whether or not the encapsulated expanding material hydrates and expands at the pH and or other conditions of interest, i.e., if the expanding material hydrates and expands in the alkaline aqueous medium at the test or downhole or other actual conditions, then the pH is above the activating pH; and conversely, if the shell is essentially impermeable at the test or surface or other actual conditions, then the pH is below the activating pH.

For purposes herein, a shell which becomes water permeable at a particular pH may include components or sections which are at least partially soluble in aqueous solutions having a pH above the activating pH, and/or which undergo a chemical reaction upon contact with aqueous solutions above the activating pH, and/or which decompose upon contact with aqueous solutions above the activating pH, and/or which undergo a phase transition upon contact with aqueous solutions above the activating pH. The shell thereby allows water infiltration or otherwise allows hydration of the expanding agent or other core material in (or from) the capsule. In embodiments, a water permeable shell includes a shell which at least partially surrounds a core, but which has or forms pores, voids, and/or discontinuities within the shell which allow water to pass through the shell and contact the core when present in an aqueous solution above the activating pH. As used herein, a water permeable shell may also include a shell which allows diffusion of water through the shell, e.g., via partial dissolution of the shell material and/or osmosis above the activating pH.

The terms capsule, encapsulated expanding agent, expanding agent capsule, and the like are used interchangeably to refer to a capsule comprising a core as a single entity disposed within a water-permeable shell or a core material dispersed throughout the shell matrix.

As used herein, capsules may comprise a single-core arrangement or configuration, i.e., a single core at least partially contained within a water permeable shell (cf. FIG. 1A) and/or may comprise a "matrix-island" arrangement or configuration in which the expanding agent is distributed at least partially within each particle or capsules as small islands within a matrix of the encapsulating or shell material (cf. FIG. 4), e.g., the expanding agent is dispersed as a discontinuous phase within the continuous shell material. Unless stated otherwise, reference to a capsule includes both single core-shell and matrix-island arrangements. In some embodiments, the core is homogenous. In other embodiments, the core may comprise various components.

As used herein for ease of reference, when a polymer is referred to as comprising a monomer, the monomer is present in the polymer is the polymerized form. The term polymer generally refers to a composition having 20 or more "mer" units. A "mer" is defined as a repeating unit of an oligomer or polymer that originally corresponded to the monomer from which the polymer is produced. For example, the "mer" of polylactic acid would be lactic acid. As used herein, unless specifically stated otherwise, the term polymer may also include an oligomer, which is defined as having 2 to 19 "mer units".

As used herein, a "polymer" may include both homopolymers (i.e., a polymer comprising essentially one monomer, and/or a copolymer, which is defined for purposes herein as a polymer comprising more than one monomer.

For purposes herein, an aliphatic moiety is defined as a linear and/or a branched saturated hydrocarbon chain. An alicyclic moiety is defined as a cyclic hydrocarbon chain, which may further include one or more heteroatoms. An olefinic moiety is defined as a linear, branched, and/or cyclic hydrocarbon chain comprising at least one carbon-carbon double or triple bond, which may further include a heteroatom. An aromatic moiety refers to a moiety comprising one or more aromatic systems, including one or more heteroaromatic systems.

For purposes herein, the percent expansion produced by setting or hardening of the cement slurry into the expanded set cement is determined according to API-10B-5 or an equivalent thereof. In this method, a ring shaped mold sealed on the top and bottom is filled to form a circular ring of cement. The mold has a stationary inner ring surrounded by an expandable outer ring which increases in circumference as the cement slurry inside the mold sets and expands. The test may be conducted at various temperatures and pressures. The percent expansion is determined by first measuring the distance M (mm) between two points on the outer ring at the time of filling the mold with the cement T_0 (e.g., measure M_0(mm) @ T_0), and then again measuring the distance between these same two points after the cement has set to form the expanded set cement. This measurement is determined at the final time T_f, as specified in the method (e.g., M_f(mm) @ T_f). The total percent expansion is then determined by multiplying the difference between the final distance and the initial distance by a constant associated with the particular mold, according to the following formula:

$$\text{Percent expansion} = (M_f - M_0) * \text{mold constant}.$$

For purposes herein, this percent expansion obtained at the final time T_f is referred to as the total percent expansion of the cement. This total percent expansion of the cement serves as the basis for all relative percent expansion determinations, as discussed herein. For purposes herein, the relative expansion of the cement slurry at a particular time (T_1), referred to as the percent relative expansion is equal to the percent expansion of the slurry (or setting cement) measured at a time T_1 divided by the total percent expansion achieved by the expanded set cement at T_f determined according to API-10B-5. For purposes herein, the percent relative expansion may be determined at standard conditions of 25°C and 1 atm of pressure, or at any suitable temperature and/or pressure specified for the intended end use. As an example, if a percent expansion at time T_1 is determined according to API-10B-5 to be 0.1%, and the total percent expansion at time T_f is determined according to the same method under the same conditions to be 1%, the percent relative expansion of the cement slurry at time T_1 would be:

$$0.1\%/1\% * 100\% = 10\% \text{ relative expansion at } T_1$$

Since the cement slurry being placed within the annulus of the wellbore is readily flowable, any expansion which occurs before the cement begins to set may increase the volume of the cement slurry, and is not thought to contribute to expansion within the annulus which produces the cement sheath transversely compressed therein. Accordingly, in embodiments, at least a percentage of the hydration of the expanding agent is delayed until after the initial set time of the cement, thereby delaying the expansion of the cement to a time after the slurry becomes more resistant to flow. This allows placement of the cement slurry within the annulus and at least partial setting of the cement prior to expansion of the cement.

In embodiments, the delay in expansion of the cement slurry is determined relative to the initial set time, the final set time, or a combination thereof for the cement slurry. The initial set time and the final set time are determined according to ASTM C191-04a, an equivalent thereof. The initial set time and/or the final set time may be determined at standard temperatures and pressures, or at the temperature and pressure specified. The relative expansion properties of the cement slurry at various times, or within various time intervals, are determined relative to the total amount of expansion (the total percent expansion) obtained by the cement slurry, utilizing the percent expansion determined according to API-10B-5.

In embodiments the composition and/or arrangement of the outer shell is selected to delay hydration of the expanding agent until a time after the outer shell is combined with the hydraulic cement. As is known to one of skill in the art, the addition of a hydraulic cement to an aqueous medium results in a substantial increase in the pH of the solution, typically from around neutral pH (e.g., 6.5 to 8.5) up to a pH in excess of 10 or 11 or more. This increase in pH results in the shell becoming (substantially more) water permeable and eventually allows an amount of water to infiltrate into the shell to hydrate and thereby expand the expanding agent which is at least initially encapsulated therein.

In embodiments the shell is selected to delay hydration of the expanding agent after being combined in the cement slurry for a time such that prior to an initial set time for the cement slurry, determined according to ASTM C191-04a, or an equivalent thereof, the percent relative expansion of the cement slurry, if any, is less than 50%, based on the total percent expansion of the expanded set cement determined according to API-10B-5.

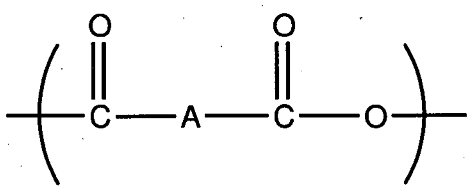
In embodiments, the shell is selected to delay hydration of the expanding agent after being combined in the cement slurry for a time such that prior to an initial set time for the cement slurry, determined according to ASTM C191-04a, or an equivalent thereof, the percent relative expansion of the cement slurry that occurs, if any, is less than 50% (or less than 40%, or less than 30%, or less than 20%, or less than 10%), based on the total percent expansion of the expanded set cement determined according to API-10B-5; and after the initial set time for the cement slurry, the percent relative expansion of the cement slurry that occurs is greater than 50% (or greater than 60%, or greater than 70%, or greater than 80%, or greater than 90%), based on the total percent expansion of the expanded set cement determined according to API-10B-5.

Utilizing this test, the ability of the shell to delay hydration of the expanding agent after being combined in the cement slurry may be determined to meet requirements of a particular cementing operation. In embodiments, other method to determine the delay of hydration of the expanding agent may be used including differential scanning calorimetry, a temperature-controlled confinement cell used to measure the effects of expanding agents under confined as shown in FIG. 5, and the like.

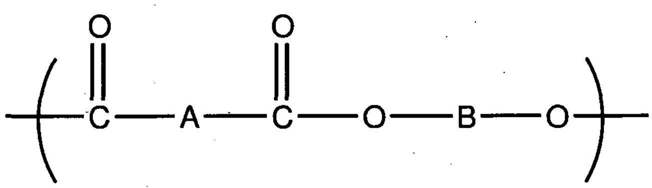
In an aspect, embodiments relate to a cement slurry comprising water, a hydraulic cement and capsules comprising an expanding agent comprising calcium oxide, magnesium oxide, calcium sulfate hemihydrate, or a combination thereof, at least partially surrounded by a shell which becomes water permeable at a pH greater than about 8 and which allows less than 50% relative expansion, based on a total percent expansion of the expanded set cement determined according to API-10B-5, prior to an initial set time for the cement slurry, and greater than 50% relative expansion, based on the total percent expansion of the expanded set cement after the initial set time for the cement slurry, determined according to ASTM C191-04a. In embodiments, greater than 50% relative expansion, based on a total percent expansion of the expanded set cement determined according to API-10B-5, occurs before a final set time for the cement slurry, determined according to ASTM C191-04a.

In embodiments, the shell comprises an inorganic oxide, a polyanhydride, a polyester, a poly(ester anhydride), a polyamide, a polyurethane, a polyether, a poly(ether urethane), a polyvinyl alcohol, a polyvinyl acetate, a polycarbonate, a polysiloxane, or a combination thereof.

In embodiments, the shell comprises a polyanhydride having the general structure:

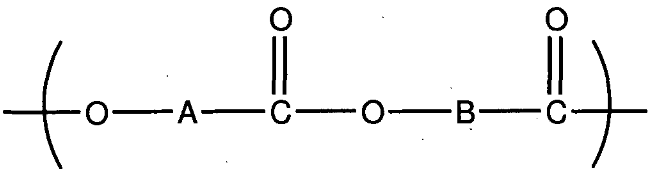

;

and/or a poly(ester anhydride) having the general structure:


;

wherein A and B are each selected from the group consisting of: an aliphatic moiety comprising 1 to 20 carbon atoms; an alicyclic moiety comprising 3 to 20 carbon atoms; an olefinic moiety comprising 2 to 20 carbon atoms; an aromatic moiety comprising 6 to 20 carbon atoms, and combinations thereof. In embodiments, the shell comprises a polyadipic anhydride moiety, a polysuberic anhydride moiety, a polysebacic anhydride moiety, or a combination thereof.

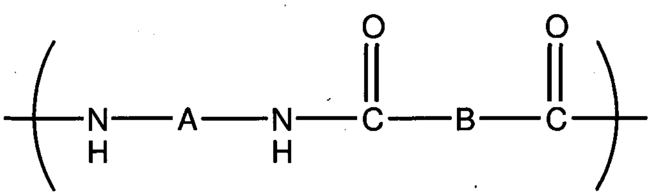
In embodiments, the shell comprises a polyester having the general structure



;

wherein A and B are each selected from the group consisting of: an aliphatic moiety comprising 1 to 20 carbon atoms; an alicyclic moiety comprising 3 to 20 carbon atoms; an olefinic moiety comprising 2 to 20 carbon atoms; an aromatic moiety comprising 6 to 20 carbon atoms, and combinations thereof. In embodiments, the shell comprises poly-glycolic acid, poly-lactic acid-c-glycolic acid, poly-L-lactic acid, poly-L/D-lactic acid, poly-L/D-lactide-co-glycolic acid, polyethylene terephthalate, or a combination thereof.

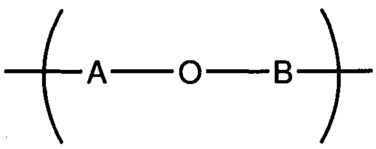
In embodiments, the shell comprises a polyamide having the general structure:



;

wherein A and B are each selected from the group consisting of: an aliphatic moiety comprising 1 to 20 carbon atoms; an alicyclic moiety comprising 3 to 20 carbon atoms; an olefinic moiety comprising 2 to 20 carbon atoms; an aromatic moiety comprising 6 to 20 carbon atoms, and combinations thereof. In embodiments, the shell comprises nylon 6, nylon 6,6, nylon 6,10, nylon 6,12, nylon 11, nylon 12, or a combination thereof.

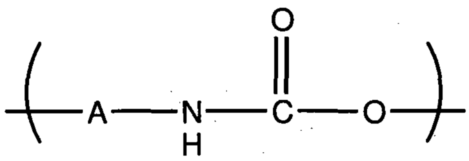
In embodiments, the shell comprises a polyether having the general structure:



;

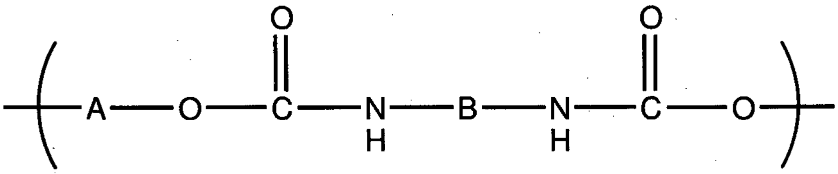
wherein A and B are each selected from the group consisting of: an aliphatic moiety comprising 1 to 20 carbon atoms; an alicyclic moiety comprising 3 to 20 carbon atoms; an olefinic moiety comprising 2 to 20 carbon atoms; an aromatic moiety comprising 6 to 20 carbon atoms, and combinations thereof.

In embodiments, the shell comprises a polyurethane having the general structure:



; and/or

a poly(ether urethane) having the general structure:



wherein A and B (when present) are each selected from the group consisting of: an aliphatic moiety comprising 1 to 20 carbon atoms; an alicyclic moiety comprising 3 to 20 carbon atoms; an olefinic moiety comprising 2 to 20 carbon atoms; an aromatic moiety comprising 6 to 20 carbon atoms, and combinations thereof.

In embodiments, the expanding agent is present in the cement slurry at a concentration between 0.1 or 1 weight percent and 30 weight percent, based on the total weight of hydraulic cement present.

In embodiments, a method to cement a subterranean well having a borehole disposed through a formation, comprises: (i) preparing a cement slurry comprising water, hydraulic cement and capsules comprising an expanding agent at least partially surrounded by a shell which becomes water permeable at a pH greater than about 8, according to one or more embodiments disclosed herein; (ii) placing the slurry in an annular region of the well between a first tubular body and a borehole wall, or between the first tubular body and a second tubular body; (iii) hardening the slurry to form an at least partially set cement; and (iv) infiltrating a portion of the water into the capsules hydrating and expanding the expanding agent to form an expanded set cement within the annular region. In embodiments, the shell is further selected to allow less than 50% relative expansion, based on a total percent expansion of the expanded set cement determined according to API-10B-5, prior to an initial set time for the cement slurry determined according to ASTM C191-04a, and greater than 50% relative expansion, based on the total percent expansion of the expanded set cement after the initial set time for the cement slurry. In embodiments, greater than 50% relative expansion, based on a total percent expansion of the expanded set cement determined according to API-10B-5, occurs before a final set time for the cement slurry, determined according to ASTM C191-04a.

In embodiments, the cement slurry comprises an amount of expanding agent sufficient to form the expanded set cement transversely compressed between, and bonded to, the first tubular body and the borehole wall, or the first tubular body and the second tubular body.

In embodiments, the bond between the first tubular body and the expanded set cement and the bond between the borehole wall and the expanded set cement are each sufficient to isolate a zone of the formation adjacent the expanded set cement.

In embodiments, the bond between the first tubular body and the expanded set cement is maintained after fluctuating the dimensions of the first tubular body in response to a temperature change, a pressure change, a mechanical disturbance resulting from a well intervention, or a combination thereof.

In embodiments, the shell is essentially impermeable to water at a pH below the target or activating pH, and allows at least 10 times greater water infiltration, or 20 times, or 30 times, or 40 times, or 50 times, or 60 times, or 70 times, or 80 times, or 90 times, or essentially fails to inhibit water infiltration above the activating pH.

In embodiments, the shell becomes water permeable at a pH greater than about 10, or a pH greater than about 10.5, or a pH greater than about 11, or a pH greater than about 11.5, or a pH equal to or greater than about 12. In embodiments, the shell is essentially impermeable to water at the pH of the makeup water used to produce the cement, and becomes water permeable at the pH of the cement formulation after a period of delay, i.e., the shell eventually becomes water permeable when combined with the hydraulic cement and water.

In embodiments, the shell comprises, or consists essentially of an inorganic component, typically an oxide such as silica, alumina, and the like, which at least partially dissolves in the aqueous solution present in the cement formulation, e.g., at a pH above 10.

In embodiments, the shell comprises, or consists essentially of an organic polymer which decomposes at the pH of the cement formulation via hydrolysis of the polymer backbone. In embodiments, the shell comprises a polyanhydride, a polyester, a poly(ester anhydride), a polyamide, a polyurethane, a polyether, a poly(ether urethane), a polyvinyl alcohol, a polyvinyl acetate, a polycarbonate, a polysiloxane, or a combination thereof. Accordingly, the shell may comprise one or more polymers, either as a blend or in individual layers or portions, and/or the polymer may comprise various linkages which result in the polymer decomposing at the pH of the cement formulation.

In embodiments, the bond between the first tubular body and the expanded set cement is maintained after fluctuating the dimensions of the first tubular body in response to a temperature change, a pressure change, a mechanical disturbance resulting from a well intervention, or a combination thereof. In embodiments, the bond between the borehole wall and the expanded set cement or the bond between the second tubular body and the expanded set cement is maintained after fluctuating the dimensions of the first tubular body in response to the temperature change, the pressure change, the mechanical disturbance resulting from the well intervention, or combinations thereof. In such embodiments, the mechanical disturbance resulting from the well intervention may comprise measuring an acoustic impedance, an amplitude, an attenuation, a bond index, or a combination thereof.

In embodiments, the expanding agent is present in the cement slurry at a concentration between 0.1 or 1 weight percent and 30 weight percent, based on the total weight of hydraulic cement present.

In embodiments, the expanding agent is present in the cement slurry at a concentration greater than or equal to about 0.1 weight percent based on the total weight of hydraulic cement present, or greater than or equal to about 0.5 weight percent, or greater than or equal to about 1 weight percent, or greater than or equal to about 5 weight percent, or greater than or equal to about 7 weight percent, or greater than or equal to about 10 weight percent, or greater than or equal to about 14 weight percent, or greater than or equal to about 20 weight percent, and less than or equal to about 30 weight percent, or less than or equal to about 25 weight percent, based on the total weight of hydraulic cement present. In embodiments, the expanding agent is present in the cement slurry at a concentration between about 1 weight percent and 30 weight percent, or between about 5 weight percent and 30 weight percent, or between about 10 weight percent and 25 weight percent, based on the total weight of hydraulic cement present.

In embodiments, the amount of expanding agent present in the slurry is suitable to produce from 0.1 percent to 5 percent total expansion of the cement slurry upon hardening into an expanded set cement as determined according to API 10B-5 or an equivalent thereof, e.g., from 0.2 to 3 percent total expansion, or from 0.5 to 2 percent total expansion.

In embodiments, the viscosity of the cement slurry during placement may be lower than 1000 cP at a shear rate of 100 s^{-1}. In embodiments, the hydraulic cement comprises Portland cement, calcium aluminate cement, fly ash, blast furnace slag, lime, silica, magnesium oxychloride, a geopolymer, zeolite, chemically bonded phosphate ceramic, diatomaceous earth, gilsonite, hematite, ilmenite, manganese tetraoxide, barite, glass or ceramic microspheres, or combinations thereof. In some embodiments the hydraulic cement consists essentially of Portland cement.

In embodiments, the capsules containing the expanding agent may be combined with the hydraulic cement and/or water in any order to make the cement slurry. In embodiments, the encapsulated expanding agent may be blended with the dry hydraulic cement, either offsite at a remote location or on-site as part of the cementing procedure, and then the blend then combined with water to make the cement slurry.

In embodiments, a method to produce a cement slurry comprises combining water and capsules comprising an expanding agent at least partially surrounded by a shell which becomes water permeable at a pH greater than an activating pH to form a first mixture having a pH less than the activating pH, e.g., a pH about 5-10 or 6-9. The method may optionally include adding a (minor) amount of an acid (i.e., less than 10 wt%) to adjust the pH. This first mixture may be subsequently combined with the hydraulic cement to produce the cement slurry according to embodiments disclosed herein. In some embodiments, the first mixture may comprise the mix water for the hydraulic cement, and depending on the impermeability of the shell material of the capsules at the first mixture pH and thus the ability to prevent hydration of the encapsulated expanding material, the first mixture can be prepared in advance of the mixture with the hydraulic cement, e.g., prepared off-site and transported to the job location, or prepared on-site and stored for an extended period, e.g., more than an hour or more than a day or more than a week before preparing the cement slurry.

In embodiments, the cement slurry according to the instant disclosure is prepared which comprises water, hydraulic cement and capsules comprising a core of an expanding agent at least partially surrounded by (e.g., encapsulated within) a pH activatable shell (see FIG. 1A). The slurry is then placed in an annular region between a first tubular body (e.g., the well casing) and a borehole wall or a second tubular body (see FIGs. 2 and 3). The slurry is then allowed to at least partially set, also referred to in the art as “harden”, i.e., allowed to set for a time greater than or equal to the first or initial set time measured for the cement slurry when determined according to ASTM C191-04a, or an equivalent thereof. Addition of the hydraulic cement to water results in a mixture having a pH above the activating pH, e.g., a pH of 10-12 or more. At this elevated pH, the shell decomposes at a much faster rate than when the shell is at a pH below the activating pH, e.g., a pH of below 10, or below 9, or below 8. Decomposition or other effects of the high pH on the shell result in the infiltration of a portion of the water present in the slurry into the capsules. As the water contacts the expanding agent, the expanding agent hydrates, causing the expanding agent to expand. Accordingly, the capsule is activated at the pH of the cement slurry. In embodiments, this expansion may cause the remaining portion of the shell to rupture, thus releasing or further reducing the inhibition of the water contacting the expanding agent, or otherwise further accelerating hydration and expansion of the expanding agent.

Expansion of the expanding agent within the partially set cement forms an expanded set cement within the annular region of the wellbore. In embodiments, the amount of expansion of the cement is sufficient to form an expanded set cement radially pre-stressed within the cement sheath, i.e., the expanded set cement is transversely compressed between the first tubular body and the borehole wall, or the first tubular body and the second tubular body.

In some embodiments, the amount of expanding agent present in the cement slurry is sufficient to produce an expanded set cement in a state of compression within the annular region which facilitates maintenance of a bond with the first tubular member and the borehole wall or second tubular member.

The method may further comprise fluctuating the dimensions of the first tubular body, e.g., allowing the dimensions of the tubular body to fluctuate in response to a temperature change, a pressure change, or a mechanical disturbance resulting from a well intervention or a combination thereof. This is a common technique applied when conducting sonic logging of the well to determine the presence and quality of the cement sheath in the annulus between the well casing the next barrier. The method may also further comprise transversely compressing the set cement between the first tubular body and the borehole wall or second tubular body to maintain bonding therewith, e.g., allowing the set cement to expand and/or to maintain the state of compression, during and/or after the dimensional fluctuation of the first tubular body.

In a further aspect, embodiments relate to methods for maintaining zonal isolation in a wellbore. A cement slurry is prepared that comprises water, hydraulic cement and capsules comprising a shell encapsulating an expanding agent core, the shell comprising a polymer which decomposes at a pH greater than 10. The slurry is then placed in an annular region between a first tubular body and a borehole wall or a second tubular body. The slurry is hardened, e.g., allowed to harden, to form an at least partially set cement. Water is infiltrated, e.g., allowed to infiltrate, into the capsules to hydrate the expanding agent in the core. The set cement is expanded to compress against and bond with the borehole wall to isolate a zone of the formation adjacent the expanded cement. The compression and bond are maintained adjacent the isolated zone after dimensions of the first tubular body are fluctuated, e.g., allowed to fluctuate in response to a temperature change, a pressure change, or a mechanical disturbance resulting from a well intervention or a combination thereof. In embodiments an acoustic logging tool is introduced into the tubular body. The tool measures acoustic impedance, amplitude, attenuation or a bond index or a combination thereof. In some embodiments, the measurements are taken azimuthally, longitudinally or both along the tubular body.

For all aspects, the expansion of the expanding agent, and thus the expansion of the cement, may be delayed for a particular period of time after initial contact of the capsules containing the expanding agent (e.g., the encapsulated expanding agent) with water. In embodiments, the capsules are "activated" to allow infiltration of water by the subjecting the capsules to a pH greater than 10.

In embodiments, the shell may comprise polymers which degrade at a pH of less than 10, but do so at a rate which allows preparation and or storage of the capsules in an aqueous mixture prior to combining with the hydraulic cement. In embodiments, less than 1 wt% of the shell decomposes over a 24 hour period, or over a 1 week period (168 hours), or over a 2 week period (336 hours) at 25°C, when the capsules are slurried in water, and the resulting mixture has a pH from about 5 to about 10 or from about 6 to about 9. Accordingly, embodiments disclosed herein may be prepared ahead of time, and then combined with the hydraulic cement just prior to placement in the wellbore.

In embodiments, a method to produce a cement slurry, comprises combining water and capsules comprising an expanding agent at least partially surrounded by a shell comprising a polymer which decomposes at a pH greater than an activating pH, optionally adding an amount of an acid or a base, to form a first mixture having a pH from about 5 to 10 or about 6 to 9; and combining the first mixture with a hydraulic cement to produce the cement slurry having a pH greater than the activating pH, e.g., greater than 10 or greater than 12, to allow infiltration of a portion of the water into the capsules hydrating the expanding agent thereby expanding the expanding agent to form an expanded set cement. In embodiments, the first mixture may be prepared at least a day before, at least a week before, or at least two weeks before preparing the cement slurry. In embodiments, the first mixture may be prepared off-site, and then transported to the wellsite where it is mixed with the hydraulic cement to form the cement slurry.

In embodiments, the ability to activate the capsules via pH further provides for a more robust expanding agent, which may be premixed or shipped and stored without hydration of the expanding agent until the capsules are combined with the cement in cement slurry. Accordingly, more of the expanding agent is available down hole even after improper storage or transport in wet conditions that sometimes occur in wellsite environments.

In some embodiments, the composition and/or configuration of the pH activated shell may be selected to delay the time between contacting the cement composition with water (i.e., preparing a cement slurry comprising water, hydraulic cement and capsules comprising an expanding agent at least partially surrounded by a shell which becomes water permeable at the pH of the cement slurry, or when otherwise exposed to a pH greater than an activating pH, e.g., above about 8, or above 9 or above 10 or above 11) and expansion of the set cement brought about by hydration and subsequent expansion of the expanding agent (e.g., infiltration of water into the capsule and/or rupture of the shell to hydrate and expand the expanding agent).

In embodiments, the selection of the pH activated shell may include selection of a plurality of layers, which may be the same or different in composition, thickness, or a combination thereof. In embodiments, the selection of the pH activated shell may include selecting the composition of the water permeable shell, increasing or decreasing the thickness of the encapsulating outer layer or layers of the water permeable shell (i.e., the number and composition of each shell layer, the thickness of each shell layer, or a combination thereof. In embodiments, inorganic oxides may be incorporated into the polymeric shell which, upon contact with the aqueous solution of the cement formulation, at least partially dissolve to form weaknesses or discontinuities within the shell thus allowing for water infiltration into the shell with subsequent activation (hydration of the expanding agent).

In embodiments, the decomposition rate of the outer layer or layers of the pH activated shell may be selected by selecting a coating composition having kinetics suitable to decompose upon contact with the water at a pH of greater than 8, or greater than 9, or greater than 10 under down hole conditions, over a suitable period of time; and/or selecting a coating composition which chemically reacts e.g., via hydrolysis with the water at the pH of the cement slurry (e.g., greater than 8, or 9, or 10, or 11) to weaken the strength of the shell and/or the solubility of the shell in a controlled manner over a suitable period of time; and/or the thickness of the outer shell may be selected to prevent water at the pH of the cement slurry from contacting the expanding agent for a suitable period of time.

For example, a thicker shell layer may increase the strength or toughness of the core to resist rupture, as well as reduce hydraulic conductance, water infiltration, or the like. Likewise, the composition of the polymer present in the shell may be selected to have a slower hydrolysis rate to further delay water infiltration into the capsule. In other examples, a combination of shell layers having different properties may be selected to delay water infiltration into the capsule, e.g., causing a longer time to dissolve, thereby delaying hydration and subsequent expansion of the expanding agent until the cement slurry is properly placed within the annulus of the well bore and has begun to set i.e., allowed to set for a time greater than or equal to the first or initial set time measured for the cement slurry when determined according to ASTM C191-04a, or an equivalent thereof.

In the figures, like numerals are used to designate like parts. As shown in FIG. 1A, the capsule 2 comprises a core 4, comprising an expanding agent, which is at least partially surrounded by a shell 6. Initially, the water is excluded by the impermeable shell 6, as shown by arrow 10.

As shown in FIG. 1B, after activation, e.g., by exposure to the pH conditions prevailing in the cement slurry, the capsule 2' comprises a core 4', comprising the expanding agent, which is at least partially surrounded by a shell 6', which has become water permeable, e.g., by at least partial dissolution, hydrolysis, decomposition, or other means of degradation of one or more components of the shell 6'. When the material of the shell 6' becomes permeable, water infiltrates as shown by arrow 10' through the activated shell 6', even though in some embodiments the shell 6' may physically remain generally intact. When the water reaches the core 4', the expanding material begins hydrating and expansion is initiated.

As shown in FIG. 1C, in an initial "A" stage, the capsule 2" comprises a core 4", comprising an expanding agent, which is at least partially surrounded by a shell 6", in a manner similar to FIGs. 1A and 1B. Initially, the water is excluded by the impermeable shell 6", as shown by arrow 10. After activation in a later stage "B", e.g., by exposure to the pH conditions prevailing in the cement slurry, the capsule 2" comprises a core 4", comprising the expanding agent, which is directly exposed to water permeation 10" through surface(s) 12", which may comprise holes or exposed areas between any remaining shell portions 6'' following removal, e.g., by at least partial dissolution, hydrolysis, decomposition, or other means of degradation of one or more components of the shell 6". When the water reaches the core 4", the expanding material begins hydrating and expansion is initiated. In the "B" stage, the core 4" is expanded and the expansion may further tear and/or rupture the shell 6", and/or otherwise enlarge the openings exposing the surfaces 12", to accelerate further water infiltration 10", hydration, and expansion of the core 4".

With reference to some embodiments, borehole 20 and tubular member 30 are shown in FIGs. 2 and 3, respectively, wherein like numerals are used to designate like parts. The cement slurry comprising the capsules according to any embodiments disclosed herein is placed in the annulus 22 around the casing or other tubular member 24, set (initial and or final) in place, and with hydration of the expanding agent, expanded as indicated at 26 to induce a state of compression and facilitate bonding. The annulus 22 is shown between the tubular member 24 and the borehole wall 20 (FIG. 2) or the tubular member 30 (FIG. 3). The logging tool 28 is then introduced to take measurements as described in some embodiments herein, for example, to map impedance and determine the presence of cement in the annulus 22 behind the tubular member 24, or the absence thereof suggesting formation of a microannulus (not shown) between the tubular member 24 and the set cement in the annulus 22.

The tubular member 24 in FIGs. 2 and 3 (and/or tubular member 30 in FIG. 3) may be dimensionally changed in length, diameter, rotational alignment, etc., e.g., with respect to the wellbore 20 (FIG. 2) or the tubular member 30 (FIG. 3), some examples of which are indicated at 32. Expansion 26 of the cement set in the annulus 22 can occur before the dimensional change 32, and according to some embodiments of the disclosure, the state of compression of the cement is maintained in the annulus 22 during and/or after the dimensional change 32, e.g., by further expansion or increased compression to accommodate the changing dimension(s). Expansion 26 of the cement set in the annulus 22 can instead and/or also occur during and/or after the dimensional change 32, and according to some embodiments of the disclosure, the state of compression of the cement can be induced in the annulus 22 during and/or after the dimensional change 32.

With reference to FIG. 2, in some embodiments a zone 34 is isolated by placement, setting (initial and or final), and expansion 26 of the cement in the annulus 22. The compression and bonding can be maintained during dimensional change 32, e.g., so that the zone 34 remains in isolation and does not fluidly communicate via the annulus 22 with other zones in the formation.

As shown in FIGs. 2 and 3, in embodiments the cement slurry comprises an amount of expanding agent sufficient to form the expanded set cement transversely compressed between (due to expansion 26) and bonded to, the first tubular member (tubular body) 24 and the borehole wall, or the first tubular member (tubular body) 24 and the second tubular member (tubular body) 30.

As shown in FIG. 2, in embodiments, the bonds between the first tubular body 24 and the expanded set cement, and between the borehole wall and the expanded set cement are each sufficient to be acoustically coupled and/or to isolate a zone 34 of the formation adjacent the expanded set cement, e.g., from another zone. In some embodiments, the compression 26 and bonding can be maintained during dimensional change 32, e.g., so that the zone 34 remains in isolation and does not fluidly communicate via the annulus 22 with other zones.

In some embodiments, as shown in FIG. 1A, the capsules 2 comprise or consist essentially of a single-core configuration, in which the expanding agent is arranged as a single core 4 at least partially surrounded by the initially impermeable shell 6, which is activated by a pH change for permeation and entry of water into the core, as illustrated in FIGs. 1B and 1C. In some embodiments, as shown in FIG. 4, the capsules 106 may comprise or consist essentially of capsules having a "matrix-island" configuration in which portions of the expanding agent 108 are dispersed as a discontinuous phase within the continuous material of the shell 110. In some embodiments, the capsules may comprise a mixture of one or more types of the single-core capsules (FIGs. 1A, 1B, 1C) and/or one or more types of the "matrix-island" configuration (FIG. 4), and/or the capsules may be a "hybrid" of large-core expanding material particles as well as smaller dispersed expanding material particles within the same shell (not shown).

In some embodiments, core-shell type particles can release or expose the encapsulated expanding agent, e.g., all at once, if the shell is ruptured, which can occur mechanically and/or by chemical degradation. As used herein, "rupture" refers to any loss of integrity of the shell whether by tearing, bursting, and so forth. Matrix-island type cores can release the islands of expanding agent upon chemical degradation and/or solubility of the matrix.

In some embodiments, although the rates of water infiltration, release of encapsulated expanding agent, and expansion of the cement may be predicted, the infiltration, release, and expansion profiles can also be observed in laboratory experiments before the particles are used. Such experiments involve exposing a sample quantity of the particles to conditions of pH and temperature which match those found in the borehole location and monitoring water infiltration and/or release of expanding agent over time, and/or formulating the cement slurry with the encapsulated particles and monitoring the expansion of the set cement upon exposure to the matching borehole conditions.

In embodiments, the initial set time and final set time for a cement slurry according to embodiments disclosed herein may be determined according to ASTM C191-04a. This may be done at standard temperatures, or at temperatures expected downhole. The expansion properties of the cement slurry upon setting may then be evaluated according to API-10B-5. The amount of expansion of the cement slurry prior to the initial set time may be determined, along with the amount of the expansion after the initial set time but before the final set time. Then the total amount of expansion of the expanded set cement may be determined.

In embodiments, the shell is selected such that the amount of expansion which occurs prior to the initial set time (according to ASTM C191-04a) is less than 1%, or less than 5%, or less than 10%, or less than 20%, or less than 30%, or less than 40%, or less than 50% of the total amount of expansion obtained by the set cement determined according to API-10B-5. In embodiments, the amount of expansion (according to API-10B-5) obtained after the initial set time but before the final set time of the cement slurry (according to ASTM C191-04a) is greater than about 50%, or greater than about 60%, or greater than about 70%, or greater than about 80%, or greater than about 90%, or greater than about 95% of the total amount of expansion obtained by the expanded set cement.

Utilizing this test, the attributes of the shell may be determined to meet requirements of a particular cementing operation.

The expanding agent may be encapsulated according to methods known in the art. Examples of documents which describe encapsulation procedures include US 3,952,741, US 4,741,401, US 4,986,354, WO 1993/0022537, WO 2003/0106809, and WO 2010/0140032, which are hereby incorporated by reference. The expanding agents are generally hydrophilic and/or water soluble and can, for example, be encapsulated in a double emulsion technique by (i) dissolving the encapsulating polymer in organic solvent, (ii) suspending the agent in particulated or powder form in the organic solution of the polymer, (iii) dispersing the resulting suspension in water, to form an emulsion in which the disperse phase is droplets of the organic solvent with agent particles suspended within these droplets, and (iv) stirring or otherwise agitating that emulsion while causing or allowing evaporation of the organic solvent, thereby forming agent particles in which the expanding agent is enclosed within a shell of the polymer. The particles can be recovered by filtration, washed, dried and stored until required for use.

Another manufacturing technique that is available involves the production of particles with an expanding agent encapsulated within an inorganic matrix, a polymer matrix, or a combination thereof. Suitable encapsulation methods include physical coating methods such as atomization coating, co-extrusion, spray coating, and the like, and/or chemical methods including solvent evaporation, phase separation-coacervation, ionic gelation, interfacial polymerization, liposomal vesicallization, sol-gel coating, nano-encapsulation, and the like. For example, in embodiments the expanding agent is mixed with a polymeric encapsulating material, e.g., in a melt or solid mixture, and then formed in discrete capsules (particles) via spray drying, extrusion with subsequent chopping or cutting into the desired lengths, and/or other methods known in the art. In embodiments, the capsules comprise essentially solid particles having an average particle size distribution ranging from about 1 to 100 micrometers.

In embodiments, a system for cementing a subterranean well in an annulus between a casing disposed within a borehole and a formation comprises a cement slurry according to one or more embodiments disclosed herein comprising water, hydraulic cement and a capsules comprising an expanding agent at least partially surrounded by a water permeable shell; and a pumping system to place a stage of the slurry in the annulus.

EMBODIMENTS LISTING

Accordingly, the present disclosure provides the following embodiments, among others:

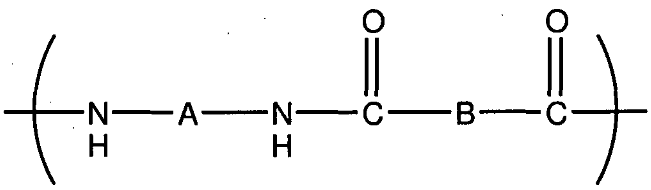
C1. Capsules comprising an expanding agent at least partially surrounded by a shell.

C2. The capsules according to embodiment C1, wherein the shell is essentially impermeable to water at a pH in the range of 6 to 9 below an activating pH of the shell, and wherein the shell becomes water permeable from exposure to at least pH in the range of 10 to 14 greater than the activating pH of the shell.

C3. The capsules according to any one of embodiments C1 or C2, wherein the expanding agent comprises calcium oxide, magnesium oxide, calcium sulfate hemihydrate, or a combination thereof.

C4. The capsules according to any one of embodiments C1 – C3, wherein the shell comprises a polyamide, an inorganic oxide, a polyanhydride, a polyester, a poly(ester anhydride), a polyurethane, a polyether, a poly(ether urethane), a polyvinyl alcohol, a polyvinyl acetate, a polysiloxane, or a combination thereof.

C5. The capsules according to any of embodiments C1 – C4, wherein the shell comprises a polyamide having the general structure:



;

wherein A and B are each selected from the group consisting of:

an aliphatic moiety comprising 1 to 20 carbon atoms;

an alicyclic moiety comprising 3 to 20 carbon atoms;

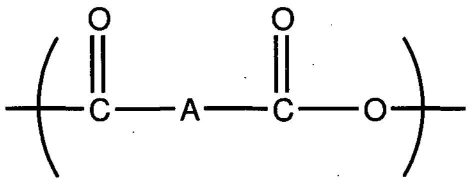
an olefinic moiety comprising 2 to 20 carbon atoms;

an aromatic moiety comprising 6 to 20 carbon atoms, and

combinations thereof.

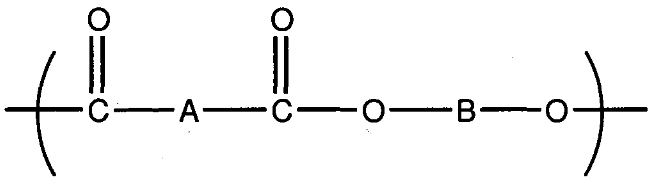
C6. The capsules according to any one of embodiments C1 – C5, wherein the shell comprises nylon 6, nylon 6,6, nylon 6,10, nylon 6,12, nylon 11, nylon 12, or a combination thereof.

C7. The capsules according to any one of embodiments C1 – C6, wherein the shell comprises a polyanhydride having the general structure



;

and/or a poly(ester anhydride) having the general structure:



;

wherein A and B are each selected from the group consisting of:

an aliphatic moiety comprising 1 to 20 carbon atoms;

an alicyclic moiety comprising 3 to 20 carbon atoms;

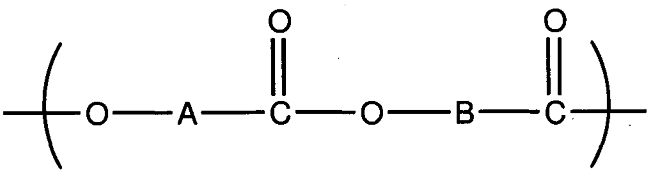
an olefinic moiety comprising 2 to 20 carbon atoms;

an aromatic moiety comprising 6 to 20 carbon atoms, and

combinations thereof.

C8. The capsules according to any one of embodiments C1 – C7, wherein the shell comprises a polyadipic anhydride moiety, a polysuberic anhydride moiety, a polysebacic anhydride moiety, or a combination thereof.

C9. The capsules according to any one of embodiments C1 – C8, wherein the shell comprises a polyester having the general structure


;

wherein A and B are each selected from the group consisting of:

an aliphatic moiety comprising 1 to 20 carbon atoms;

an alicyclic moiety comprising 3 to 20 carbon atoms;

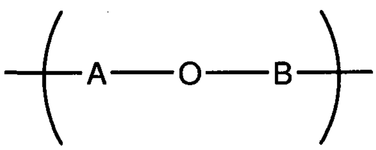
an olefinic moiety comprising 2 to 20 carbon atoms;

an aromatic moiety comprising 6 to 20 carbon atoms, and

combinations thereof.

C10. The capsules according to any one of embodiments C1 – C9, wherein the shell comprises poly-glycolic acid, poly-lactic acid-c-glycolic acid, poly-L-lactic acid, poly-L/D-lactic acid, poly-L/D-lactide-co-glycolic acid, polyethylene terephthalate, or a combination thereof.

C11. The capsules according to any one of embodiments C1 – C10, wherein the shell comprises a polyether having the general structure:


;

wherein A and B are each selected from the group consisting of:

an aliphatic moiety comprising 1 to 20 carbon atoms;

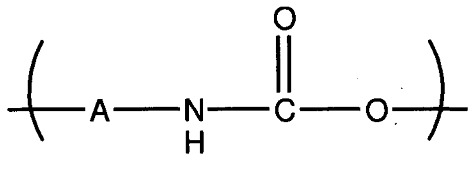
an alicyclic moiety comprising 3 to 20 carbon atoms;

an olefinic moiety comprising 2 to 20 carbon atoms;

an aromatic moiety comprising 6 to 20 carbon atoms, and

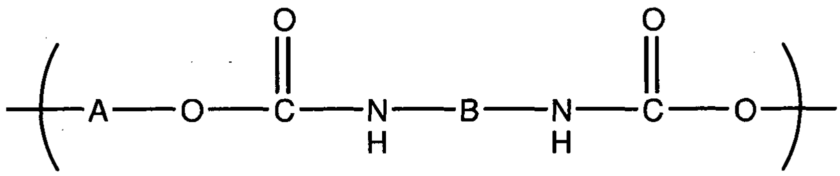
combinations thereof.

C12. The capsules according to any one of embodiments C1 – C11, wherein the shell comprises a polyurethane having the general structure:



;

and/or a poly(ether urethane) having the general structure:



wherein A and B are each selected from the group consisting of:

an aliphatic moiety comprising 1 to 20 carbon atoms;

an alicyclic moiety comprising 3 to 20 carbon atoms;

an olefinic moiety comprising 2 to 20 carbon atoms;

an aromatic moiety comprising 6 to 20 carbon atoms, and

combinations thereof.

C13. The capsules according to any one of embodiments C1 – C12 in an aqueous medium at a pH below the activation pH.

C14. The capsules according to any one of embodiments C1 – C12 in a cement slurry comprising hydraulic cement and water at a pH above the activation pH, wherein the expanding agent is present in the cement slurry at a concentration between 0.1 weight percent and 30 weight percent, based on the total weight of the hydraulic cement present.

C15. The capsules according to any one of embodiments C1 – C12 in a dry blend with hydraulic cement.

E1. A method to cement a subterranean well having a borehole disposed through a formation, comprising:

i) preparing a cement slurry comprising water, hydraulic cement, and the capsules according to any one of embodiments C1 – C12;

(ii) placing the slurry in an annular region of the well between a first tubular body and a borehole wall, or between the first tubular body and a second tubular body;

(iii) hardening the slurry to form an at least partially set cement; and

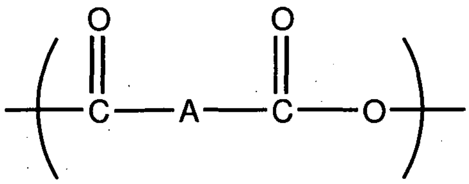
(iv) hydrating and expanding the expanding agent to form an expanded set cement within the annular region.

E2. The method according to embodiment E1 wherein the cement slurry comprises a pH above the activating pH.

E3. The method according to embodiment E1 or E2, wherein the expanding agent comprises calcium oxide, magnesium oxide, calcium sulfate hemihydrate, or combinations thereof.

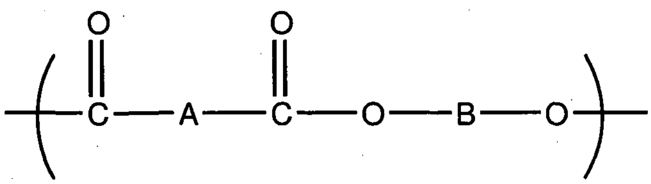
E4. The method according to any one of embodiments E1 – E3, wherein the shell comprises a polyamide, a polyanhydride, a polyester, a poly(ester anhydride), a polyurethane, a polyether, a poly(ether urethane), a polyvinyl alcohol, a polyvinyl acetate, a polysiloxane, or a combination thereof.

E5. The method according to any one of embodiments E1 – E4, wherein the shell comprises a polyanhydride having the general structure



;

and/or a poly(ester anhydride) having the general structure:



;

wherein A and B are each selected from the group consisting of:

an aliphatic moiety comprising 1 to 20 carbon atoms;

an alicyclic moiety comprising 3 to 20 carbon atoms;

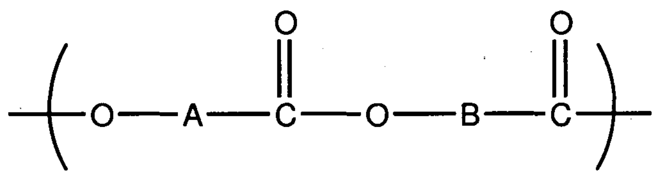
an olefinic moiety comprising 2 to 20 carbon atoms;

an aromatic moiety comprising 6 to 20 carbon atoms, and

combinations thereof.

E6. The method according to any one of embodiments E1 – E5, wherein the shell comprises a polyadipic anhydride moiety, a polysuberic anhydride moiety, a polysebacic anhydride moiety, or a combination thereof.

E7. The method according to any one of embodiments E1 – E6, wherein the shell comprises a polyester having the general structure



;

wherein A and B are each selected from the group consisting of:

an aliphatic moiety comprising 1 to 20 carbon atoms;

an alicyclic moiety comprising 3 to 20 carbon atoms;

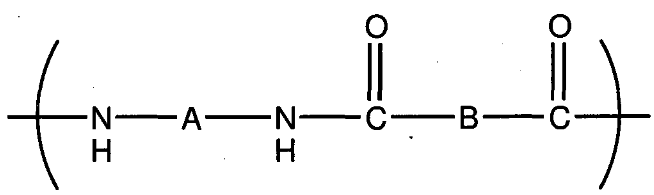
an olefinic moiety comprising 2 to 20 carbon atoms;

an aromatic moiety comprising 6 to 20 carbon atoms, and

combinations thereof.

E8. The method according to any one of embodiments E1 – E7, wherein the shell comprises poly-glycolic acid, poly-lactic acid-c-glycolic acid, poly-L-lactic acid, poly-L/D-lactic acid, poly-L/D-lactide-co-glycolic acid, polyethylene terephthalate, or a combination thereof.

E9. The method according to any one of embodiments E1 – E8, wherein the shell comprises a polyamide having the general structure:



;

wherein A and B are each selected from the group consisting of:

an aliphatic moiety comprising 1 to 20 carbon atoms;

an alicyclic moiety comprising 3 to 20 carbon atoms;

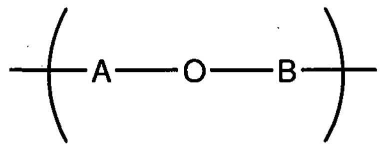
an olefinic moiety comprising 2 to 20 carbon atoms;

an aromatic moiety comprising 6 to 20 carbon atoms, and

combinations thereof.

E10. The method according to any one of embodiments E1 – E9, wherein the shell comprises nylon 6, nylon 6,6, nylon 6,10, nylon 6,12, nylon 11, nylon 12, or a combination thereof.

E11. The method according to any one of embodiments E1 – E10, wherein the shell comprises a polyether having the general structure:



;

wherein A and B are each selected from the group consisting of:

an aliphatic moiety comprising 1 to 20 carbon atoms;

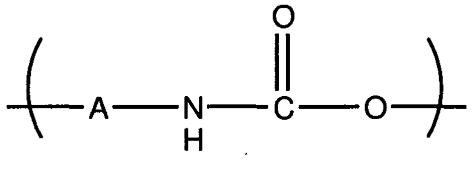
an alicyclic moiety comprising 3 to 20 carbon atoms;

an olefinic moiety comprising 2 to 20 carbon atoms;

an aromatic moiety comprising 6 to 20 carbon atoms, and

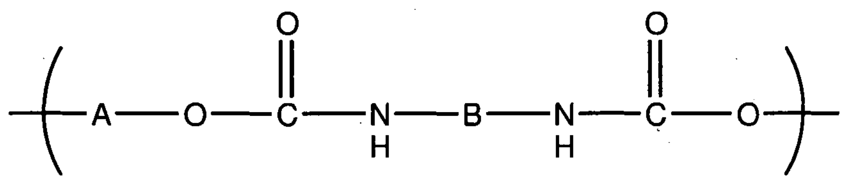
combinations thereof.

E12. The method according to any one of embodiments E1 – E11, wherein the shell comprises a polyurethane having the general structure:



;

and/or a poly(ether urethane) having the general structure:



wherein A and B are each selected from the group consisting of:

an aliphatic moiety comprising 1 to 20 carbon atoms;

an alicyclic moiety comprising 3 to 20 carbon atoms;

an olefinic moiety comprising 2 to 20 carbon atoms;

an aromatic moiety comprising 6 to 20 carbon atoms, and

combinations thereof.

E13. The method according to any one of embodiments E1 – E12, wherein the cement slurry comprises an amount of expanding agent sufficient to form the expanded set cement transversely compressed between, and bonded to, the first tubular body and the borehole wall, or the first tubular body and the second tubular body.

E14. The method according to any one of embodiments E1 – E13, further comprising isolating a zone of the formation adjacent the expanded set cement.

E15. The method according to any one of embodiments E1 – E14, wherein the bond between the first tubular body and the expanded set cement and the bond between the borehole wall and the expanded set cement are each sufficient to isolate a zone of the formation adjacent the expanded set cement.

E16. The method according to any one of embodiments E1 – E15, wherein the expanding agent is present in the cement slurry at a concentration between 1 weight percent and 30 weight percent, based on the total weight of hydraulic cement present.

E17. The method according to any one of embodiments E1 – E16, wherein the bond between the first tubular body and the expanded set cement is maintained after fluctuating the dimensions of the first tubular body in response to a temperature change.

E18. The method according to any one of embodiments E1 – E17, wherein the bond between the first tubular body and the expanded set cement is maintained after fluctuating the dimensions of the first tubular body in response to a pressure change.

E19. The method according to any one of embodiments E1 – E18, wherein the bond between the first tubular body and the expanded set cement is maintained after fluctuating the dimensions of the first tubular body in response to a mechanical disturbance resulting from a well intervention.

E20. The method according to any one of embodiments E1 – E19, wherein the bond between the first tubular body and the expanded set cement is maintained after fluctuating the dimensions of the first tubular body in response to the temperature change, the pressure change, the mechanical disturbance resulting from a well intervention, or a combination thereof.

E21. The method according to any one of embodiments E1 – E20, wherein the shell is selected to allow less than 50% relative expansion, based on a total percent expansion of the expanded set cement determined according to API-10B-5, prior to an initial set time for the cement slurry determined according to ASTM C191-04a, and greater than 50% relative expansion, based on the total percent expansion of the expanded set cement after the initial set time for the cement slurry.

E22. The method according to any one of embodiments E1 – E21 wherein greater than 50% relative expansion, based on a total percent expansion of the expanded set cement determined according to API-10B-5, occurs before a final set time for the cement slurry, determined according to ASTM C191-04a.

E23. The method according to any one of embodiments E1 – E22, wherein the shell is selected to allow less than 50% relative expansion, based on a total percent expansion of the expanded set cement determined according to API-10B-5, to occur prior to an initial set time for the cement slurry determined according to ASTM C191-04a, and greater than 50% relative expansion to occur after the initial set time for the cement slurry.

S1. A system for cementing a subterranean well in an annulus between a casing disposed within a borehole and a formation comprising the capsules in the cement slurry according to embodiment C14.

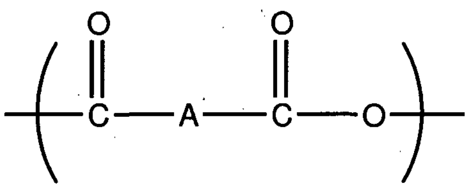
S2. The system of embodiment S1, further comprising a pumping system to place the cement slurry in the annulus.

S3. A system for cementing a subterranean well in an annulus between a casing disposed within a borehole and a formation comprising: a cement slurry comprising water, hydraulic cement and capsules comprising an expanding agent at least partially surrounded by a shell which becomes water permeable at a pH greater than about 10 to allow infiltration of a portion of the water into the capsules hydrating the expanding agent thereby expanding the expanding agent to form an expanded set cement; and a pumping system suitable to position the cement slurry in the annulus.

S4. The system according to any one of embodiments S1 – S3, wherein the expanding agent comprises calcium oxide, magnesium oxide, calcium sulfate hemihydrate, or combinations thereof.

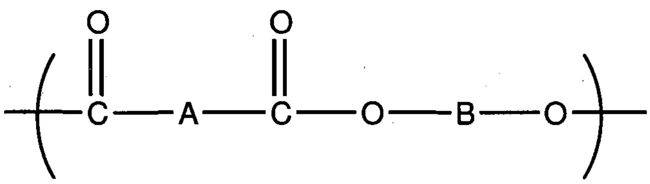
S5. The system according to any one of embodiments S1 – S4, wherein the shell comprises a polyanhydride, a polyester, a poly(ester anhydride), a polyamide, a polyurethane, a polyether, a poly(ether urethane), a polyvinyl alcohol, a polyvinyl acetate, a polysiloxane, or a combination thereof.

S6. The system according to any one of embodiments S1 – S5, wherein the shell comprises a polyanhydride having the general structure



;

and/or a poly(ester anhydride) having the general structure:



;

wherein A and B are each selected from the group consisting of:

an aliphatic moiety comprising 1 to 20 carbon atoms;

an alicyclic moiety comprising 3 to 20 carbon atoms;

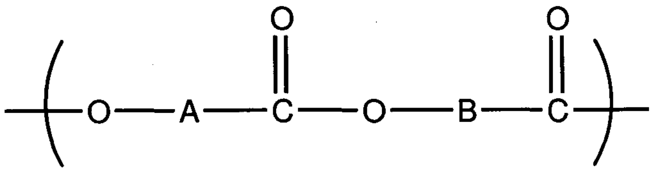
an olefinic moiety comprising 2 to 20 carbon atoms;

an aromatic moiety comprising 6 to 20 carbon atoms, and

combinations thereof.

S7. The system according to any one of embodiments S1 – S6, wherein the shell comprises a polyadipic anhydride moiety, a polysuberic anhydride moiety, a polysebacic anhydride moiety, or a combination thereof.

S8. The system according to any one of embodiments S1 – S7, wherein the shell comprises a polyester having the general structure



;

wherein A and B are each selected from the group consisting of:

an aliphatic moiety comprising 1 to 20 carbon atoms;

an alicyclic moiety comprising 3 to 20 carbon atoms;

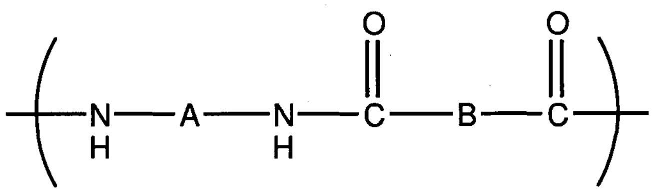
an olefinic moiety comprising 2 to 20 carbon atoms;

an aromatic moiety comprising 6 to 20 carbon atoms, and

combinations thereof.

S9. The system according to any one of embodiments S1 – S8, wherein the shell comprises poly-glycolic acid, poly-lactic acid-c-glycolic acid, poly-L-lactic acid, poly-L/D-lactic acid, poly-L/D-lactide-co-glycolic acid, polyethylene terephthalate, or a combination thereof.

S10. The system according to any one of embodiments S1 – S9, wherein the shell comprises a polyamide having the general structure:



;

wherein A and B are each selected from the group consisting of:

an aliphatic moiety comprising 1 to 20 carbon atoms;

an alicyclic moiety comprising 3 to 20 carbon atoms;

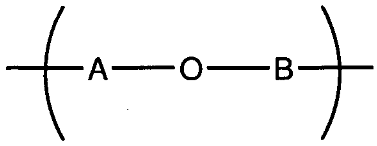
an olefinic moiety comprising 2 to 20 carbon atoms;

an aromatic moiety comprising 6 to 20 carbon atoms, and

combinations thereof.

S11. The system according to any one of embodiments S1 – S10, wherein the shell comprises nylon 6, nylon 6,6, nylon 6,10, nylon 6,12, nylon 11, nylon 12, or a combination thereof.

S12. The system according to any one of embodiments S1 – S11, wherein the shell comprises a polyether having the general structure:


;

wherein A and B are each selected from the group consisting of:

an aliphatic moiety comprising 1 to 20 carbon atoms;

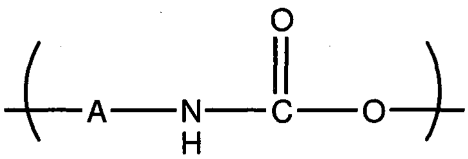
an alicyclic moiety comprising 3 to 20 carbon atoms;

an olefinic moiety comprising 2 to 20 carbon atoms;

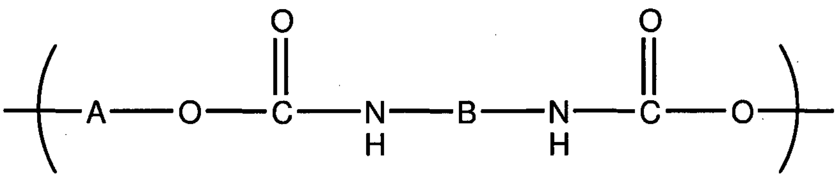
an aromatic moiety comprising 6 to 20 carbon atoms, and

combinations thereof.

S13. The system according to any one of embodiments S1 – S12, wherein the shell comprises a polyurethane having the general structure:


;

and/or a poly(ether urethane) having the general structure:



wherein A and B are each selected from the group consisting of:

an aliphatic moiety comprising 1 to 20 carbon atoms;

an alicyclic moiety comprising 3 to 20 carbon atoms;

an olefinic moiety comprising 2 to 20 carbon atoms;

an aromatic moiety comprising 6 to 20 carbon atoms, and

combinations thereof.

S14. The system according to any one of embodiments S1 – S13, wherein the cement slurry comprises an amount of expanding agent sufficient to form the expanded set cement transversely compressed between, and bonded to, the first tubular body and the borehole wall, or the first tubular body and the second tubular body.

S15. The system according to any one of embodiments S1 – S14, wherein the bond between the first tubular body and the expanded set cement and the bond between the borehole wall and the expanded set cement are each sufficient to isolate a zone of the formation adjacent the expanded set cement.

S16. The system according to any one of embodiments S1 – S15, wherein the bond between the first tubular body and the expanded set cement is maintained after fluctuating the dimensions of the first tubular body in response to a temperature change, a pressure change, a mechanical disturbance resulting from a well intervention, or a combination thereof.

S17. The system according to any one of embodiments S1 – S16, wherein the expanding agent is present in the cement slurry at a concentration between 0.1 weight percent and 30 weight percent, based on the total weight of hydraulic cement present.

S18. The system according to any one of embodiments S1 – S17, wherein the shell is selected such that less than 50% relative expansion occurs, based on a total percent expansion of the expanded set cement determined according to API-10B-5, prior to an initial set time for the cement slurry determined according to ASTM C191-04a, and greater than 50% relative expansion of the cement occurs after the initial set time for the cement slurry.

S19. The system according to any one of embodiments S1 – S18, wherein greater than 50% relative expansion of the cement occurs before a final time of setting for the cement slurry, determined according to ASTM C191-04a.

S20. The system according to any one of embodiments S1 – S19, wherein greater than 50% relative expansion of the cement occurs before after a final time of setting for the cement slurry, determined according to ASTM C191-04a.

M1. A method to produce a cement slurry, comprising:

i) combining water and the capsules according to any one of embodiments C1 – C12 to form a first mixture of the capsules in aqueous medium at a pH below the activation pH;

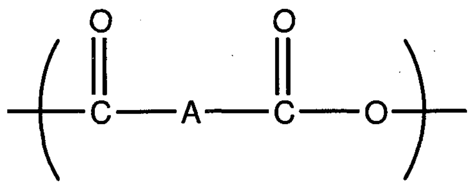
ii) combining the first mixture with hydraulic cement to produce the cement slurry having a pH greater than the activating pH; and

iii) delaying the infiltration.

M2. The method according to embodiment M1, wherein the expanding agent comprises calcium oxide, magnesium oxide, calcium sulfate hemihydrate, or combinations thereof.

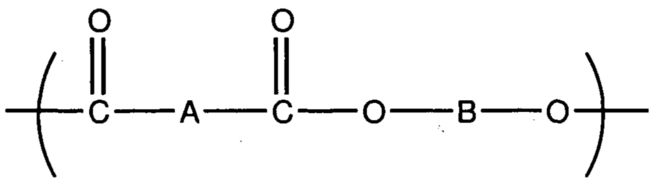
M3. The method according to embodiment M1 or M2, wherein the shell comprises a polyamide, a polyanhydride, a polyester, a poly(ester anhydride), a polyurethane, a polyether, a poly(ether urethane), a polyvinyl alcohol, a polyvinyl acetate, a polycarbonate, a polysiloxane, or a combination thereof.

M4. The method according to any one of embodiments M1 – M3, wherein the shell comprises a polyanhydride having the general structure



;

and/or a poly(ester anhydride) having the general structure:



;

wherein A and B are each selected from the group consisting of:

an aliphatic moiety comprising 1 to 20 carbon atoms;

an alicyclic moiety comprising 3 to 20 carbon atoms;

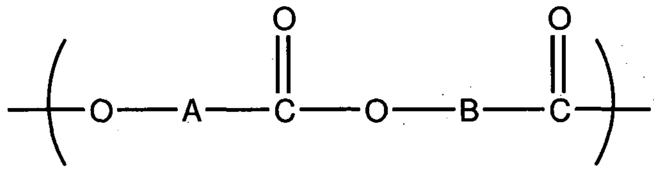
an olefinic moiety comprising 2 to 20 carbon atoms;

an aromatic moiety comprising 6 to 20 carbon atoms, and

combinations thereof.

M5. The method according to any one of embodiments M1 – M4, wherein the shell comprises a polyadipic anhydride moiety, a polysuberic anhydride moiety, a polysebacic anhydride moiety, or a combination thereof.

M6. The method according to any one of embodiments M1 – M5, wherein the shell comprises a polyester having the general structure



;

wherein A and B are each selected from the group consisting of:

an aliphatic moiety comprising 1 to 20 carbon atoms;

an alicyclic moiety comprising 3 to 20 carbon atoms;

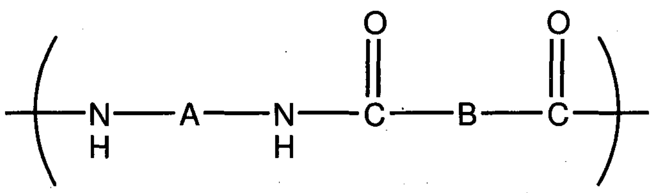
an olefinic moiety comprising 2 to 20 carbon atoms;

an aromatic moiety comprising 6 to 20 carbon atoms, and

combinations thereof.

M7. The method according to any one of embodiments M1 – M6, wherein the shell comprises poly-glycolic acid, poly-lactic acid-c-glycolic acid, poly-L-lactic acid, poly-L/D-lactic acid, poly-L/D-lactide-co-glycolic acid, polyethylene terephthalate, or a combination thereof.

M8. The method according to any one of embodiments M1 – M7, wherein the shell comprises a polyamide having the general structure:



;

wherein A and B are each selected from the group consisting of:

an aliphatic moiety comprising 1 to 20 carbon atoms;

an alicyclic moiety comprising 3 to 20 carbon atoms;

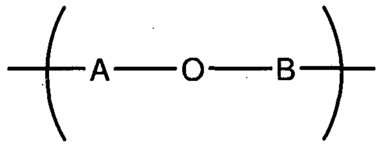
an olefinic moiety comprising 2 to 20 carbon atoms;

an aromatic moiety comprising 6 to 20 carbon atoms, and

combinations thereof.

M9. The method according to any one of embodiments M1 – M8, wherein the shell comprises nylon 6, nylon 6,6, nylon 6,10, nylon 6,12, nylon 11, nylon 12, or a combination thereof.

M10. The method according to any one of embodiments M1 – M9, wherein the shell comprises a polyether having the general structure:



;

wherein A and B are each selected from the group consisting of:

an aliphatic moiety comprising 1 to 20 carbon atoms;

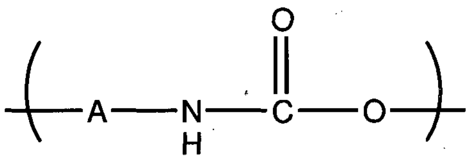
an alicyclic moiety comprising 3 to 20 carbon atoms;

an olefinic moiety comprising 2 to 20 carbon atoms;

an aromatic moiety comprising 6 to 20 carbon atoms, and

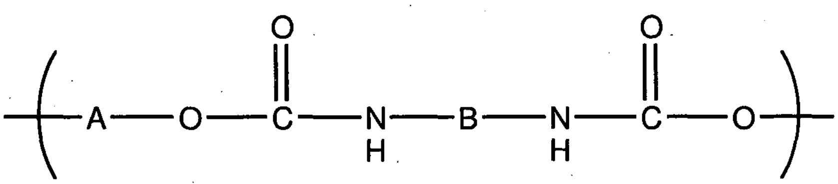
combinations thereof.

M11. The method according to any one of embodiments M1 – M10, wherein the shell comprises a polyurethane having the general structure:



;

and/or a poly(ether urethane) having the general structure:



wherein A and B are each selected from the group consisting of:

an aliphatic moiety comprising 1 to 20 carbon atoms;

an alicyclic moiety comprising 3 to 20 carbon atoms;

an olefinic moiety comprising 2 to 20 carbon atoms;

an aromatic moiety comprising 6 to 20 carbon atoms, and

combinations thereof.

M12. The method according to any one of embodiments M1 – M11, wherein the cement slurry comprises an amount of expanding agent sufficient to form the expanded set cement transversely compressed between, and bonded to, a first tubular body and the borehole wall, or a first tubular body and a second tubular body.

M13. The method according to any one of embodiments M1 – M12, wherein the expanding agent is present in the cement slurry at a concentration between 0.1 weight percent and 30 weight percent, based on the total weight of hydraulic cement present.

M14. The method according to any one of embodiments M1 – M13, wherein the shell is selected such that less than 50% relative expansion occurs, based on a total percent expansion of the expanded set cement determined according to API-10B-5, prior to an initial set time for the cement slurry determined according to ASTM C191-04a, and greater than 50% relative expansion of the cement occurs after the initial set time for the cement slurry.

M15. The method according to any one of embodiments M1 – M14, wherein greater than 50% relative expansion of the cement occurs before a final time of setting for the cement slurry, determined according to ASTM C191-04a.

M16. The method according to any one of embodiments M1 – M14, wherein greater than 50% relative expansion of the cement occurs before after a final time of setting for the cement slurry, determined according to ASTM C191-04a.

EXAMPLES

The following examples are provided to more fully illustrate the disclosure. These examples are not intended to limit the scope of the disclosure in any way.

To measure the effects of expanding agents under confined conditions, a temperature-controlled confinement cell as shown in FIG. 5 was employed. Radial confinement is provided by a hollow steel cylinder **201** with ID = 2.86 cm (1.125 in.) and OD = 7.62 cm (3 in.). The cylinder is sealed at the bottom with a removable metallic plug **202** that screws into the bottom and seals with two O-rings. This cell is designed such that the axial confinement from the top is provided by a piston **207** that slides easily inside the steel cylinder and is connected by a rod **209** to a programmable mechanical testing machine with a 5-kN load cell.

The steel cylinder can be screwed inside a heating/insulator chamber **203** where a glycol bath is heated up with a resistance heater **204**. Tests can be performed at temperatures between room temperature and about 95°C. The upper limit is defined by the inability to prevent water escaping from the cement as vapor, since the device is not pressure-tight. Two thermocouples are placed near the heater and near the cement sample. They are connected to the heater power supply box and are used to maintain a fixed set-point temperature.

Two general modes of operation can be used with the expansion cell: fixed displacement of the piston (in which case the compressive load is measured) and fixed load applied to the piston (in which case the displacement of the piston is measured). The experiments here are conducted in fixed displacement mode.

To simulate hydration of cement placed against a permeable formation containing water, a porous ceramic disk **205** saturated with water can be placed on top of the cement sample **206**, with a layer of filter paper between to keep the disk clean. The piston is then inserted into the cylinder until it makes contact with the porous disk. Additional water **208** is poured on top of the piston, and then finally a layer of high-boiling-point silicon oil is added to prevent evaporation of the water. Holes in the piston allow water access between the sample and borehole. As the cement and expanding agent react, volume lost to chemical shrinkage is replaced by external water flowing into the slurry from above, keeping the pores of the sample saturated. To simulate hydration of cement placed against a tight formation that supplies no water to the cement, the piston is placed directly in contact with the cement and a thick layer of lubricant is used to prevent water evaporation from the specimen. In this case, chemical shrinkage desaturates the pore system, causing some shrinkage that may not have been compensated by the encapsulated expanding agent.

Figure 6A qualitatively compares the hydration profiles of an untreated expanding agent and an encapsulated (delayed) expanding agent. The delay is tuned to the cement setting time, indicated by the dashed vertical line. The kinetics remains similar once the expanding agent is released. With the non-encapsulated (untreated) expanding agent, hydration of the expanding agent begins essentially on contact with water. The majority of the hydration occurs before the cement starts setting.

The expansion of the cement generates stress in the cement only after the cement has started setting (after the initial set time). Figure 6B qualitatively shows the measured compressive stress for the two systems, a comparative untreated (non-encapsulated) expanding agent and an encapsulated (delayed) expanding agent according to embodiments disclosed herein. The initial set time of the cement is qualitatively observed in the figure as the time when stress starts being measured. Other means of determining the initial set time include consistency (viscosity), calorimetry since the cement setting reaction is exothermic, and the like. In this example, over 70% of the untreated expanding agent has been hydrated before the cement began setting. Accordingly, in the absence of encapsulation, only 30% of the expanding agent is available to contribute to forming compressive stress within the cement as it sets within the confined space of the annulus. In contrast, the inventive encapsulated (delayed) expanding agent shows essentially no hydration of the expanding agent until after the cement begins to set. Accordingly, in the inventive example, essentially 100% of the expanding agent is available for hydration and thus essentially 100% of the expanding agent is able to generate compressive stress within the cement as it sets within the confined space of the annulus, as displayed in Figure 6B.

Examples 1 and 2 – poly lactic-acid degradation

Experiments showing the effect of water contacting the expanding agent were conducted. Storage of the expanding agent may result in contact with water due to storage in humid conditions or due to premixing with the mix water. In the example shown in FIG. 7 two identical formulations were compared containing an expanding agent (MgO/CaO mixture), detailed in Table 1. These data show a properly stored material Example 1 (slurry A), compared to an expanding agent which had been exposed to wet conditions Example 2 (slurry B). As these data show, the slurry viscosity is significantly lower when prepared using the expanding agent that was properly stored in dry conditions. Once the expanding agent contacts water, a significant increase in viscosity occurs.

Table 1: Effect of water on expanding agent

Property/Component	Example 1 - Slurry A Dry expanding agent	Example 2 - Slurry B Wet expanding agent
Slurry density	1900 kg/m3	1900 kg/m3
Class G cement (mass by weight of cement)	100%	100%
Dry MgO/CaO (mass by weight of cement)	5%	-
MgO/CaO exposed to humidity (mass by weight of cement)	-	5%
Antifoam (volume by weight of cement)	4L/t	4L/t
Dispersant (volume by weight of cement)	10L/t	10L/t

Examples 3 and 4 – polylactic-acid degradation

In the following examples, the stability of various encapsulating agents were compared in aqueous solutions having a neutral pH (6.5-7.5) and at a pH of 13, typical of cement slurry formulations.

In Example 3, an aqueous solution of poly lactic-acid (PLA) having a pH of 7 was prepared and allowed to age at 25°C for 1 week. The degradation of the PLA was determined to be less than 0.5 weight percent per week.

In Example 4, an aliquot of the solution used in Example 3 was adjusted to a pH of 13 with $Ca(OH)_2$. The solution was allowed to age at 25°C. Complete degradation of the PLA occurred in less than 45 minutes under these conditions.

Examples 5 and 6 Nylon 6 degradation

As sample of Nylon 6 was aged at 130°C with agitation in an aqueous brine solution at neutral pH (~7). The data are shown in FIG. 9. As these data show, the degradation of Nylon 6 at 130°C is slow, less than 2 weight percent per week.

Another piece of the same Nylon 6 sample was aged in an identical way at a pH of 12.6 (buffered with saturated $Ca(OH)_2$). These data are shown in FIG. 10. As these data show, the degradation of Nylon 6 is much faster at elevated pH with ~68 weight percent degradation after 1 week and complete degradation after 3 weeks under these conditions.

Although only a few example embodiments have been described in detail above, those skilled in the art will readily appreciate that many modifications are possible in the example embodiments without materially departing from this invention. Accordingly, all such modifications are intended to be included within the scope of this disclosure as defined in the following claims. In the claims, means-plus-function clauses are intended to cover the structures described herein as performing the recited function and not only structural equivalents, but also equivalent structures. Thus, although a nail and a screw may not be structural equivalents in that a nail employs a cylindrical surface to secure wooden parts together, whereas a screw employs a helical surface, in the environment of fastening wooden parts, a nail and a screw may be equivalent structures. It is the express intention of the applicant not to invoke 35 U.S.C. § 112 (f) for any limitations of any of the claims herein, except for those in which the claim expressly uses the words 'means for' together with an associated function.

CLAIMS

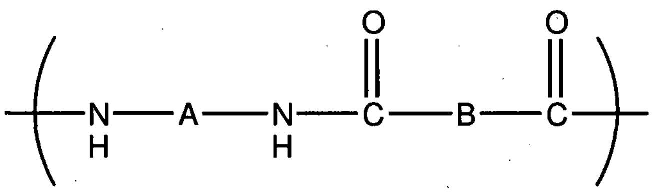
We Claim:

1. Capsules comprising an expanding agent at least partially surrounded by a shell, wherein the shell is essentially impermeable to water at a pH in the range of 6 to 9 below an activating pH of the shell, and wherein the shell becomes water permeable from exposure to at least one pH in the range of 10 to 14 greater than the activating pH of the shell.

2. The capsules according to claim 1, wherein the expanding agent comprises calcium oxide, magnesium oxide, calcium sulfate hemihydrate, or a combination thereof.

3. The capsules according to claim 1 or claim 2, wherein the shell comprises a polyamide, an inorganic oxide, a polyanhydride, a polyester, a poly(ester anhydride), a polyurethane, a polyether, a poly(ether urethane), a polyvinyl alcohol, a polyvinyl acetate, a polycarbonate, a polysiloxane, or a combination thereof.

4. The capsules according to any one of claims 1 to 3, wherein the shell comprises a polyamide having the general structure:



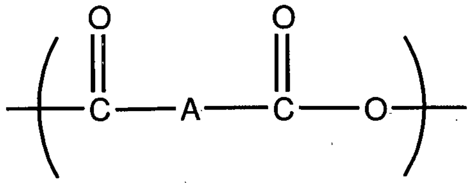
;

wherein A and B are independently selected from the group consisting of:

an aliphatic moiety comprising 1 to 20 carbon atoms;
an alicyclic moiety comprising 3 to 20 carbon atoms;
an olefinic moiety comprising 2 to 20 carbon atoms;
an aromatic moiety comprising 6 to 20 carbon atoms, and
combinations thereof.

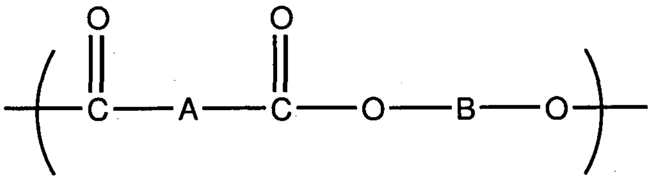
5. The capsules according to any one of claims 1 to 4, wherein the shell comprises nylon 6, nylon 6,6, nylon 6,10, nylon 6,12, nylon 11, nylon 12, or a combination thereof.

6. The capsules according to any one of claims 1 to 5, wherein the shell comprises a polyanhydride having the general structure



;

and/or a poly(ester anhydride) having the general structure:



;

wherein A and B are independently selected from the group consisting of:

aliphatic moieties comprising 1 to 20 carbon atoms;

alicyclic moieties comprising 3 to 20 carbon atoms;

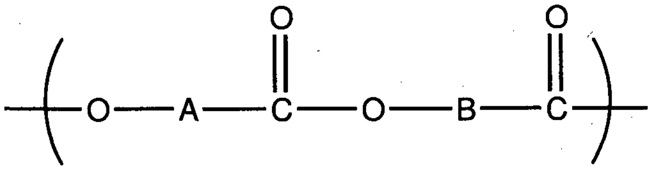
olefinic moieties comprising 2 to 20 carbon atoms;

aromatic moieties comprising 6 to 20 carbon atoms, and

combinations thereof.

7. The capsules according to any one of claims 1 to 6, wherein the shell comprises a polyadipic anhydride moiety, a polysuberic anhydride moiety, a polysebacic anhydride moiety, or a combination thereof.

8. The capsules according to any one of claims 1 to 7, wherein the shell comprises a polyester having the general structure



;

wherein A and B are independently selected from the group consisting of:

an aliphatic moiety comprising 1 to 20 carbon atoms;

an alicyclic moiety comprising 3 to 20 carbon atoms;

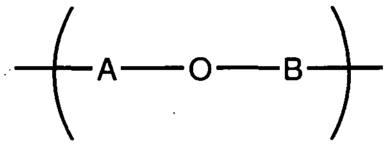
an olefinic moiety comprising 2 to 20 carbon atoms;

an aromatic moiety comprising 6 to 20 carbon atoms, and

combinations thereof.

9. The capsules according to any one of claims 1 to 8, wherein the shell comprises poly-glycolic acid, poly-lactic acid-co-glycolic acid, poly-L-lactic acid, poly-L/D-lactic acid, poly-L/D-lactide-co-glycolic acid, polyethylene terephthalate, or a combination thereof.

10. The capsules according to any one of claims 1 to 9, wherein the shell comprises a polyether having the general structure

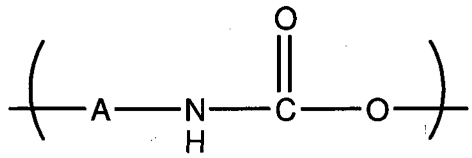


;

wherein A and B are independently selected from the group consisting of:

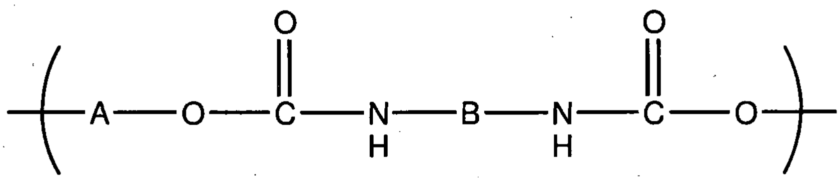
an aliphatic moiety comprising 1 to 20 carbon atoms;
an alicyclic moiety comprising 3 to 20 carbon atoms;
an olefinic moiety comprising 2 to 20 carbon atoms;
an aromatic moiety comprising 6 to 20 carbon atoms, and
combinations thereof.

11. The capsules according to any one of claims 1 to 10, wherein the shell comprises a polyurethane having the general structure:



;

and/or a poly(ether urethane) having the general structure:



wherein A and B are independently selected from the group consisting of:

an aliphatic moiety comprising 1 to 20 carbon atoms;
an alicyclic moiety comprising 3 to 20 carbon atoms;
an olefinic moiety comprising 2 to 20 carbon atoms;

an aromatic moiety comprising 6 to 20 carbon atoms, and combinations thereof.

12. The capsules according to any one of claims 1 to 11 in an aqueous medium at a pH below the activation pH.

13. The capsules according to any one of claims 1 to 11 in a cement slurry comprising hydraulic cement and water at a pH above the activation pH, wherein the expanding agent is present in the cement slurry at a concentration between 0.1 weight percent and 30 weight percent, based on the total weight of the hydraulic cement present.

14. The capsules according to any one of claims 1 to 11 in a dry blend with hydraulic cement.

15. A method to cement a subterranean well having a borehole disposed through a formation, comprising:

(i) preparing a cement slurry comprising water, hydraulic cement, the capsules according to any one of claims 1 to 11, and a pH above the activating pH;

(ii) placing the slurry in an annular region of the well between a first tubular body and a borehole wall, or between the first tubular body and a second tubular body;

(iii) hardening the slurry to form an at least partially set cement; and

(iv) hydrating and expanding the expanding agent to form an expanded set cement within the annular region.

15. The method according to claim 14, wherein the cement slurry comprises an amount of expanding agent sufficient to form the expanded set cement transversely compressed between, and bonded to, the first tubular body and the borehole wall, or the first tubular body and the second tubular body.

16. The method according to claim 14 or claim 15, further comprising isolating a zone of the formation adjacent the expanded set cement.

17. The method according to claim 15 or claim 16, wherein the bond between the first tubular body and the expanded set cement is maintained after fluctuating the dimensions of the

first tubular body in response to a temperature change, a pressure change, a mechanical disturbance resulting from a well intervention, or a combination thereof.

18. The method according to any one of claims 14 to 17, wherein the shell is selected to allow less than 50% relative expansion, based on a total percent expansion of the expanded set cement determined according to API-10B-5, to occur prior to an initial set time for the cement slurry determined according to ASTM C191-04a, and greater than 50% relative expansion, based on the total percent expansion of the expanded set cement determined according to API-10B-5, to occur after the initial set time for the cement slurry determined according to ASTM C191-04a.

19. A system for cementing a subterranean well in an annulus between a casing disposed within a borehole and a formation, comprising: the capsules in the cement slurry according to claim 13; and a pumping system to place the cement slurry in the annulus.

20. A method to produce a cement slurry, comprising:

combining water and the capsules according to any one of claims 1 to 11 to form a first mixture of the capsules in aqueous medium at a pH below the activation pH;

combining the first mixture with hydraulic cement to produce the cement slurry having a pH greater than the activating pH; and

delaying the infiltration.

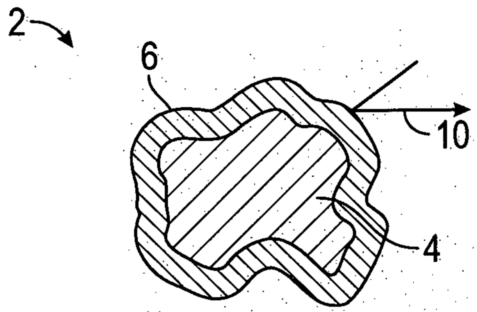


FIG. 1A

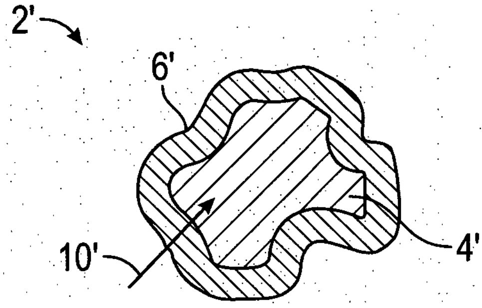


FIG. 1B

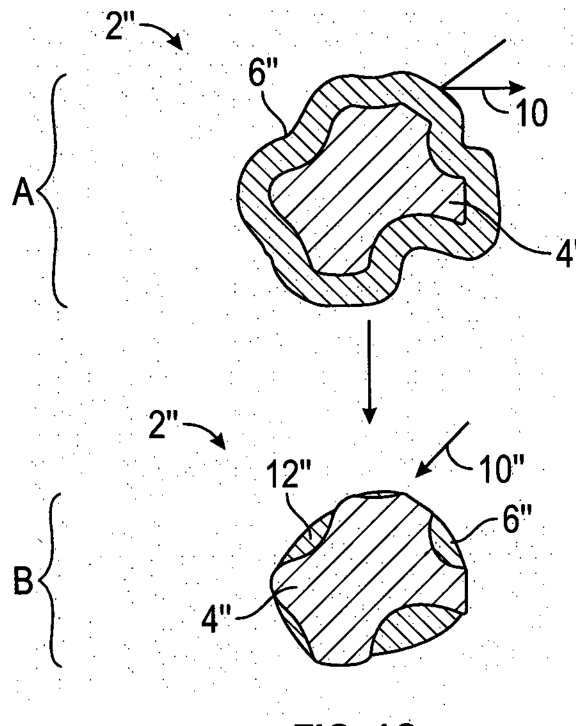


FIG. 1C

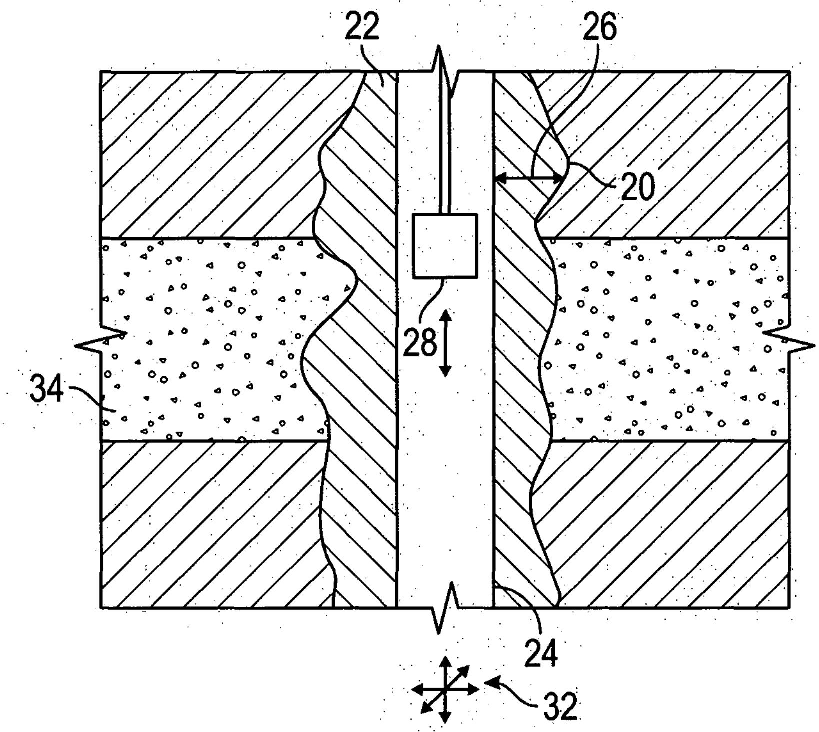


FIG. 2

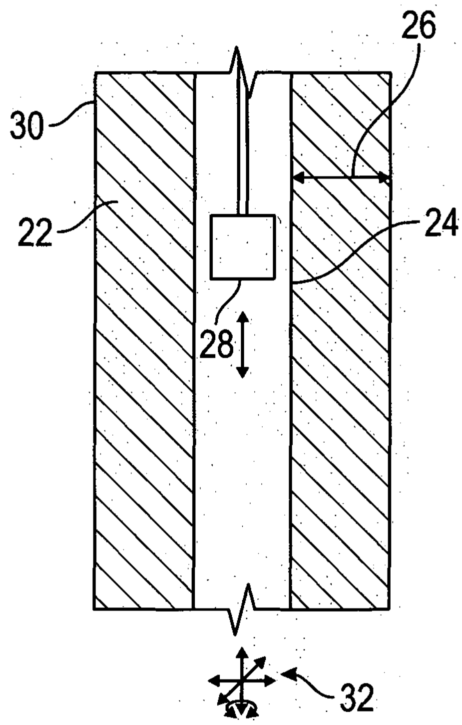


FIG. 3

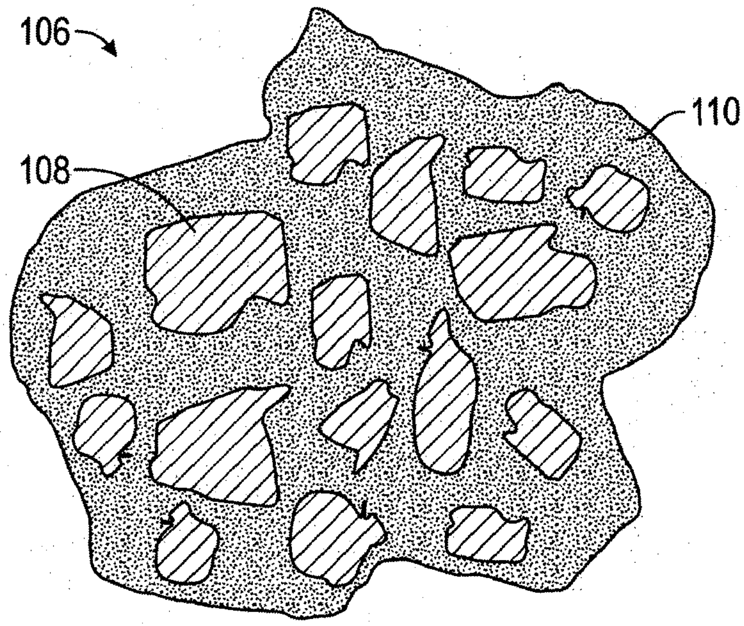


FIG. 4

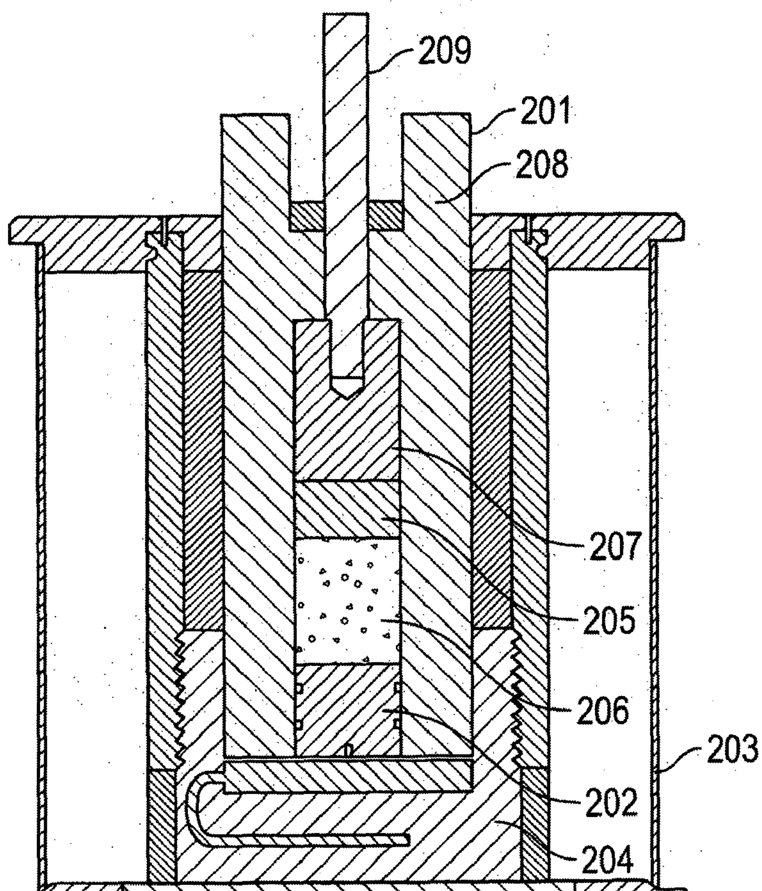


FIG. 5

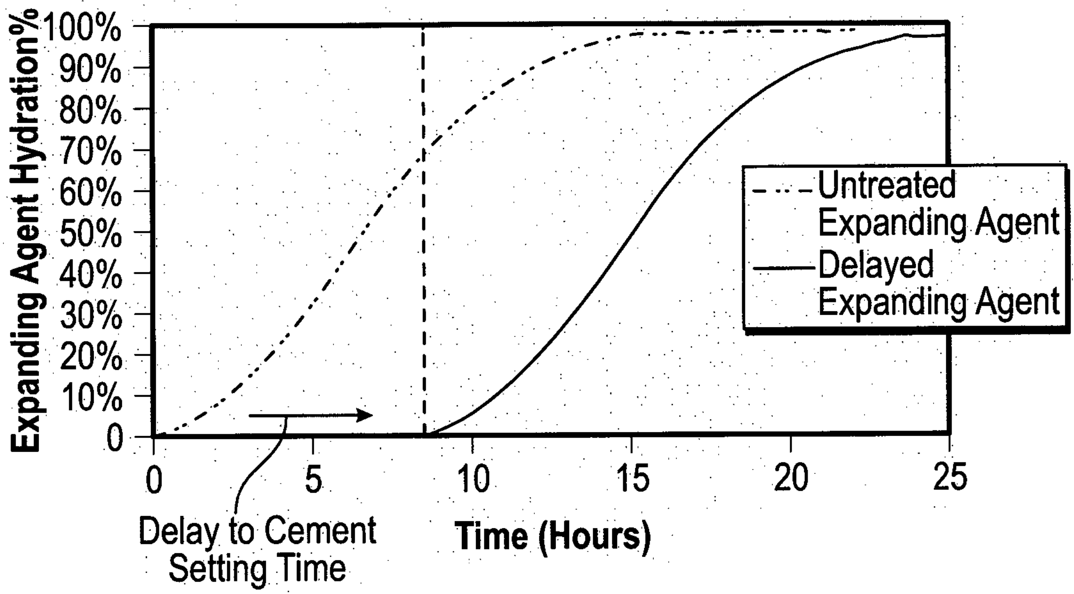

Expanding Agent Hydration%
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0
0
5
10
15
20
25
Untreated
Expanding Agent
Delayed
Expanding Agent
Delay to Cement
Setting Time
Time (Hours)

FIG. 6A

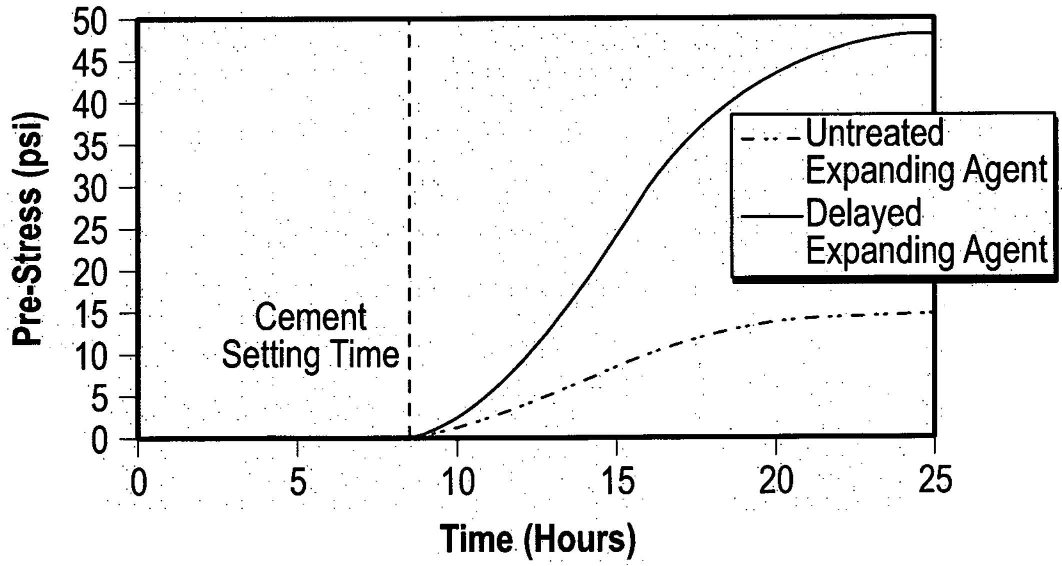
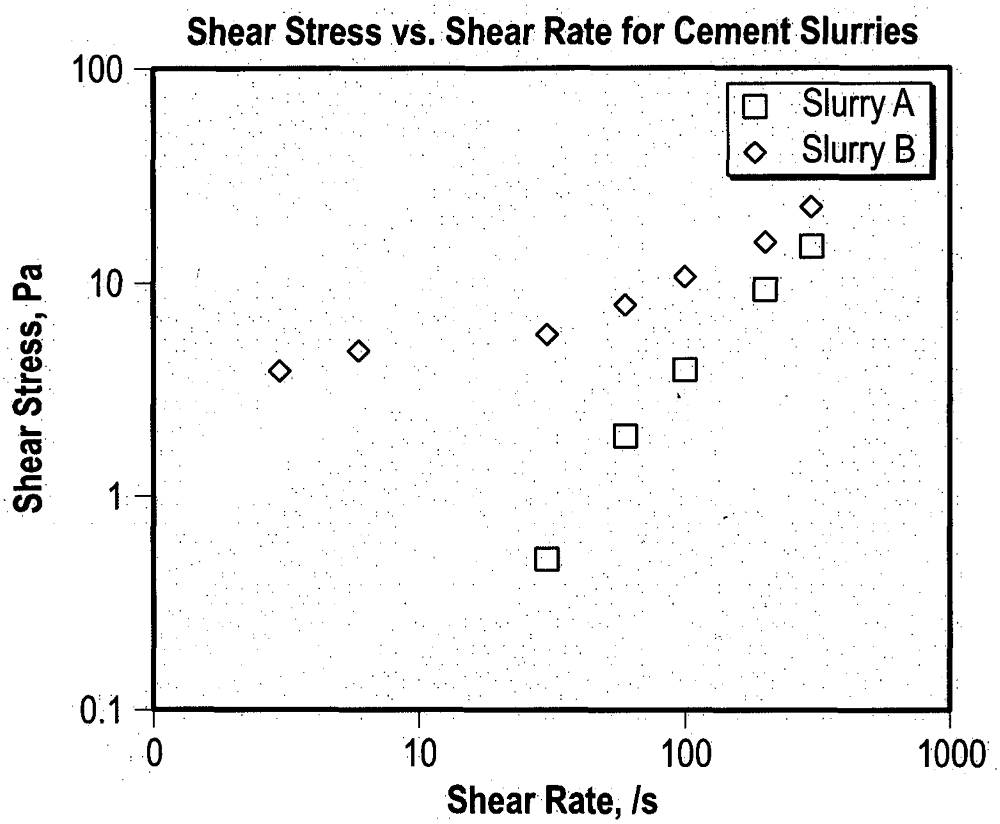
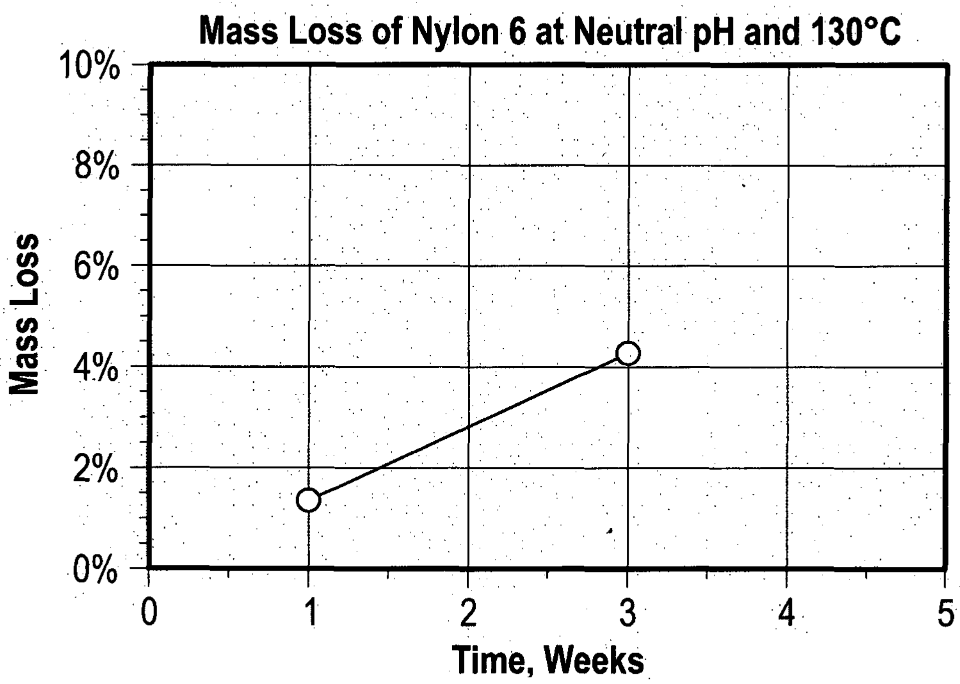

Pre-Stress (psi)
50
45
40
35
30
25
20
15
10
5
0
0
5
10
15
20
25
Untreated
Expanding Agent
Delayed
Expanding Agent
Cement
Setting Time
Time (Hours)

FIG. 6B



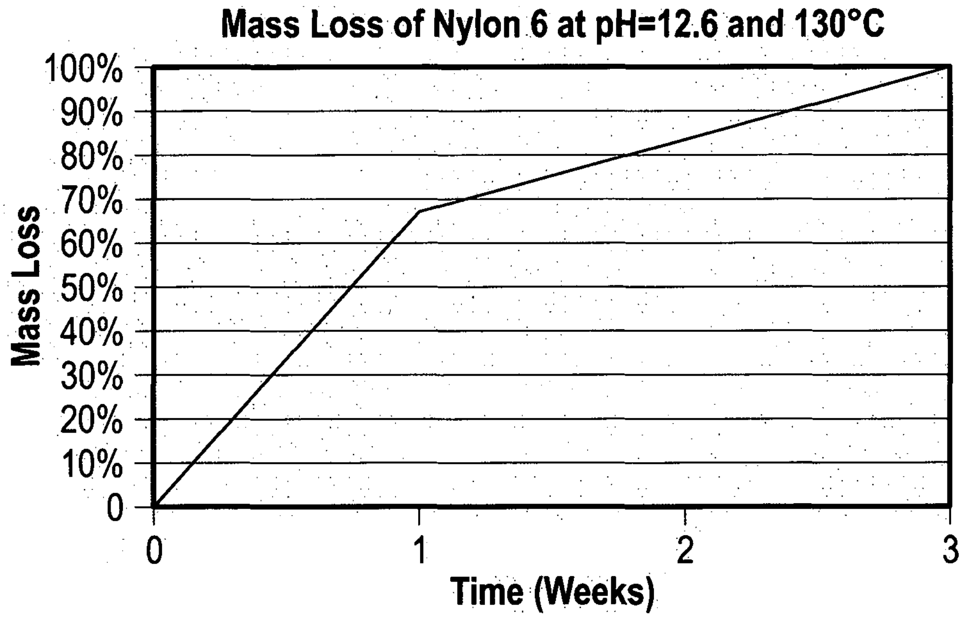
Shear Stress vs. Shear Rate for Cement Slurries
100
10
1
0.1
Shear Stress, Pa
0
10
100
1000
Shear Rate, /s
Slurry A
Slurry B

FIG. 7



Mass Loss of Nylon 6 at Neutral pH and 130°C
10%
8%
6%
4%
2%
0%
Mass Loss
0
1
2
3
4
5
Time, Weeks

FIG. 8



Mass Loss of Nylon 6 at pH=12.6 and 130°C
Mass Loss
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0
0
1
2
3
Time (Weeks)

FIG. 9

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2016/000272

A. CLASSIFICATION OF SUBJECT MATTER
INV. C04B28/02 C04B20/10 C09K8/473
ADD.

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)
C04B C09K

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

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

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2005/167107 A1 (RODDY CRAIG W [US] ET AL) 4 August 2005 (2005-08-04) pages 2,5, paragraphs [0017], [0027], [0020],; claims 17,21 -----	1-13, 15-21
X	DE 37 04 783 A1 (HOERLING LUDWIG CHEM [DE]) 25 August 1988 (1988-08-25) column 1 - column 2; claims 1,2 -----	1,2
X	US 5 650 004 A (YON MICHAEL D [US]) 22 July 1997 (1997-07-22) claim 6 -----	1-3
X	CA 946 427 A (FULLER CO) 30 April 1974 (1974-04-30) pages 4,9; claims 1,3,6 -----	1,2,14
	-/--	

[X] Further documents are listed in the continuation of Box C.

[X] 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

"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	Date of mailing of the international search report
4 November 2016	14/11/2016

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Authorized officer

Philippart, Anahí

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2016/000272

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2013/023949 A2 (EVONIK DEGUSSA GMBH [DE]; KATUSIC STIPAN [DE]; KRESS PETER [DE]; FISCH) 21 February 2013 (2013-02-21) pages 3,13,14; claims 1,6,10,11 -----	1-3
X	US 5 118 527 A (WILSON ALFONZO L [US]) 2 June 1992 (1992-06-02) abstract; claims 2,9 -----	1-3
A	WO 2015/195596 A1 (SCHLUMBERGER SERVICES PETROL [FR]; SCHLUMBERGER CA LTD [CA]; SCHLUMBER) 23 December 2015 (2015-12-23) pages 10,11; claim 1 -----	15
A	US 4 332 619 A (GANDY RICHARD G ET AL) 1 June 1982 (1982-06-01) cited in the application abstract; claims 1,4 -----	1,15-21

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/IB2016/000272

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			DE	2155825	A1	18-05-1972
			FR	2114404	A5	30-06-1972
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			WO	2013023949	A2	21-02-2013
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WO 2015195596	A1	23-12-2015	NONE			
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			US	4332619	A	01-06-1982