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

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
19 January 2017 (19.01.2017)

WIPO | PCT

(10) International Publication Number
WO 2017/011655 A1

(51) International Patent Classification:
C08L 33/18 (2006.01) *C08L 63/00* (2006.01)
C08L 33/02 (2006.01)

(21) International Application Number:
PCT/US2016/042276

(22) International Filing Date:
14 July 2016 (14.07.2016)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
62/192,461 14 July 2015 (14.07.2015) US

(71) Applicant: **WEIR SLURRY GROUP, INC.** [—/US]; 2701 South Stoughton Road, Madison, WI 53716 (US).

(72) Inventor: **LANE, Timothy**; 3459 South 700 West, Salt Lake City, UT 84119 (US).

(74) Agents: **KHATRI, Vishal, V.** et al.; Jones Day, 250 Vesey Street, New York, NY 10281-1047 (US).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, 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.

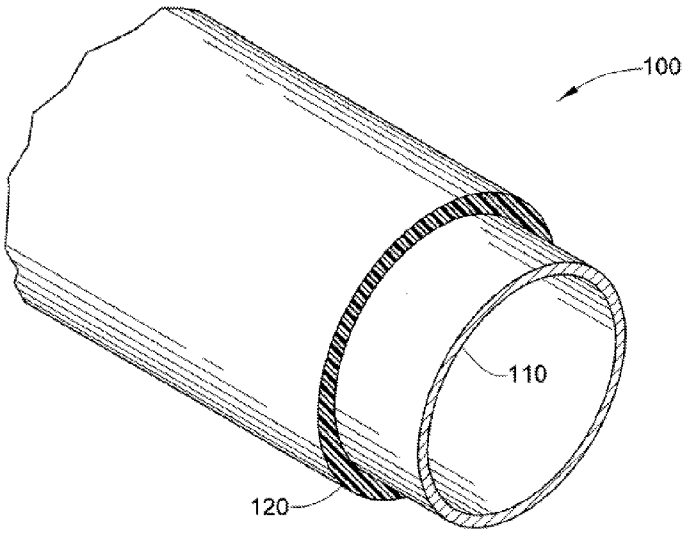
(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK,

[Continued on next page]

WO 2017/011655 A1

(54) Title: SWELLABLE RUBBER COMPOSITIONS

FIG. 1



[Continued on next page]

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))*

(57) Abstract: This disclosure relates to swellable compositions for use with oil and gas field equipment including, for example, swellable packers. Further, the present disclosure also relates to compositions, systems and methods for sealing a region between the wellbore wall and the packer-conduit assembly. The composition comprises a super absorbent polymers, an elastomer; a rubber; a sulfur curing agent; a silica; and a powder super absorbent polymer.

SWELLABLE RUBBER COMPOSITIONS

CROSS REFERENCE TO RELATED APPLICATION

[0001] This application claims the benefit of priority from U.S. Provisional Application No. 62/192,461, filed July 14, 2015. The foregoing related application, in its entirety, is incorporated herein by reference.

FIELD OF THE DISCLOSURE

[0002] The present disclosure relates to swellable rubber compositions and, more particularly, to swellable rubber compositions for use with oil and gas field equipment including, for example, swellable packers. The present disclosure also relates to systems and methods for sealing a region between the wellbore wall and the packer-conduit assembly.

BACKGROUND OF THE DISCLOSURE

[0003] Conventionally, well conduits were cemented into place in the wellbore. However, the use of cement is sometimes not desirable because it may reduce or interfere with the production of the well. With the introduction of non-cemented wells, open hole packers came into use. Initially, the packer designs were mechanical in nature, and, eventually, swellable packers were introduced.

[0004] Swellable packers were initially designed to swell when exposed to oil-based fluids. More recently, swellable packers that swell in the presence of water-based fluids (e.g., brine) are also in use. However, these swellable packers have drawbacks because the rubber composition is not always acceptable for use in wells and/or the rubber does not sufficiently swell when it contacts saline formation water. Moreover, it is oftentimes necessary to swell the packer as soon as possible during well operations. If the swell rate of the packer is too slow, the well operations will be delayed, which can be extremely costly to the well operator. Accordingly, there is a need for swellable packers that have sufficient swell rates and hold at high pressures in downhole conditions (for example, saline environment, high temperatures).

[0005] Granular super absorbent polymers (SAP) have been used in the art to produce swellable packers because granular SAP achieves high volume swell at high temperature. The granular SAP particles are less expensive and swell faster than non-granular SAP particles. It is oftentimes believed that larger SAP particles are better because the larger particles lead to faster swell rates and larger swell area as compared to smaller/non-granular SAP particles. However, surprisingly it was found that high levels of leaching associated with large SAP particles not only reduce the swell potential of these compounds, but the leaching creates large perforations in the rubber. These perforations

produce weak points which will lead to failure when the rubber is stressed. An analogy for this would be perforated paper which when stressed will split at the perforation line.

[0006] In addition, elastomer compositions may be more difficult to process where higher amounts of granular SAPs are mixed into the composition. For example, the higher level of granular SAP may result in an unacceptable level of mixing, and the granular SAP may not be properly incorporated into the composition. In short, there is a desire to have higher loads of SAPs in the swellable packer, but not at the expense of deterioration of the other physical and/or chemical properties of the packer or the processing of elastomeric composition used for forming the swellable packer.

[0007] The present disclosure is directed to producing a swellable elastomeric composition with higher loads of SAPs wherein the composition has acceptable physical and/or chemical properties during processing, after forming and/or curing of the swellable packer, as well as when it is placed into use.

[0008] It has been unexpectedly found that by using powder SAPs, higher loads of powder SAPs may be incorporated into the elastomeric composition (as compared to loading with granular SAPs), and that the swellable composition has acceptable physical and/or chemical properties during processing, after forming and/or curing of the swellable packers, as well as when it is placed into use in the wellbore.

[0009] It has also been unexpectedly found, as disclosed herein, that higher loads of powder SAPs in the elastomeric composition result in packers with excellent swell rates in brines, low leaching and acceptable physical and/or chemical properties when subjected to the high temperature and/or high pressure conditions that occur in a wellbore.

[0010] The present disclosure is directed to elastomeric compositions and swellable packers that achieve a predictable and suitable swell rate (swelling as a function of time) such that the packer may be subjected to higher pressure in a timelier manner.

[0011] The present disclosure is also directed to swellable packers that have acceptable physical and/or chemical properties when subjected to brine type conditions, higher temperature conditions, and/or higher pressure conditions, such as those, for example, that may occur in a wellbore.

[0012] The present disclosure is directed to swellable compositions, and the packers produced using such swellable compositions, that swell at a suitable predictable rate and amount and are able to withstand high pressures and high temperatures without substantial physical failures, such as tearing and/or perforation.

[0013] Accordingly, it is desirable to have a swellable composition that is more acceptable for use with oil and gas field equipment, including, for example, a swellable packer.

SUMMARY OF THE DISCLOSURE

[0014] Exemplary embodiments described herein may provide for a swellable rubber composition comprising: an elastomer; a water-soluble resin; a curing agent and/or agents; a filler; and a powder super absorbent polymer (SAP).

[0015] Exemplary embodiments described herein may provide for a swellable rubber composition comprising: an elastomer; a butadiene rubber; a sulfur curing agent; a silica; and a powder super absorbent polymer.

[0016] Exemplary embodiments described herein may provide a swellable rubber composition comprising: a nitrile elastomer; a rubber; a sulfur curing agent; a silica; and a powder super absorbent polymer.

[0017] Exemplary embodiments described herein may provide a swellable rubber composition comprising: at least one nitrile rubber elastomer; at least one styrene butadiene rubber; carbon black; dioctyl phthalate; fumed silica; zinc oxide; an antiozonant; an antidegradant; a tackifier; sulfur; tetramethhylthiuram disulfide; an inhibitor; at least one powder super absorbent polymer; and stearic acid.

[0018] In exemplary embodiments, the at least one nitrile rubber elastomer is a hydrogenated nitrile elastomer having a percent hydrogenation from about 70 percent to about 91 percent.

[0019] In exemplary embodiments, the elastomer has a Mooney viscosity ML 1+4 (100 degrees Celsius) of about 47 to about 72.

[0020] In an exemplary embodiment, the at least one nitrile rubber elastomer may be a hydrogenated nitrile elastomer having a percent unsaturation of about 9 percent to about 30 percent.

[0021] In exemplary embodiments, the powder super absorbent polymer may be present in 125 to 175 Phr.

[0022] In exemplary embodiments, the powder super absorbent polymer may be present in 170 to 210 Phr.

[0023] In exemplary embodiments, the powder super absorbent polymer may be present in 190 to 210 Phr or in 185 to 215 Phr.

[0024] In exemplary embodiments, the powder super absorbent polymer may be present in at least 150 Phr, 175 Phr, 190 Phr, 200 Phr, 225 Phr or 250 Phr.

[0025] In exemplary embodiments, at least one powder super absorbent polymer and at least one granular super absorbent polymer may be present in the swellable rubber composition; and the at least one powder super absorbent polymer may comprise at least 50%, 60%, 70%, 80%, 90% or 95% by weight of a total super absorbent polymer incorporated into the swellable rubber.

[0026] In exemplary embodiments, the total amount of super absorbent polymer is selected such that, after curing, a cured swellable rubber packer may be capable of expanding in water and/or brine without significantly compromising the physical properties of the rubber composition and/or without significantly leaching and/or without significantly perforating.

[0027] In exemplary embodiments, the powder super absorbent polymer may have an average particle size of about 10 to 120 μm or about 20 to 100 μm, (e.g., about 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, 100, 105, 110, 115 or 120 μm).

[0028] In exemplary embodiments, the powder super absorbent polymer may have an average particle size of less than or equal to about 20, 30, 40, 50, 60, 70, 80, 90, 100, 110 or 120 μm.

[0029] In exemplary embodiments, the powder super absorbent polymer may consist essentially of particle sizes of less than or equal to about 20, 30, 40, 50, 60, 70, 80, 90, 100, 110, 120 or 130 μm.

[0030] In exemplary embodiments, about 70%, 75%, 80%, 85%, 90%, or 95% the powder super absorbent polymer may have particle sizes of less than or equal to about 20, 30, 40, 50, 60, 70, 80, 90, 100, 110, 120 or 130 μm.

[0031] In exemplary embodiments, the powder super absorbent polymer may comprise about 120 to 220, about 165 to 225, about 170 to 210 or about 190 to 200 (e.g., 120, 125, 130, 135, 140, 145, 150, 155, 160, 165, 170, 175, 180, 185, 190, 195, 200, 205, 210, 215 or 220) Phr.

[0032] In exemplary embodiments, the powder super absorbent polymer may comprise one or more of the following: poly-electrolytes, polyacyrlates (e.g., sodium polyacrylate), polyacryamide-co-polyacrylates (e.g., polyacryamide-co-potassium acrylate), polyacrylamides (e.g., potassium polyacrylamide), acrylic acids, hydrophilic clays, bentonite (e.g., sodium bentonite, potassium bentonite, calcium bentonite, or wyoming bentonite), wood, cork, and/or cellulose fibers.

[0033] In exemplary embodiments, the granular super absorbent polymer may comprise one or more of the following: poly-electrolytes, polyacyrlates (e.g., sodium polyacrylate), polyacryamide-co-polyacrylates (e.g., polyacryamide-co-potassium acrylate), polyacrylamides (e.g., potassium polyacrylamide), acrylic acids, hydrophilic clays, bentonite (e.g., sodium bentonite, potassium bentonite, calcium bentonite, or wyoming bentonite), wood, cork, and/or cellulose fibers.

[0034] In exemplary embodiments, the powder super absorbent polymer may be potassium polyacrylate polyacrylamide copolymer that has a mean particle size of approximately 35 μm, a median particle size of approximately 35 μm with a standard deviation of approximately 10 μm, and substantially no particles over approximately 63 μm in the powder.

[0035] In exemplary embodiments, the powder super absorbent polymer may be potassium polyacrylate polyacrylamide copolymer wherein no, or substantially no, particles are over approximately 63 μm in the powder.

[0036] In exemplary embodiments, the powder super absorbent polymer may be potassium polyacrylate polyacrylamide copolymer wherein no, or substantially no, particles are over approximately 75 μm in the powder.

[0037] In exemplary embodiments, the powder super absorbent polymer may be potassium polyacrylate polyacrylamide copolymer wherein no, or substantially no, particles are over approximately 50 μm, 55 μm, 60 μm, 65 μm, 70 μm, 75 μm, 80 μm, 85 μm, 90 μm, 95 μm, 100 μm, 110 μm, 115 μm or 125 μm in the powder.

[0038] In exemplary embodiments, the powder super absorbent polymer may have no, or substantially no, particles are over approximately 63 μm in the powder.

[0039] In exemplary embodiments, the powder super absorbent polymer may have no, or substantially no, particles are over approximately 75 μm in the powder.

[0040] In exemplary embodiments, the powder super absorbent polymer may have no, or substantially no, particles are over approximately 50 μm, 55 μm, 60 μm, 65 μm, 70 μm, 75 μm, 80 μm, 85 μm, 90 μm, 95 μm, 100 μm, 110 μm, 115 μm or 125 μm in the powder.

[0041] In exemplary embodiments, the swellable rubber composition, after curing, may be configured to swell by at least about 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, 90%, 100%, 110%, 120%, 130%, 140%, 150%, 160%, 170%, 180%, 190%, 200%, 210%, 220%, 230%, 240% or 250% by volume in an about 5% weight/volume brine solution without substantially compromising the physical properties of the cured rubber composition and/or without significantly leaching and/or without significantly perforating.

[0042] In exemplary embodiments, the swellable rubber composition, after curing, may be configured to swell by at least about 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, 90%, 100%, 110%, 120%, 130%, 140%, 150%, 160%, 170%, 180%, 190%, 200%, 210%, 220%, 230%, 240% or 250% by volume in an about 16% weight/volume brine solution without substantially compromising the physical properties of the rubber composition and/or without significantly leaching and/or without significantly perforating.

[0043] In exemplary embodiments, the swellable composition, after curing, may swell by at least 50%, 60%, 65%, 70%, 75% or 80% by volume in approximately 96 hours in a 5% brine solution at 200 degrees Fahrenheit.

[0044] In exemplary embodiments, the swellable composition, after curing, may swell by at least 50%, 60%, 65%, 70%, 75% or 80% by volume in approximately 96 hours in a 16% brine solution at 200 degrees Fahrenheit.

[0045] In exemplary embodiments, the swellable rubber composition, after curing, may be configured to swell while being subjected to a temperature of about 200 degrees Fahrenheit.

[0046] In exemplary embodiments, the swellable rubber composition, after curing, may be configured to swell while being subjected to a temperature of about 275 degrees Fahrenheit.

[0047] In exemplary embodiments, the swellable rubber composition, after curing, may be configured to swell while being subjected to a pressure of at least about 3000, 4000, 5000 or 6000 psi.

[0048] In exemplary embodiments, the swellable rubber composition, after curing, may be configured to substantially swell within 2, 3, 4 or 5 days.

[0049] In exemplary embodiments, the swellable rubber composition, after curing, may have a Shore A hardness of at least about 20, 25 or 30.

[0050] In exemplary embodiments, the swellable rubber composition, after curing and substantially swelling, may have a Shore A hardness of at least about 20, 25 or 30.

[0051] Exemplary embodiments described herein may provide for a swellable packer that may comprise: a conduit, and a swellable rubber composition according to one or more of the swellable compositions disclosed herein wrapped around at least a portion of the conduit and cured.

[0052] Exemplary embodiments described herein may provide for a swellable packer manufactured by causing the swellable rubber composition of one or more of the embodiments disclosed herein to cure after the swellable rubber composition has been wrapped around at least a portion of the conduit.

[0053] Exemplary embodiments described herein may provide for a method of sealing a region between wellbore wall and the swellable packer-conduit assembly, wherein the swellable packer-conduit assembly comprises a conduit and a swellable packer at least partially surrounding the outer surface of the conduit, comprising: locating a swellable packer-conduit assembly in a region of the wellbore in a manner so as to seal said space upon swelling of the swellable body, the swellable body being susceptible to being in contact with water, water based fluid and/or formation water present in the wellbore, according to one or more of the embodiments disclosed herein.

[0054] Exemplary embodiments described herein may provide for a swellable rubber composition comprising: about 10 parts per hundred (Phr) of an elastomer; about 90 Phr of a butadiene rubber; about 150 Phr of a powder SAP, about 45 Phr of fumed silica.

[0055] Exemplary embodiments described herein may provide for a swellable rubber composition comprising: about 10 parts per hundred (Phr) of an elastomer; about 90 Phr of a butadiene rubber; about 192 Phr of a powder SAP, about 45 Phr of fumed silica.

[0056] In exemplary embodiments, the elastomer may be one or more combinations of butadiene acrylonitrile copolymer, nitrile rubber, hydrogenated nitrile rubber, NBR, hydrogenated NBR, highly saturated nitrile, HNR, HNBR, carboxylated NBR (XNBR), CR, EPDM, ACM, NR, SBR, BR, natural rubber, synthetic polyisoprene, butyl rubbers (IIR) CSM, Silicone, fluoro rubbers, and perfluoro rubbers, tetrafluoro ethylene propylene rubber).

[0057] In exemplary embodiments, the salt may be one or more combinations of metal containing salts, such as metal chlorides (e.g., sodium chloride, potassium chloride, or calcium chloride), metal phosphates (e.g., $Ca_3(PO_4)_2$), metal carbonates (e.g., $CaCO_3$ or $BaCO_3$), metal oxides (e.g., MgO), metal sulfides (e.g., ZnS), metal hydroxides (e.g., $Fe(OH)_2$), metal sulfates (e.g., $BaSO_4$), metal acetates, metal bicarbonates, metal formates, metal hydrosulphides, metal imides, metal nitrates, metal nitrides; dissociating salts; and non-metal salts (e.g., NH_4Cl).

[0058] In exemplary embodiments, the super absorbent polymer, clays, and/or natural swelling materials may comprise one or more combinations of poly-electrolytes, polyacyrlates (e.g., sodium polyacrylate), polyacryamide-co-polyacrylates (e.g., polyacryamide-co-potassium acrylate), polyacrylamides (e.g., potassium polyacrylamide), acrylic acids, hydrophilic clays, bentonite (e.g., sodium bentonite, potassium bentonite, calcium bentonite, or wyoming bentonite), wood, cork, and/or cellulose fibers.

[0059] In exemplary embodiments, the swellable rubber composition may further comprise a general purpose plasticiser for rubber products, such as phthalate esters (e.g., dioctyl phthalate), trimellitates, sebacates, adipates, terephthalates, benzoates, dibenzoates, organophosphates, gluterates, or azelates.

[0060] In exemplary embodiments, the swellable rubber composition may further comprise carbon black, for example, in about 5 to about 15 Phr.

[0061] In exemplary embodiments, the swellable rubber composition may further comprise dioctyl phthalate(DOP), for example, in about 3 to about 9 Phr.

[0062] In exemplary embodiments, the swellable rubber composition may further comprise zinc oxide, for example, in about 3 to about 9 Phr.

[0063] In exemplary embodiments, the swellable rubber composition may further comprise an antiozonant, for example, in about 0.5 to about 2 Phr.

[0064] In exemplary embodiments, the swellable rubber composition may further comprise antidegradant, for example, in about 0.2 to 2.5 Phr.

[0065] In exemplary embodiments, the swellable rubber composition may further comprise a tackifier, for example, in about 1 to about 5 Phr.

[0066] In exemplary embodiments, the swellable rubber composition may further comprise an inhibitor, for example, in about 0.1 to about 0.6 Phr.

[0067] In exemplary embodiments, the swellable rubber composition may further comprise stearic acid, for example, in about 0.5 to about 3 Phr.

[0068] Exemplary embodiments described herein may provide for a swellable rubber composition as described herein wherein the swellable cured rubber composition may be configured to swell by at least about 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, 90%, 100%, 110%, 120%, 130%, 140%, 150%, 160%, 170%, 180%, 190%, 200%, 210%, 220%, 230%, 240% or 250% by volume.

[0069] Exemplary embodiments described herein may provide for a swellable rubber composition as described herein wherein the swellable cured rubber composition may be configured to swell by at least about 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, 90%, 100%, 110%, 120%, 130%, 140%, 150%, 160%, 170%, 180%, 190%, 200%, 210%, 220%, 230%, 240% or 250% by volume in about 5% brine solution.

[0070] Exemplary embodiments described herein may provide for a swellable rubber composition as described herein wherein the swellable cured rubber composition may be configured to swell by at least about 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, 90%, 100%, 110%, 120%, 130%, 140%, 150%, 160%, 170%, 180%, 190%, 200%, 210%, 220%, 230%, 240% or 250% by volume in about 10% brine solution.

[0071] Exemplary embodiments described herein may provide for a swellable rubber composition as described herein wherein the swellable cured rubber composition may be configured to swell by at least about 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, 90%, 100%, 110%, 120%, 130%, 140%, 150%, 160%, 170%, 180%, 190%, 200%, 210%, 220%, 230%, 240% or 250% by volume in about 16% brine solution.

[0072] Exemplary embodiments described herein may provide for a swellable rubber composition as described herein wherein the swellable cured rubber composition may be configured to swell by at least about 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, 90%, 100%, 110%, 120%, 130%, 140%, 150%, 160%, 170%, 180%, 190%, 200%, 210%, 220%, 230%, 240% or 250% by volume in about 20% brine solution.

[0073] Other aspects, features, and advantages will become apparent from the following detailed description when taken in conjunction with the accompanying drawings, which are a part of this disclosure and which illustrate, by way of example, principles of inventions disclosed.

DETAILED DESCRIPTION OF THE DRAWINGS

[0074] Notwithstanding any other forms that may fall within the scope of the disclosure as set forth in the Summary, specific embodiments will now be described by way of example and with reference to the accompanying drawings in which:

[0075] Figure 1 illustrates an exemplary embodiment of a sectional view of a swellable packer assembly comprising a rubber coating surrounding a conduit and capable of swelling in the presence of water and/or water formations.

[0076] Figures 2A-C illustrate graphical representations of the percent swell versus time in hours for swellable compositions tested in a solution with 5% brine at 200 degrees Fahrenheit, each swellable composition having SAPs of different particle sizes.

[0077] Figures 3A-C illustrate graphical representations of the percent swell versus time in hours for swellable compositions tested in a solution with 16% brine at 200 degrees Fahrenheit, each swellable composition having SAPs of different particle sizes.

[0078] Figures 4A-C illustrate graphical representations of the percent swell versus time in hours for swellable compositions tested in a solution with 5% brine at 275 degrees Fahrenheit, each swellable composition having SAPs of different particle sizes.

[0079] Figures 5A-C illustrate graphical representations of the percent swell versus time in hours for swellable compositions tested in a solution with 16% brine at 275 degrees Fahrenheit, each swellable composition having SAPs of different particle sizes.

[0080] Figures 6A-C illustrate graphical representations of percent swell versus SAP loading in Parts Per Hundred Rubber (Phr) for swellable compositions after four days in a solution with 5% brine at 200 degrees Fahrenheit, each swellable composition having SAPs of different particle sizes, where the SAP loading to achieve a 75% swell by the fourth day has been predicted.

[0081] Figure 7A illustrates a graphical representation of the percent leaching versus SAP loading in Phr for swellable compositions tested in a solution with, each swellable composition having SAPs of different particle sizes. The composition used in Figure 7A is Composition A disclosed herein with different levels of SAP.

[0082] Figures 7B-E depict photographical test results relating to leaching.

[0083] Figure 8 illustrates a graphical representation of the percent swell versus time in hours for swellable compositions tested in a solution with 5% brine at 200 degrees Fahrenheit, each swellable composition having a powder SAP and having different SAP loading in Phr.

[0084] Figure 9 illustrates two pucks exposed to 16% brine at 275 degrees Fahrenheit after one week of testing. The left puck sample used 10% NBR rubber, and the right puck sample used 10% HNBR.

[0085] Figure 10 illustrates a packer with physical failure or perforation where granular SAP (load 150 Phr, large granular) has been used in the rubber formulation.

[0086] Figures 11A-B depict graphical representations of test results from the packer described in Example 1 that was tested in a solution of 16% brine at a temperature of 275 degrees Fahrenheit.

[0087] Figure 12 depicts a graphical representation of test results from the packer described in Example 1 that was tested in a solution of 5% brine at a temperature of 275 degrees Fahrenheit.

DETAILED DESCRIPTION

[0088] The present disclosure is directed to the unexpected discovery that swellable rubber compositions with higher levels of powder super absorbent particles (SAPs) may provide both the desired swell rate and excellent physical properties for downhole conditions as compared to the same formulation containing granular SAP.

[0089] In exemplary embodiments, granular SAP(s) means SAPs where a substantial portion of the particles are at least 150 μm. As used herein, a substantial portion may mean at least 50%, 60%, 70% or 80% of the particles, or more. Alternatively, granular SAP means SAPs were the mean particle size is at least 150 μm.

[0090] In exemplary embodiments, medium size granular SAP means SAPs with a particle size distribution from about 150 μm to about 400 μm wherein at least 50%, 60%, 70% or 80% of the individual particles or more fall within this range.

[0091] In exemplary embodiments, large size granular SAP means SAPs with a particle size distribution from about 400 μm to about 1000 μm wherein approximately 50%, 60%, 70% or 80% of the individual particles or more fall within this range.

[0092] In exemplary embodiments, powder SAP means SAPs where a substantial portion of the particles are less than or equal to 50 μm, 75 μm, 100 μm, 125 μm, or 150 μm. As used herein a substantial portion may mean at least 50%, 60%, 70%, 80% or 90% of the particles, or more. Alternatively, powder SAP(s) means SAPs were the mean particle size is less than or equal to about 50 μm, 75 μm, 100 μm, 125 μm, or 150 μm. In exemplary embodiments, the powder SAP may

contain less than or equal to about 5%, 10%, 15%, 20%, 25%, 30%, 35%, 40%, 45% or 50% granular SAP particles.

[0093] In exemplary embodiments, water means water, water solutions, downhole water-based solutions, aqueous-based solutions, and/or brines. Some embodiments of the present disclosure swell in the presence of water, water solutions, downhole water-based solutions, aqueous-based solutions, brines, and/or oil- or hydrocarbon-based fluid. As used herein, the term "brine" is meant to refer to a water-based fluid containing alkaline or earth-alkaline chlorides salt, such as sodium chloride, calcium chloride, sulphates and carbonates. The swelling characteristics may be variable in relation to the variability in salt concentration and/or temperature, among other things. That is, for examples, as the salt concentration increases, the amount of swell may decrease. The numerical percents for brines disclosed herein are percents by volume unless otherwise stated.

[0094] Figure 1 illustrates an exemplary embodiment of a sectional view of a swellable packer assembly comprising a rubber coating, which is capable of swelling in the presence of water and/or water formations, such as brines, and oil- or hydrocarbon-based fluid. As shown, the swellable packer assembly 100 comprises a conduit 110 with a swellable rubber 120 wrapped around the conduit 110. In exemplary embodiments, the conduit 110 may be made of a suitable metal. In exemplary embodiments, the rubber 120 may be vulcanized to the conduit 110 such that the combination has a substantially unitary construction. In exemplary embodiments, the swellable packer assembly 100 may be designed to reduce and/or minimize extrusion of the rubber during use. In exemplary embodiments, end rings (not shown) may be provided to protect the ends of the rubber 120, or, alternatively, the end portions of the rubber 120 may be tapered (not shown) to more easily move through the well to the desired depth. The swellable packer 100 may be produced using a number of suitable techniques, for example, pressure molding, injection molding, extruding, calendar wrapping, strip winding an elastomeric composition described herein.

[0095] In exemplary embodiments, the swellable rubber composition and/or cured packer may comprise an elastomer, such as a thermoset elastomer capable of withstanding high temperatures for a prolonged period of time and that swells in the presence of water or a water-based fluid. In exemplary embodiments, the swellable rubber composition and/or cured packer may comprise an elastomer, such as a thermoset elastomer capable of withstanding high temperatures for a prolonged period of time and that swells in the presence of water or a water-based fluid and/or in the presence of an oil- or hydrocarbon-based fluid.

[0096] As used herein, for example, the elastomer may be one or more of the following: butadiene acrylonitrile copolymer, nitrile rubber, NBR, hydrogenated nitrile rubber, hydrogenated NBR, highly saturated nitrile, HNR, HNBR, carboxylated NBR (XNBR), CR, EPDM, ACM, NR,

SBR, BR, natural rubber, synthetic polyisoprene, butyl rubbers (IIR), CSM, Silicone, fluoro rubbers, perfluoro rubbers, tetrafluoro ethylene propylene rubber (FEPM) and combinations thereof.

[0097] For example, the at least one nitrile rubber elastomer is a hydrogenated nitrile elastomer having a percent hydrogenation from about 70 percent to about 91. For example the hydrogenated nitrile elastomer may have a Mooney viscosity ML 1+4 (100 degrees Celsius) of about 47 to about 72. In other embodiments, the hydrogenated nitrile elastomer may have a percent unsaturation of about 9 percent to about 30 percent. Examples of the hydrogenated nitrile elastomer that are commercially available from Zetpol® include 0020, 1020L, 2020L, and 2030L.

[0098] In exemplary embodiments, the swellable rubber composition and/or cured packer may also comprise a cement, a Portland cement, or one or more reactive filler materials, such as cement, cementations material, metal oxide, and mixtures thereof, which react and swell upon contact with water and/or stiffen the rubber composite. In exemplary embodiments, the cement may result in improvements in the physical properties of the rubber, such as increased volume and increased modulus. For example, the filler may be a reactive filler, a reinforcing reactive filler, a sealing system, cement clinker, silicate, aluminate, ferrite or combinations thereof.

[0099] In exemplary embodiments, the swellable rubber composition and/or cured packer may comprise a water soluble resin, which may increase the swelling rate and the degree of swell of the elastomer. Exemplary water soluble resins that may be used comprise polyethylene oxide, carboxymethyl cellulose, polyvinyl pyrrolidone, hydroxyethyl cellulose, hydroxypropyl cellulose or combinations thereof.

[00100] In exemplary embodiments, the swellable rubber composition typically includes a curing agent and/or curing system. Non-limiting examples are sulfur-based curing agents or peroxide curing agents. Co-agents may also be included. The curing system may be selected to be suitable with the polymers used in the swellable rubber composition.

[00101] The present disclosure is directed, at least in part, to the use of powder grades of SAPs that may be incorporated into swellable compositions at higher concentrations without detriment to the process ability and/or the quality of the elastomer rubber composition used for producing the swellable compositions and swellable packers, both before and after curing occurs. Certain embodiments are directed to the use of powder SAPs; however, in other embodiments, granular and powder SAPs are used in combination. The present disclosure contemplates that granular and powder grades may be combined in the swellable compositions disclosed herein and in the swellable packers disclosed herein. It has been unexpectedly found that increased loading of powder SAPs may be achieved (as compared to loading with granular SAPs) without degrading, or substantially degrading, the desired physical properties of the elastomer rubber composition, the cured packers and/or the

cured packer after swelling. Some exemplary embodiments disclosed herein are directed to certain swellable rubber compositions, and other embodiments are directed to using powder grades in swellable packers that have other types of rubber based elastomeric compositions.

[00102] The swellable non-elastomeric material contributes to the high volume swell at high temperature and/or high pressures, which characterizes the swellable rubber compositions, according to certain embodiments. This swellable non-elastomeric material includes SAPs, as well as other swellable organic or inorganic materials. Examples of SAPs include, but are not limited to, partially neutralized polyacrylic acid sodium salt, crosslinked isoprene-maleic acid salt, starch-polyacrylic acid salt, crosslinked carboxylmethyl cellulose (CMC), and/or polyvinyl alcohol-acrylic acid salt. Examples of swellable organic acid salts include sodium acetate, sodium formate, sodium acrylate, and the like. Examples of swellable inorganic materials include carbonates of sodium, potassium, lithium, calcium, magnesium or the like. The sodium carbonate may be used in the form of soda ash instead of pure sodium carbonate. The swellable non-elastomeric material may be a single swellable non-elastomeric material or a mixture of two or more swellable non-elastomeric material. Other non-limiting examples include Polyacrylic acid, polymethacrylic acid, polyacrylamide, polyethyleneoxide, polyethylene glycol, polypropylene oxide, poly (acrylic acid-co-acrylamide), polymers made from zwitterionic monomers, which include N, N-dimethyl- N-acryloyloxyethyl-N-(3-sulfopropyl)-ammonium betaine, N, N-dimethyl-N-acrylamidopropyl- N-(2-carboxymethyl)-ammonium betaine, N, N-dimethyl-N-acrylamidopropyl-N-(3- sulfopropyl)-ammonium betaine, 2-(methylthio)ethyl methacryloyl-S-(sulfopropyl)-sulfonium betaine, 2-[(2-acryloylethyl)dimethylammonio]ethyl 2-methyl phosphate, [(2- acryloylethyl)dimethylammonio] methyl phosphonic acid, 2-(acryloyloxyethyl)-2'- (trimethylammonium)ethyl phosphate, 2-methacryloyloxy ethyl phosphorylcholine, 2-[(3- acrylamidopropyl)dimethylammonio]ethyl 2'-isopropyl phosphate, 1-vinyl-3-(3- sulfopropyl)imidazolium hydroxide, (2-acryloxyethyl)carboxymethyl methylsulfonium chloride, 1 -(3-sulfopropyl)-2-vinylpyridinium betaine, N-(4-sulfobutyl)-N-methyl-N,N-diallylamine ammonium betaine, N,N-diallyl-N-methyl-N-(2-sulfoethyl)ammonium betaine or the like. Other non-limiting examples are poly-electrolytes, polyacyrlates (e.g., sodium polyacrylate), polyacryamide-co-polyacrylates (e.g., polyacryamide-co-potassium acrylate), polyacrylamides (e.g., potassium polyacrylamide), acrylic acids, hydrophilic clays, bentonite (e.g., sodium bentonite, potassium bentonite, calcium bentonite, or wyoming bentonite), wood, cork, and/or cellulose fibers.

[00103] In exemplary embodiments, the swellable rubber may comprise silica (or other filler particles) to reinforce the rubber compound. In certain embodiments, the silica may be fumed silica.

[00104] In exemplary embodiments, the swellable rubber may comprise a salt, such as particles or fine particles of salt, which are incorporated into the swellable rubber to, for example, allow

migration of water, water-based fluids, salt-containing water-based fluids, and/or water formations, such as brines, into the swellable rubber by osmosis so as to introduce swelling of the swellable rubber upon migration of the water, water-based fluids, salt-containing water-based fluids, and/or water formations into the swellable rubber. Examples of salt may comprise one or more of the following metal containing salts, such as metal chlorides (e.g., sodium chloride, potassium chloride, or calcium chloride), metal phosphates (e.g., $Ca_3(PO_4)_2$), metal carbonates (e.g., $CaCO_3$ or $BaCO_3$), metal oxides (e.g., MgO), metal sulfides (e.g., ZnS), metal hydroxides (e.g., $Fe(OH)_2$), metal sulfates (e.g., $BaSO_4$), metal acetates, metal bicarbonates, metal formates, metal hydrosulphides, metal imides, metal nitrates, metal nitrides, dissociating salts, and non-metal salts (e.g., NH_4Cl).

[00105] In exemplary embodiments, the swellable rubber may comprise a general purpose plasticiser for rubber products, such as phthalate esters (e.g., dioctyl phthalate), trimellitates, sebacates, adipates, terephthalates, benzoates, dibenzoates, organophosphates, gluterates or azelates.

[00106] In exemplary embodiments, the swellable rubber may comprise a material to reinforce a rubber compound to improve physical properties and/or color the product, such as pigments or carbon black (N-550).

[00107] In exemplary embodiments, the swellable rubber may comprise a material that reacts with the filler particles and acts as an activator in the cure system, such as zinc oxide. Together with the zinc oxide, the rubber may further comprise stearic acid, which reacts to produce zinc stearate - an intermediate in the vulcanization mechanism.

[00108] In exemplary embodiments, the swellable rubber may comprise a water-soluble, waxy solid for use as a process aid and lubricant during the rubber mixing process, such as polyethylene glycol.

[00109] In exemplary embodiments, the swellable rubber may comprise about 100 parts per hundred rubber (Phr) (i.e., the compositions comprise about 100 parts of an elastomer or combinations of elastomers) of an elastomer, about 40 Phr of polyethylene oxide, about 20 Phr of ionic peroxide cure and/or peroxide curing with a co-agent, about 126 Phr of a salt, and about 65 Phr of an SAP, clay, and/or other swelling material. In exemplary embodiments, the swellable rubber may further comprise any combination of one or more of: about 35 Phr of a cement or Portland cement, about 30 Phr of silica, about 10 Phr of dioctyl phthalate, about 8 Phr of N-550 (carbon black), about 5 Phr of zinc oxide, about 1 Phr of stearic acid, and/or about 10 Phr of PEG6000 (polyethylene glycol).

[00110] In exemplary embodiments, a swellable rubber composition as described herein may be configured to swell by at least about 50%, 60%, 70%, 80%, 90%, 100%, 110%, 120%, 130%, 140%, 150%, 160%, 170%, 180%, 190%, 200%, 210%, 220%, 230%, 240%, or 250% in brine solution, for

example, a 3-30% brine solution, such as 5%, 10%, 15%, 20%, 25%, or 30 % brine. The brine solution may comprise water with dissolved alkali metal salts (e.g., NaCl or KCl) and/or alkaline-earth metal salts (e.g., $CaCl_2$, $CaCO_3$, or $MgCl_2$). In exemplary embodiments, a swellable rubber composition as described herein may be configured to swell by at least the same or similar amounts in oil- or hydrocarbon-based fluids.

[00111] In exemplary embodiments, the swellable rubber may comprise the following composition (Composition A):

Material Description	**Parts Per Hundred (Phr)**
Nitrile Rubber (e.g. NIPOL DN3350)	5 – 15 (e.g. 10)
Styrene Butadiene Rubber (e.g. SBR 1502, Astlett)	75 – 105 (e.g. 90)
Fumed Silica (e.g. HISIL 190G)	40 – 50 (e.g. 45)
Carbon Black (e.g. N234)	5 – 15 (e.g. 8)
Dioctyl Phthalate(DOP)	3 – 9 (e.g. 6)
Zinc Oxide	3 - 7 (e.g. 5)
Antiozonant (e.g. 6PPD)	0.5 – 2 (e.g. 1)
Antidegradant (e.g. TMQ)	0.5 – 2.5 (e.g. 1.5)
Tackifier (e.g. KORESIN BASF)	1 – 5 (e.g. 3)
Potassium polyacrylate polyacrylamide copolymer (e.g. SAP) powder (mean particle size 35 μm, median particle size 35 μm, standard deviation of 10 μm, and substantially no particles over 75 μm)	125 – 175 (e.g. 150)
Sulfur	0.5 – 1.5 (e.g. 1)
Tetramethylthiuram disulfide(TMTD)	1 – 3 (e.g. 2)
Inhibitor (e.g. PVI, Akrochem CTP or retarder CTP)	0.3 – 0.7 (e.g. 0.5)
Stearic Acid	0.5 – 3 (e.g. 1)

[00112] In exemplary embodiments, the swellable rubber may comprise the following composition (Composition B):

Material Description	**Parts Per Hundred (Phr)**
hydrogenated saturated nitrile rubber (e.g. Zetpol 2030L)	5 – 15 (e.g. 10)
Styrene Butadiene Rubber (e.g. SBR 1502, Astlett)	75 – 105 (e.g. 90)
Fumed Silica (e.g. HISIL 190G)	40 – 50 (e.g. 45)
Carbon Black (e.g. N234)	5 – 15 (e.g. 8)
Dioctyl Phthalate(DOP)	3 – 9 (e.g. 6)
Zinc Oxide	3 to 7 (e.g. 5)
Antiozonant (e.g. 6PPD)	0.5 – 2 (e.g. 1)
Antidegradant (e.g. TMQ)	0.5 – 2.5 (e.g. 1.5)
Tackifier (e.g. KORESIN BASF)	1 – 5 (e.g. 3)
Potassium polyacrylate polyacrylamide copolymer (e.g. SAP) powder (mean particle size 35 μm, median particle size 35 μm, standard deviation of 10 μm, and substantially no particles over 75 μm)	180 – 220 (e.g. 205)
Sulfur	0.5 – 1.5 (e.g. 1)
Tetramethylthiuram disulfide(TMTD)	1 – 3 (e.g. 2)
Inhibitor (e.g. PVI, Akrochem CTP or retarder CTP)	0.3 – 0.7 (e.g. 0.5)
Stearic Acid	0.5 – 3 (e.g. 1)

[00113] In exemplary embodiments, the swellable rubber may comprise the following composition (Composition C):

Material Description	**Parts Per Hundred (Phr)**
acrylonitrile butadiene rubber (NBR) (e.g. Nipol DN3350, Zeon)	5 – 15 (e.g. 10)
Styrene Butadiene Rubber (e.g. SBR 1502, Astlett)	75 – 105 (e.g. 90)
Fumed Silica (e.g. HISIL 190G, PPG)	40 – 50 (e.g. 45)
Carbon Black (e.g. N234)	5 – 15 (e.g. 8)
Dioctyl Phthalate(DOP)	3 – 9 (e.g. 6)
Zinc Oxide	3 to 7 (e.g. 5)
Antiozonant (e.g. 6PPD, Eastman)	0.5 – 2 (e.g. 1)
Antidegradant (e.g. TMQ)	0.5 – 2.5 (e.g. 1.5)
Tackifier (e.g. KORESIN BASF)	1 – 5 (e.g. 3)
Potassium polyacrylate polyacrylamide copolymer (e.g. SAP, Evonik) powder and substantially no particles t over 75 μm	200 – 210 (e.g. 205)
Sulfur	0.5 – 1.5 (e.g. 1)
Tetramethylthiuram disulfide(TMTD)	1 – 3 (e.g. 2)
Inhibitor (e.g. PVI, Akrochem CTP or retarder CTP)	0.25 – 0.75 (e.g. 0.5)
Stearic Acid	0.5 – 3 (e.g. 1)

[00114] In exemplary embodiments, the swellable rubber may comprise the following composition (Composition D):

Material Description	**Parts Per Hundred (Phr)**
acrylonitrile butadiene rubber (NBR) (e.g. Nipol DN3350, Zeon)	5 – 15 (e.g. 10)
Styrene Butadiene Rubber (e.g. SBR 1502, Astlett)	75 – 105 (e.g. 90)
Fumed Silica (e.g. HISIL 190G, PPG)	40 – 50 (e.g. 45)
Carbon Black (e.g. N234)	5 – 15 (e.g. 8)
Dioctyl Phthalate(DOP)	3 – 9 (e.g. 6)
Zinc Oxide	3 to 7 (e.g. 5)
Antiozonant (e.g. 6PPD, Eastman)	0.5 – 2 (e.g. 1)
Antidegradant (e.g. TMQ)	0.5 – 2.5 (e.g. 1.5)
Tackifier (e.g. KORESIN BASF)	1 – 5 (e.g. 3)
Potassium polyacrylate polyacrylamide copolymer (e.g. SAP, Evonik) powder and substantially no particles over 75 μm	185 – 210 (e.g. 197)
Sulfur	0.5 – 1.5 (e.g. 1)
Tetramethylthiuram disulfide(TMTD)	1 – 3 (e.g. 2)
Inhibitor (e.g. PVI, Akrochem CTP or retarder CTP)	0.25 – 0.75 (e.g. 0.5)
Stearic Acid	0.5 – 3 (e.g. 1)

[00115] In exemplary embodiments, the swellable rubber may comprise the following composition (Composition E):

Material Description	**Parts Per Hundred (Phr)**
acrylonitrile butadiene rubber (NBR) (e.g. Nipol DN3350, Zeon)	5 – 15 (e.g. 10)
Styrene Butadiene Rubber (e.g. SBR 1502, Astlett)	75 – 105 (e.g. 90)
Fumed Silica (e.g. HISIL 190G)	40 – 50 (e.g. 45)
Carbon Black (e.g. N234)	5 – 15 (e.g. 8)
Dioctyl Phthalate(DOP)	3 – 9 (e.g. 6)
Zinc Oxide	3 to 7 (e.g. 5)
Antiozonant (e.g. 6PPD)	0.5 – 2 (e.g. 1)
Antidegradant (e.g. TMQ)	0.5 – 2.5 (e.g. 1.5)
Tackifier (e.g. KORESIN BASF)	1 – 5 (e.g. 3)
Potassium polyacrylate polyacrylamide copolymer (e.g. SAP, Evonik) powder and substantially no particles over 75 μm	200 – 210 (e.g. 205)
Sulfur	0.5 – 1.5 (e.g. 1)
Mercaptobenzothiazole disulfide (MBTS)	1 – 3 (e.g. 2)
Methyl Methacrylate Butadiene Styrene (MBS)	0.25- 0.75 (e.g. 0.5)
Stearic Acid	0.5 – 3 (e.g. 1)

[00116] In exemplary embodiments, the swellable rubber may comprise the following composition (Composition F):

Material Description	**Parts Per Hundred (Phr)**
acrylonitrile butadiene rubber (NBR) (e.g. Nipol DN3350, Zeon)	5 – 15 (e.g. 10)
Polybutadiene Rubber (BR) (e.g. KBR 01, Kumho)	75 – 105 (e.g. 90)
Fumed Silica (e.g. HISIL 190G, PPG)	40 – 50 (e.g. 45)
Carbon Black (e.g. N234)	5 – 15 (e.g. 8)
Dioctyl Phthalate(DOP)	3 – 9 (e.g. 6)
Zinc Oxide	3 to 7 (e.g. 5)
Antiozonant (e.g. 6PPD, Eastman)	0.5 – 2 (e.g. 1)
Antidegradant (e.g. TMQ)	0.5 – 2.5 (e.g. 1.5)
Tackifier (e.g. KORESIN BASF)	1 – 5 (e.g. 3)
Potassium polyacrylate polyacrylamide copolymer (e.g. SAP, Evonik) powder and substantially no particles over 75 μm	200 – 210 (e.g. 205)
Sulfur	0.5 – 1.5 (e.g. 1)
Tetramethylthiuram disulfide(TMTD)	1 – 3 (e.g. 2)
Inhibitor (e.g. PVI, Akrochem CTP or retarder CTP)	0.25 – 0.75 (e.g. 0.5)
Stearic Acid	0.5 – 3 (e.g. 1)

[00117] In exemplary embodiments, the swellable rubber may comprise the following composition (Composition G):

Material Description	**Parts Per Hundred (Phr)**
acrylonitrile butadiene rubber (NBR) (e.g. Nipol DN3350, Zeon)	35 – 55 (e.g. 45)
Polybutadiene Rubber (BR) (e.g. KBR 01, Kumho)	35 – 55 (e.g. 45)
hydrogenated saturated nitrile rubber (e.g. Zetpol 2030L)	5 – 15 (e.g. 10)
Fumed Silica (e.g. HISIL 190G, PPG)	40 – 50 (e.g. 45)
Carbon Black (e.g. N234)	5 – 15 (e.g. 8)
Dioctyl Phthalate(DOP)	3 – 9 (e.g. 6)
Zinc Oxide	3 to 7 (e.g. 5)
Antiozonant (e.g. 6PPD, Eastman)	0.5 – 2 (e.g. 1)
Antidegradant (e.g. TMQ)	0.5 – 2.5 (e.g. 1.5)
Tackifier (e.g. KORESIN BASF)	1 – 5 (e.g. 3)
Potassium polyacrylate polyacrylamide copolymer (e.g. SAP, Evonik) powder and substantially no particles over 75 μm	200 – 210 (e.g. 205)
Sulfur	0.5 – 1.5 (e.g. 1)
Tetramethylthiuram disulfide(TMTD)	1 – 3 (e.g. 2)
Inhibitor (e.g. PVI, Akrochem CTP or retarder CTP)	0.25 – 0.75 (e.g. 0.5)
Stearic Acid	0.5 – 3 (e.g. 1)

[00118] In exemplary embodiments, the swellable rubber may comprise the following composition (Composition H):

Material Description	Parts Per Hundred (Phr)
acrylonitrile butadiene rubber (NBR) (e.g. Nipol DN4050, Zeon)	85 – 115 (e.g. 100)
Silica (e.g. Ultrasil VN3, Evonik)	20 – 40 (e.g. 30)
Carbon Black (e.g. N550)	5 – 15 (e.g. 8)
Polyethylene Glycol (e.g. PEG 6000)	5 – 15 (e.g. 10)
Polyethylene Oxide (e.g. PEO-3)	35-45 (e.g. 40)
Dioctyl Phthalate(DOP)	7 – 13 (e.g. 10)
Zinc Oxide	3 to 7 (e.g. 5)
Antiozonant (e.g. 6PPD, Eastman)	0.5 – 2 (e.g. 1)
Antidegradant (e.g. TMQ)	0.5 – 2.5 (e.g. 1.5)
Tackifier (e.g. KORESIN BASF)	1 – 5 (e.g. 3)
Potassium polyacrylate polyacrylamide copolymer (e.g. SAP) powder and substantially no particles over 75 μm	75 – 125 (e.g. 100)
Sulfur	1.5 – 2.5 (e.g. 2)
4,4'-dithiodimorpholine (DTDM)	0.5 – 1.5 (e.g. 1)
Mercaptobenzothiazole (MBT)	0.25 – 0.75 (e.g. 0.5)
Stearic Acid	0.5 – 3 (e.g. 1)

[00119] In exemplary embodiments, the swellable rubber may comprise the following composition (Composition I):

Material Description	Parts Per Hundred (Phr)
acrylonitrile butadiene rubber (NBR) (e.g. Nipol DN3350, Zeon)	7 – 13 (e.g. 10)
Ethylene Propylene Diene Terpolymer monomer rubber (EPDM) (e.g. Buna EPT 3950, Lanxess)	80 – 100 (e.g. 90)
Fumed Silica (e.g. HISIL 190G, PPG)	40 – 50 (e.g. 45)
Carbon Black (e.g. N234)	5 – 15 (e.g. 10)
Polyethylene Glycol (e.g. PEG 6000)	3 – 7 (e.g. 5)
Zinc Oxide	3 to 7 (e.g. 5)
Vinyltris(2-methoxyethoxy)silane (e.g. JHV172, Chemspec)	2 – 6 (e.g. 4)
Trioctyl Trimellitate (e.g. TOTM, Hallstar)	4 – 8 (e.g. 6)
Tackifier (e.g. KORESIN BASF)	1 – 5 (e.g. 3)
Potassium polyacrylate polyacrylamide copolymer (e.g. SAP, Evonik) powder and substantially no particles over 75 μm	205 – 225 (e.g. 215)
Sulfur	0.5 – 1.5 (e.g. 1)
Tetramethylthiuram disulfide(TMTD)	1 – 3 (e.g. 2)
Vanox ZMTI (Vanderbilt)	1.5 – 2.5 (e.g. 2)
Accelerator Zinc Dibenzyl Dithiocarbamate (ZBED)	0.5 – 1.5 (e.g. 1)
Stearic Acid	0.5 – 3 (e.g. 1)

[00120] In exemplary embodiments, the swellable rubber may comprise the following composition (Composition J):

Material Description	**Parts Per Hundred (Phr)**
hydrogenated saturated nitrile rubber (e.g. Zetpol 2030L)	5 – 15 (e.g. 10)
Natural rubber (e.g. SVR10)	75 – 105 (e.g. 90)
Peptizer (e.g., Struktol A60)	1 – 4 (e.g. 2.5)
Fumed Silica (e.g. HISIL 190G)	40 – 50 (e.g. 45)
Carbon Black (e.g. N234)	5 – 15 (e.g. 8)
Dioctyl Phthalate(DOP)	3 – 9 (e.g. 6)
Zinc Oxide	3 to 7 (e.g. 5)
Antiozonant (e.g. 6PPD)	0.5 – 2 (e.g. 1)
Antidegradant (e.g. TMQ)	0.5 – 2.5 (e.g. 1.5)
Tackifier (e.g. KORESIN BASF)	1 – 5 (e.g. 3)
Potassium polyacrylate polyacrylamide copolymer (e.g. SAP) powder (mean particle size 35 μm, median particle size 35 μm, standard deviation of 10 μm, and substantially no particles over 63 μm)	185 – 215 (e.g. 197)
Sulfur	0.5 – 1.5 (e.g. 1)
Tetramethylthiuram disulfide(TMTD)	1 – 3 (e.g. 2)
Inhibitor (e.g. PVI, Akrochem CTP or retarder CTP)	0.3 – 0.7 (e.g. 0.5)
Stearic Acid	0.5 – 3 (e.g. 1)

[00121] In exemplary embodiments, the swellable rubber may comprise the following composition (Composition K):

Material Description	**Parts Per Hundred (Phr)**
hydrogenated saturated nitrile rubber (e.g. Zetpol 2030L)	5 – 15 (e.g. 10)
Synthetic polyisoprene (e.g. Natsyn 2200)	75 – 105 (e.g. 90)
Fumed Silica (e.g. HISIL 190G)	40 – 50 (e.g. 45)
Carbon Black (e.g. N234)	5 – 15 (e.g. 8)
Dioctyl Phthalate(DOP)	3 – 9 (e.g. 6)
Zinc Oxide	3 to 7 (e.g. 5)
Antiozonant (e.g. 6PPD)	0.5 – 2 (e.g. 1)
Antidegradant (e.g. TMQ)	0.5 – 2.5 (e.g. 1.5)
Tackifier (e.g. KORESIN BASF)	1 – 5 (e.g. 3)
Potassium polyacrylate polyacrylamide copolymer (e.g. SAP) powder and substantially no particles over 75 μm)	180 – 220 (e.g. 205)
Sulfur	0.5 – 1.5 (e.g. 1)
Tetramethylthiuram disulfide(TMTD)	1 – 3 (e.g. 2)
Inhibitor (e.g. PVI, Akrochem CTP or retarder CTP)	0.3 – 0.7 (e.g. 0.5)
Stearic Acid	0.5 – 3 (e.g. 1)

[00122] In exemplary embodiments, the swellable rubber may comprise the following composition (Composition L):

Material Description	**Parts Per Hundred (Phr)**
hydrogenated saturated nitrile rubber (e.g. Zetpol 2030L)	80 – 100 (e.g. 90)
Styrene Butadiene Rubber (e.g. SBR 1502, Astlett)	5 – 20 (e.g. 10)
Fumed Silica (e.g. HISIL 190G)	40 – 50 (e.g. 45)
Carbon Black (e.g. N234)	5 – 15 (e.g. 8)
Dioctyl Phthalate(DOP)	3 – 9 (e.g. 6)
Zinc Oxide	3 to 7 (e.g. 5)
Antiozonant (e.g. 6PPD)	0.5 – 2 (e.g. 1)
Antidegradant (e.g. TMQ)	0.5 – 2.5 (e.g. 1.5)
Tackifier (e.g. KORESIN BASF)	1 – 5 (e.g. 3)
Potassium polyacrylate polyacrylamide copolymer (e.g. SAP) powder and substantially no particles over 75 μm	160 – 180 (e.g. 170)
Sulfur	0.5 – 1.5 (e.g. 1)
Tetramethylthiuram disulfide(TMTD)	1 – 3 (e.g. 2)
Inhibitor (e.g. PVI, Akrochem CTP or retarder CTP)	0.3 – 0.7 (e.g. 0.5)
Stearic Acid	0.5 – 3 (e.g. 1)

[00123] EXAMPLE 1

[00124] Packers having one or more of the materials listed in Composition B within the identified ranges were prepared and tested. Tests were conducted in 5% brine and 16% brine. Both of the packers were prepared and tested under similar conditions.

[00125] The packer tested in 16% brine was prepared and tested as follows. The base pipe was five feet in length and had an outer diameter of 4.5 inches. The swellable rubber was applied to the base pipe using a wrapping technique. The outer diameter after adding the swellable rubber formulation was approximately 5.7 inches. Diameter of the packer was measured in one foot increments from the low pressure side to the high pressure side. The swellable rubber formulation was cured at 330 degrees Fahrenheit at a pressure of 70 psi for 2.5 hours. After curing, the hardness was measured at random locations, and the hardness was from approximately 86 to 92 Shore A. The packer was inspected, and no bonding issues were detected. The packer was placed in 16% brine solution at a temperature of 275 degrees Fahrenheit and at a pressure of about 300 psi for multiple days. The packer was then subjected to a differential pressure of at least 5000 psi before being removed and inspected. The above described data and measurements are reproduced below in Table 1.

Table 1.

Base Pipe OD (in)	4.5”
Packer OD (in)	5.7”
Fluid Type	
Record the Rubber Type	Composition B (above)
Element Length (Feet)	5
Temperature (°F)	275
Salinity (%)	16%
Refresh Schedule (Hours)	0
Pressure Requirements (PSI)	5000
Expected Contact Time (Days)	5
Time to Apply Pressure (Days)	17
Manufacturing	Calendar Wrap
Temperature (°F)	330
Pressure (PSI)	70
Time Duration (hrs.)	2.5
Nylon Wrap Pull (Pounds)	100

Dia. #0 (in):	5.69	Dia. #1 (in):	5.7	Dia. #2 (in):	5.7
Dia. #3 (in):	5.7	Dia. #4 (in):	5.7	Dia. #5 (in):	5.69

Hardness Test. #1:	92	Hardness Test #2:	90	Hardness Test #3 :	89
Hardness Test. #4:	88	Hardness Test #5:	86	Hardness Test #6 :	90

[00126] The outer diameter after swelling was around 6 inches. Diameter of the packer was measured in one foot increments from the low pressure side to the high pressure side. The Shore A hardness varied from approximately 32 to 48. After being subjected to the test conditions for multiple days, the swelled packer was able to withstand a differential pressure of greater than 5000 psi. Measurements on the packer after the test are reproduced below in Table 2. Graphical representations of test results are depicted in Figures 11A-B. As shown in Figure 11A, pressure was incrementally applied up to a pressure differential between the high pressure side and the low pressure side of over 5000 psi, and the pressure differential was maintained for over one hour. As shown in Figure 11B, pressure of over 5000 psi was instantaneously applied up to a pressure differential between the high pressure side and the low pressure side of over 5000 psi, and the pressure differential was maintained for over one hour.

Table 2.

Dia. #0 (in):	N/A		Dia. #1 (in):	N/A		Dia. #2 (in):	N/A
Dia. #3 (in):	6		Dia. #4 (in):	6		Dia. #5 (in):	6.03

	0:00 (Top)	3:00	6:00	9:00
Hardness Test. #1 :	36	32	42	42
Hardness Test. #2 :	37	42	40	42
Hardness Test. #3 :	42	42	38	40
Hardness Test. #4 :	42	42	36	35
Hardness Test. #5 :	46	48	37	43
Hardness Test. #6 :	43	42	42	42

[00127] The packer tested in 5% brine was prepared and tested as follows. The base pipe was five feet in length and had an outer diameter of 4.5 inches. The swellable rubber was applied to the base pipe using a wrapping technique. The outer diameter after adding of the swellable rubber formulation was approximately 5.7 inches. Diameter of the packer was measured in one foot increments from the low pressure side to the high pressure side. The swellable rubber formulation was cured at 330 degrees Fahrenheit at a pressure of 70 psi for 2.5 hours. After curing, the hardness was measured at random locations and the hardness was from approximately 90 to 95 Shore A. The packer was inspected, and no bonding issues were detected. The packer was placed in 5% brine solution at a temperature of 275 degrees Fahrenheit and a pressure of over 5000 psi for multiply days. The packer was then removed and inspected. The above described data is reproduced below in Table 3.

Table 3.

Base Pipe OD (in)	4.5”
Packer OD (in)	5.7”
Fluid Type	
Record the Rubber Type	Composition B (above)
Element Length (Feet)	5
Temperature (°F)	275
Salinity (%)	5%
Refresh Schedule (Hours)	0
Pressure Requirements (PSI)	5000
Expected Contact Time (Days)	2
Time to Apply Pressure (Days)	8
Manufacturing	Calendar Wrap
Temperature (°F)	330
Pressure (PSI)	70
Time Duration (hrs.)	2.5
Nylon Wrap Pull (Pounds)	100

Dia. #0 (in):	5.69	Dia. #1 (in):	55.69	Dia. #2 (in):	5.7
Dia. #3 (in):	5.7	Dia. #4 (in):	5.7	Dia. #5 (in):	5.7
Hardness Test. #1:	91	Hardness Test #2:	91	Hardness Test #3:	95
Hardness Test. #4:	92	Hardness Test #5:	92	Hardness Test #6:	90

[00128] The outer diameter after swelling was approximately 6 inches. Diameter of the packer was measured in one foot increments from the low pressure side to the high pressure side. The Shore A hardness varied from approximately 32 to 50. After being subjected to the test conditions for multiple days the swelled packer was able to withstand a differential pressure of greater than 5000 psi. Measurements on the packer after the test are reproduced below in Table 4. A graphical representation of test results are depicted in Figure 12. As shown in Figure 12, pressure was incrementally applied up to a pressure differential between the high pressure side and the low pressure side of over 5000 psi, and the pressure differential was maintained for over one hour.

Table 4.

Dia. #0 (in):	N/A	Dia. #1 (in):	5.98	Dia. #2 (in):	5.98
Dia. #3 (in):	5.98	Dia. #4 (in):	5.97	Dia. #5 (in):	6.05

	0:00 (Top)	3:00	6:00	9:00
Hardness Test. #1 :	37	37	33	32
Hardness Test. #2 :	35	40	35	33
Hardness Test. #3 :	39	47	33	33
Hardness Test. #4 :	35	42	38	34
Hardness Test. #5 :	47	46	50	41
Hardness Test. #6 :	43	42	42	38

[00129] EXAMPLE 2

[00130] Samples of swellable packers were prepared using SAPs with three different particles sizes. Pucks of the swellable packers were produced based on the formulation set forth in Composition A. A first composition was prepared based on Composition A using powder SAP at 110 Phr, 130 Phr, 150 Phr and 170 Phr loads. A second composition was prepared based on Composition A using a medium size granular SAP at 110 Phr, 130 Phr, 150 Phr and 170 Phr loads. A third composition was prepared based on Composition A using a large size granular SAP at 110 Phr, 130 Phr, 150 Phr and 170 Phr loads. The types of SAPs used and the particles sizes are set forth in Table 5 below. The particle size distributions of the SAPs in Table 5 were measured from the actual lots used in this example.

Particle size (μm)			
	Powder	Medium Granular	Large Granular
Mean	35.33	298.67	666.23
Median	5	261	652
Std dev	10.61	97.72	161.09

Table 5: SAP Particle Size Comparisons

[00131] The sample pucks were tested at 200 degrees Fahrenheit in a solution with 5% brine by volume and in a solution with 16% brine by volume. The sample pucks were also tested at 275

degrees Fahrenheit in a solution with 5% brine by volume and in a solution with 16% by volume brine. The test results from this test are set forth below in Table 6.

	1	2	3	4	5	6	7	8	9	10	11	12
Powder SAP	110 phr			130 phr			150 phr			170 phr		
Medium Granular SAP		110 phr			130 phr			150 phr			170 phr	
Large Granular SAP			110 phr			130 phr			150 phr			170 phr
Physical Properties												
Tensile Strength	781	502	351	695	421	401	542	390	336	655	376	294
Elongation	360	335	289	224	229	238	225	208	164	66	219	256
Hardness (shore A)	93	88	89	91	87	95	94	91	95	95	94	93
Specific Gravity	1.26	1.26	1.25	1.30	1.27	1.28	1.27	1.28	1.29	1.28	1.25	1.29
SAP Leaching, 0%/200°F/7 days	1	2	3	4	5	6	7	8	9	10	11	12
Jar Mass (M_j)	180.1	178.35	180.02	178.36	180.23	180.14	178.21	180.03	178.34	178.44	180.14	180.16
Button Mass (M_b)	15.26	15.21	14.83	15.52	15.43	15.56	15.81	15.45	15.34	16.04	15.69	15.47
Total Mass After Drying (M_{final})	180.69	180.7	180.85	179.42	180.48	185.06	179.48	180.17	180.48	179.75	184.75	185.7
SAP Mass (M_{sap})	0.59	2.37	3.77	1.06	3.25	4.92	1.27	3.14	5.14	1.31	4.81	5.54
Leaching % (L)	3.87	15.58	25.25	6.63	21.06	30.63	8.03	20.32	33.51	8.17	25.38	35.81
Puck Swelling	1	2	3	4	5	6	7	8	9	10	11	12
200 °F, 5% brine Day 4 Swell (%)	38.63	35.75	35.08	45.97	48.31	76.89	52.85	57.02	57.06	62.62	44.75	82.9
200 °F, 16% brine Day 4 Swell (%)	22.08	25.17	30.88	26.53	32.66	36.02	32.55	37.11	36.36	37.49	29.43	43.47
275 °F, 5% brine Day 4 Swell (%)	55.26	54.59	62.57	63.37	77	76.89	71.25	84.56	100.62	81.33	80.53	98.67
275 °F, 16% brine Day 4 Swell (%)	30.2	39.9	35.62	36.27	41.9	39.73	32.59	48.16	55.04	54.21	46.39	70.52

Table 6: Test Results for Example 2

[00132] Figures 2A-C, 3A-C, 4A-C, and 5A-C depict graphical representations of some of the test results using composition A. Figures 2A-2C, 4A-4C, and 5A-5B show that, in simulated downhole conditions of 200 Fahrenheit 5% brine, 275 Fahrenheit 5% brine, and 275 Fahrenheit 16% brine, the compositions comprising medium and large granular SAPs swelled faster and had a higher percent swell (volume) as compared to the compositions comprising powder SAPs at respective varying loads. Figures 3A-3C demonstrate that, in simulated downhole conditions of 200 Fahrenheit 16% brine, compositions comprising medium and large granular SAP swell more similarly to compositions comprising powder SAPs at respective varying loads. The data shown in Figures 3A-3C is expected, as 200 Fahrenheit 16% brine conditions is considered to be a challenging environment for swelling, e.g., these conditions result in a slower swelling rate and smaller swelling volume compared to less saline conditions and higher temperatures. As shown in the results in Figures 2A-2C, 4A-4C, and 5A-5C, it is expected that, if the test at 200 Fahrenheit 16% brine was performed for more hours, the larger granular SAP at the higher loads would show a higher percent swell and a faster swell than the powder SAP. Accordingly, these tests results demonstrate that one of ordinary skill in the art would be encouraged to select medium or large granular SAP for packer elastomers to achieve the fastest swell rates and highest swell volumes as compared to powdered SAP.

[00133] Further testing comparing powder SAP, medium granular SAP, and large granular SAP was conducted. As used herein, one method for measuring the leaching of SAP from Composition A is as follows. However, other methods may also be used. The rubber is molded into a button of approximately 15g. The exact mass of the button is measured and recorded. The button is placed in a container of known mass with approximately 375 mL distilled water. The button must be completely

immersed in the water. The container is sealed and placed in an oven at about 200 degrees Fahrenheit for approximately 7 days. At this time, the rubber button is removed. Leached SAP on the surface of the button is scraped into the jar. The jar is placed back in the oven for approximately 3 days to evaporate the water, leaving dried SAP. The mass of the jar + SAP is measured and the mass of the jar is subtracted from this value, providing the mass of SAP that has leached from the rubber button. The percent leaching is calculated by dividing the leached SAP mass from the initial mass of the rubber button. It was discovered that granular SAPs demonstrate a significantly higher percentage of leaching as compared to powder SAPs. For example, as shown in Figure 7A, the composition comprising the larger granular SAP exhibited leaching of approximately 25% for the lowest SAP loading, and the percent leaching increased for the composition comprising the larger granular SAP as the SAP loading increased (i.e., up to greater than approximately 35% leaching at SAP loading of approximately 170 Phr). The composition comprising the medium granular SAP exhibited leaching of approximately 15% for the lowest SAP loading, and the percent leaching increased for the composition comprising the medium granular SAP as the SAP loading increased (i.e., up to approximately 30% leaching at SAP loading of approximately 170). Unexpectedly, the composition comprising the powder SAP exhibited leaching of less than approximately 5% for the lowest SAP loading. The percent leaching increased for the composition comprising the powder SAP as the SAP loading increased (i.e., up to less than approximately 10% leaching at SAP loading of approximately 170). However, the rate of leaching increase as the SAP loading increased for the composition comprising the powder SAP was surprisingly and observably less than the rate of leaching increase as the SAP loading increased for the granular SAPs. Notably, the powdered SAP samples leach by less than half the amount of both of the granular SAPs.

[00134] Figure 7B depicts a photograph of a leach test on the three cured compositions. In this example, the test was conducted in distilled water at 200 approximately degrees Fahrenheit for approximately 7 days. The left jar contains a swellable composition having the powder SAP, and no visible evidence of leaching can be observed. The middle jar contains a swellable composition having the medium granular SAP, and considerable leaching can be observed. The right jar contains a swellable composition having the large granular SAP, and substantial leaching can be observed, so much so that the composition no longer contacts the bottom of the jar and is suspended in the solution.

[00135] As another example, Figures 7C-E depict the effect of leaching on cured swellable compositions. Figure 7C shows a puck prior to swell testing. Leaching can reduce the swell potential of a cured composition and create a higher likelihood of perforations in the composition (e.g., which can lead to failure of the composition, such as when the composition is stressed). The left puck

sample in Figures 7D-E contains a swellable composition comprising the large granular SAP with a load of 150 Phr. As shown in Figure 7D, the surface of the left puck sample comprising large granular SAP is highly pitted and rough due at least in part to leaching. Further, Figure 7E shows that the left puck sample comprising large granular SAP has torn from the ring. The middle puck sample in Figures 7D-E with a load of 150 Phr contains a swellable composition comprising the medium granular SAP. As shown in Figure 7D, the surface of the middle puck sample comprises some perforations in the composition, though not to the extent as seen in the left puck sample. Furthermore, as shown in Figure 7E, tearing from the ring is less visible in the middle sample as compared to the left sample. The right puck sample in Figures 7D-E contains a swellable composition comprising the powder SAP with a load of 150 Phr. As shown in Figure 7D, the right puck sample surface is substantially smooth no visible perforations. Similarly, Figure 7E does not show any tearing of the composition from the ring in the right puck. Additionally, it was surprisingly noticed that the amount of swell of the right puck appeared to be similar to the left and middle pucks (large and medium granular SAPs). Accordingly, as disclosed herein (and surprisingly), the use of SAP powdered grades in exemplary embodiments results in swellable packers with acceptable amounts of swell as well as suitable physical properties such that these packers may be used in high temperature and/or high pressure well bores applications.

[00136] It was discovered that high levels of leaching and/or less flexibility in the swellable composition with granular SAP particles. Leaching can reduce the swell potential of a swellable composition, and it can create tears and/or perforations in the rubber. These tears and/or perforations may produce weak points, which lead to failure when the rubber is stressed. Figure 10 is a failed packer illustrating that the rubber has been ripped off down the length of the rubber when it was exposed to high pressure. The leaching data in Figures 7D-E and the failed packer in Figure 10 demonstrate that the physical properties of swellable packers can generally deteriorate with high loads of granular SAPs.

[00137] EXAMPLE 3

[00138] Figures 6A-C depict percent swell versus SAP loading for swellable packers exposed to a solution with 5% brine by volume at 200 degrees Fahrenheit for four days, which were created, in part, using data from Example 2 (Composition A). Based on the data, a linear, or substantially linear, relationship between percent swell and SAP loading is depicted for powder SAP, medium granular SAP, and large granular SAP. The predicted compounding level to achieve 75% swell for the three SAPs is illustrated in Figures 6A-C.

[00139] As depicted in Figure 6A, the predicted SAP loading to achieve a 75% swell using the powder SAP is approximately 205 Phr. A maximum load level for the powder SAP has not been

determined, but it is greater than the predicted load to achieve a 75% swell in four days in the aforementioned environment of approximately 205 Phr. Therefore, it is predicted that a 75% swell in four days in the aforementioned environment is attainable for a swellable composition using powder SAP.

[00140] Figure 6B depicts the predicted SAP loading to achieve a 75% swell using the medium granular SAP as approximately 190 Phr. In this example, the maximum load for medium granular SAP in such swellable compositions was determined to be approximately 170 Phr (e.g., due at least in part to the amount of leaching that would occur at medium granular SAP at loads of greater than 170 Phr). Therefore, it is predicted that a 75% swell in four days in the aforementioned environment may not be attainable for a swellable composition using only medium granular SAP.

[00141] Figure 6C depicts the predicted SAP loading to achieve a 75% swell using the large granular SAP as approximately 160 Phr. In this example, the maximum load for large granular SAP in such swellable compositions was determined to be approximately 150 Phr. Therefore, it is predicted that a 75% swell in four days in the aforementioned environment may not be attainable for a swellable composition using only large granular SAP.

[00142] Accordingly, it was surprisingly discovered that increasing the quantity of powder SAP beyond the max load of the medium or large granular SAP in a swelling composition resulted in the powder SAP composition having improved swelling rate and volume characteristics along with improved physical characteristics (no tearing or perforations). Moreover, the 205 Phr powder SAP composition was easily combined and had no manufacturing problems. Medium or large granular SAP could not be combined with the swelling composition to achieve the 75% swell in four days (e.g., the granular SAP falls out of the formula and becomes unmanageable).

[00143] EXAMPLE 4

[00144] Two puck samples of a swellable composition were prepared with 205 Phr of the powder SAP. The powder SAP was mixed using an internal mixer (e.g., which can assist in fly loss). One composition contained 10% of NBR rubber (Nipol DN3350). The other composition contained 10% of HNBR (Zetpol 2030L). The resulting compositions exhibited excellent green strength and acceptable milling and manipulation properties. Data relating to these two compositions is reproduced in Table 7 below. As predicted in Example 3, 205 Phr loading of the powder SAP achieves 75% swell within four days in a solution having 5% brine by volume at 200 degrees Fahrenheit. The composition having HNBR (Zetpol 2030) exhibited a greater swell rate after four days in three of the four environments. Use of HNPR (Zetpol 2030) may offer improved thermal stability at higher temperatures and may further minimize leaching. As depicted in Figure 8, the swell rate of swellable compositions comprising powder SAP increased as the SAP loading increased.

Figure 9 depicts the two puck samples exposed to a solution having 16% brine by volume at 275 degrees Fahrenheit after one week of testing. The left puck sample used 10% NBR rubber (Nipol DN3350), and the right puck sample used 10% HNBR (Zetpol 2030L).

		205 phr, 10% DN3350	205 phr, 10% HNBR
96 hour Swell %	200 °F, 5% brine	75.8	77.8
	200 °F, 16% brine	46.5	47.2
	275 °F, 5% brine	98.4	96.0
	200 °F, 16% brine	65.4	66.9

Table 7: 205 Phr of Powder SAP Swell Data

[00145] As depicted in Figure 8, the swell rate of swellable compositions comprising powder SAP increased as the SAP loading increased.

[00146] Other Non-limiting Exemplary Embodiments

[00147] Further advantages of the claimed subject matter will become apparent from the following examples describing certain embodiments of the claimed subject-matter.

[00148] Example 1A. A method of sealing a region between a wall and a swellable packer-conduit assembly, wherein the swellable packer-conduit assembly comprises a conduit and a swellable packer at least partially surrounding the outer surface of the conduit, the method comprising: locating the swellable packer-conduit assembly in a region with a surrounding wall; permitting the swellable packer-conduit assembly to be exposed to water, water based fluid, and/or formation water while the swellable packer-conduit assembly is surrounded by the surrounding wall; permitting the swellable packer-conduit assembly to be exposed toheat while the swellable packer-conduit assembly is surrounded by the surrounding wall; waiting for a duration of time such that the swellable packer can swell to substantially seal the region between the surrounding wall and the swellable packer-conduit assembly.

[00149] Example 2A. The method of Example 1A, wherein the swellable packer comprises a powder super absorbent polymer present in at least about 150 Phr, 175 Phr, 197 Phr, 200 Phr, 205 Phr or 225 Phr.

[00150] Example 3A. The method of Example 1A or 2A, wherein the heat comprises a temperature of about 200 degrees Fahrenheit.

[00151] Example 4A. The method of Example 1A or 2A, wherein the heat comprises a temperature of about 275 degrees Fahrenheit.

[00152] Example 5A. The method of one or more of Examples 1A-4A, wherein the water, water based fluid, and/or formation water is an about 5% weight/volume brine solution.

[00153] Example 6A. The method of one or more of Examples 1A-4A, wherein the water, water based fluid, and/or formation water is an about 16% weight/volume brine solution.

[00154] Example 7A. The method of one or more Examples 1A-6A, wherein the swellable packer swells by at least about 50%, 60%, 65%, 70%, 75%, 80%, or 90% by volume.

[00155] Example 8A. The method of one or more of Examples 1A-7A, wherein the duration of time is about 2, 3, 4, or 5 days.

[00156] Example 9A. The method of one or more of Examples 1A-8A, wherein the seal between the surrounding wall and the swelled swellable packer-conduit assembly can withstand being subjected to a pressure of at least about 3000, 4000, 5000, 6000, 70000, or 8000 psi.

[00157] Example 10A. The method of one or more Examples 1A-9A, wherein the swellable packer comprises a swellable rubber composition comprising:

(i) a combination of an elastomer, a butadiene rubber, a sulfur curing agent, a silica, and a powder super absorbent polymer;

(ii) a combination of a nitrile elastomer, a rubber, a sulfur curing agent, a silica, and a powder super absorbent polymer; or

(iii) a combination of at least one nitrile rubber elastomer, at least one styrene butadiene rubber, carbon black, dioctyl phthalate, fumed silica, zinc oxide, an antiozonant, an antidegradant, a tackifier, sulfur, tetramethhylthiuram disulfide, an inhibitor, at least one powder super absorbent polymer, and stearic acid.

[00158] Example 11A. The method of one or more Examples 1A-10A, wherein the seal between the surrounding wall and the swelled swellable packer-conduit assembly can withstand being subjected to pressures of at least about 5000 psi and temperatures of at least about 200 degrees Fahrenheit and maintain the seal.

[00159] Example 12A. The method of one or more Examples 1A-10A, wherein the seal between the surrounding wall and the swelled swellable packer-conduit assembly can withstand being subjected to pressures of at least about 5000 psi and temperatures of at least about 275 degrees Fahrenheit and maintain the seal.

[00160] Example 1B. A method of sealing a region between a wellbore wall and a swellable packer-conduit assembly, wherein the swellable packer-conduit assembly comprises a conduit and a

swellable packer at least partially surrounding the outer surface of the conduit, the method comprising: locating the swellable packer-conduit assembly in a region of the wellbore; permitting the swellable packer-conduit assembly to be exposed to water, water based fluid, and/or formation water while the swellable packer-conduit assembly is in the wellbore; permitting the swellable packer-conduit assembly to be exposed to heat while the swellable packer-conduit assembly is in the wellbore; waiting for a duration of time such that the swellable packer can swell to substantially seal the region between the wellbore wall and the swellable packer-conduit assembly.

[00161] Example 2B. The method of Example 1B, wherein the swellable packer comprises a powder super absorbent polymer present in at least about 150 Phr, 175 Phr, 197 Phr, 200 Phr, 205 Phr or 225 Phr.

[00162] Example 3B. The method of Example 1B or 2B, wherein the heat comprises a temperature of about 200 degrees Fahrenheit.

[00163] Example 4B. The method of Example 1B or 2B, wherein the heat comprises a temperature of about 275 degrees Fahrenheit.

[00164] Example 5B. The method of one or more of Examples 1B-4B, wherein the water, water based fluid, and/or formation water is an about 5% weight/volume brine solution.

[00165] Example 6B. The method of one or more of Examples 1B-4B, wherein the water, water based fluid, and/or formation water is an about 16% weight/volume brine solution.

[00166] Example 7B. The method of one or more Examples 1B-6B, wherein the swellable packer swells by at least about 50%, 60%, 65%, 70%, 75%, 80%, or 90% by volume.

[00167] Example 8B. The method of one or more of Examples 1B-7B, wherein the duration of time is about 2, 3, 4, or 5 days.

[00168] Example 9B. The method of one or more of Examples 1B-8B, wherein the seal between the wellbore wall and the swelled swellable packer-conduit assembly can withstand being subjected to a pressure of at least about 3000, 4000, 5000, 6000, 7000, or 8000 psi.

[00169] Example 10B. The method of one or more Examples 1B-9B, wherein the swellable packer comprises a swellable rubber composition comprising:

(i) a combination of an elastomer, a butadiene rubber, a sulfur curing agent, a silica, and a powder super absorbent polymer;

(ii) a combination of a nitrile elastomer, a rubber, a sulfur curing agent, a silica, and a powder super absorbent polymer; or

(iii) a combination of at least one nitrile rubber elastomer, at least one styrene butadiene rubber, carbon black, dioctyl phthalate, fumed silica, zinc oxide, an antiozonant, an antidegradant, a

tackifier, sulfur, tetramethhylthiuram disulfide, an inhibitor, at least one powder super absorbent polymer, and stearic acid.

[00170] Example 11B. The method of one or more Examples 1B-10B, wherein the seal between the wellbore wall and the swelled swellable packer-conduit assembly can withstand being subjected to pressures of at least about 5000 psi and temperatures of at least about 200 degrees Fahrenheit and maintain the seal.

[00171] Example 12B. The method of one or more Examples 1B-10B, wherein the seal between the wellbore wall and the swelled swellable packer-conduit assembly can withstand being subjected to pressures of at least about 5000 psi and temperatures of at least about 275 degrees Fahrenheit and maintain the seal.

[00172] Example 1C. A swellable rubber composition comprising: an elastomer; a butadiene rubber; a sulfur curing agent; a silica; and a powder super absorbent polymer.

[00173] Example 2C. A swellable rubber composition comprising: a nitrile elastomer; a rubber; a sulfur curing agent; a silica; and a powder super absorbent polymer.

[00174] Example 3C. A swellable rubber composition comprising: at least one nitrile rubber elastomer; at least one styrene butadiene rubber; carbon black; dioctyl phthalate; fumed silica; zinc oxide; an antiozonant; an antidegradant; a tackifier; sulfur; tetramethhylthiuram disulfide; an inhibitor; at least one powder super absorbent polymer; and stearic acid.

[00175] Example 4C. The swellable rubber composition of one or more of Examples 1C-3C, wherein the powder super absorbent polymer is present in about 125 to 175 Phr.

[00176] Example 5C. The swellable rubber composition of one or more of Examples 1C-4C, wherein the powder super absorbent polymer is present in about 170 to 210 Phr.

[00177] Example 6C. The swellable rubber composition of one or more of Examples 1C-5C, wherein the powder super absorbent polymer is present in at least about 150 Phr, 175 Phr, 200 Phr or 225 Phr.

[00178] Example 7C. The swellable rubber composition of one or more of Examples 1C-6C, wherein the powder super absorbent polymer and at least one granular super absorbent polymer is present in the swellable rubber; and wherein the powder super absorbent polymer comprises at least 50%, 60%, 70%, 80%, 90%, or 95% by weight of a total super absorbent polymer incorporated into the swellable rubber.

[00179] Example 8C. The swellable rubber composition of one or more of Examples 1C-7C, wherein the total super absorbent polymer is selected such that, after curing, a cured swellable rubber

packer is capable of expanding in water and/or brine without compromising the physical properties of the rubber and/or without significantly leaching and/or without significantly perforating.

[00180] Example 9C. The swellable rubber composition of one or more of Examples 1C-8C, wherein the powder super absorbent polymer has an average particle size of about 10 to 120 μm or about 20 to 100 μm, (e.g., about 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, 100, 105, 110, 115 or 120 μm).

[00181] Example 10C. The swellable rubber composition of one or more of Examples 1C-9C, wherein the powder super absorbent polymer has an average particle size of less than or equal to about 20, 30, 40, 50, 60, 70, 80, 90, 100, 110 or 120 μm.

[00182] Example 11C. The water swellable rubber composition of one or more of Examples 1C-10C, wherein the powder super absorbent polymer consists essentially of particle sizes of less than or equal to about 20, 30, 40, 50, 60, 70, 80, 90, 100, 110, 120 or 130 μm.

[00183] Example 12C. The swellable rubber composition of one or more of Examples 1C-11C, further comprising about 120 to 220 (e.g., 120, 125, 130, 135, 140, 145, 150, 155, 160, 165, 170, 175, 180, 185, 190, 195, 200, 205, 210, 215, 220) Phr of powder super absorbent polymer.

[00184] Example 13C. The swellable rubber composition of one or more of Examples 1C-12C, wherein the powder super absorbent polymer comprises one or more of the following: poly-electrolytes, polyacyrlates (e.g., sodium polyacrylate), polyacryamide-co-polyacrylates (e.g., polyacryamide-co-potassium acrylate), polyacrylamides (e.g., potassium polyacrylamide) and/or acrylic acids.

[00185] Example 14C. The swellable rubber composition of one or more of Examples 1C-13C, wherein the granular super absorbent polymer comprises one or more of the following: poly-electrolytes, polyacyrlates (e.g., sodium polyacrylate), polyacryamide-co-polyacrylates (e.g., polyacryamide-co-potassium acrylate), polyacrylamides (e.g., potassium polyacrylamide) and/or acrylic acids.

[00186] Example 15C. The swellable rubber composition of one or more of Examples 1C-13C, wherein the powder super absorbent polymer is a potassium polyacrylate polyacrylamide copolymer that has a mean particle size of approximately 35 μm, a median particles size of approximately 35 μm with a standard deviation of approximately 10 μm and substantial no particles over approximately 75 μm in the powder.

[00187] Example 16C. The swellable rubber composition of one or more of Examples 1C-15C, wherein the swellable rubber composition after curing is configured to swell by at least about 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, 90%, 100%, 110%, 120%, 130%, 140%, 150%, 160%, 170%, 180%, 190%, 200%, 210%, 220%, 230%, 240% or 250% by volume in an about 5%

weight/volume brine solution without substantially compromising the physical properties of the cured rubber and/or without significantly leaching and/or without significantly perforating.

[00188] Example 17C. The swellable rubber composition of one or more of Examples 1C-16C, wherein the swellable rubber composition after curing is configured to swell by at least about 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, 90%, 100%, 110%, 120%, 130%, 140%, 150%, 160%, 170%, 180%, 190%, 200%, 210%, 220%, 230%, 240% or 250% by volume in an about 16% weight/volume brine solution without substantially compromising the physical properties of the rubber and/or without significantly leaching and/or without significantly perforating.

[00189] Example 18C. The swellable rubber composition of one or more of Examples 1C-17C, wherein the swellable rubber composition after curing is configured to swell while being subjected to a temperature of about 200 degrees Fahrenheit.

[00190] Example 19C. The swellable rubber composition of one or more of Examples 1C-17C, wherein the water swellable rubber composition after curing is configured to swell while being subjected to a temperature of about 275 degrees Fahrenheit.

[00191] Example 20C. The swellable rubber composition of one or more of Examples 1C-19C, wherein the swellable rubber composition after curing is configured to swell while being subjected to a pressure of at least about 3000, 4000, 5000, 6000, 7000, or 8000 psi.

[00192] Example 21C. The swellable rubber composition of one or more of Examples 1C-20C, wherein the swellable rubber composition after curing is configured to substantially swell within 2, 3, 4 or 5 days.

[00193] Example 22C. The swellable rubber composition of one or more of Examples 1C-21C, wherein the swellable rubber composition after curing has a Shore A hardness of at least 20, 25 or 30.

[00194] Example 23C. The swellable rubber composition of one or more of Examples 1C-21C, wherein the swellable rubber composition after curing and substantially swelling has a Shore A hardness of at least 20, 25 or 30.

[00195] Example 24C. A swellable packer comprising: a conduit, and a swellable rubber composition according to one or more of Examples 1C-23C, wrapped around at least a portion of the conduit and cured.

[00196] Example 25C. A swellable packer manufactured by causing the swellable rubber composition of one or more of Examples 1C-23C to cure after the swellable rubber composition has been wrapped around at least a portion of the conduit.

[00197] Example 26C. A method of sealing a region between wellbore wall and the swellable packer-conduit assembly, wherein the swellable packer-conduit assembly comprises a conduit and a

swellable packer at least partially surrounding the outer surface of the conduit, comprising: locating a swellable packer-conduit assembly in a region of the wellbore in a manner so as to seal said space upon swelling of the swellable body, the swellable body being susceptible to being in contact with water, water based fluid, and/or formation water present in the wellbore, according to one or more of Examples 1C-23C.

[00198] While exemplary embodiments have been shown and described herein, one skilled in the art would understand that such embodiments are provided by way of example only. The following claims define the scope of the invention, and methods and structures within the scope of these claims and their equivalents are included in this disclosure.

[00199] In the foregoing description of exemplary embodiments, specific terminology has been used for the sake of clarity. However, the invention is not intended to be limited to the specific terms selected, and it is to be understood that each specific term includes all technical equivalents that operate in the same or similar manner to accomplish the same or similar technical purpose. Terms such as "front" and "rear," "inner" and "outer," "above" and "below," "upper" and "lower," and the like are used as words of convenience to provide reference points and are not to be construed as limiting terms. A term such as "at least" is a number greater than zero as described herein.

[00200] The reference in this specification to any prior publication (or information derived from it), or to any matter that is known, is not, and should not be taken as, an acknowledgement, admission, or any form of suggestion that prior publication (or information derived from it) or known matter forms part of the common general knowledge in the field of endeavor to which this specification relates.

[00201] In this specification, the word "comprising" is to be understood in its "open" sense, that is, in the sense of "including," and thus not limited to its "closed" sense, that is, in the sense of "consisting only of." A corresponding meaning is to be attributed to the corresponding words "comprise," "comprised," "comprises," includes, has, and derivatives thereof, where they appear.

[00202] In addition, the foregoing describes only some embodiments of the invention(s), and alterations, modifications, additions, and/or changes can be made thereto without departing from the scope and spirit of the disclosed embodiments, the embodiments being illustrative and not restrictive.

[00203] Furthermore, invention(s) have been described in connection with what are presently considered to be the most practical and preferred embodiments. It is to be understood that the invention is not to be limited to the disclosed embodiments, but, on the contrary, is intended to cover various modifications and equivalent arrangements included within the spirit and scope of the invention(s). Also, the various embodiments described above may be implemented in conjunction with other embodiments. For example, aspects of one embodiment may be combined with aspects of

another embodiment to realize yet other embodiments. Further, each independent feature or component of any given assembly may constitute an additional embodiment.

NAI-1501538259v1

What is Claimed is:

1. A swellable rubber composition comprising:
an elastomer;
a butadiene rubber;
a sulfur curing agent;
a silica; and
a powder super absorbent polymer.

2. A swellable rubber composition comprising:
a nitrile elastomer;
a rubber;
a sulfur curing agent;
a silica; and
a powder super absorbent polymer.

3. A swellable rubber composition comprising:
at least one nitrile rubber elastomer;
at least one styrene butadiene rubber;
carbon black;
dioctyl phthalate;
fumed silica;
zinc oxide;
an antiozonant;
an antidegradant;
a tackifier;
sulfur;
tetramethhylthiuram disulfide;
an inhibitor;
at least one powder super absorbent polymer; and
stearic acid.

4. The swellable rubber composition of one or more of claims 1-3, wherein the powder super absorbent polymer is present in 125 to 175 Phr.

5. The swellable rubber composition of one or more of claims 1-4, wherein the powder super absorbent polymer is present in 170 to 210 Phr.

6. The swellable rubber composition of one or more of claims 1-5, wherein the powder super absorbent polymer is present in at least 150 Phr, 175 Phr, 200 Phr or 225 Phr.

7. The swellable rubber composition of one or more of claims 1-6, wherein the powder super absorbent polymer and at least one granular super absorbent polymer is present in the swellable rubber composition; and wherein the powder super absorbent polymer comprises at least 50%, 60%, 70%, 80%, 90% or 95% by weight of a total super absorbent polymer incorporated into the swellable rubber composition.

8. The swellable rubber composition of one or more of claims 1-7, wherein the total super absorbent polymer is selected such that, after curing, a cured swellable rubber packer is capable of expanding in water and/or brine without compromising the physical properties of the rubber composition and/or without significantly leaching and/or without significantly perforating.

9. The swellable rubber composition of one or more of claims 1-8, wherein the powder super absorbent polymer has an average particle size of about 10 to 120 μm or about 20 to 100 μm, (e.g., about 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, 100, 105, 110, 115 or 120 μm).

10. The swellable rubber composition of one or more of claims 1-9, wherein the powder super absorbent polymer has an average particle size of less than or equal to about 20, 30, 40, 50, 60, 70, 80, 90, 100, 110 or 120 μm.

11. The swellable rubber composition of one or more of claims 1-10, wherein the powder super absorbent polymer consists essentially of particle sizes of less than or equal to about 20, 30, 40, 50, 60, 70, 80, 90, 100, 110, 120 or 130 μm.

12. The swellable rubber composition of one or more of claims 1-11, further comprising about 120 to 220 (e.g., 120, 125, 130, 135, 140, 145, 150, 155, 160, 165, 170, 175, 180, 185, 190, 195, 200, 205, 210, 215, 220) Phr of powder super absorbent polymer.

13. The swellable rubber composition of one or more of claims 1-12, wherein the powder super absorbent polymer comprises one or more of the following: poly-electrolytes, polyacyrlates (e.g., sodium polyacrylate), polyacryamide-co-polyacrylates (e.g., polyacryamide-co-potassium acrylate), polyacrylamides (e.g., potassium polyacrylamide) and/or acrylic acids.

14. The swellable rubber composition of one or more of claims 1-13, wherein the granular super absorbent polymer comprises one or more of the following: poly-electrolytes, polyacyrlates (e.g., sodium polyacrylate), polyacryamide-co-polyacrylates (e.g., polyacryamide-co-potassium acrylate), polyacrylamides (e.g., potassium polyacrylamide) and/or acrylic acids.

15. The swellable rubber composition of one or more of claims 1-13, wherein the powder super absorbent polymer is a potassium polyacrylate polyacrylamide copolymer that has a mean particle size of approximately 35 μm, a median particle size of approximately 35 μm with a standard deviation of approximately 10 μm, and substantially no particles over approximately 63 μm in the powder.

16. The swellable rubber composition of one or more of claims 1-15, wherein the swellable rubber composition, after curing, is configured to swell by at least about 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, 90%, 100%, 110%, 120%, 130%, 140%, 150%, 160%, 170%, 180%, 190%, 200%, 210%, 220%, 230%, 240% or 250% by volume in an about 5% weight/volume brine solution without substantially compromising the physical properties of the cured rubber composition and/or without significantly leaching and/or without significantly perforating.

17. The swellable rubber composition of one or more of claims 1-16, wherein the swellable rubber composition, after curing, is configured to swell by at least about 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, 90%, 100%, 110%, 120%, 130%, 140%, 150%, 160%, 170%, 180%, 190%, 200%, 210%, 220%, 230%, 240% or 250% by volume in an about 16% weight/volume brine solution without substantially compromising the physical properties of the rubber composition and/or without significantly leaching and/or without significantly perforating.

18. The swellable rubber composition of one or more of claims 1-17, wherein the swellable rubber composition, after curing, is configured to swell while being subjected to a temperature of about 200 degrees Fahrenheit.

19. The swellable rubber composition of one or more of claims 1-17, wherein the swellable rubber composition, after curing, is configured to swell while being subjected to a temperature of about 275 degrees Fahrenheit.

20. The swellable rubber composition of one or more of claims 1-19, wherein the swellable rubber composition, after curing, is configured to swell while being subjected to a pressure of at least about 3000, 4000, 5000, 6000, 7000, or 8000 psi.

21. The swellable rubber composition of one or more of claims 1-20, wherein the swellable rubber composition, after curing, is configured to substantially swell within 2, 3, 4 or 5 days.

22. The swellable rubber composition of one or more of claims 1-21, wherein the swellable rubber composition, after curing, has a Shore A hardness of at least about 20, 25 or 30.

23. The swellable rubber composition of one or more of claims 1-21, wherein the swellable rubber composition, after curing and substantially swelling, has a Shore A hardness of at least about 20, 25 or 30.

24. A swellable packer comprising:

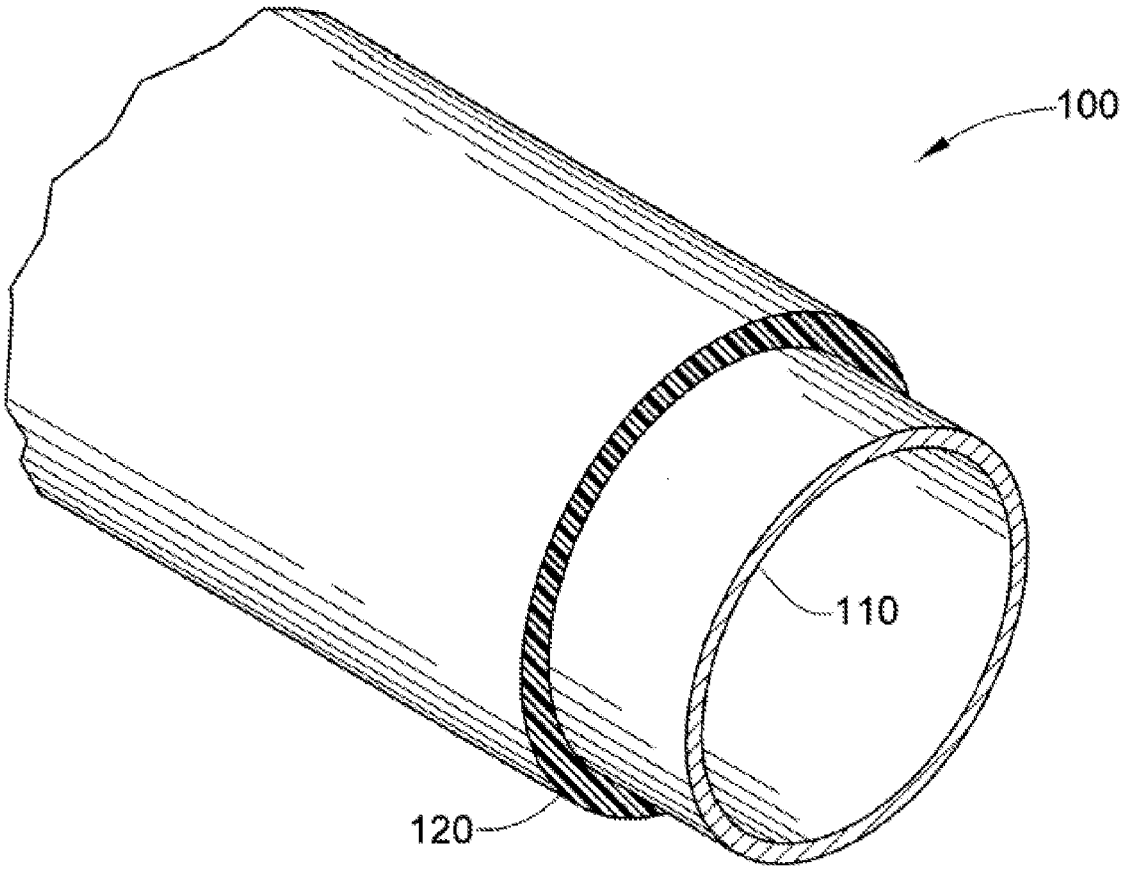
a conduit, and

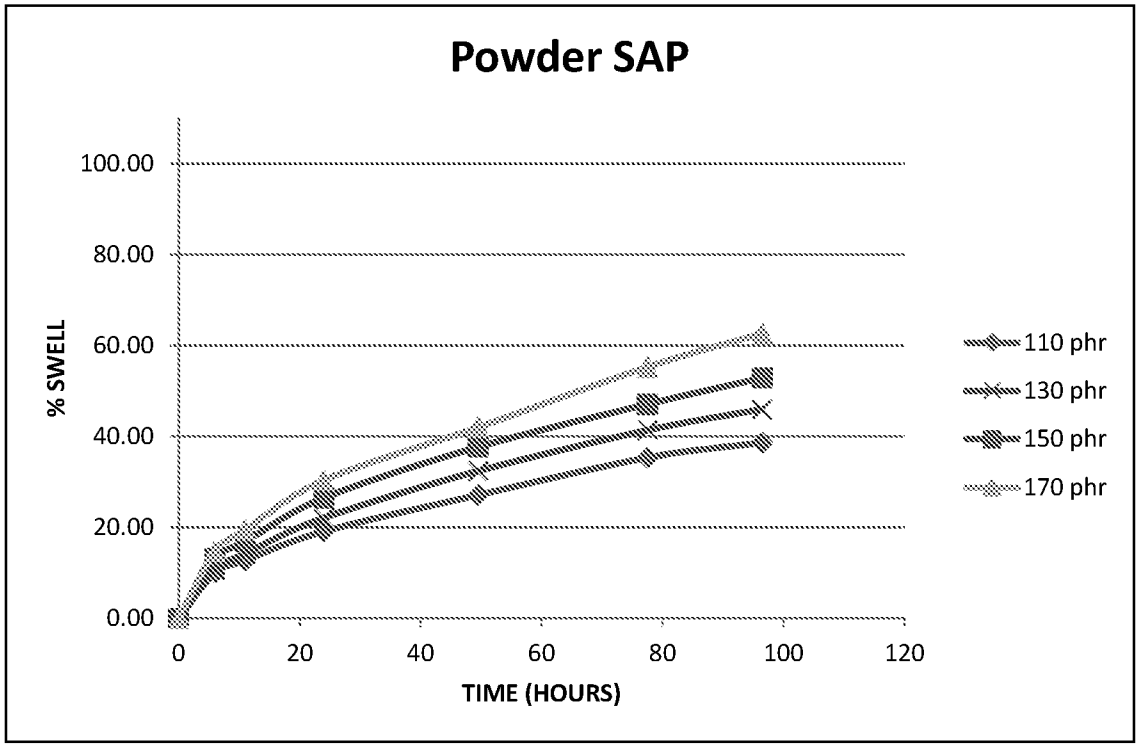
a swellable rubber composition according to one or more of claims 1-23, wrapped around at least a portion of the conduit and cured.

25. A swellable packer manufactured by causing the swellable rubbercomposition of one or more of claims 1-23 to cure after the swellable rubber composition has been wrapped around at least a portion of the conduit.

26. A method of sealing a region between wellbore wall and the swellable packer-conduit assembly, wherein the swellable packer-conduit assembly comprises a conduit and a swellable packer at least partially surrounding the outer surface of the conduit, comprising: locating a swellable packer-conduit assembly in a region of the wellbore in a manner so as to seal said space upon swelling of the swellable body, the swellable body being susceptible to being in contact with water, water based fluid and/or formation water present in the wellbore, according to one or more of claims 1-23.

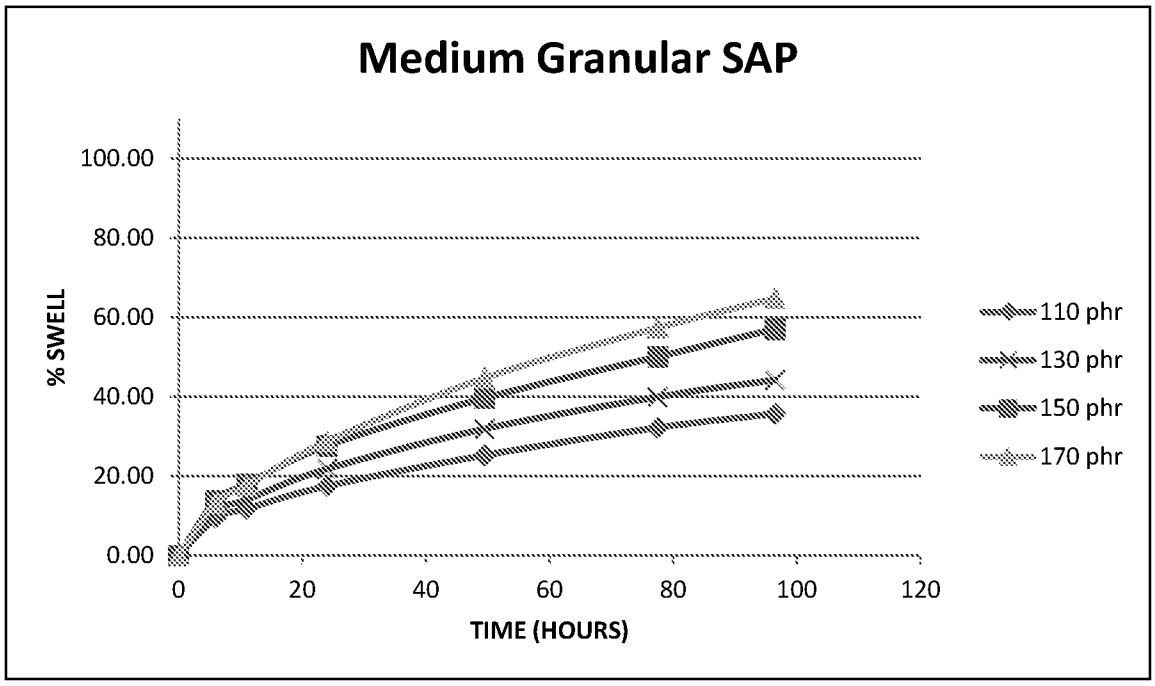
FIG. 1





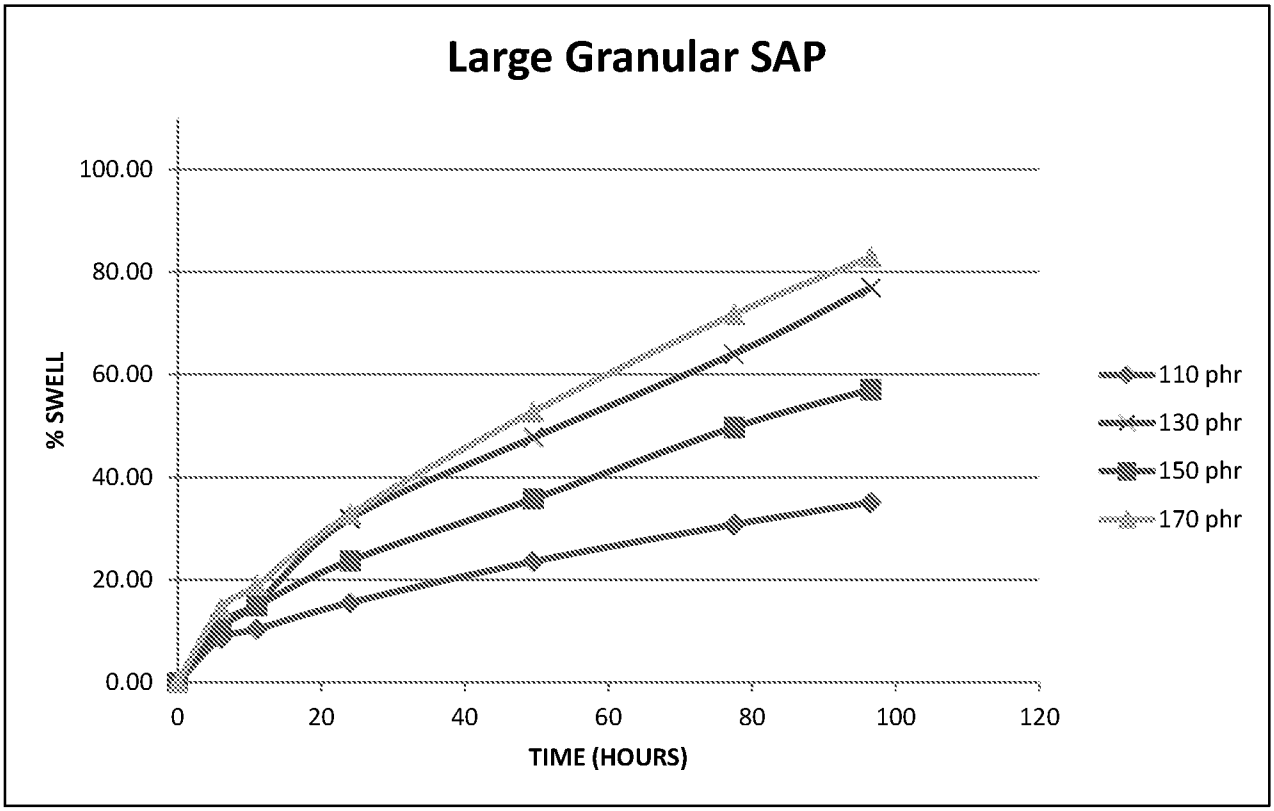
Swelling in 5% Brine, 200°F

FIG. 2A



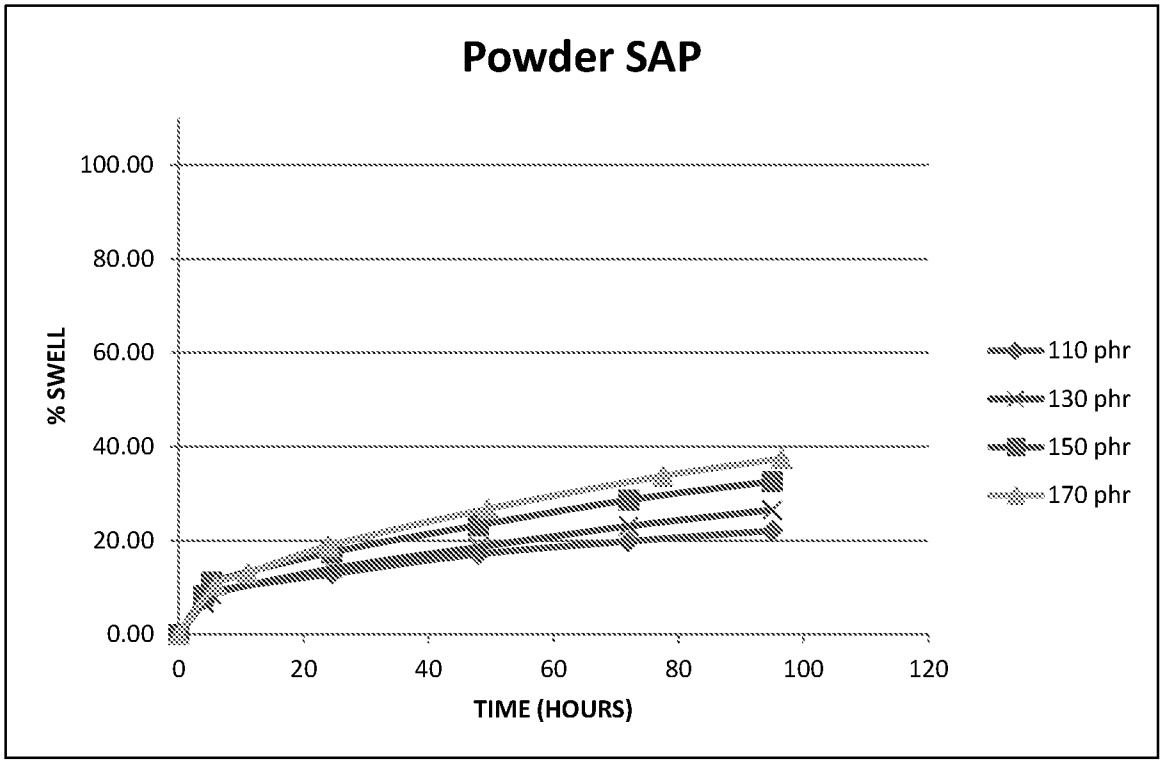
Swelling in 5% Brine, 200°F

FIG. 2B



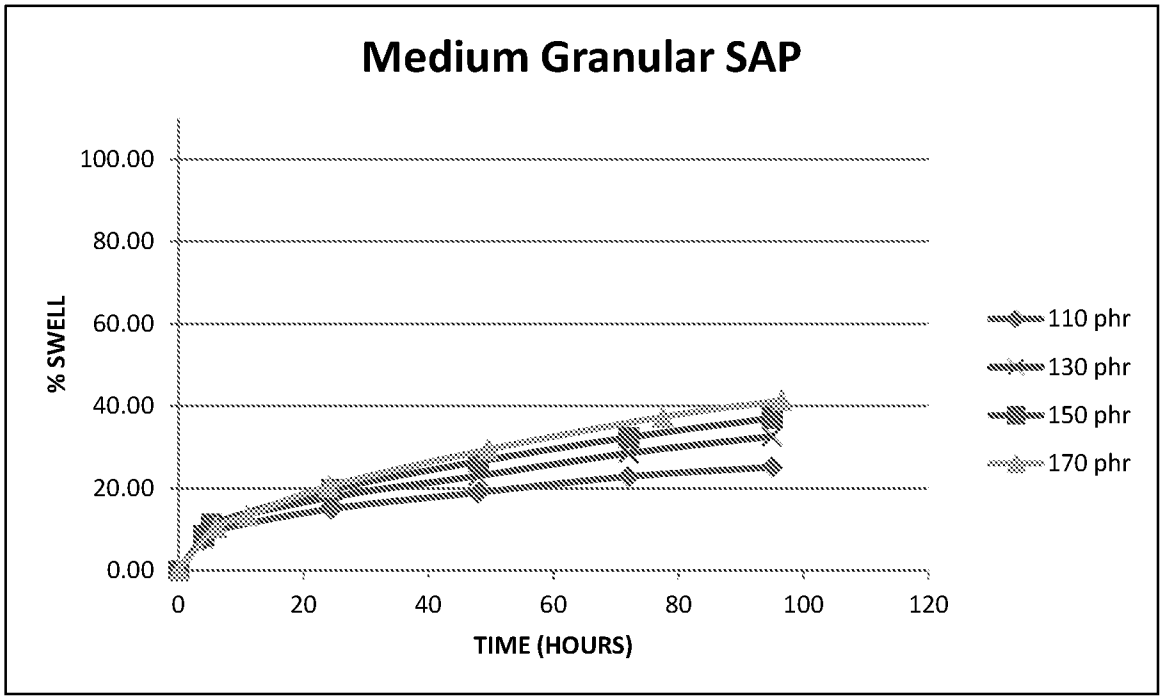
Swelling in 5% Brine, 200°F

FIG. 2C



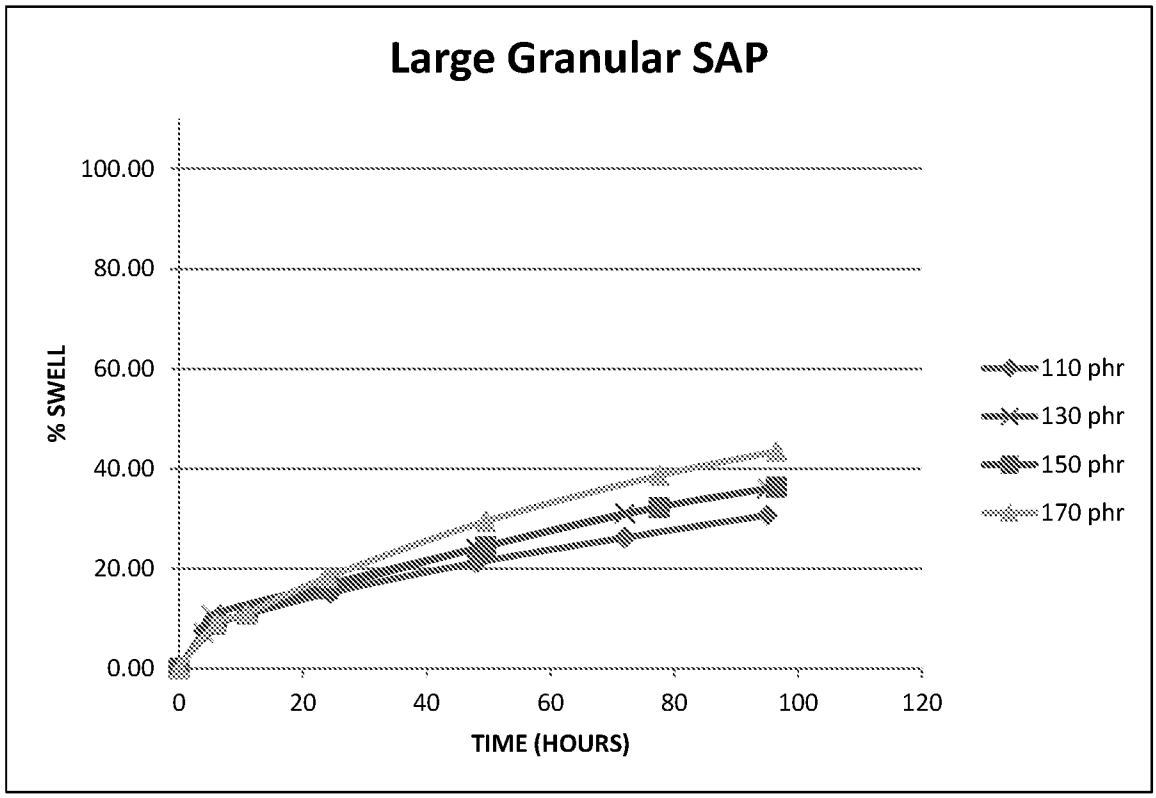
Swelling in 16% Brine, 200°F

FIG. 3A



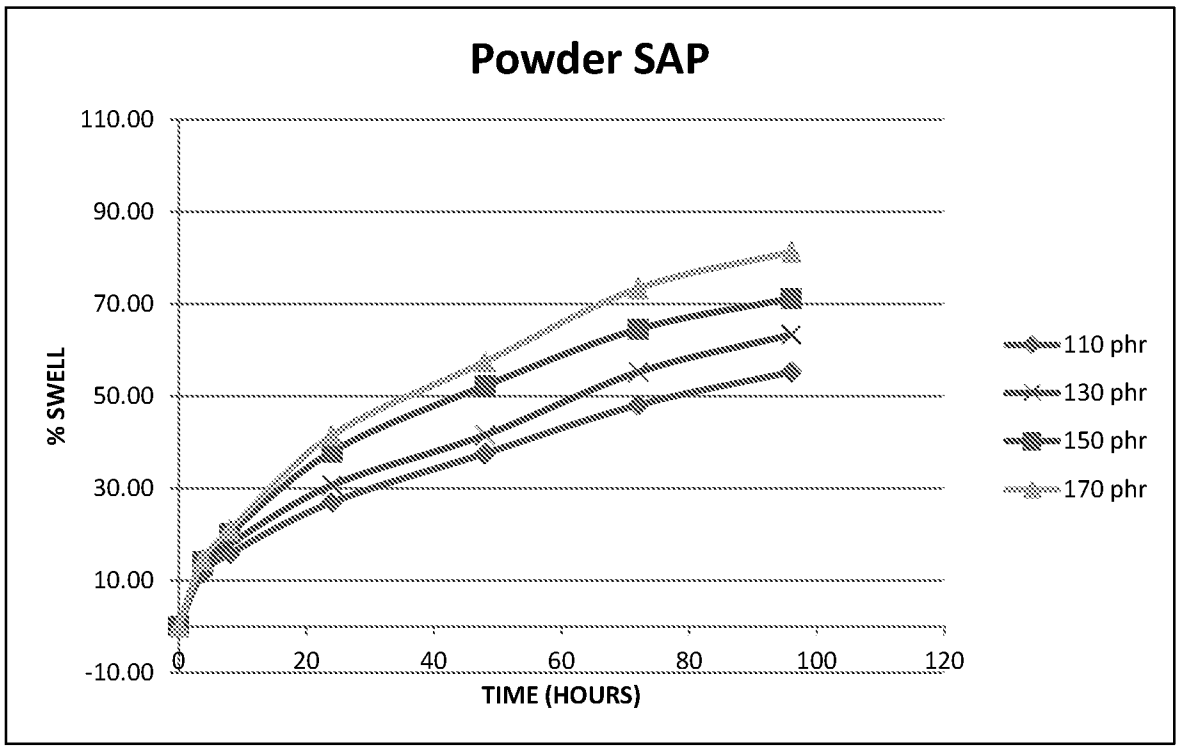
Swelling in 16% Brine, 200°F

FIG. 3B



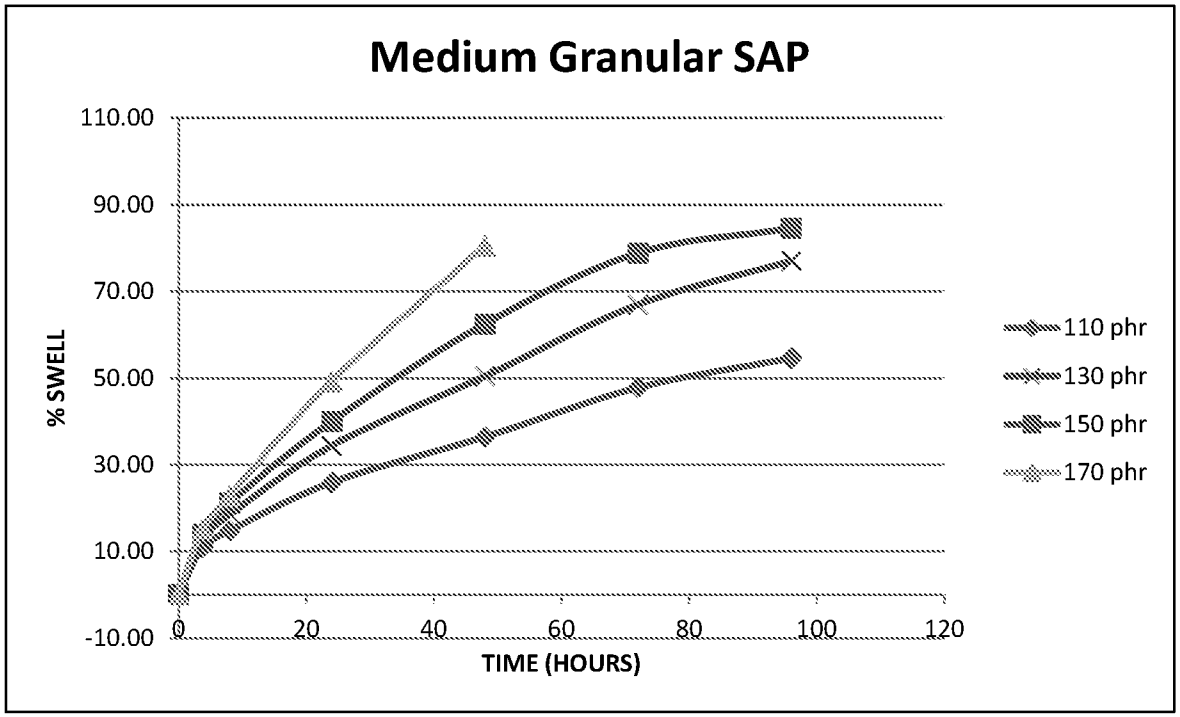
Swelling in 16% Brine, 200°F

FIG. 3C



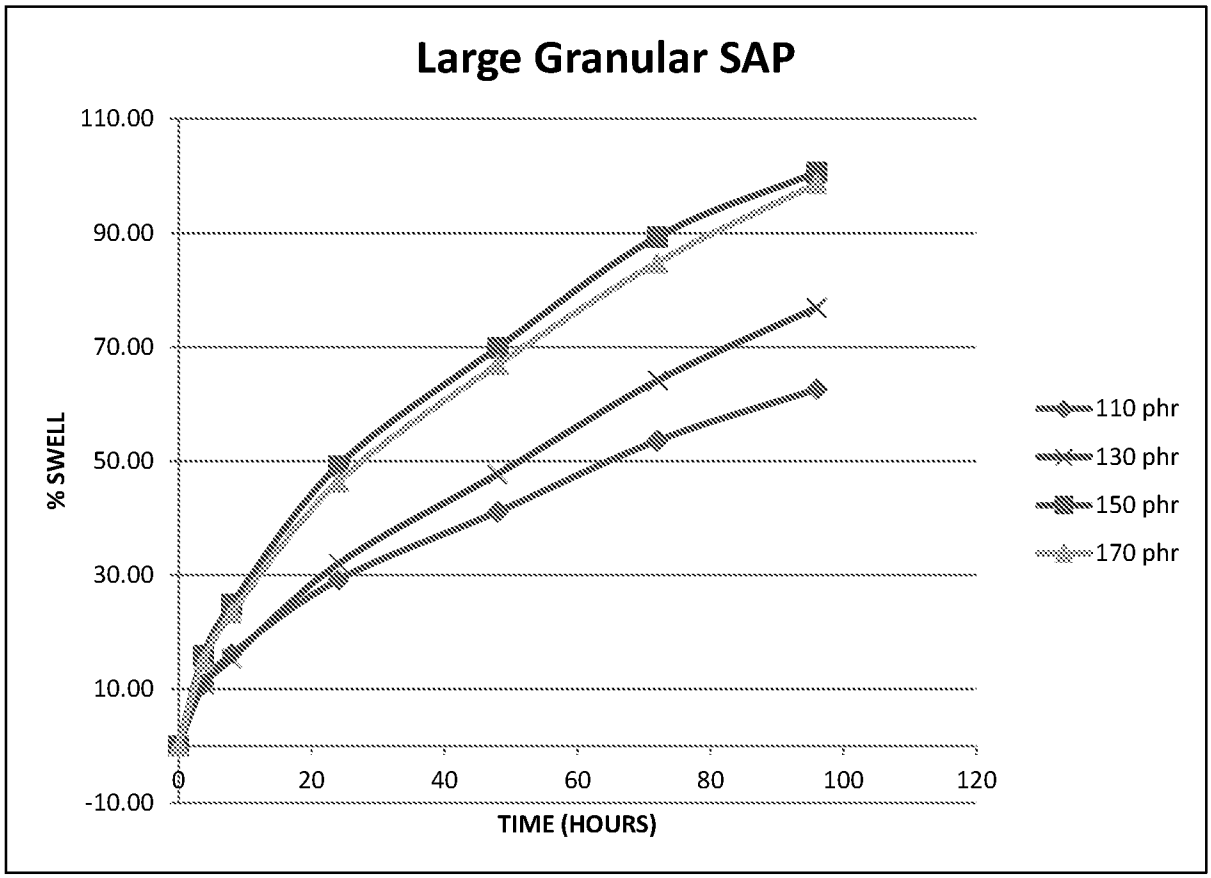
Swelling in 5% Brine, 275°F

FIG. 4A



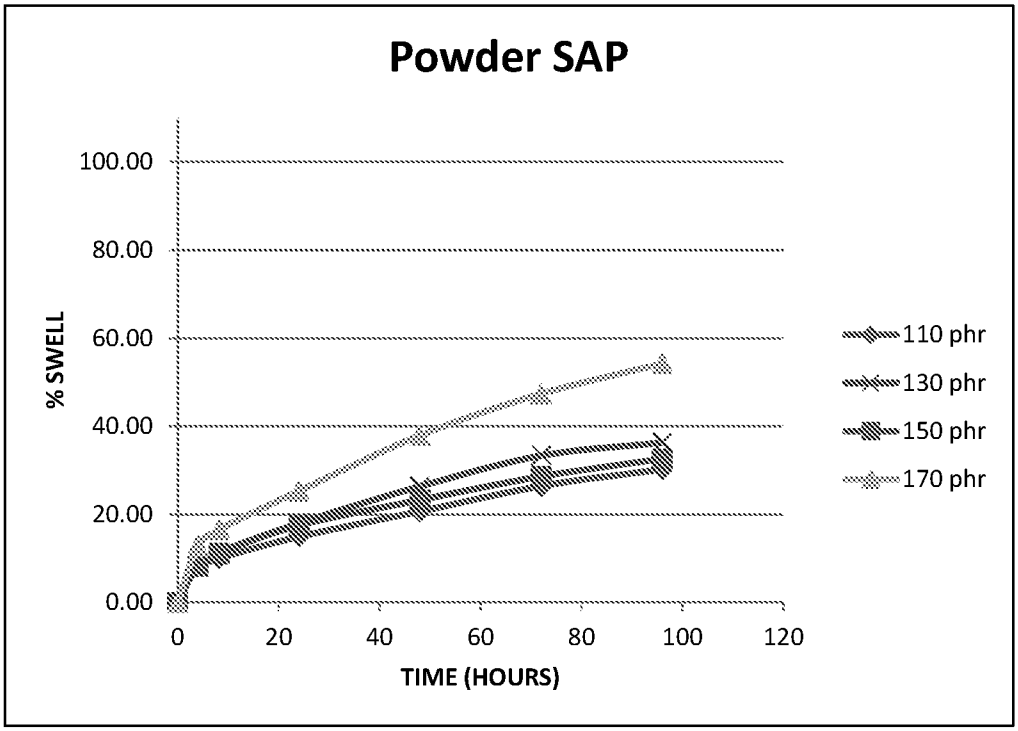
Swelling in 5% Brine, 275°F

FIG. 4B



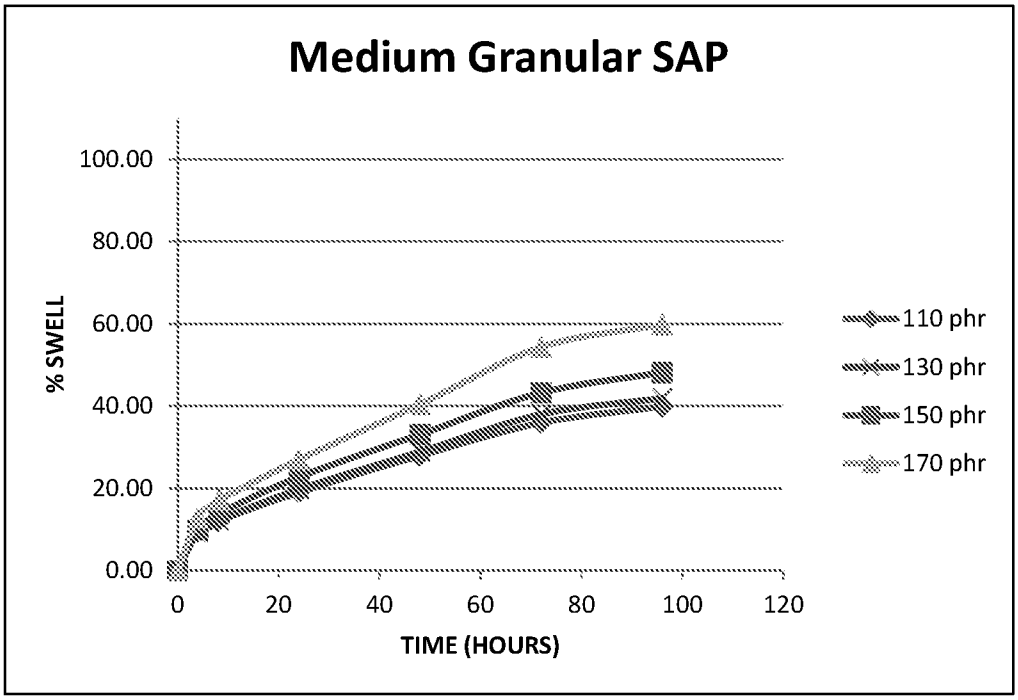
Swelling in 5% Brine, 275°F

FIG. 4C



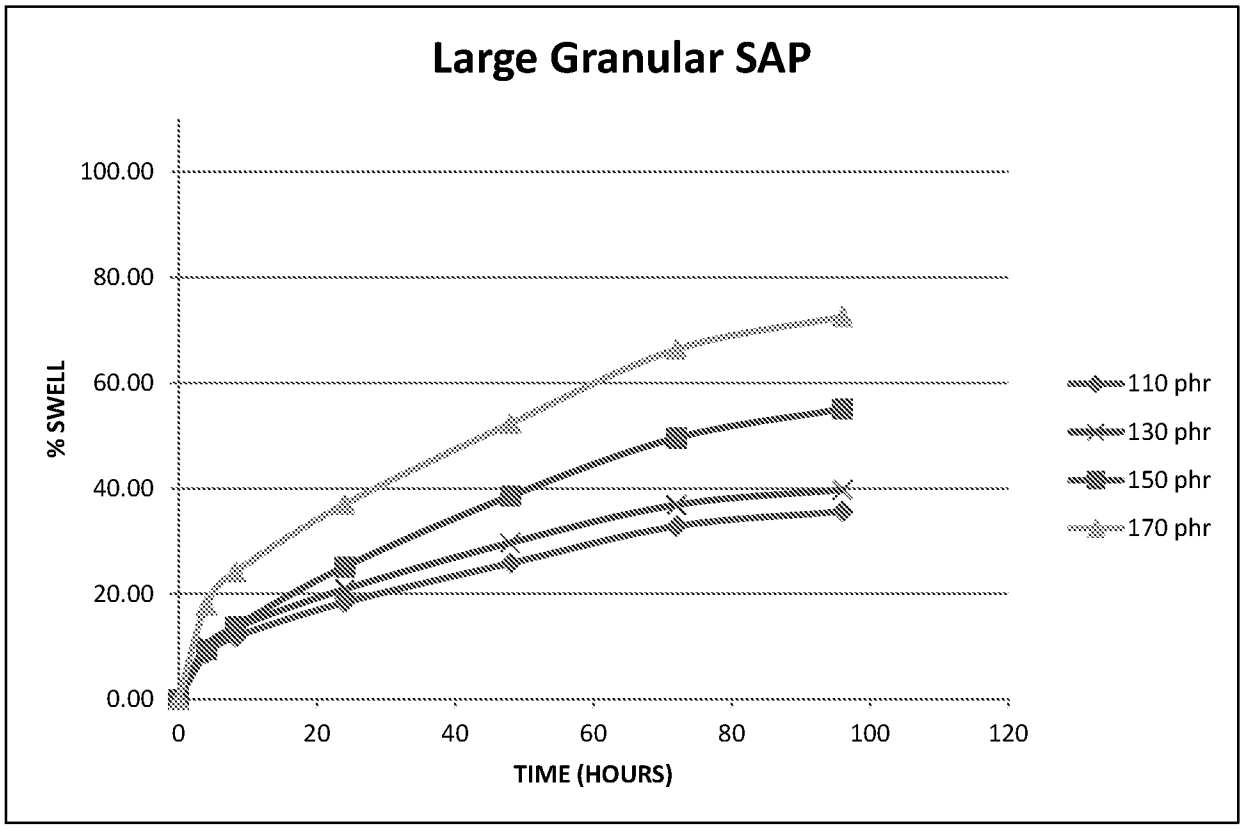
Swelling in 16% Brine, 275°F

FIG. 5A



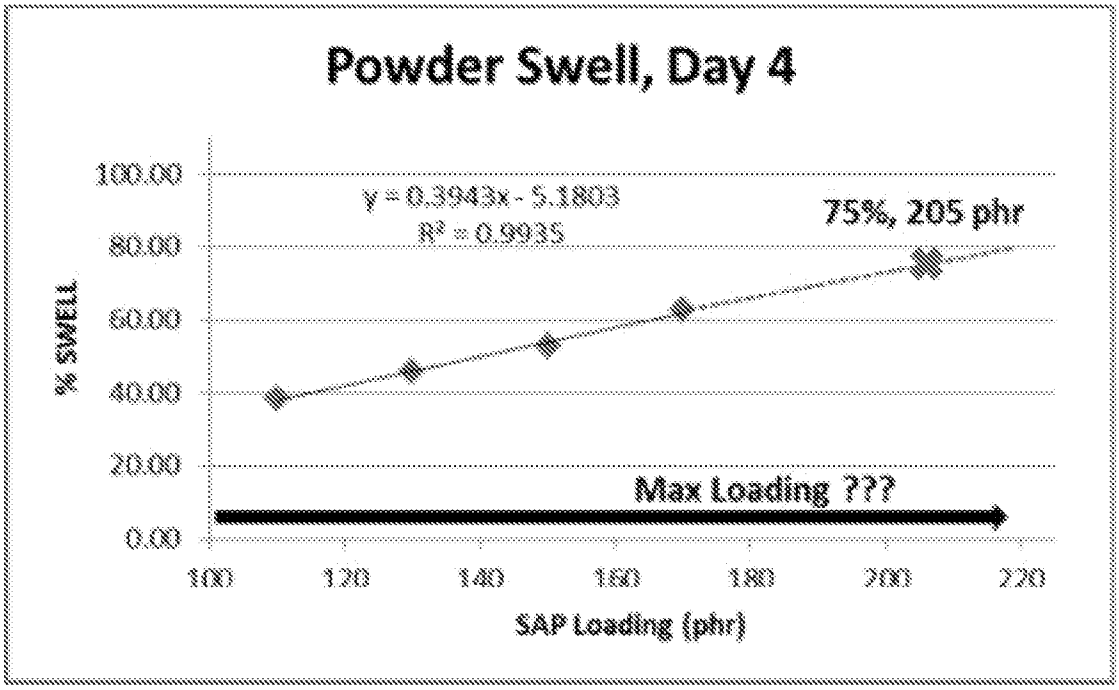
Swelling in 16% Brine, 275°F

FIG. 5B



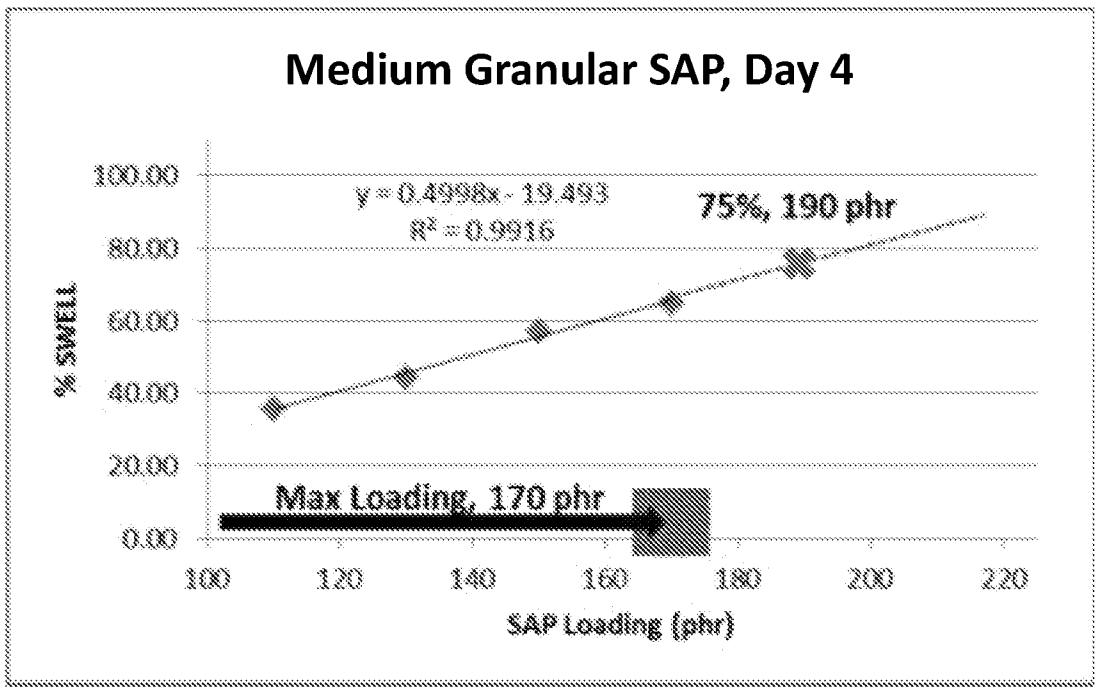
Swelling in 16% Brine, 275°F

FIG. 5C



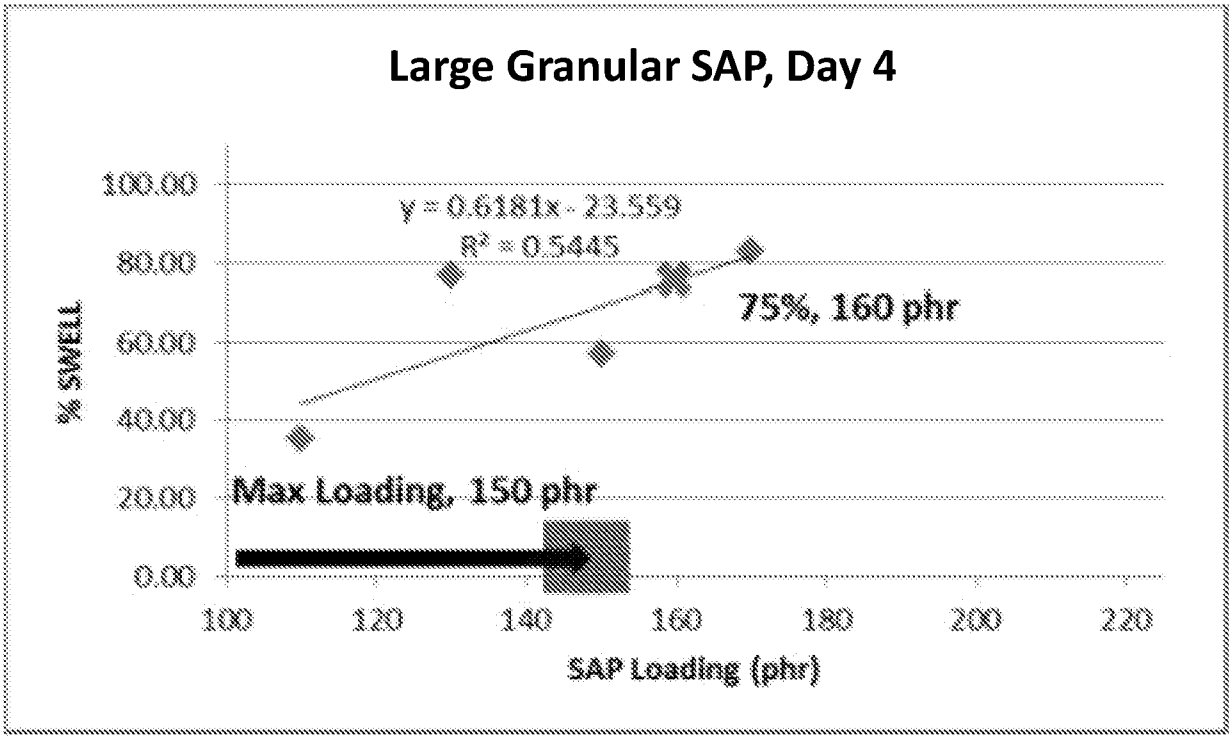
Day 4 Swell vs. SAP Loading (5% Brine, 200°F)

FIG. 6A



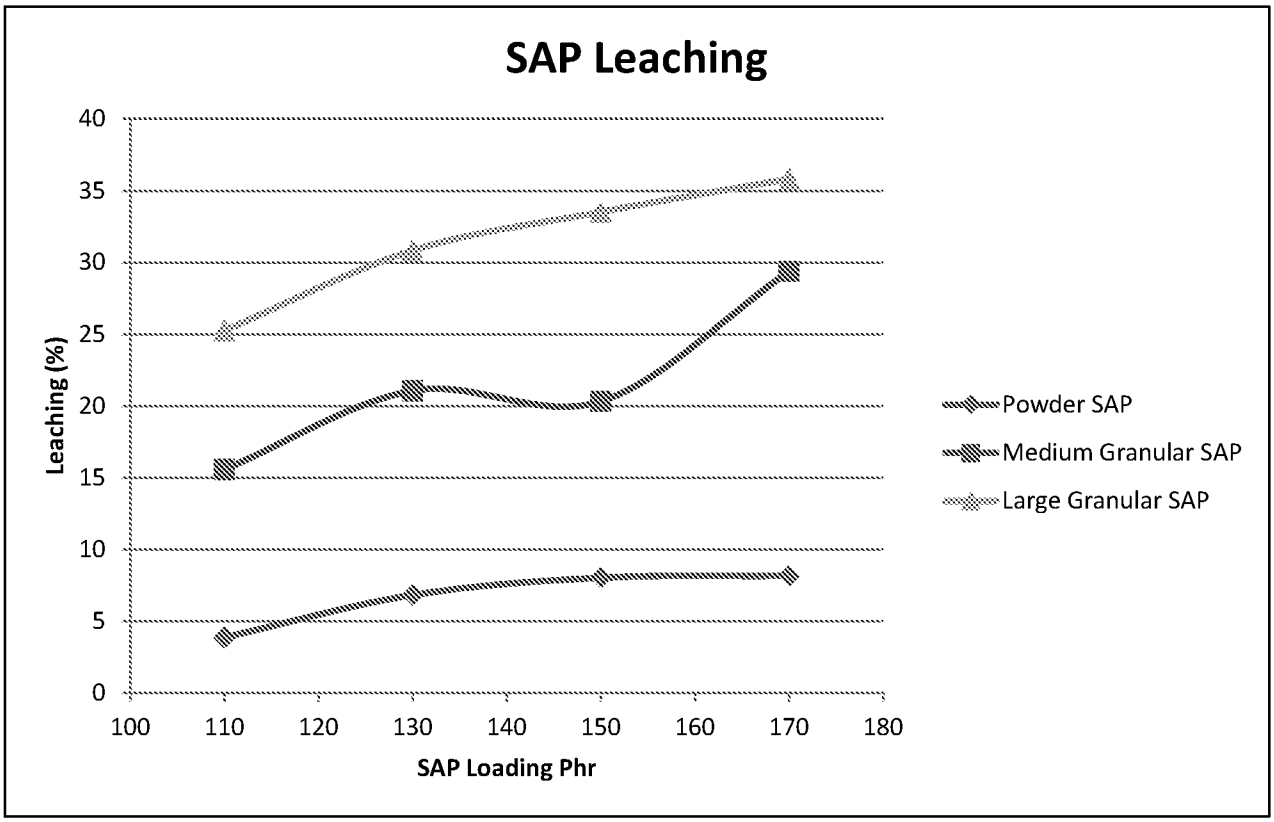
Day 4 Swell vs. SAP Loading (5% Brine, 200°F)

FIG. 6B



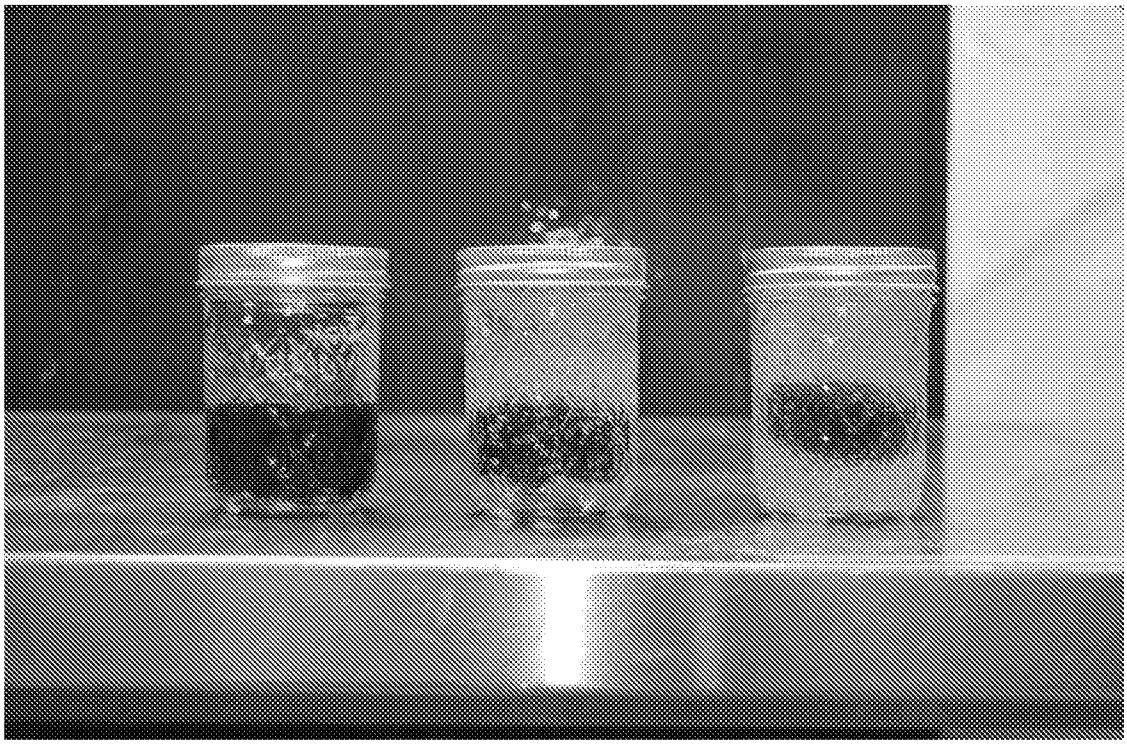
Day 4 Swell vs. SAP Loading (5% Brine, 200°F)

FIG. 6C



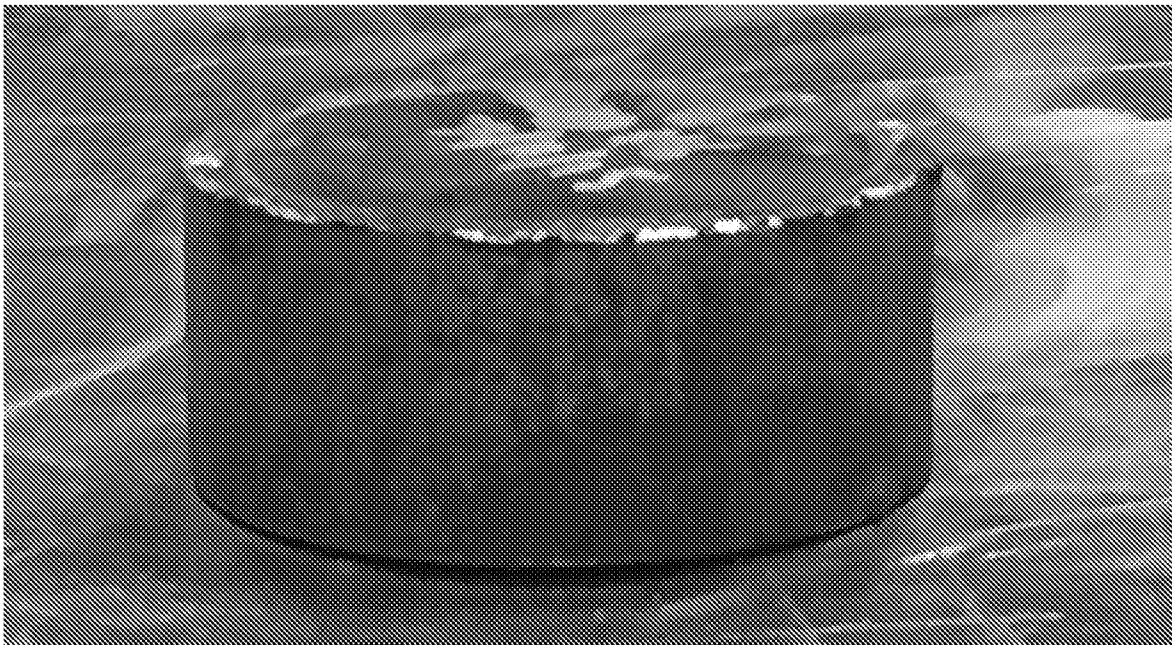
SAP Leaching Comparison

FIG. 7A



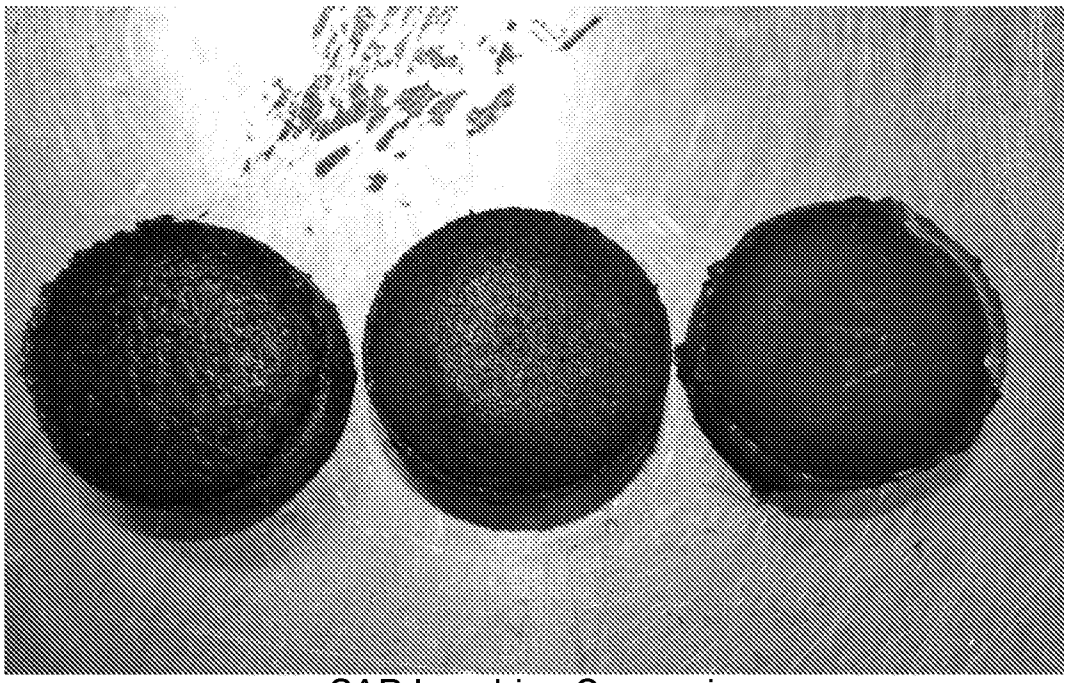
SAP Leaching Comparison

FIG. 7B



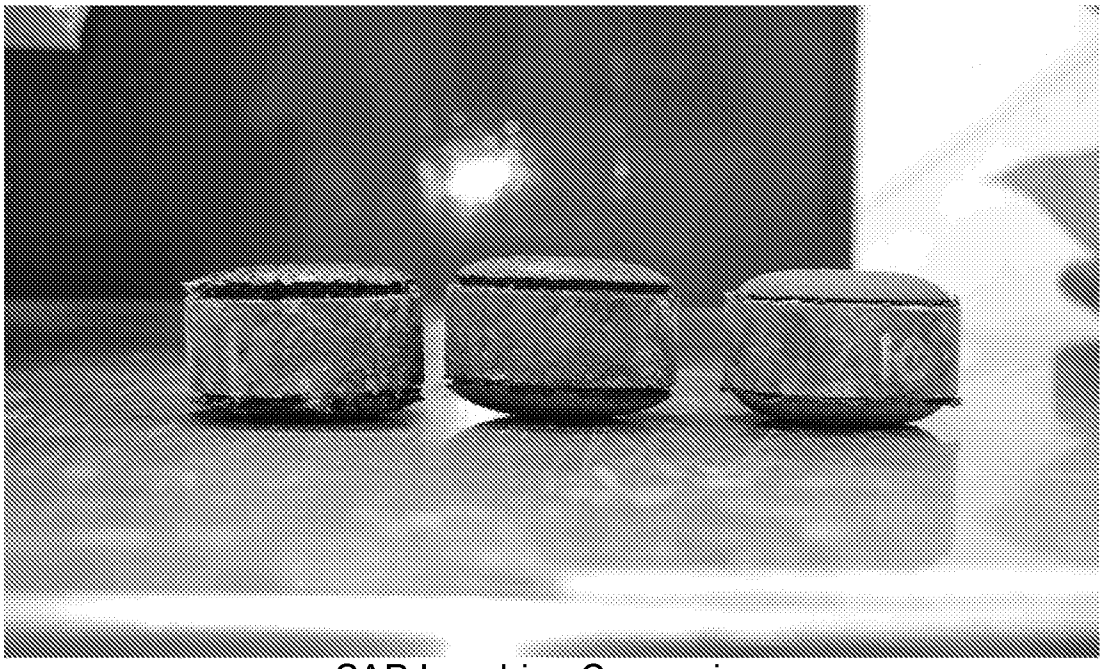
SAP Leaching Comparison

FIG. 7C



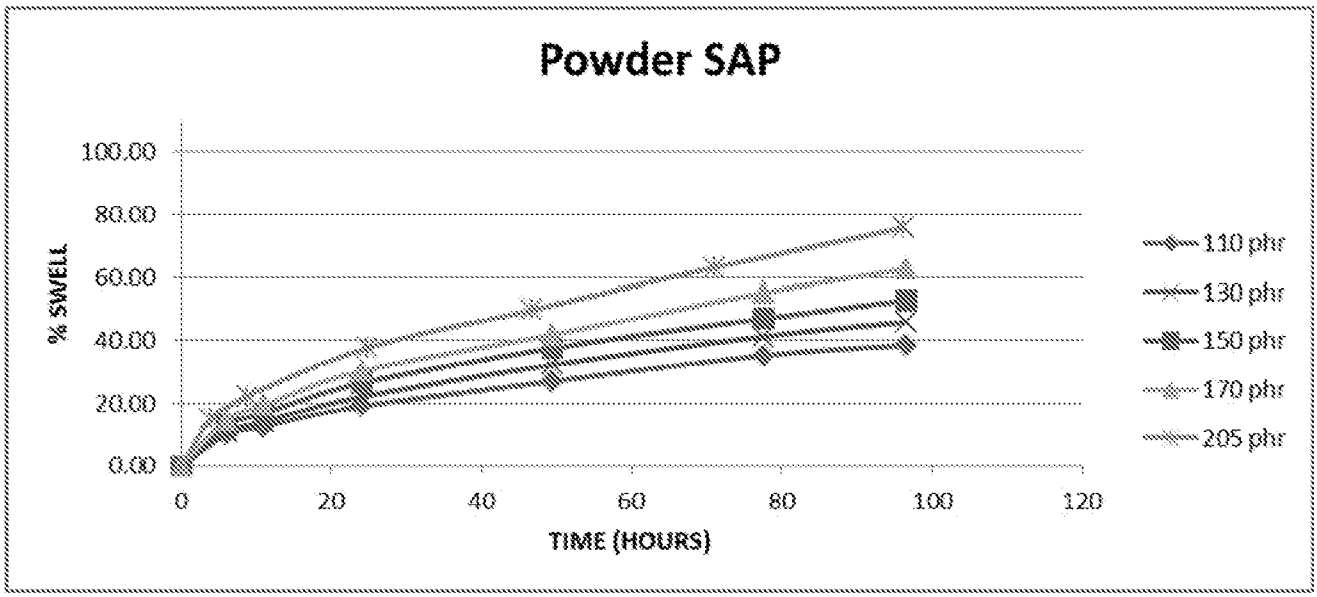
SAP Leaching Comparison

FIG. 7D



SAP Leaching Comparison

FIG. 7E



Swell Comparison, Powder SAP (5% Brine, 200°F)

FIG. 8

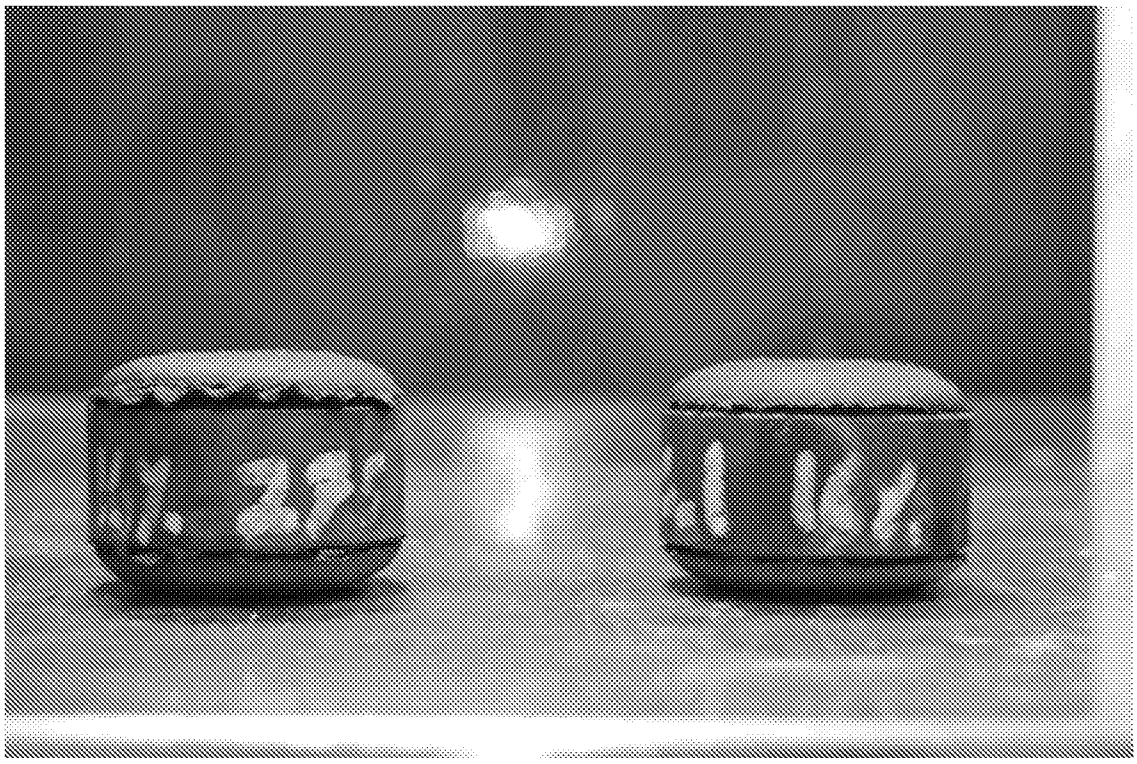
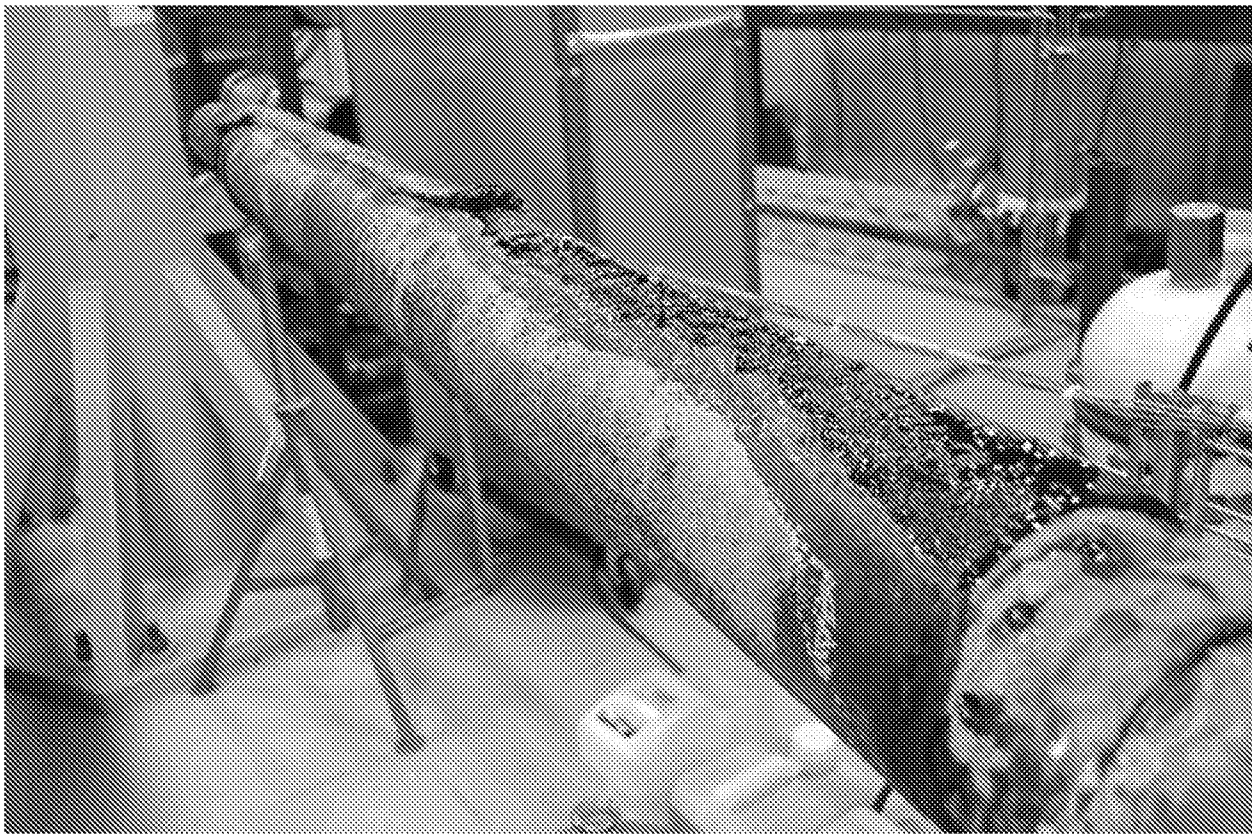


FIG. 9



Packer with Granular SAP Perforation Failure

FIG. 10

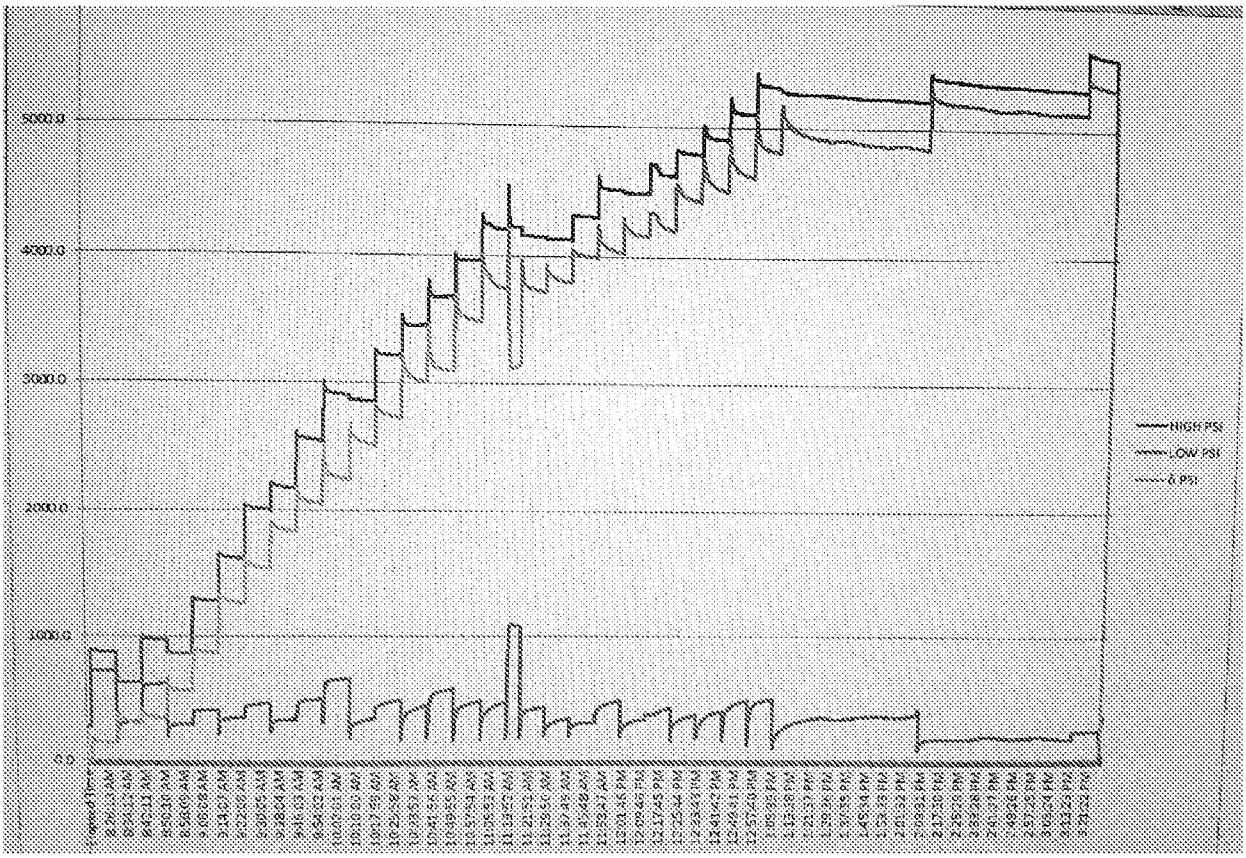


FIG. 11A

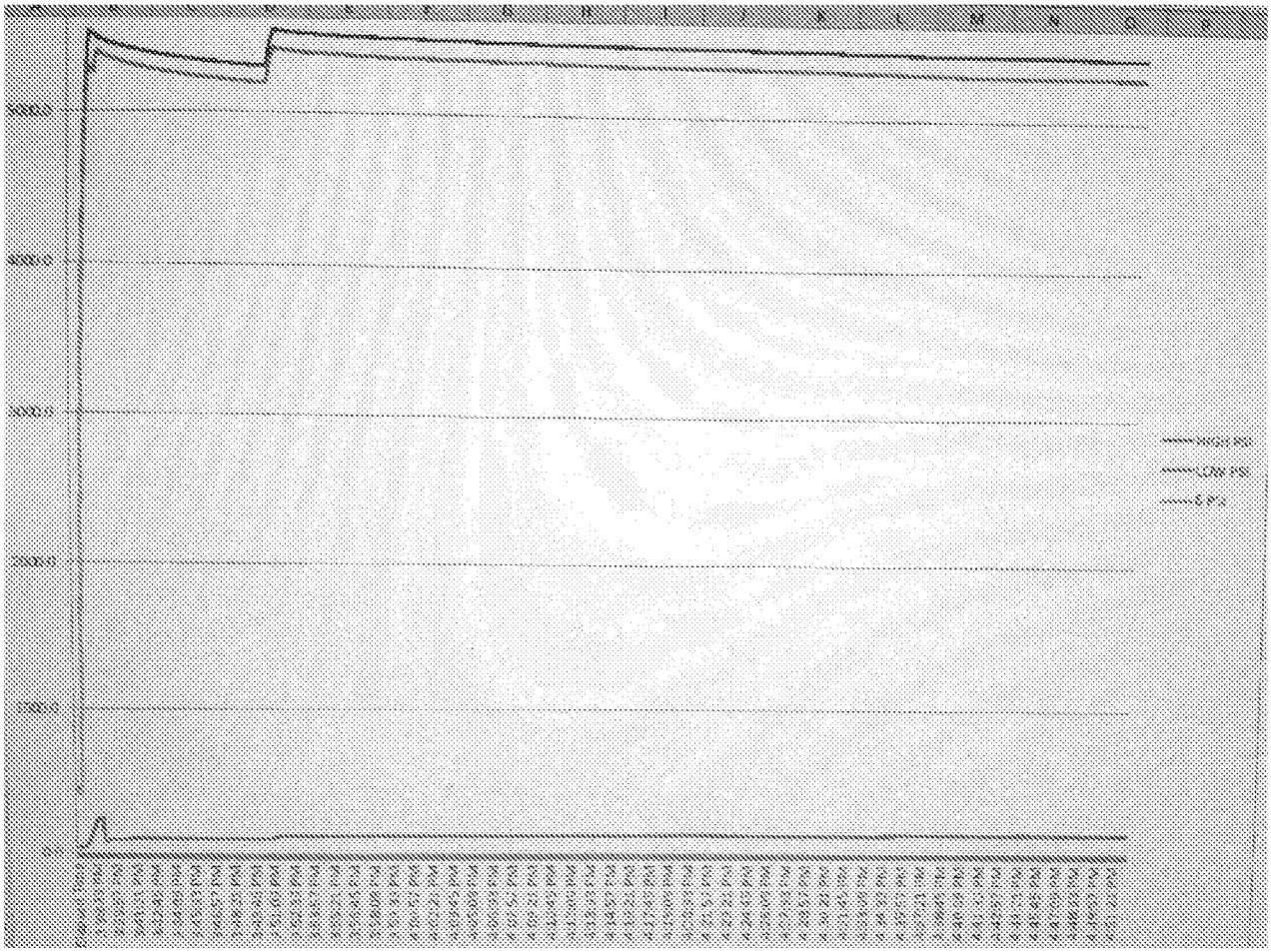


FIG. 11B

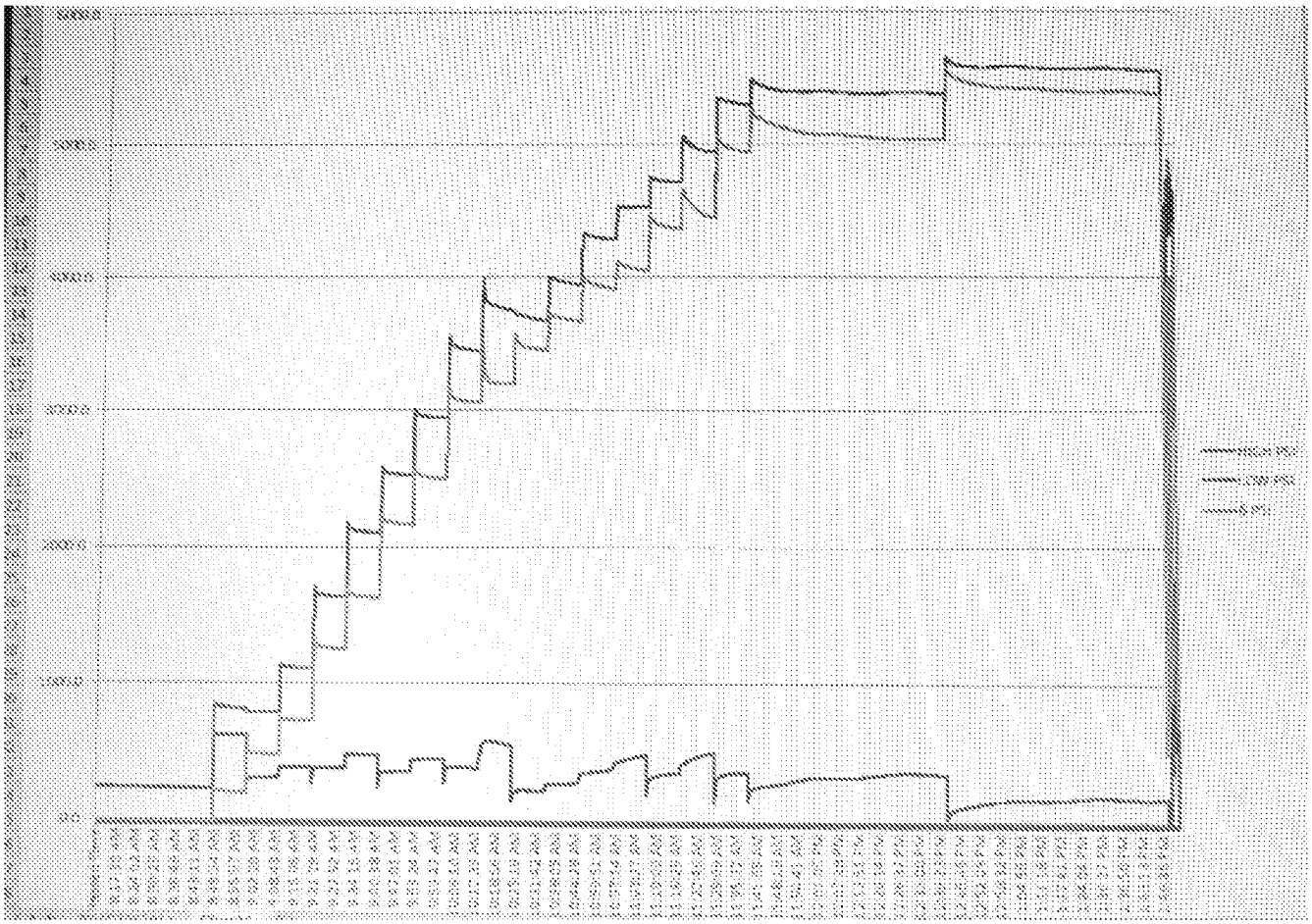


FIG. 12

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 16/42276

A. CLASSIFICATION OF SUBJECT MATTER
IPC(8) - C08L 33/18, C08L 33/02; C08L 63/00 (2016.01)
CPC - C08L 15/005, C08L 33/18, C08L 9/02, C08L 2205/03
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)
IPC(8) - C08L 33/18, C08L 33/02, C08L 63/00 (2016.01)
CPC - C08L 15/005, C08L 33/18, C08L 9/02, C08L 2205/03

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
CPC- B01J20/28011, B01J2220/445, C08L1/286, E21B33/1208, E21B33/1208, C08L15/005, C08L33/18 and Y10T137/0324 (Search terms - See below)

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
PatBase and Google. Search terms: swell, expand, enlarge, rubber, elastomer, polybutadiene, butadiene, sulfur, sulphur, silica, sand, super, polymer, absorbent, sap, nitrile, acrylonitrile, copolymer, nbr, hnr, hnbr, dioctyl, phthalate, inhibit, stearic, acid and fume.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X --- Y	US 200/0066838 A1 (Zhang et al.) 20 March 2008 (20.03.2008) Entire document, especially para [0039], [0041]-[0064] and [0078]	1, 4/1 ---------- 2, 3 and 4/(2,3)
Y	US 2013/0274397 A1 (Choi et al.) 17 October 2013 (17.10.2013). Entire document, especially para [0084]	2, 3 and 4/(2,3) 3 and 4/3
Y	US 7,910,682 B2 (Okamoto et al.) 22 March 2011 (22.03.2011) Entire document, especially col 46, ln 9-10 andcol 51, ln 48. C 3 and 4/3	

☐ Further documents are listed in the continuation of Box C. ☐

* 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
06 September 2016	27 SEP 2016
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-8300	Authorized officer: Lee W. Young PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 16/42276

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☒ Claims Nos.: 5-26.
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.