A swellable apparatus for filling a space in oil or gas apparatus and method of forming an apparatus is described. The apparatus comprises a hydrocarbon swellable body formed from an elastomeric material selected to expand on exposure to a hydrocarbon fluid such as EPDM. The swellable body has a first surface which is exposed to a hydrocarbon fluid, a first (inner) portion, and a second portion disposed between the first portion and the surface. The first portion comprises a fluid permeability structure which differs from the fluid permeability structure of the second portion. In one embodiment, the cross-linking density of an outer portion of the body is greater than the cross-linking density of an inner portion of the body.
Fig. 2
Fig. 5
**Fig. 6A**

![Graph 6A](image)

**Fig. 6B**

![Graph 6B](image)
SWELLABLE APPARATUS AND METHOD OF FORMING

CROSS-REFERENCE TO RELATED APPLICATIONS


FIELD OF THE INVENTION

[0002] The present invention relates to a swellable apparatus for filling a space in oil or gas apparatus and a method of forming such a swellable apparatus.

BACKGROUND

[0003] Well packers are used to create seals in downhole environments. Typically, a well packer is used to form a seal in the annular space between a casing and a tubular located in the casing or between a drilled hole and a tubular located in the drilled hole. Instead of mechanical or inflatable well packers, it is known to form well packers from a material that swells upon contact with hydrocarbons present in the downhole environment.

[0004] The material is selected to expand on exposure to at least one predetermined fluid, which may be a hydrocarbon fluid or an aqueous fluid. The packer may be run to a downhole location in its unexpanded state, where it is exposed to a wellbore fluid and caused to expand. The design, dimensions, and swelling characteristics are selected such that the swellable mantle expands to create a fluid seal in the annulus, thereby isolating one wellbore section from another. Swellable packers have several advantages over conventional packers, including passive actuation, simplicity of construction, and robustness in long term isolation applications. Examples of swellable packers and suitable materials are described in GB 2411918.

[0005] Typically a packer will be constructed for a specific application and incorporated into a casing string or other tool string by means of threaded couplings. Swellable packers are typically constructed from multiple layers of uncured elastomeric material, such as ethylene propylene diene monomer (EPDM) rubber. Multiple layers are overlaid on a mandrel or tubular in an uncured form to build up a mantle of the required dimensions. The mantle is subsequently cured, e.g. by heat curing or air curing. The outer surface of the swellable mantle is then machined using a lathe to create a smooth cylindrical surface. This method produces a fully cured, unitary swellable mantle capable of sealing large differential pressures.

[0006] It is important to control the swell rate of the swellable material of the packer. Swellable materials used to form the expanding portion of the packer will begin to swell as soon as they are exposed to triggering fluids. Thus the packers may begin to expand as they contact drilling oil wellbore fluids during run-in to their desired location in the wellbore. However, it is desirable for the packer outer diameter (OD) to be small during run-in to avoid contact with obstructions, for example washout zones. When the packer is in its desired location, it is advantageous for the packer to swell to its fully swelled condition providing a seal in the wellbore in a short time. It is therefore advantageous to have a swelling rate profile which takes account of the run-in time of the packer and the possible exposure of the packer to triggering fluid during run in. In particular, it may be desirable to impede or retard the swelling of the packer during an early stage of exposure to a triggering fluid, but increase the rate of during a later stage of exposure.

[0007] EP 1315883 discloses a packer system comprising a core of a first elastomer, and an external elastomer which consists of a material having a lower diffusion rate of hydrocarbons compared with the elastomer which constitutes the core.

[0008] In certain applications it is desirable to have a swellable packer that swells on exposure to hydrocarbons and water. Such well packers comprise material that is capable of swelling upon contact with hydrocarbons and material that is capable of swelling upon contact with water or brine. Such materials may be referred to as “hybrid” swelling materials. A swellable packer that swells upon contact with both hydrocarbons and water may provide a proper seal during both the initial and the subsequent stages of production. More specifically, during an early stage of production the production fluid may be comprised essentially of hydrocarbons and during later stages of production the water content of the production fluid may increase.

[0009] WO 05/012686 discloses a swellable material for downhole applications comprising an elastomeric matrix material to which has been added super absorbent polymer (SAP) particles. Such SAP particles can be classified into starch systems, cellulose systems and synthetic resin systems. The SAPs have hydrophilic characteristics by virtue of the presence of alcohols, carboxylic acids, amides or sulphuric acids. Cross-linking between the particles creates a three dimensional network. A compound is mixed with and bound to the material to maintain the desired diffusion gradient and allow for continued absorption of water (and thus continued swelling) in aqueous conditions.

[0010] US 2007/0021245 discloses oilfield elements and assemblies comprising elastomeric compositions capable of swelling in oil and water. The compositions comprise the reaction product of linear or branched polymers having residual ethylenic unsaturation with an unsaturated organic monomer having at least one acidic reactive moiety.

[0011] One object of the invention is to provide an alternative swellable apparatus which facilitates control or selection of swelling characteristics such as swelling rate during exposure to wellbore fluids.

[0012] The present inventor has appreciated certain shortcomings of known well packers formed of material capable of swelling upon contact with hydrocarbons and water. In particular, swelling of hybrid materials may be inadequate or slow in aqueous (water or brine) conditions.

[0013] One drawback of blending water swellable bodies such as superabsorbent polymers with elastomers is that the bodies which are embedded in the elastomer may migrate towards the surface of the elastomer that is exposed to water. This can cause the swellable material to have non uniform swelling. In some cases, blisters may develop on the surface of the elastomer that is exposed to water. If these blisters burst open, they will leave cracks or openings in the elastomer.

SUMMARY

[0014] It is therefore an object of the present invention to provide a swellable apparatus configured to fill a space in oil or gas apparatus that addresses such shortcomings.
It is a further object for the present invention to provide a method of forming swellable apparatus for filling a space in oil or gas apparatus.

According to a first aspect of the invention, there is provided a swellable apparatus for filling a space in oil or gas apparatus, the swellable apparatus comprising a unitary hydrocarbon swellable body formed from an elastomeric material selected to expand on exposure to a hydrocarbon fluid, the hydrocarbon swellable body having an first surface which, in use, is exposed to a hydrocarbon fluid, a first portion, and a second portion disposed between the first portion and the first surface, wherein the first portion comprises a fluid permeability structure which differs from the fluid permeability structure of the second portion.

In this context, the term “unitary” means cured or otherwise formed into a single body or mass. In this specification, elastomeric material means a synthetic or natural material displaying elastomeric or rubber-like characteristics, and includes compositions comprising polymeric and non-polymeric additives including stabilizers, fillers, co-agents and others.

The first surface is preferably an outer surface exposed to a wellbore fluid, but in an alternative configuration the first surface is exposed to a triggering fluid, which may be delivered internally or via a fluid delivery system.

The permeability of the hydrocarbon swellable body may be varied by varying the cross-linking density of the elastomeric material in parts of the hydrocarbon swellable body. The cross-linking density of the first portion may be less than the cross-linking density of the second portion. The composition of the elastomeric material may otherwise be the same in the first and second portions.

Thus according to a second aspect of the invention, there is provided a swellable apparatus for filling a space in oil or gas apparatus, the swellable apparatus comprising a hydrocarbon swellable body formed from a cross-linked elastomeric material selected to expand on exposure to a hydrocarbon fluid, the hydrocarbon swellable body having a first surface which, in use, is exposed to a hydrocarbon fluid, wherein the cross-linking density of the elastomeric material varies in the hydrocarbon swellable body.

Embodiments of the second aspect of the invention may comprise preferred and optional features of the first aspect and vice versa.

Different parts of the hydrocarbon swellable body may therefore have different cross-linking densities. By varying the cross-linking density of the material which makes up the body, the diffusion rate, and thus the swelling rate, of the swellable apparatus is affected. A higher cross-linking density reduces the diffusion rate of hydrocarbon fluid when compared with a lower cross-linking density. The apparatus thus has a permeability structure which varies in the body. The invention may therefore provide a unitary body of cured elastomeric material which facilitates control and/or selection of swelling characteristics.

Preferably, the extent of cross-linking in the hydrocarbon swellable body decreases in an inward direction from the first surface. The hydrocarbon swellable body may have a first surface directed towards a hydrocarbon fluid and a second surface, wherein the extent of cross-linking in the hydrocarbon swellable body decreases in a direction from the first surface to the second surface.

More specifically, an extent of cross-linking at an outer surface of the hydrocarbon swellable body may be higher than an extent of cross-linking within the hydrocarbon swellable body, the outer surface, in use, coming into contact with the first fluid. In use, a high extent and/or density of cross-linking at the outer surface may control or retard an uptake of hydrocarbon molecules by the hydrocarbon swellable body whilst allowing a part of the hydrocarbon swellable body having a lower extent of cross-linking to have faster penetration of the hydrocarbon molecules and thus faster swelling.

A greater extent of cross-linking at the first surface may reduce a rate of uptake of hydrocarbon molecules by the hydrocarbon swellable body. Therefore, an extent of cross-linking at the first surface may be predetermined to set a predetermined rate of uptake of hydrocarbon molecules. This has advantages in certain wellbore environments where it is desirable for swelling of the apparatus to be retarded, for example during run-in of the apparatus to its required depth. An elastomer having an increased cross-linking density may have a reduced tendency to suffer from migration of the water swellable body towards the surface of the elastomer that is exposed to water and thus reduce non-uniform swelling.

More specifically, the extent of cross-linking at the surface of the hydrocarbon swellable body may be between about 10 and about 100 times higher than at a location in the hydrocarbon swellable body spaced apart from the first surface of the hydrocarbon swellable body.

Alternatively or in addition, the permeability of the hydrocarbon swellable body may be varied by varying the macroscopic bond structure of the elastomeric material. Thus different parts of the body may have different macroscopic bond structures. This may be achieved by incorporating in a part of the swellable body of a polymer additive or a plurality of specific polymer additives, which may comprise a semi-crystalline rubber and/or polyoctenamer such as VESTENAMER®.

The preferred additive is VESTENAMER®®, but the additive may comprise one or more rubbers as described in trans-Polyoctenamer by Draxler, Marl A. & Kautschuk, Gummi, Kunststoffe, 34, Nr. 3/1981, pp. 185-190; and 25 Jahre Polyoctenamer-der Entwicklungsgang eines Synthesekautschucks vom Laborpraparat zum industriellen Rohstoff, by Draxler, Marl A., Kautschuk, Gummi Kunststoffe, 42, Nr. 10/1989, pp. 868-874, incorporated herein by reference.

Thus the inner portion of the swellable body may incorporate a semi-crystalline rubber or polyoctenamer to provide a macroscopic bond structure, whereas an outer portion of the swellable body disposed towards the outer surface of the body may not have a semi-crystalline rubber or polyoctenamer incorporated therein.

It is believed that the addition of a semi-crystalline rubber polyoctenamer results in a macroscopic bond structure which increases the permeability of the apparatus to increase the access of the water to the water swellable bodies. Thus access pathways are provided by the macroscopic bond structure of the material. The macroscopic bond structure also improves the retention of the water swellable body in the hydrocarbon swellable body.

More specifically, the polymer additive, such as VESTENAMER®, may comprise between about 5% and about 15% of a volume of the swellable apparatus.

In an alternative embodiment of the invention, the swellable apparatus comprises one or more foaming agents or blowing agents. A chemical foaming agent decomposes to release a gas when heated to its activation temperature. A
range of different chemical foaming agents may be used with the invention. One example is a dinitrosopentamethylene tetraamine (DNPT) such as OPEx® 80, available from Uniroyal Chemical. Another suitable additive is based on the family of azodicarbonamide type chemicals, for example, those provided by Lanxess Group under the POROFOUR® brand.

[0033] The foaming agent may be incorporated into the swellable apparatus during mixing, and subsequently treated, for example by heating to decompose and impart a cellular structure to the EPDM matrix material. Preferably, the cellular structure is an open cellular structure. Thus the cellular structure may provide one or more fluid pathways within the hydrocarbon swellable body, which increases the permeability of the swellable apparatus.

[0034] The swellable apparatus may comprise a plurality of water swellable bodies. The plurality of water swellable bodies may, for example, be embedded in the hydrocarbon swellable body such that the water swellable bodies are spaced apart from each other. The water swellable bodies may be evenly and uniformly spaced apart from each other.

[0035] Alternatively or in addition, the hydrocarbon swellable body may comprise at least one pathway therethrough. Thus, at the least one pathway may provide for the passage of water comprised in the second fluid through the hydrocarbon swellable body. The provision of at least one pathway may provide for ease of access of water to the water swellable body, e.g. compared with known swellable apparatus.

[0036] The at least one pathway may be configured to permit the passage of water molecules but prevent the passage of hydrocarbon molecules contained in the first fluid. This limits or eliminates the effect that providing pathways in the apparatus has on the hydrocarbon-swelling characteristics of the apparatus.

[0037] Thus, the at least one pathway may allow for the passage of water molecules. Alternatively or in addition, the at least one pathway may have a diameter of less than about 1000 microns. Thus, the at least one pathway may prevent the passage of the at least one water swellable body, when the at least one water swellable body is embedded in the hydrocarbon swellable body.

[0038] More specifically, the at least one pathway may have a diameter of less than about 100 microns and may preferably be about 40 microns. Such a dimension means that hydrocarbon molecules may not readily pass through the pathway.

[0039] Alternatively or in addition, the swellable apparatus may be configured such that the at least one pathway may extend from an outer surface of the hydrocarbon swellable body through the hydrocarbon swellable body to the at least one water swellable body, the outer surface, in use, coming into contact with the first and second fluids.

[0040] Alternatively or in addition, the pathway may comprise a bore. The bore may, for example, be formed by perforation of the hydrocarbon swellable body. The perforation may be a mechanical perforation, and may be formed by penetrating the hydrocarbon swellable body with a pin, needle or spike, or may be a perforation formed by a laser, for example in a micro-drilling process.

[0041] Alternatively or in addition, the pathway may comprise a macroscopic bond structure between the hydrocarbon swellable body and the at least one water swellable body. Such a macroscopic bond structure may, for example, be formed by the inclusion of a polymer material, which may be a semi-crystalline rubber and/or polyoctenamer such as VESTENAMER®.

[0042] More specifically, the polymer material, such as VESTENAMER®, may comprise between about 5% and about 15% of a volume of the swellable apparatus.

[0043] Changing at least one of a number of pathways and a density of pathways per unit area of the outer surface of the hydrocarbon swellable body may provide for control of access of water molecules to the at least one water swellable body. Thus, at least one of the number of pathways and the pathway density may be increased to increase access of a selected fluid to the at least one swellable body. Hence, changing at least one of the number of pathways and the pathway density may control an uptake of an aqueous fluid by the water swellable body whilst not affecting an uptake of a hydrocarbon fluid by the hydrocarbon swellable body.

[0044] Alternatively or in addition, the hydrocarbon swellable body may comprise a polymer. Alternatively or in addition, the hydrocarbon swellable body may comprise an elastomer.

[0045] Alternatively or in addition, the hydrocarbon swellable body may comprise ethylene propylene diene monomer rubber (EPDM). Alternatively or in addition, the hydrocarbon swellable body may be operative to swell upon contact with the first fluid by diffusion of hydrocarbon molecules into the hydrocarbon swellable body. Alternatively or in addition, the water swellable body may comprise a polymer.

[0046] More specifically, the water swellable body may comprise a Super Absorbent Polymer (SAP), which may be an acrylic acid and sodium acrylate copolymer such as AQUALIC®. Alternatively or in addition, the water swellable body may comprise a salt, such as NaCl or CaCl2. Alternatively or in addition, the water swellable body may be operative to swell upon contact with water by means of diffusion of water molecules into the water swellable body. More specifically, where the water swellable body comprises a salt, the water swellable body may be operative to swell upon contact with water by means of osmosis.

[0047] Alternatively or in addition, the hydrocarbon swellable body may comprise between about 35% and about 50% of a volume of the swellable apparatus and the water swellable body may comprise between about 15% and about 40% of the volume of the swellable apparatus. In use, such a composition may provide for an increase in volume for the swellable apparatus from the unswellen condition to the swollen condition of up to about 300% an environment such as that found in a downhole oil well. For example, within 2-3 weeks of exposure to a 100 degree Celsius fluid mixture containing both a hydrocarbon-based liquid and low salinity aqueous solution.

[0048] More specifically, the hydrocarbon swellable body may comprise between about 40% and about 45% of the volume of the swellable apparatus.

[0049] Alternatively or in addition, the water swellable body may comprise between about 25% and about 35% of the volume of the swellable apparatus.

[0050] Alternatively or in addition, the swellable apparatus may comprise a filler, such as carbon black or silica oxide. More specifically, the filler may comprise between about 15% and about 30% of a volume of the swellable apparatus.

[0051] Alternatively or in addition, the swellable apparatus may comprise an activator, which is operative to form a sul-
...phurating compound. More specifically, the activator may comprise at least one of zinc oxide and stearic acid. When zinc oxide and stearic acid are present a zinc sulphurating compound may be formed. More specifically, the stearic acid may comprise less than about 2% of a volume of the swellable apparatus.

Alternatively or in addition, the swellable apparatus may comprise a metal oxide, such as zinc oxide. In the curing process the zinc oxide may activate an organic accelerator. Suitable organic accelerators include zinc diacrylate (ZDA), zinc dimethacrylate (ZDMA), triallyl cyanate (TAC), or triallyl isocyanate (TAIC®), including those available from Sartomer Company, Inc of Pennsylvania, USA. An unreacted portion of the zinc oxide may remain available to neutralize sulphur-bearing acidic decomposition products formed during vulcanization. Adequate levels of zinc oxide can contribute markedly to chemical reinforcement, scorch control and resistance to heat-aging and compression fatigue.

More specifically, the metal oxide may comprise less than about 5% of a volume of the swellable apparatus.

Alternatively or in addition, at least one of the first fluid and the second fluid may be comprised in a downhole fluid present in a downhole environment. More specifically, the downhole fluid may comprise at least one of: a completion brine; a water-based drilling mud; an oil-based drilling mud; formation water; and a production fluid, e.g. oil or gas from a well being produced.

Thus, the swellable apparatus may be used, e.g. in a well packer, where it may be activated by water-based completion fluids. After a completion operation and during a well production phase, the swellable apparatus may be used to form a seal, even though the swellable may then be mainly exposed to hydrocarbons.

Alternatively or in addition, the swellable apparatus may be operative to increase in volume from an unswollen condition to a swollen condition by up to about 300% when in contact with at least one of the first fluid and the second fluid. Thus, the swellable apparatus may be operative to swell based on simultaneous swelling of both the hydrocarbon swellable body and the water swellable body.

According to a third aspect of the invention, there is provided a swellable material for filling a space in oil or gas apparatus, the swellable material selected to swell on exposure to a wellbore fluid, wherein the swellable material comprises an elastomeric material and an additive comprising a semi-crystalline rubber and/or a polycrystomer.

The preferred additive is VESTENAMER®, but the additive may comprise one or more rubbers as described in trans-Polyoctamener by Draxler, Marl A. & Kautschuk, Gummi, Kunststoffe, 34, Nr. 3/1981, pp. 185-190; and 25 Jahre Polyoctamener-der Entwicklungsgang eines Synthesekautschuks vom Laborpraparat zum industriellen Rohstoff, by Draxler, Marl A., Kautschuk, Gummi Kunststoffe, 42, Nr. 10/1989, pp. 868-874, incorporated herein by reference.

Thus the swellable material may incorporate a semi-crystalline rubber or polycrystomer to provide a macroscopic bond structure. It is believed that the addition of a semi-crystalline rubber and/or a polycrystomer results in a macroscopic bond structure which increases the permeability of the material to increase the access of wellbore fluids into the swellable material or a body formed therefrom. Thus access pathways are provided by the macroscopic bond structure of the material. The macroscopic bond structure also improves the retention of a water swellable body such as an SAP in a swellable body.

The elastomeric material may be an ethylene propylene copolymer such as EPDM.

More specifically, the polymer additive, such as VESTENAMER®, may comprise between about 5% and about 15% of a volume of the swellable apparatus.

Embodiments of the third aspect of the invention may comprise preferred and optional features of the first or second aspects of the invention and vice versa.

According to a fourth aspect of the invention, there is provided an oil or gas tool comprising the swellable apparatus of the first, second or third aspects of the invention. The tool may be a downhole tool, and may be a wellbore packer, anchor or centraliser.

Embodiments of the fourth aspect of the invention may comprise preferred and optional features of the first to third aspects of the invention and vice versa.

According to a fifth aspect of the invention, there is provided a method of forming a swellable apparatus for filling a space in oil or gas apparatus, the method comprising the steps of: providing an elastomeric material selected to expand on exposure to a hydrocarbon fluid; curing the elastomeric material to form a unitary hydrocarbon swellable body; treating the elastomeric material such that a first portion of the hydrocarbon swellable body comprises a fluid permeability structure which differs from the fluid permeability structure of a second portion of the hydrocarbon swellable body.

The method may include the steps of providing a sheet of hydrocarbon swellable material, forming a substantially cylindrical mantle from the sheet of hydrocarbon swellable material. The method may comprise the steps of forming multiple layers of the hydrocarbon swellable material on a mandrel or tubular.

The multiple layers may be formed by wrapping a sheet of hydrocarbon swellable material onto the mandrel or tubular. A cross-linking agent may be applied to the surface of one or more layers. For example, the outermost layers may be coated with a cross-linking agent. The multiple layers may be of an uncured elastomeric material.

Alternatively, or in addition, the method may comprise the step of incorporating an additive into the elastomeric material. The additive may be a pathway forming material with the hydrocarbon swellable material and the water swellable material. Alternatively, or in addition, the additive may be a chemical foaming agent. The pathway forming material may comprise a polymer, which may be a semi-crystalline rubber and/or polycrystomer such as VESTENAMER®.

Alternatively or in addition, the method may comprise treating the hydrocarbon swellable material such that an outer surface of the hydrocarbon swellable body has a higher extent of cross-linking than within the hydrocarbon swellable body. The elastomeric material may be treated by applying a cross-linking agent. The cross-linking agent may be selectively applied to parts of the hydrocarbon swellable body. More specifically, treating the hydrocarbon swellable material may comprise providing a curing material on an uncured outer surface of the hydrocarbon swellable body.

More specifically, the curing material may comprise at least one of: a cure accelerator; and a curing agent. Cure accelerators or curing agents are well and widely known to those skilled in the art of elastomer or polymer science.
Alternatively or in addition, providing the curing material may comprise at least one of spraying and painting at least one application (e.g. such that it forms a temporary coating to be absorbed by the swellable material) of the curing material onto the outer surface of the hydrocarbon swellable member.

More specifically, the curing material may be provided on the outer surface before the swellable member is cured. The process of curing the swellable member will be well known to persons skilled in the art. More specifically, skilled persons will have a full understanding of parameters associated with temperatures and pressures required to cure swellable members formed of an elastomer; such a process will be familiar to skilled persons as vulcanisation. It will be appreciated that peroxide curing and/or sulphur curing may be used with the present invention.

Alternatively or in addition, the curing material may be dissolved as an aqueous solution or in a solvent.

More specifically, the curing material may have a predetermined concentration when in the form of an aqueous solution or solvent. Thus, the concentration may be changed from one curing step to another such that when the curing material is applied to an outer surface of the hydrocarbon swellable member an extent of cross-linking may be controlled.

In one embodiment of the invention a curing material is provided on the outer surface of a fully or substantially cured material prior to a re-curing process to change the cross-linking structure of the material.

Embodiments of the fifth aspect of the invention may comprise preferred and optional features of the first to fourth aspects of the invention and vice versa.

The present inventor has appreciated the feature of varying an extent of cross-linking across the hydrocarbon swellable body has particular application to a hybrid swellable material. Thus, from a sixth aspect of the present invention there is provided a swellable apparatus for filling a space in oil or gas apparatus, the swellable body comprising a hydrocarbon swellable body and at least one water swellable body,

the swellable apparatus, in use, being operative to fill the space in oil or gas apparatus when in a swollen condition, the swellable apparatus adopting the swollen condition when at least one of the hydrocarbon swellable body and the at least one water swellable body are swollen, the hydrocarbon swellable body swelling upon contact with a first fluid comprising a hydrocarbon; and the at least one water swellable body swelling upon contact with a second fluid comprising water, the hydrocarbon swellable body having a structure that varies as to an extent of cross-linking across the hydrocarbon swellable body.

More specifically, an extent of cross-linking at an outer surface of the hydrocarbon swellable body may be higher than an extent of cross-linking within the hydrocarbon swellable body, the outer surface, in use, coming into contact with the first fluid.

Alternatively or in addition, the swellable apparatus may be configured such that the hydrocarbon swellable body is operative to control access of the second fluid to the at least one water swellable body.

Embodiments of the sixth aspect of the invention may comprise preferred and optional features of the first to fifth aspects of the invention and vice versa.

According to a seventh aspect of the present invention, there is provided a method of forming a swellable apparatus for filling a space in oil or gas apparatus, the method comprising: incorporating a hydrocarbon swellable material and a water swellable material, the hydrocarbon swellable material forming a hydrocarbon swellable body and the water swellable material forming at least one water swellable body, the hydrocarbon swellable material and the water swellable material being incorporated such that, in use, the formed hydrocarbon swellable body swells upon contact with a first fluid comprising a hydrocarbon and the at least one water swellable body swells upon contact with a second fluid comprising water, and treating the hydrocarbon swellable body such that an extent of cross-linking of the hydrocarbon swellable body varies across the hydrocarbon swellable body.

More specifically, the hydrocarbon swellable body may be treated such that an outer surface of the hydrocarbon swellable body has a higher extent of cross-linking than within the hydrocarbon swellable body.

Alternatively or in addition, the hydrocarbon swellable material and the water swellable material may be further incorporated such that, in use, the hydrocarbon swellable body is operative to control access of the second fluid to the at least one water swellable body.

Embodiments of the seventh aspect of the invention may comprise preferred and optional features of the sixth aspect of the invention and vice versa.

According to an eighth aspect of the invention, there is provided a method of forming a swellable material for filling a space in oil or gas apparatus, the swellable material selected to swell on exposure to a wellbore fluid, the method comprising the step of combining an elastomeric material and an additive comprising a semi-crystalline rubber and/or a polyacrylamer.

The method may comprise the additional step of curing the formed elastomeric material and additive.

Embodiments of the eighth aspect of the invention may comprise preferred and optional features of the third aspect of the invention and vice versa.

BRIEF DESCRIPTION OF THE DRAWINGS

There will now be described, by way of example only, embodiments of the invention with reference to the following drawings, of which:

FIG. 1 is a cross-section of a wellbore packer comprising swellable apparatus in accordance with an embodiment of the invention;

FIG. 2 is a longitudinal section of a downhole tool comprising swellable apparatus in accordance with an embodiment of the invention;

FIG. 3 is a schematic line drawing of a material for the swellable apparatus of FIG. 2;

FIG. 4 is a schematic view of the swellable apparatus of the downhole centraliser tool of FIG. 2;

FIG. 5 is a graph of swelling profile for samples of a swellable apparatus in accordance with embodiments of the invention;

FIG. 6A is a graph of swelling profile for two samples of swellable material in water;

FIG. 6B is a graph of swelling profile for two samples of swellable material in a hydrocarbon fluid; and
FIG. 7 is a cross-section of a wellbore packer in accordance with an alternative embodiment of the invention.

DETAILED DESCRIPTION

Referring firstly to FIG. 1, there is shown in cross section a wellbore packer which comprises a swellable material in accordance with an embodiment of the invention. The packer, generally shown at 10, comprises a swellable mantle 12 disposed on a tubular 14. The packer is configured to be disposed in a wellbore such that its outer surface 16 is exposed to wellbore fluids. In this example, the swellable mantle 12 is formed from an elastomeric material comprises an ethylene propylene diene monomer (EPDM) rubber, selected to swell on exposure to a hydrocarbon fluid. The swellable mantle 12 has a cross-linking density which varies across its cross section. An inner volume or core 18 comprises a relatively low density of cross-linking of the elastomeric material. An outer volume 20, disposed between the outer surface 16 and the inner volume 18, has a relatively high cross-linking density. The volume 20 has a lower permeability and swell rate to wellbore fluids by virtue of its increased cross-linked density. Thus the diffusion of the well fluids into the body is retarded by the relatively highly cross-linked volume 20.

The volume 20 of high cross-linking is achieved by coating the outer surface of the formed swellable mantle with a cross-linking accelerator such as zinc diacrylate (ZDA). The cross-linking accelerator is coated on to the outer surface by spraying or brushing, and allowed to penetrate into the swellable mantle 12. Subsequently, the swellable mantle may be cured or re-cured to cause the cross-linking to occur and create a uniaxial hydrocarbon swellable body with the relatively high density cross-linked region 20.

Although in FIG. 1 the high cross-linked region 20 appears to have a discrete boundary with the relatively low cross-linked region 18, in practice there is a region of continuous change in cross-linking density due to the gradual penetration of the cross-linking agent into the swellable mantle 12. The relative thickness of the high cross-linked region 20, and the relative densities of cross-linking in the volumes can be varied by changing the amount of cross-linking accelerator applied to the outer surface, and the time it is allowed to penetrate into the swellable mantle before the curing or re-curing process is performed.

FIG. 2 shows generally at 100 a swellable centraliser of an alternative embodiment of the invention, located downhole in a subterranean wellbore 112. The centraliser 100 is provided with a swellable apparatus 116, which can swell in the presence of hydrocarbon and aqueous wellbore fluids to fill the annular space 118. To achieve this, the swellable apparatus 116 is formed from a “hybrid” material containing both hydrocarbon and water swellable bodies, as described in more detail with reference to FIG. 3. Access to the water and hydrocarbon swellable bodies by hydrocarbons and water, which will be present in wellbore fluids, is controlled by the structure of the swellable material.

The swellable material 120 has a hydrocarbon swellable body in the form of an ethylene propylene diene monomer rubber (EPDM) elastomer matrix, together with water swellable bodies 132 in the form of super absorbent polymers (SAPs) embedded within the matrix 122. The polymer bodies 132 are evenly distributed and spaced apart from each other throughout the material. Upon being brought into contact with hydrocarbon molecules, the EPDM matrix is caused to swell, while the super absorbent polymers swell upon contact with water. This ensures proper performance of the swellable apparatus to seal the wellbore annulus around the centraliser tool in the presence of both water and hydrocarbon based well fluids, and in the presence of fluids consisting of water and hydrocarbons are mixed together.

In this example, hydrocarbon molecules diffuse into the EPDM matrix and water molecules diffuse into the super absorbent polymers. The EPDM matrix makes up about 40% of the material volume, while the super absorbent polymers make up a further 20% of the volume. This helps to achieve the desired swelling behaviour. Further, the material volume includes a silica oxide filler, a zinc oxide and stearic acid.

Relative quantities of the above mentioned components used in forming the swellable material of this example are specified in Table A below:

<table>
<thead>
<tr>
<th>Component</th>
<th>Phr</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>EPDM (calendering grade)</td>
<td>100</td>
<td>39.2%</td>
</tr>
<tr>
<td>HAF N530 Carbon Black</td>
<td>48</td>
<td>18.8%</td>
</tr>
<tr>
<td>Processing Oil</td>
<td>20</td>
<td>7.8%</td>
</tr>
<tr>
<td>Zinc Oxide</td>
<td>5</td>
<td>2.0%</td>
</tr>
<tr>
<td>Peroxide (pure)</td>
<td>5</td>
<td>2.0%</td>
</tr>
<tr>
<td>Co-agent (TAC or TAIC)</td>
<td>2</td>
<td>0.8%</td>
</tr>
<tr>
<td>Stearic Acid</td>
<td>1</td>
<td>0.4%</td>
</tr>
<tr>
<td>VESTENAMER®</td>
<td>10</td>
<td>3.9%</td>
</tr>
<tr>
<td>Water Absorbent Resin (AQUALIC®)</td>
<td>64</td>
<td>25.1%</td>
</tr>
<tr>
<td><strong>TOTAL</strong></td>
<td>255</td>
<td>100.0%</td>
</tr>
</tbody>
</table>

FIG. 4 provides a more detailed view of the apparatus shown in FIGS. 2 and 3. The apparatus is formed from the material 120 described with reference to FIG. 3.

In FIG. 4 the apparatus is additionally shown having a number of sub-micron pathways 140 through the material 120. The pathways 140 provide access for water molecules from the wellbore environment 142 through the surface region 144 of the wellbore apparatus 100 to the water absorbing polymers. In this example, the pathways 140 are created by mechanical perforations through the material 120. The pathways 140 are sized to permit water molecules to pass readily through the bores. However, hydrocarbon molecules do not readily pass through the pathways. The density of pathways 140 is selected to provide adequate access of water for the required swelling properties, such as rate and volume expansion, of the swellable apparatus 100.

The perforations are produced in an automated process using a perforating roller body, such as described in U.S. Pat. No. 3,646,639. In alternative embodiments the perforations may be formed using a laser or micro-drilling process using a system of CO2 lasers.

The swellable hybrid material is vulcanised to produce cross-linking of the EPDM matrix 122. In this example, the swellable apparatus has a strongly cross-linked surface region 146, followed below by a region 148 of intermediate cross-linking, and a further main region 150 that is cross-linked to a still lesser degree. The extent of cross-linking controls access of hydrocarbon molecules to the hydrocarbon swellable matrix 122, such that the swelling behaviour of the apparatus in the presence of hydrocarbons can be selected appropriately.

In this case, the cross-linking at the surface is strong to retard the uptake of hydrocarbon molecules and the degree and/or speed of hydrocarbon-activated swelling, while in
other regions, which are cross-linked to a lesser extent, hydrocarbon molecules that have been taken up are allowed to diffuse more effectively throughout the material.

In order to create such a cross-linked structure, a cross-linking or curing agent such as zinc diacylate (ZDA) is coated onto the outer surface by spraying or brushing. The variable cross-linking profile in this example is substantially continuous, due to the diffusion of the cross-linking agent into the swellable body.

In order to create such a cross-linked structure, a cross-linking or curing agent such as zinc diacylate (ZDA) is deposited onto the outer surface by spraying or brushing. This may be carried out during the construction of the packer apparatus before curing to adjust the cross-linking characteristics and, in turn, the nature of the swelling. The EPDM component of the material is cross-linked upon curing of the EPDM.

Samples of the swellable material with the composition specified in Table A were placed in tap water at a controlled temperature of 80 degrees Celsius, and the mass changes were measured over a period of several days. FIG. 5 is a graph of water-swell profile for samples having a number of different perforation densities. In each case the perforations were mechanically formed in the sample using a perforating needle. The data show that perforating the material has a marked effect on the swell profile. For example, at around 15 days, the sample with 1050 perforations per square inch (approximately 6.45 square cm) had increased in mass by around 200%, compared with an increase of around 75% for the unperforated case. The sample with 132 perforations per square inch (approximately 6.45 square cm) had increased in mass by around 112%. The data also show the maximum mass increases to be higher where the perforation density is higher.

To measure the effect on the swelling profile in a hydrocarbon fluid, samples of the same material composition with no perforations, 16 perforations, 64 perforations and 132 perforations per square inch (approximately 6.45 square cm) were placed in the special kerosine Clairsol 350 MEIFTM at a controlled temperature of 80 degrees Celsius. The mass increase of the samples was measured, and the data showed no significant effect on swelling profile, i.e. the perforations did not significantly affect the penetration of the hydrocarbon into the body.

Samples of the material composition specified in Table A were compared with a similar composition with the VESTENAMER® omitted. Samples of each composition were placed in tap water at a controlled temperature of 80°C. FIG. 6A is a plot of percentage mass change versus time for the respective samples. The data show a clear increase in swell profile for the swellable material containing VESTENAMER® compared to the swellable material with no VESTENAMER®.

Identical samples were placed in Clairsol 350 MEIFTM at a controlled temperature of 80°C to model the effect of the VESTENAMER® in a hydrocarbon well fluid environment, with the measured mass increase plotted in FIG. 6B. The data show an improved swell rate and improved maximum swell increase for the swellable material with the VESTENAMER®, compared to the swellable material without VESTENAMER®.

It is believed that the addition of the VESTENAMER® results in a macroscopic bond structure within the material which increases the permeability to wellbore fluids. This increases the access of water contained in a wellbore fluid to the water swellable bodies in the elastomer. In addition, the macroscopic bond structure increases the permeability of the apparatus to hydrocarbon fluids. The data also show that the addition of the VESTENAMER® increases the maximum swell increase of the material. Although the examples shown relate to VESTENAMER®, the addition of other semi-crystalline rubbers and/or polyoctenamers also falls within the scope of the invention. Thus in particular embodiments, the access pathways providing access for water molecules to the super absorbing polymer bodies may be formed by the macroscopic bond structure of the material itself.

FIG. 7 is a cross sectional view through a packer in accordance with an alternative embodiment of the invention. The packer, generally shown at 200, is similar to the packer 10 of FIG. 1, but differs in its construction. The packer comprises an expanding portion 215 of cylindrical form located on a tubular 214. The packer is formed by forming multiple wraps 202a, 202b, and 202c of an elastomeric material 230 on the tubular 214. The elastomeric material 230 consists of a substantially rectangular sheet. In this example, the elastomeric material 230 is extruded EPDM and is uncur. The elastomeric material will typically be formed in a continuous length of several tens of metres, and may conveniently be deployed from a storage reel.

The lowermost layer 202a of the material is secured to the tubular 214 by a bonding agent, which may be a cyanoacrylate based adhesive. The multiple layer construction allows treatments to be applied to different parts of the swellable mantle. In this embodiment, the outer surfaces of the two outermost layers 202a, 202c of the material are coated with a cross-linking agent such as ZDA. This may be applied to the material prior to its application to the tubular over selected areas of the material. Alternatively, the treatment may be applied to the different layers during application onto the tubular.

When the expanding portion is formed it is cured, for example by a heat curing process, to form a unitary body of hydrocarbon swellable material. A cross-linking accelerator has been selectively applied to an outer volume of the expanding portion, resulting in an inner volume 218 with relatively low cross-linking density, compared with an outer volume 220 with relatively high cross-linking density.

In an alternative embodiment (not illustrated), the elastomeric material 230 is replaced by a sheet material of a hybrid swellable material, such as that described with reference to FIGS. 2 to 4. In another alternative embodiment, the permeability structure of the swellable body is affected by creating a macroscopic bond structure. This is achieved by incorporating a semi-crystalline rubber such as VESTENAMER® in a part of the sheet material. For example, the innermost layers of the expanding portion may incorporate VESTENAMER®, whereas the outermost layers do not. Curing of the material to a unitary body of hydrocarbon swellable material results in a varying macroscopic structure across the cross-section of the body, and thus a variation in permeability to hydrocarbon fluids, even if molecular cross-linking density is the same across the body.

The invention provides a swellable apparatus for filling a space in oil or gas apparatus and method of forming an apparatus is described. The apparatus comprises a hydrocarbon swellable body formed from an elastomeric material selected to expand on exposure to a hydrocarbon fluid such as
EPDM. The swellable body has a first surface which is exposed to a hydrocarbon fluid, a first (inner) portion, and a second portion disposed between the first portion and the surface. The first portion comprises a fluid permeability structure which differs from the fluid permeability structure of the second portion. In one embodiment, the cross-linking density of an outer portion of the body is greater than the cross-linking density of an inner portion of the body.

[0122] The presently described invention provides a number of benefits. Importantly, it provides apparatus which facilitates control or selection of swelling characteristics such as swelling rate during exposure to wellbore fluids. It allows for controlled swelling behaviour in the presence of both hydrocarbon and water that may typically be encountered in operations in wells. It provides for reliability of performance of swellable apparatus in different conditions.

[0123] Various modifications and improvements may be made without departing from the scope of the invention herein described. Combinations of features other than those specifically claimed are within the scope of the invention.

1-29. (canceled)
30. A swellable apparatus for filling a space in an oil or gas apparatus, the swellable apparatus comprising:

a unitary hydrocarbon swellable body formed from an elastomeric material selected to expand on exposure to a hydrocarbon fluid, the hydrocarbon swellable body having a first surface which is exposed to a hydrocarbon fluid during operation, a first portion, and a second portion disposed between the first portion and the first surface,

wherein the first portion comprises a fluid permeability structure which differs from a fluid permeability structure of the second portion.

31. The apparatus as claimed in claim 30, wherein the cross-linking density of the elastomeric material in the first portion of the hydrocarbon swellable body differs from the cross-linking density of the elastomeric material in the second portion of the hydrocarbon swellable body.

32. The apparatus as claimed in claim 31, wherein the cross-linking density of the elastomeric material in the second portion is greater than the cross-linking density of the elastomeric material in the first portion.

33. The apparatus as claimed in claim 31, wherein the hydrocarbon swellable body comprises a second surface, and the extent of cross-linking in the hydrocarbon swellable body decreases in a direction from the first surface to the second surface.

34. The apparatus as claimed in claim 30, wherein one of the first or second portions of the hydrocarbon swellable body comprises an additive comprising a semi-crystalline rubber.

35. The apparatus as claimed in claim 34, wherein one of the first or second portions of the hydrocarbon swellable body comprises a polyoctenamer.

36. The apparatus as claimed in claim 35, wherein the polyoctenamer comprises between about 5% and about 15% of a volume of the first or second portion of the hydrocarbon swellable body.

37. The apparatus as claimed in claim 30, wherein one of the first or second portions of the hydrocarbon swellable body comprises an additive comprising one or more chemical foaming agents.

38. The apparatus as claimed claim 30, further comprising a plurality of water swellable bodies embedded in the hydrocarbon swellable body.

39. The apparatus as claimed in claim 30, wherein the hydrocarbon swellable body comprises at least one pathway for the passage of water in a wellbore fluid through the hydrocarbon swellable body.

40. A method of forming a swellable apparatus for filling a space in an oil or gas apparatus, the method comprising the steps of:

- providing an elastomeric material selected to expand on exposure to a hydrocarbon fluid;
- curing the elastomeric material to form a unitary hydrocarbon swellable body; and
- treating the elastomeric material such that a first portion of the hydrocarbon swellable body comprises a fluid permeability structure which differs from the fluid permeability structure of a second portion of the hydrocarbon swellable body.

41. The method as claimed in claim 40, comprising the additional steps of:

- providing a sheet of hydrocarbon swellable material; and
- forming a substantially cylindrical mantle from the sheet of hydrocarbon swellable material.

42. The method as claimed in claim 41, comprising the additional step of forming multiple layers of the hydrocarbon swellable material on a mandrel or tubular.

43. The method as claimed in claim 41, comprising the additional step of wrapping a sheet of hydrocarbon swellable material onto a mandrel or tubular.

44. The method as claimed in claim 40, comprising the additional step of incorporating an additive into the elastomeric material, the additive comprising a chemical foaming agent.

45. The method as claimed in claim 40, comprising the additional step of incorporating an additive into the elastomeric material, the additive comprising a semi-crystalline rubber.

46. The method as claimed in claim 40, comprising the additional step of treating the hydrocarbon swellable material such that a second portion of the hydrocarbon swellable body has a higher extent of cross-linking than a first portion of the hydrocarbon swellable body.

47. The method as claimed in claim 46, comprising the additional step of applying a cross-linking agent selectively to parts of the hydrocarbon swellable body.

48. The method as claimed in claim 47, comprising the additional steps of:

- forming multiple layers of the hydrocarbon swellable material on a mandrel or tubular; and
- applying a cross-linking agent to the surface of one or more layers prior to curing the elastomeric material.

49. A swellable apparatus for filling a space in an oil or gas apparatus, the swellable apparatus comprising:

- a hydrocarbon swellable body formed from a cross-linked elastomeric material selected to expand on exposure to a hydrocarbon fluid, the hydrocarbon swellable body having a first surface which is exposed to a hydrocarbon fluid during operation, wherein the cross-linking density of the elastomeric material varies in the hydrocarbon swellable body.

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