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(54) Title of the Invention: Process
Abstract Title: Process for producing a suspension of temperature-sensitive water-swellable microgel particles

(57) A process for producing a suspension of temperature-sensitive water-swellable microgel particles having a solids loading of at least 10% wt/v comprises polymerizing, in a reactor vessel containing a polar solvent and an anionic surfactant, one or more temperature-sensitive monomers, optionally in the presence of one or more non-temperature sensitive co-monomers, with an organic cross-linking agent and with from 0.25% to 2.5% wt/wt (with respect to the total monomer including optional co-monomer) of a free radical initiator; wherein the initiator is fed into the reactor vessel at a steady rate over at least 10% of the period required for the polymerization to reach 90% completion. Also shown is a method of modifying the permeability of water in a subterranean hydrocarbon reservoir.

GB 2524232 A

PROCESS

This invention relates to processes for producing a suspension of temperature-sensitive water-swellable microgel particles having solids loadings of at least 10% weight/volume (wt/v).

This invention also relates to compositions and processes for the recovery of hydrocarbon fluids from a subterranean reservoir and more particularly to compositions comprising microgel suspensions that modify the permeability of subterranean formations, thereby increasing the mobilization and/or recovery rate of hydrocarbon fluids present in the formations.

Processes for modifying the permeability to water of subterranean hydrocarbon-bearing rock formations are particularly useful in the field of hydrocarbon recovery, for example, in the recovery of crude oil from a petroleum reservoir.

In the first stage of hydrocarbon recovery from a subterranean formation (referred to as "primary recovery"), natural pressure in the formation forces hydrocarbon fluids towards production wells where they can flow or are pumped to a surface production facility. However, formation pressure is generally sufficient only to recover around 10 to 20 percent of the total hydrocarbon present in a subterranean formation. Accordingly "secondary recovery" techniques are applied to recover hydrocarbon from subterranean formations in which the hydrocarbon fluids no longer flow by natural forces.

Secondary recovery techniques rely on the supply of external energy to increase the pressure in a subterranean formation. One such technique involves the injection of water (for example, aquifer water, river water, seawater or produced water) or a gas (for example, carbon dioxide, flue gas, or produced gas) into the subterranean formation via a network of injection wells to drive the hydrocarbon fluids towards one or more production wells. The injection of water during secondary recovery is commonly referred to as water flooding while the injection of gas during secondary recovery is commonly referred to as gas flooding. Additionally, if the injected fluid (water or gas) encourages movement of normally immobile residual oil or other hydrocarbons, such a process is termed tertiary recovery.

The efficiency of water flooding or gas flooding techniques depends on a number of variables, including the permeability of the formation and the viscosity of the hydrocarbon

fluids in the formation.

A prevalent problem with secondary and tertiary recovery projects relates to the heterogeneity of the reservoir rock strata. The mobility of the injected fluid typically is different from the hydrocarbon. For instance, when the injected fluid is more mobile than the hydrocarbon various mobility control processes are required to make the sweep of the reservoir more uniform and the consequent hydrocarbon recovery more efficient. Unfortunately, such processes have limited value when high permeability zones, commonly called "thief zones" or "streaks" exist within the reservoir rock. The injected fluid flows preferentially through these thief zones following a low resistance path from the injection well to the production well. In such cases the injected fluid does not effectively sweep the hydrocarbon from adjacent, lower permeability zones of the reservoir.

Flow diversion involves changing the path of the injected fluid through the reservoir so that it contacts and displaces more oil. Numerous physical and chemical treatment methods have been used to divert injected fluids from the thief zones.

Generally, when a treatment is applied in the region of the reservoir close to a producing well it is usually termed a water (or gas) shut-off treatment. Generally, when it is applied to the region of the reservoir close to an injection well it is termed a profile control or conformance control treatment. Generally, when a chemical treatment is capable of propagating deep within a thief zone before being activated to block the thief zone, it is referred to as deep reservoir flow diversion.

In cases where the thief zone(s) are isolated from the lower permeability adjacent zones, mechanical seals or "plugs" can be set in the well to block the entrance of the injected fluid into the thief zone from an injection well or the exit of the injected fluid from the thief zone into a production well. If the fluid enters or leaves the thief zone from the bottom of the well, cement can also be used to fill the well bore to above the zone of ingress or egress.

When the completion of the well allows the injected fluid to enter both the thief and the adjacent zones, a cement squeeze is often a suitable means of isolating the watered out thief zone. Certain cases, however, are not amenable to such methods because communication exists between layers of the reservoir rock outside the reach of cement. Typical examples of this are when fractures or rubble zones or washed out caverns exist

behind the casing. In such instances chemical gels, capable of moving through pores in reservoir rock have been applied to seal the thief zones.

A few "deep reservoir flow diversion" processes have been developed with the aim of reducing the permeability in a substantial proportion of the thief zone and, or at a

5   significant distance from the injection and production wells. The use of swellable cross linked superabsorbent polymer microparticles for modifying the permeability of subterranean formations is disclosed in U.S. Pat. Nos. 5,465,792 and 5,735,349. However, swelling of the superabsorbent microparticles described therein is induced by changes of the carrier fluid from hydrocarbon to aqueous or from water of high salinity to water of

10   low salinity.

Deep reservoir flow diversion may also be achieved by injecting polymeric microparticles comprising polymeric chains linked together via thermally labile hydrolysable crosslinkers and non-thermally labile crosslinkers, as disclosed in U.S. Pat. Nos. 6,454,003, 6,709,402, 6,984,705 and 7,300,973. The suspension of microparticles

15   travels through the thief zones and is progressively heated to a temperature at which the thermally labile crosslinkers hydrolyze and are broken and the microparticles absorb water, swell and block the pores of the reservoir rock. The permeability of the thief zones is thereby reduced and subsequently injected fluid is diverted into the lower permeability zones to displace hydrocarbon towards a producing well.

20   Microgels are defined in the International Union of Pure and Applied Chemistry (IUPAC) Compendium of Chemical Terminology (the Gold Book) as a particle of gel of any shape with an equivalent diameter of approximately 0.1 to 100 μm. Typically, microgels are intramolecularly crosslinked polymeric macromolecules that undergo structural changes in response to external triggers. In particular, microgels can take up

25   solvent molecules and so swell, but can also release the solvent molecules and collapse as conditions change and the solvent becomes a non-solvent. A particular class of microgels are temperature-sensitive microgels, which swell/collapse in response to changes in temperature.

UK Patent Application publication GB 2262117 relates to conformance control of a

30   reservoir where high formation temperatures are encountered comprising the steps of (a) injecting at ambient temperature into the formation a latex solution containing particles which flocculate, shrink and harden at higher temperatures, and a solution of an ionic

compound as a promoter, (b) allowing the solution to flow through a zone or zones of relatively high permeability in the formation under increasing temperature conditions, and (c) allowing the latex particles to flocculate, shrink and harden at a location where the temperature is sufficiently high to promote this effect. According to GB 2262117, when

5   the particles flocculate, shrink and harden, they form a more effective blocking agent than the dispersed, expanded and softer particles. It is stated in GB 2262117 that suitable latex particles may be prepared by polymerizing or copolymerizing various acrylamides, for example N-isopropylacrylamide. However, the dispersions of GB 2262117 are all produced at the desired particle concentration for the fluid that is to be injected into the

10   reservoir, the maximum concentration of microparticles produced in the examples being 0.1%.

Methods of synthesizing poly(N-isopropylacrylamide) microgels using "surfactant free emulsion polymerization" are disclosed in Pelton R H and Chibante P (1986); Preparation of Aqueous Lattices with N-isopropylacrylamide; Colloids and Surfaces; 20,

15   247-256. The typical solids loading achieved via this method is 0.5% wt/v, although concentrations of 1% wt/v may be achieved.

McPhee W; Tam K C; Pelton R; Poly(N-isopropylacrylamide) Latices Prepared with Sodium Dodecyl Sulphate; Journal of Colloid and Interface Science; (1993) 156, 24-30 discloses a method of synthesizing poly(N-isopropylacrylamide) microgels using an

20   "emulsion polymerization technique", stabilized by the surfactant sodium dodecyl sulphate. In this paper, solids loading of up to 1.4% wt/v are disclosed.

Hydrocarbon recovery is generally carried out in remote and/or inaccessible locations, such as from subsea reservoirs (with fluids being injected into the reservoir from a platform or floating vessel), and transporting large volumes of low concentration

25   microgel suspensions to such locations may generally be difficult and/or uneconomic, for example owing to the costs and difficulties of handling and shipping such large volumes. It may also be uneconomic to dry such dilute suspensions, because of the high volumes of solvent that must be removed, resulting in high energy costs for evaporating large volumes of solvent, and also because of the loss of relatively high proportions of microgel in the

30   drying process (e.g. loss through the dryer flue).

The use of conventional methods for preparing suspensions of temperature-sensitive water-swellable microgel particles has been found to be unsuitable for producing

suspensions having higher solids loading, for example solids loading of at least 10% wt/v, particularly because at such increased loadings coagulation occurs during the polymerization process, so that the resulting material is not suitable for use as a temperature-sensitive water-swellable microgel.

5   There remains a need for alternative methods for producing suspensions of temperature-sensitive water-swellable microgel particles having solids loadings of at least 10% wt/v.

Thus, according to the present invention there is provided a process for producing a suspension of temperature-sensitive water-swellable microgel particles having a solids

10   loading of at least 10% wt/v, the process comprising polymerizing, in a reactor vessel containing a polar solvent and an anionic surfactant, one or more temperature-sensitive monomers, optionally in the presence of one or more non-temperature sensitive co-monomers, with an organic cross-linking agent and with from 0.25% to 2.5% wt/wt (with respect to the total monomer including optional co-monomer) of a free radical initiator;

15   wherein the initiator is fed into the reactor vessel at a steady rate over at least 10% of the period required for the polymerization to reach 90% completion.

Also according to another aspect of the present invention, there is provided a process for producing dried temperature-sensitive water-swellable microgel particles, the process comprising producing a suspension of temperature-sensitive water-swellable

20   microgel particles having a solids loading of at least 10% wt/v by a process of the invention and drying the suspension.

Also according to another aspect of the present invention, there is provided a process for producing a concentrated suspension of temperature-sensitive water-swellable microgel particles, the process comprising producing a suspension of temperature-sensitive

25   water-swellable microgel particles having a solids loading of at least 10% wt/v by a process of the present invention and partially drying the temperature-sensitive water-swellable microgel suspension, or producing dried temperature-sensitive water-swellable microgel particles by a process of the present invention and redispersing the dried particles in a solvent, in particular, an aqueous solvent, wherein the concentrated suspension of

30   temperature-sensitive microgel particles has a solids loading of at least 15% wt/v, preferably, at least 20% wt/v.

Preferably, the concentrated suspension of temperature-sensitive water swellable

microgel particles has a solids loading of less than 30% wt/v, in particular, less than 25% wt/v.

By a suspension of "temperature-sensitive water-swellable" microgel particles is meant that the microgel particles of the suspension have a volume phase transition temperature (VPTT) at which the degree of swelling of the microgel particles, when dispersed in a solvent, changes dramatically. Typically, the microgel particles absorb solvent molecules and swell when dispersed in a solvent, in particular, an aqueous solvent, at below the VPTT and desorb solvent molecules and shrink in size at or above the VPTT. Typically, the microgel particles of the dispersion have a VPTT in the range of 30 to 100°C, preferably 30 to 70°C.

Flocculation of the shrunken microgel particles occurs at or above a critical flocculation temperature (CFT). Typically, the microgel particles of the dispersion have a CFT in the range of 30 to 100°C, preferably, 30 to 70°C.

The present invention solves the technical problem defined above by the process of producing temperature-sensitive water-swellable microgel suspensions having solids loadings of at least 10% wt/v in a reactor vessel by feeding an initiator into the reactor vessel at a steady rate over at least 10% of the period required for the polymerization to reach 90% completion.

By a "steady rate" it is meant that during the period or periods when the initiator is fed into the reactor vessel, the rate at which it is fed varies by no more than ±25% from the average rate over the period of addition. Preferably, the rate at which the initiator is fed into the reactor vessel varies by no more than ±20%, more preferably, by no more than ±10%, most preferably, by no more than ±5% from the average rate over the period of addition.

The rate at which the initiator is fed into the reactor vessel refers to the rate of addition from all sources; for example, if initiator is fed into the reaction vessel from two separate sources, the rate of addition refers to the combined rate of addition from each source.

The period required for the polymerization to reach 90% completion refers to the time required for at least 90% of the temperature-sensitive monomers to be incorporated in polymer chains, from commencement of addition of the initiator. The degree of polymerization in a reactor vessel at a particular time may be determined by measuring the

amount of polymer and/or unpolymerized monomer present in the reactor vessel. The time required for polymerization to reach 90% completion for a particular combination of reactants and reaction conditions may be calculated based on known information, where available, or may be determined by simple experimentation.

5   In at least some examples of the present invention, the period required for the polymerization to reach 90% completion is at least 1 hour, for example at least 2 hours or at least 3 hours, from commencement of addition of the initiator.

In at least some examples of the present invention, the initiator is fed into the reactor vessel over at least 50% of the period required for the polymerization to reach 90%

10   completion, preferably over at least 75% of the period required for the polymerization to reach 90% completion, more preferably over at least 85% of the period required for the polymerization to reach 90% completion, for example, over the entire period required for the polymerization to reach 90% completion.

In at least some examples of the present invention, the initiator is fed into the

15   reactor vessel over the course of at least 30 minutes, preferably, at least 60 minutes.

In at least some examples of the present invention, the initiator is fed into the reactor vessel at an average rate of from 0.125% wt/wt (with respect to the total monomer including optional co-monomer) per hour to 5% wt/wt (with respect to the total monomer including optional co-monomer) per hour, or from 0.5% wt/wt (with respect to the total

20   monomer/co-monomer) per hour to 2.0% wt/wt (with respect to the total monomer including optional co-monomer) per hour.

In at least some examples of the present invention, the initiator is fed into the reactor vessel over a single continuous period, the rate of addition of initiator to the reactor vessel being steady over the entire period. In at least some examples of the present

25   invention, the initiator is fed into the reactor vessel discontinuously, i.e. the initiator is fed into the reactor vessel over 2 or more separate periods separated by periods during which initiator is not fed into the reactor vessel. As discussed herein, where the initiator is fed into the reactor vessel discontinuously, the rate at which the initiator is fed, excluding the periods when it is not being fed into the reactor vessel, is kept steady.

30   Preferably, the suspension of temperature-sensitive water-swellable microgel particles has a solids loading of from 10% wt/v to 25% wt/v, in particular, from 12.5% wt/v to 20% wt/v.

In at least some examples of the present invention, the average hydrodynamic diameter (average particle diameter when solvated with water) is in the range 70 nm to 1.5 μm, preferably 150 to 750 nm, in particular, 350 to 750 nm. The particles become smaller as they are heated to at or above the VPTT, so that, in at least some examples of the present invention, the particle size is 50 to 350 nm, preferably 100 to 275 nm.

By "temperature-sensitive monomers" is meant monomers that impart the desired temperature sensitivity and water-solubility to a polymer incorporating the monomers. Such polymers may be:

1) a homopolymer of the temperature-sensitive monomer;

2) a co-polymer of two or more temperature-sensitive monomers; or

3) a co-polymer of one or more temperature-sensitive monomers with one or more "non-temperature-sensitive" co-monomers.

By "non-temperature-sensitive co-monomer" is meant that a polymer comprised solely of such co-monomer or comonomers would not exhibit temperature-sensitivity.

In at least some examples of the present invention, the temperature-sensitive monomer is N-ethylacrylamide, N-isopropylacrylamide, N-isopropylmethacrylamide, vinyl methyl ether, N-vinyl caprolactam or mixtures thereof. In at least some examples of the present invention, very pure temperature-sensitive monomer is used, for example at least 99% or at least 99.9% pure.

In at least some examples of the present invention, one or more non-temperature-sensitive co-monomers are polymerized with the one or more temperature-sensitive monomers, the non-temperature sensitive co-monomer being, for example, a non-temperature sensitive acrylamide (for example, methyl acrylamide, N-methyl acrylamide, dimethylacrylamide, diethylacrylamide, and N-hydroxyethylacrylamide), acrylic acid, methacrylic acid, ethylacrylic acid, n-butyl acrylate, methyl methacrylate, ethyl methacrylate, hydroxyethyl methacrylate, 2-(dimethylamino)ethylmethacrylate, 2-(diethylamino)ethylmethacrylate, 2-acrylamido-2-methylpropane sulfonic acid (AMPS), styrene, 4-vinylpyridine, N-vinyl formamide, N-vinyl pyrrolidone, ethylene oxide, ethylene imine, maleic acid, fumaric acid, ethylene glycol vinyl ether, ethylene glycol methyl ether methacrylate or azobenzene containing monomer.

In at least some examples of the present invention, the amount of non-temperature sensitive co-monomer incorporated into the co-polymer is less than 55 mol%, for example

less than 30 mol%, or less than 20 mol%.

In at least some examples of the present invention, the free radical initiator is an azo compound, for example, azobisisobutyronitrile (AIBN), 4,4'-azobis(4-cyanovaleric acid) (ACVA) or 2,2'-azobis(2-methylpropionamidine) dihydrochloride; an inorganic compound, for example, potassium persulfate or ammonium persulfate; or a redox couple, for example, benzoyl peroxide/dimethylaminopyridine and potassium persulfate/sodium metabisulfite.

Generally, the total amount of free radical initiator fed to the reaction vessel is from 0.25% to 2.5% wt/wt (with respect to the total monomer/co-monomer). In at least some examples of the present invention, the total amount of free radical initiator fed into the reactor vessel is from 0.5% to 2.0% wt/wt (with respect to the total monomer/co-monomer).

Any suitable cross-linking agent may be used in the process of the invention. In at least some examples of the present invention, the cross-linking agent is N',N-methylene-bis acrylamide, ethyleneglycol dimethacrylate, isoprene, divinyl benzene, allyl methacrylate or diallyl phthalate.

Any suitable amount of cross-linking agent may be used in the process of the invention. In at least some examples of the present invention, the amount of cross-linking agent is from 0.25% to 2.5% wt/wt (with respect to the total monomer/co-monomer).

Any suitable anionic surfactant may be used in the process of the invention. In at least some examples of the present invention, the anionic surfactant is an ammonium or Group IA metal salt of a C_8 to C_{18} carboxylic acid, a C_8 to C_{18} hydrocarbyl sulphate or a C_8 to C_{18} hydrocarbyl phosphate ester. Optionally, the anionic surfactant is an ammonium or Group IA metal salt of a branched C_8 to C_{18} carboxylic acid, C_8 to C_{18} hydrocarbyl sulphate or C_8 to C_{18} hydrocarbyl phosphate ester. In at least some examples of the present invention, the anionic surfactant is a lithium, potassium or sodium salt of a C_8 to C_{18} hydrocarbyl sulphate or phosphate ester, for example sodium dodecyl sulphate.

Any suitable amount of anionic surfactant may be used in the process of the present invention. In at least some examples of the present invention, the amount of anionic surfactant present in the reactor vessel during the process of the present invention is from 1% to 3.5% wt/wt (with respect to the total monomer/co-monomer), for example 1.5% to 3% wt/wt, or 2% to 2.5% wt/wt.

Any suitable polar solvent may be used in the process of the invention. In at least some examples of the present invention, the polar solvent is an aqueous solvent. The aqueous solvent may be a brine having salts dissolved therein.

The polymerization process of the present invention may be carried out at any
5   suitable temperature. In at least some examples of the present invention, the polymerization process is carried out at a temperature of from 50 to 90°C, for example 60 to 80°C.

The polymerization process of the present invention may be carried out under any suitable conditions. In at least some examples of the present invention, the process is
10   carried out in an oxygen-free atmosphere, which allows for a controlled reaction by reducing termination brought about by oxygen radicals. In at least some examples of the present invention, oxygen is removed by purging the reactants and the reactor vessel with nitrogen before the polymerization is carried out.

In the polymerization process of the present invention, all of the components of the
15   polymerization reaction, other than the free radical initiator, may be contained in the reactor vessel before the start of the reaction. However, in at least some examples of the present invention, one or more components other than the free radical initiator, may be added to the reaction vessel, for example, over the same time period as the initiator. Thus, in at least some examples of the present invention, the monomer is fed into the reactor
20   vessel over the same time period as the initiator. Alternatively or additionally, in at least some examples of the present invention, when the polymerization is carried out in the presence of a co-monomer, the co-monomer is fed into the reactor vessel over the same period as the initiator. Where additional components of the reaction are fed into the reactor vessel, they may be fed as a combined feed with the free radical initiator or they may be
25   fed separately.

Any suitable reactor vessel may be used for carrying out the present invention. In at least some examples of the present invention, the reactor vessel includes components providing a sufficiently high shear rate to the contents of the reactor vessel such that there is a limited temperature difference across the reactor vessel, for example a temperature
30   difference of no more than 7.5°C, preferably, not more than 5°C across the entire vessel. Preferably, the shear rate in the reactor vessel is at least 0.5 millisecond^{-1}, preferably, at least 1 millisecond^{-1}, more preferably, at least 5 milliseconds^{-1}, for example, at least 10

milliseconds^{-1}.

In the process for producing dried temperature-sensitive water-swellable microgel particles according to the present invention any suitable method of drying may be used, for example freeze drying or spray drying, preferably spray drying.

5   Dried temperature-sensitive water-swellable microgel particles produced by the process of the present invention may be dried sufficiently that they may be stored and transported as powder materials, or they may optionally be further processed to form granules or other solid forms, for example, tablets.

Where the powder is processed to form solid forms such as granules or tablets,

10   additives such as binders or disintegrants may be optionally incorporated into the granules or tablets.

By "disintegrant" is meant an additive that aids the break-up of the granules or tablets such that the microgel particles are released from the granules or tablets and become dispersed in an aqueous solvent. Suitable disintegrants include additives that swell in the

15   presence of water, for example, sodium carboxymethylcellulose, alginates, polyvinylpyrrolidone (PVP), for example, PVP-K30 and PVP-K90; additives that dissolve in water, for example, sodium chloride, potassium chloride, calcium chloride; and, surfactants that increase the wettability of the granules or tablet. Suitable optional binders include starches, sugars, for example, lactose, sugar alcohol, for example, xylitol, sorbitol

20   and maltitol, and cellulose or modified cellulose, for example, microcrystalline cellulose and hydroxypropyl cellulose.

The present invention also provides a process for producing a concentrated suspension of temperature-sensitive water-swellable microgel particles, for example by partially drying a microgel suspension having a solids loading or at least 10% wt/v

25   obtained by the process of the present invention, or by redispersing dried temperature-sensitive water-swellable microgel particles produced according to the present invention in a solvent. Any suitable solvent may be used to redisperse the dried particles, for example water, methanol, ethanol, glycol (for example, ethylene glycol) and mixtures thereof. Electrolytes, for example salts, may be added to the dispersion.

30   Dried temperature-sensitive water-swellable microgel particles (including granules or tablets formed from compacted dried temperature-sensitive water-swellable microgel particles) and concentrated suspensions of temperature-sensitive water-swellable microgel

particles obtainable by the processes of the present invention are relatively convenient to handle, transport and use compared to low concentration suspensions of temperature-sensitive microgel particles. Such dried and/or concentrated suspensions of temperature-sensitive water-swellable microgel particles are therefore particularly convenient for use in

5 modifying the permeability to water of thief zones of hydrocarbon-bearing reservoirs.

According to the present invention there is yet further provided a process for modifying the permeability to water of at least one thief zone of a subterranean hydrocarbon reservoir comprising:

(a) dispersing dried temperature-sensitive water-swellable microgel particles and/or a

10 concentrated suspension of temperature-sensitive water-swellable microgel particles obtainable by the process of the present invention in an injection water at below the critical flocculation temperature for the microgel particles, thereby forming a dispersion of hydrated microgel particles in the injection water, wherein the hydrated microgel particles are capable of shrinking and flocculating above the critical flocculation temperature (CFT)

15 and the microgel particles are selected to have a CFT that corresponds to a threshold temperature encountered in the thief zone, and wherein (i) the injection water has an ionic compound dissolved therein at a concentration effective to promote flocculation of the microgel particles at above the CFT, and/or (ii) the water associated with the reservoir rock of the thief zone has an ionic compound dissolved therein at a concentration effective to

20 promote flocculation of the microgel particles at above the CFT;

(b) injecting the dispersion formed in (a) down a well and into the high permeability thief zone or zones such that the dispersion flows through the thief zone or zones, so that the microgel particles shrink and flocculate at a location within the thief zone or zones where the temperature is above the threshold temperature, thereby reducing the

25 permeability of the thief zone or zones to water.

The well into which the dispersion is injected to block a thief zone or zones may be an injection well or a production well. Where the dispersion is injected into a production well, the well is taken off production prior to injection of the dispersion from the production well into the high permeability thief zone or zones (termed a "squeeze"

30 treatment).

Although the initial temperature of the reservoir may be in the range of 80 to 140°C, substantial cooling of the thief zone may have occurred during a waterflood. Accordingly,

the threshold temperature for flocculation of the microgel particles may be less than the original reservoir temperature (prior to waterflooding), for example, may be in the range of 25 to 100°C, preferably, 35 to 80°C. The person skilled in the art will understand that the extent of cooling of the thief zone in the near wellbore region of a production well is likely

5   to be less than the extent of cooling of the thief zone in the near wellbore region of an injection well.

Where the dispersion is injected from a production well into a thief zone or zones, if necessary, ambient temperature water (for example, seawater, estuarine water, river water, lake water or desalinated water having a temperature of about 3 to 15°C), may be injected

10   into the thief zone ahead of the dispersion of the microgel particles in order to cool the production well and thief zone thereby mitigating the risk of premature flocculation of the microgel particles.

The person skilled in the art will understand that the microgel particles of the injected dispersion should have a VPTT and a CFT at or above the threshold temperature in the

15   thief zone such that the microgel particles shrink in size and flocculate at the desired location within the thief zone or zones of the reservoir.

The thief zone or zones of the reservoir may be a layer of reservoir rock having a permeability that is at least 3 times greater, preferably, at least 4 times greater than the permeability of adjacent hydrocarbon-bearing formations of the reservoir. For example,

20   the by-passed adjacent hydrocarbon-bearing layers of the reservoir may have a permeability, for example, in the range of 30 to 100 millidarcies while the thief layer may have a permeability, for example, in the range of 90 to less than 6,000 millidarcies, in particular, 90 to 1,000 millidarcies, with the proviso that the thief layer has a permeability at least 3 times greater, preferably, at least 4 times greater than that of the adjacent by-

25   passed layers of the reservoir. Where the thief zone is of relatively low permeability, for example, has a permeability in the range of 90 to 1,000 millidarcies, it is believed that at least a portion of the microgel particles may either bind to the surface of the pores of the rock matrix or "filter out" such that the microgel particles deposit within the pore space of the rock matrix in the near wellbore region of the well, for example, at a radial distance of

30   less than 5 metres from the well. However, any microgel particles that penetrate deeper into the reservoir may form a further block when the particles reach a portion of the thief zone that is at or above the threshold temperature owing to shrinkage and flocculation of

the microgel particles. Thus, for relatively low permeability thief zones, flow diversion may occur in the near wellbore region of a well and potentially deeper within the reservoir.

The thief zone or zones of the reservoir may also be a super conductor layer. A super conductor layer is a highly permeable interbedded layer of a reservoir, for example, a

5   conglomerate layer of the reservoir. By "conglomerate" layer is meant a layer of a reservoir comprising poorly consolidated clasts of relatively large size (for example, pebbles or cobbles). Typically, the pebbles of a conglomerate layer may be regarded as having a size in the range of 4 to 64 mm while cobbles are regarded as having a size from 64 to 256 mm. Owing to the poorly consolidated nature of conglomerate layers, the

10   permeabilities of these layers are very high, for example, a conglomerate layer may have a permeability in the range of 6 to 15 Darcies, in particular, 6 to 10 Darcies.

In the case of a poorly consolidated conglomerate layer, the dispersion of hydrated microgel particles may penetrate a significant distance into the layer before encountering the threshold temperature at which the microgel particles flocculate. Where the dispersion

15   is injected from an injection well into a poorly consolidated conglomerate layer, it is preferred that the dispersion penetrates at least 10%, preferably, at least 20% of the interwell distance between the injection well and production well before encountering the threshold temperature at which the microgel particles flocculate and block the formation rock. Accordingly, where the thief zone is a super conductor layer, the process of

20   modifying the permeability of the thief layer may be regarded as a deep reservoir flow diversion process.

The thief zone or zones of the reservoir may also be a layer of reservoir rock having fractures therein that may be up to several hundreds of metres in length. Depending on the temperature of the surrounding rock and on the length of the fracture, the dispersion of

25   hydrated microgel particles may penetrate a significant distance into a fracture, for example, to the fracture tip, before encountering the threshold temperature at which the microgel particles flocculate and block the fracture.

The microgel particles may be added to the injection water stream in the form of a concentrated dispersion, in the form of a powder or in the form of disintegratable granules

30   or tablets. If desired, powder or granules/tablets may be added to a portion of an injection water stream, for example, in a mixing vessel, thereby forming a concentrated dispersion of microgel particles that is subsequently blended into the remainder of the injection water.

Thus, a side stream may be taken from the injection water and is passed to the mixing vessel, and the concentrated dispersion is then withdrawn from the mixing vessel and is blended with the remainder of the injection water stream.

It is also envisaged that a concentrated suspension of the microgel, or a microgel powder or granules or tablets formed from the microgel powder may be dosed directly into the injection water. Thus, the injection water stream typically has a sufficient velocity and turbulence to disperse the microgel powder in the injection water or to disintegrate the granules or tablets and uniformly disperse the microgel particles in the injection water.

Where the microgel particles are prone to being degraded by bacteria, as is the case for poly(ethylacrylamide) based microgel particles, a bactericide may be added to the injection water or may be blended with the microgel powder or microgel concentrate or may be incorporated into the microgel granules or tablets.

In at least some examples of the process for modifying the permeability to water of a thief zone, the injection water is seawater, estuarine water, brackish water, lake water, river water, desalinated water, produced water or aquifer water.

By "produced water" is meant water produced in the process of recovering hydrocarbons from the subterranean hydrocarbon-bearing rock formation or in any other process.

The ionic compound that is dissolved in the injection water may be inorganic, e.g. sodium chloride, potassium chloride, or calcium chloride, or may be organic, e.g. a polyelectrolyte, for example, poly(styrene sulphonate) or carboxy methyl cellulose. Preferably, the ionic compound is inorganic. In the absence of an ionic compound or when the ionic compound is present in the injection water (the aqueous phase of the dispersion) at below the effective concentration, either no flocculation of the microgel particles is achieved or there is insufficient flocculation of the microgel particles to set up a block in the thief zone or zones of the formation. It has been found that the concentration of inorganic ionic promoter in the aqueous phase of the dispersion should typically be at least 500 ppm wt/v, preferably, at least 2,000 ppm wt/v, more preferably, at least 3000 ppm wt/v in order to set up a block in the thief zone or zones. In at least some examples of the present invention, the injection water comprises sodium chloride at a concentration of at least 0.03 mol% (1,750 ppm wt/v).

Accordingly, where the microgel particles are dispersed in an injection water selected

from seawater, estuarine water, brackish water and produced water or combinations thereof, the amount of naturally occurring inorganic salts dissolved in the injection water is sufficient to achieve flocculation of the microgel particles at above the threshold temperature. However, where the injection water is selected from fresh water (e.g. river water or lake water) or from desalinated water (for example, produced by reverse osmosis of a high salinity water, for example, seawater or estuarine water or a produced water), it may be necessary to add an ionic compound to the injection water in order to achieve an effective concentration of ionic compound. Where the microgel particles are added to the injection water in the form of a powder, it is envisaged that the ionic compound could be mixed in powdered form with the dried microgel particles or may be coated onto the surface of the microgel particles. Additionally or alternatively, the ionic compound may be dissolved in the aqueous medium of the microgel before drying and therefore becomes incorporated in the interstitial space of the dried microgel particles. Where the dried microgel particles are formed into granules or tablets, an ionic compound may be blended with the microgel particles prior to forming the granules or tablets or an ionic compound may be coated onto the surface of the granules or tablets. The amount of ionic compound that is incorporated into the powder or disintegratable granules or tablets should be sufficient to give an effective concentration of ionic compound at the location in the thief zone where the threshold temperature is at or above the CFT for the microgel particles.

It is also envisaged that the water associated with the reservoir rock of the thief zone may have an ionic compound dissolved therein at a concentration effective to promote flocculation of the microgel particles at above the CFT. The water associated with the reservoir rock is commonly termed "formation water" and is typically a mixture of the connate water and water injected during a waterflood. The person skilled in the art will understand that the previously injected water may be a saline water, for example, seawater, estuarine water, a saline aquifer water, or a produced water.

Without wishing to be bound by any theory, it is believed that flocculation of the microgel particles blocks the thief zone or zones. Accordingly, subsequently injected water (for example, an injection water selected from seawater, produced water, estuarine water, brackish water, lake water, river water and desalinated water) is diverted away from the thief zones and into neighboring lower permeability zones of the reservoirs. The net result is that more water passes through the previously unswept zones, with more oil and

less water being swept towards the production well.

Owing to the difference in permeability between the thief zone(s) and adjacent hydrocarbon-bearing formations of the reservoir, most of the injected dispersion enters a thief zone. However, if desired, packers may be arranged above and below a thief zone in order to mitigate the risk of the dispersion of microgel particles entering adjacent poorly swept layers of the reservoir.

The VPTT and CFT of the microgel particles may be readily determined by the person skilled in the art. The VPTT and CFT of the microgel particles may be adjusted by appropriate selection of comonomers and also by varying the molar ratios of the comonomers thereby allowing dispersions of microgel particles to be prepared that match the threshold temperature within the thief zone or zones where it is desired to form the block of flocculated microgel particles. For example, it has been found that the threshold temperature for flocculation of microgel particles comprising cross-linked poly(N-isopropylacrylamide) (NIPAM) is in the range of 32 to 34°C, the threshold temperature for flocculation of microgel particles comprising cross-linked poly(N-isopropylmethacrylamide) is about 44°C, whilst the threshold temperature for flocculation of microgel particles comprising cross-linked N-ethyl acrylamide is about 78°C. Intermediate threshold temperatures can be obtained for cross-linked copolymers of NIPAM and N-ethyl acrylamide containing varying molar ratios of the comonomers. Owing to the low cost of N-methyl acrylamide, copolymers comprising N-methyl acrylamide are particularly preferred, for example, copolymers of NIPAM and N-methyl acrylamide comprising up to 30 mol% of structural units derived from N-methylacrylamide, for example, 10 to 20 mol%, of structural units derived from N-methyl acrylamide. It has been found that where a NIPAM copolymer contains up to 30 mol%, preferably, 10 to 20 mol% of structural units derived from N-methyl acrylamide that this does not interfere with the ability of the microgel particles to shrink and flocculate.

Typically, when heated to above the threshold temperature, the shrunken microgel particles have a diameter in the range of 100 to 400 nm, preferably, 200 to 300 nm. Generally, the average particle diameter of the shrunken microgel particles is typically at least 30% smaller, for example, at least 40% smaller than the original average hydrodynamic diameter. However, the flocs of microgel particles that form above the threshold temperature are sufficiently large to bridge the pore throats of high permeability

thief zone or bridge fractures in a fractured rock layer.

In at least some examples of the present invention, the amount of dried microgel particles and/or concentrated microgel suspension mixed into the injection water is in the range of 500 to 10,000 parts-per-million on a weight by volume basis (ppm wt/v), for example 1,000 to 6,000 ppm wt/v or 2,000 to 5,500 ppm wt/v.

In at least some examples of the present invention, the dispersion is injected continuously or intermittently, preferably, continuously, into the formation for up to 4 weeks, for example for 5 to 15 days.

In at least some examples of the present invention, the dried microgel particles and/or concentrated microgel suspension is added to a low salinity injection water having a total dissolved solids content of from 300 to 10,000 ppm wt/v, preferably, 3,000 to 8,000 ppm wt/v and having a multivalent cation content less than the multivalent cation content of the connate water of the subterranean hydrocarbon-bearing rock formation.

In at least some examples of the present invention, the CFT for flocculation of the microgel particles is from 25 to 100°C, in particular,35 to 80°C.

The invention will now be described by way of example only with reference to the following experiments and examples in which suspensions according to the present invention are labeled numerically as Suspension 1, Suspension 2, etc. and suspensions not according to the present invention and labeled alphabetically as Suspension A, Suspension B, etc.

Preparation of a Suspension of Temperature-Sensitive Microgel Particles Having a Solids Loading of 10% wt/v

An attempt was made to produce a microgel suspension having a solids loading of 10% wt/v by a conventional emulsion polymerization technique (Suspension A). 2.5g of a temperature-sensitive monomer (N-isopropylacrylamide/NIPAM) was dissolved in 25ml ultra pure water to which was also added 0.05 g of a cross-linking agent (N', N-methylene-bis acrylamide/MBA), 0.0625 g of an anionic surfactant (sodium dodecyl sulphate/SDS) and 0.0375 g of a free radical initiator (potassium persulfate/KPS). The reactants were combined in a suitably sized reaction vessel. Before mixing, both the reaction vessel and all of the reactants were purged to remove oxygen, and the vessel was sealed following mixing. A very pure NIPAM monomer (99.9% purity) was used. The reaction vessel was heated to obtain a solution temperature of 70°C, and the solution was stirred for 5 hours

during which time the microgel composition coagulated rather than forming a stable dispersion.

Two further attempts were made to produce suspensions having solids loadings of 10% wt/v using the method employed for Suspension A (Suspension B and Suspension C). For Suspension B, the amount of MBA was reduced to 0.0125g and the amount of SDS was reduced to 0.05 g, whilst the amount of KPS was maintained at 0.0375 g. For Suspension C, 0.025 g of MBA was used together with 0.05 g of SDS, and the amount of KPS was reduced to 0.025 g. In both cases, stable suspensions were not obtained.

Suspensions A, B and C are not according to the present invention because the free radical initiator was not fed into the reactor vessel over at least 10% of the period required for the polymerization to reach 90% completion.

A suspension having a solids loading of at least 10% wt/v (Suspension 1) according to the present invention was prepared by a method corresponding to the method used for preparing Suspensions A, B and C, but adapted so that the free radical initiator was fed into the reactor vessel over at least 10% of the period required for the polymerization to reach 90% completion. Specifically, 2.5 g NIPAM was dissolved in 7.5ml ultra pure water, 0.025 g MBA was dissolved in 5ml ultra pure water and 0.05 g SDS was dissolved in 2.5ml ultra pure water. The MBA and SDS solutions were combined with the NIPAM solution, and the combined mixture was transferred into a suitably sized reactor vessel which was then degassed for 30 minutes with a stirrer rate of 300 rpm. 0.025 g KPS was then dissolved in 10ml degassed ultra pure water, and the solution was transferred to a degassed syringe. The syringe was attached to a syringe housing, incorporating a syringe pump, previously attached to the reactor vessel, and a delivery rate of 10ml per hour was set for the syringe pump. The reactor vessel was heated so that a solution temperature of 70°C was achieved, and the syringe pump was then activated. After 1 hour the entire KPS solution had been pumped into the reactor vessel and the reaction was allowed to continue for a further 4 hours.

After 5 hours a stable suspension of temperature-sensitive water-swellable microgel particles had been obtained, and the properties of the suspension were investigated further to determine particle size before and after heat activated collapse (using conventional dynamic light scattering techniques) and also to measure the Polydispersity Index before and after collapse. The Polydispersity Index was calculated from the size data generated

by dynamic light scattering using standard algorithms, for example those defined in the ISO standard document 13321:1996 E. A low PI value indicates a highly monodisperse suspension, whilst a higher number indicates greater variability in particle size.

Three further microgel compositions according to the present invention having a solids loading of 10% wt/v were prepared in the same way as Suspension 1 (Suspensions 2, 3 and 4). For Suspension 2, the amounts of MBA and KPS were both increased to 0.05 g, whilst the amount of SDS was maintained at 0.05 g. For Suspension 3, the amount of KPS was increased to 0.05 g, whilst the amount of MBA was maintained at 0.025 g, and the amount of SDS was maintained at 0.05 g. For Suspension 4, the amount of MBA was increased to 0.05 g, and the amount of KPS was increased to 0.0375 g, whilst the amount of SDS was maintained at 0.05 g. In each case, the KPS was dissolved in 10ml ultra pure water, and the injection rate was set at 10ml per hour.

Suspensions 2, 3 and 4 all formed stable suspensions by the end of the reaction period, and were further tested to determine particle size and Polydispersity Index values before and after collapse.

Compositions for each of Suspensions A to C and 1 to 4, together with particle size and Polydispersity Index values, are shown in Table 1.

Table 1

	NIPAM		MBA		SDS		KPS		Injection	Dispersion Conditions	PARTICLE SIZE		POLYDISPERSITY INDEX	
	wt/v	g	wt/wt	g	wt/wt	g	wt/wt	g			Before collapse (nm)	After collapse (nm)	Before collapse (nm)	After collapse (nm)
Suspension A	10%	2.5	2.0%	0.05	2.5%	0.0625	1.5%	0.0375	NO	Coagulated	N/A	N/A	N/A	N/A
Suspension B		2.5	0.5%	0.0125	2.0%	0.05	1.5%	0.0375	NO	Coagulated	N/A	N/A	N/A	N/A
Suspension C	10%	2.5	1.0%	0.025	2.0%	0.05	1.0%	0.025	NO	Coagulated	N/A	N/A	N/A	N/A
Suspension 1	10%	2.5	1.0%	0.025	2.0%	0.05	1.0%	0.025	YES	Stable dispersion	193.6	112.6	0.0639	0.0594
Suspension 2	10%	2.5	2.0%	0.05	2.0%	0.05	2.0%	0.05	YES	Stable dispersion	247.0	165.7	0.1041	0.0968
Suspension 3	10%	2.5	1.0%	0.025	2.0%	0.05	2.0%	0.05	YES	Stable dispersion	216.5	138.9	0.0295	0.0257
Suspension 4	10%	2.5	2.0%	0.05	2.0%	0.05	1.5%	0.0375	YES	Stable dispersion	210.5	136.2	0.0179	0.0115

The results in Table 1 show that injecting the free radical initiator into the reactor vessel at a steady rate over at least 10% of the period required for the polymerization to reach 90% completion allows for the production of stable suspensions of temperature-sensitive water-swellable microgel particles having solids loadings of at least 10% wt/v.

5 Production of a Suspension of Temperature-Sensitive Water-Swellable Microgel Particles Having a Solids Loading of 15% wt/v

A suspension of temperature-sensitive water-swellable microgel particles having a solids loading of 15% wt/v (Suspension 5) according to the present invention was prepared by the method used to prepared Suspensions 1 to 4, but with an increased concentration of

10 temperature-sensitive monomer (NIPAM). Thus, 3.75 g NIPAM (15% wt/v) was combined with 0.075 g cross-linking agent (BA) (2% wt/wt) and 0.075 g anionic surfactant (SDS) (2% wt/wt) in 15ml ultra pure water, and transferred to a suitably sized reaction vessel. 0.0563 g free radical initiator (KPS) (1.5% wt/wt) was dissolved in 10ml ultra pure water, which was injected into the heated reactor vessel at a rate of 10ml per hour for 1

15 hour, and the reaction was allowed to continue for a further 4 hours. At the end of the reaction period a stable suspension had formed. The suspension was examined by transmission electromicroscopy, which showed that the particle size was relatively uniform. The critical flocculation temperature (CFT) of Suspension 5 in 0.3 molar sodium chloride was 28°C.

20 Production of a Suspension of Temperature-Sensitive Water-Swellable Microgel Particles Incorporating an Acrylamide Co-Monomer and Having a Solids Loading of 15.75% wt/v

A suspension of temperature-sensitive water-swellable microgel particles having a solids loading of 15.75% wt/v (Suspension 6) according to the present invention was prepared by the method of Suspension 5, but incorporating 5% wt/wt (as a percentage of

25 the total monomer/co-monomer) acrylamide co-monomer. Specifically, the reaction was carried out as set out for Suspension 5, but the free radical initiator (KPS) was dissolved in only 5ml ultra pure water, whilst 0.1875 g acrylamide co-monomer was also dissolved in 5ml ultra pure water. The KPS and acrylamide co-monomer were then combined, to give a combined volume of 10ml, which was injected into the reactor vessel at a rate of 10ml per

30 hour as for Suspension 5. After 1 hour all of the KPS/co-monomer had been injected into the reactor vessel, and the reaction was allowed to continue for a further 4 hours. At the completion of the reaction period a stable suspension was found to have been formed

having a relatively uniform particle size and a critical flocculation temperature (CFT) in 0.3 molar sodium chloride of 30°C.

Production of a Suspension of Temperature-Sensitive Water Swellable Microgel Particles Having a Solids Loading of 20% wt/v

5   A suspension of temperature-sensitive water-swellable microgel particles having a solids loading of 20% wt/v (Suspension 7) according to the present invention was prepared by the method of Suspension 5, but with the amount of temperature-sensitive monomer (NIPAM) increased to 20% wt/v. The amount of free radical initiator (KPS) was also reduced to 1.0% wt/wt. Thus, 5 g of temperature-sensitive monomer (NIPAM) (20% wt/v)

10   was combined with 0.1 g of cross-linking agent (MBA) (2% wt/wt) and 0.1 g of anionic surfactant (SDS) (2% wt/wt) in 15ml ultra pure water, and transferred to a suitably sized reaction vessel. 0.05 g free radical initiator (KPS) (1% wt/wt) was dissolved in 10ml ultra pure water, which was injected into the heated reaction vessel at a constant rate of 10ml per hour for 1 hour. The reaction was then allowed to continue for a further 4 hours. After

15   cooling a stable dispersion was found to have been produced. In contrast, a further suspension (Suspension D) having the same composition as Suspension 7 (i.e. 20% wt/v NIPAM, 2% wt/wt MBA, 2% wt/wt SDS and 1.0% wt/wt KPS), but produced according to the method used for Suspensions A to C, was found to coagulate and to not form a stable dispersion. Suspension D is not according to the present invention because the free radical

20   initiator is not added to the reactor vessel over at least 10% of the period required for the polymerization to reach 90% completion.

Effect of Increasing Amounts of Acrylamide Comonomer on the Critical Flocculation Temperature of the Microgel Particles

Suspensions of temperature-sensitive water-swellable microgel particles having a solids

25   loading of 15% wt/v were prepared using the method described above but with varying amounts of acrylamide comonomer of 5, 10, 15 and 20% wt/wt of the total weight of monomer (Suspensions 8 to 11 respectively). The critical flocculation temperature (CFT) for these suspensions is given in Table 2 below.

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Table 2

	Acrylamide Comonomer (%)	Critical Flocculation Temperature (°C)
Suspension 8	5	36
Suspension 9	10	40
Suspension 10	15	42
Suspension 11	20	52

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Claims:

1. A process for producing a suspension of temperature-sensitive water-swellable microgel particles having a solids loading of at least 10% wt/v, the process comprising polymerizing, in a reactor vessel containing a polar solvent and an anionic surfactant, one or more temperature-sensitive monomers, optionally in the presence of one or more non-temperature sensitive co-monomers, with an organic cross-linking agent and with from 0.25% to 2.5% wt/wt (with respect to the total monomer including optional co-monomer) of a free radical initiator; wherein the initiator is fed into the reactor vessel at a steady rate over at least 10% of the period required for the polymerization to reach 90% completion.

2. A process as claimed in claim 1, wherein the rate at which the initiator is fed into the reactor vessel varies by no more than ±20%, preferably no more than ±5% from the average rate over the period of addition, most preferably wherein the rate is constant.

3. A process as claimed in claim 1 or claim 2, wherein the period required for the polymerization to reach 90% completion is at least 1 hour, preferably at least 2 hours, more preferably at least 3 hours.

4. A process as claimed in any preceding claim, wherein the initiator is fed into the reactor vessel over at least 50% of the period required for the polymerization to reach 90% completion, preferably over at least the entire period required for the polymerization to reach 90% completion.

5. A process as claimed in any preceding claim, wherein the initiator is fed into the reactor vessel over the course of at least 30 minutes, preferably at least 60 minutes.

6. A process as claimed in any preceding claim, wherein the initiator is fed into the reactor vessel at an average rate of from 0.125% wt/wt (with respect to the total monomer/co-monomer) per hour to 5% wt/wt (with respect to the total monomer/co-monomer) per hour, preferably from 0.5% wt/wt (with respect to the total monomer/co-monomer) per hour to 2.0% wt/wt (with respect to the total monomer/co-monomer) per hour.

7. A process as claimed in any preceding claim, wherein the initiator is fed into the reactor vessel over a single continuous period, or wherein the initiator is fed into the reactor vessel discontinuously.

8. A process as claimed in any preceding claim, wherein the suspension of temperature-sensitive water-swellable microgel particles has a solids loading of from 10%

wt/v to 25% wt/v, preferably from 12.5% wt/v to 20% wt/v.

9.   A process as claimed in any preceding claim, wherein the temperature-sensitive monomer is N-ethylacrylamide, N-isopropylacrylamide, N-isopropylmethacrylamide, vinyl methyl ether, N-vinyl caprolactam or mixtures thereof.

10.   A process as claimed in any preceding claim, wherein the non-temperature-sensitive co-monomer, where present, is acrylamide, methyl acrylamide, N-methyl acrylamide, dimethylacrylamide, diethylacrylamide, N-hydroxyethylacrylamide, acrylic acid, methacrylic acid, ethylacrylic acid, n-butyl acrylate, methyl methacrylate, ethyl methacrylate, hydroxyethyl methacrylate, 2-(dimethylamino)ethylmethacrylate, 2-(diethylamino)ethylmethacrylate, 2-acrylamido-2-methylpropane sulfonic acid (AMPS), styrene, 4-vinylpyridine, N-vinyl formamide, N-vinyl pyrrolidone, ethylene oxide, ethylene imine, maleic acid, fumaric acid, ethylene glycol vinyl ether, ethylene glycol methyl ether methacrylate, azobenzene containing monomer or mixtures thereof.

11.   A process as claimed in any preceding claim, wherein the amount of co-monomer incorporated into the copolymer is less than 55 mol%, preferably less than 30 mol%, particularly less than 20 mol%.

12.   A process as claimed in any preceding claim, wherein the free radical initiator is an azo compound, for example, azobisisobutyronitrile (AIBN), 4,4'-azobis(4-cyanovaleric acid) (ACVA) or 2,2'-azobis(2-methylpropionamidine) dihydrochloride; an inorganic compound, for example, potassium persulfate or ammonium persulfate; or a redox couple, for example, benzoyl peroxide/dimethylaminopyridine and potassium persulfate/sodium metabisulfite.

13.   A process as claimed in any preceding claim, wherein the total amount of free radical initiator fed into the reactor vessel is from 0.5% to 2.0% wt/wt (with respect to the total monomer including optional co-monomer).

14.   A process as claimed in any preceding claim, wherein the cross-linking agent is N',N-methylene-bis acrylamide, ethyleneglycol dimethacrylate, isoprene, divinyl benzene, allyl methacrylate or diallyl phthalate.

15.   A process as claimed in any preceding claim, wherein the amount of cross-linking agent is from 0.25% to 2.5% wt/wt (with respect to the total monomer including optional co-monomer).

16.   A process as claimed in any preceding claim, wherein the anionic surfactant is an

ammonium or Group IA metal salt of an, optionally branched, C_8 to C_{18} carboxylic acid or an, optionally branched, C_8 to C_{18} hydrocarbyl sulphate or C_8 to C_{18} hydrocarbyl phosphate ester; preferably a lithium, potassium or sodium salt of a C_8 to C_{18} hydrocarbyl sulphate or C_8 to C_{18} hydrocarbyl phosphate ester, more preferably sodium dodecyl sulphate.

17.   A process as claimed in any preceding claim, wherein the amount of anionic surfactant is from 1% to 3.5% wt/wt (with respect to the total monomer including optional co-monomer), preferably 1.5% to 3% wt/wt, more preferably 2% to 2.5% wt/wt.

18.   A process as claimed in any preceding claim, wherein the polar solvent is water, optionally further comprising a salt.

19.   A process as claimed in any preceding claim, wherein the polymerization is carried out at a temperature of from 50 to 90°C, preferably 60 to 80°C.

20.   A process as claimed in any preceding claim, wherein the monomer is fed into the reactor vessel over the same time period as the initiator.

21.   A process as claimed in any preceding claim, wherein the polymerization is carried out in the presence of a co-monomer, and the co-monomer is fed into the reactor vessel over the same time period as the initiator.

22.   A process for producing dried temperature-sensitive water-swellable microgel particles, the process comprising producing a microgel suspension having a solids loading of at least 10% wt/v by a process as claimed in any preceding claim and drying the microgel suspension to remove the polar solvent.

23.   A process as claimed in claim 22, wherein the microgel suspension is dried by spray drying.

24.   A process for producing a concentrated suspension of temperature-sensitive water-swellable microgel particles, the process comprising producing a microgel suspension having a solids loading of at least 10% wt/v by a process as claimed in any of claims 1 to 21 and partially drying the microgel suspension, or producing dried temperature-sensitive water-swellable microgel particles by a process as claimed in claim 22 or claim 23 and redispersing the dried particles in a solvent.

25.   A process for modifying the permeability to water of at least one thief zone of a subterranean hydrocarbon reservoir comprising:

(a)   dispersing dried temperature-sensitive water-swellable microgel particles and/or a concentrated suspension of temperature-sensitive water-swellable microgel particles

obtainable by the process of the present invention in an injection water at below the critical flocculation temperature for the microgel particles, thereby forming a dispersion of hydrated microgel particles in the injection water, wherein the hydrated microgel particles are capable of shrinking and flocculating above the critical flocculation temperature (CFT) and the microgel particles are selected to have a CFT that corresponds to a threshold temperature encountered in the thief zone, and wherein (i) the injection water has an ionic compound dissolved therein at a concentration effective to promote flocculation of the microgel particles at above the CFT, and/or (ii) the water associated with the reservoir rock of the thief zone has an ionic compound dissolved therein at a concentration effective to promote flocculation of the microgel particles at above the CFT;

(b)   injecting the dispersion formed in step (a) down a well and into the high permeability thief zone or zones such that the dispersion flows through the thief zone or zones so that the microgel particles shrink and flocculate at a location within the thief zone or zones where the temperature is above the threshold temperature, thereby reducing the permeability of the thief zone or zones to water.

26.   A process as claimed in claim 25, wherein the injection water is seawater, estuarine water, brackish water, lake water, river water, desalinated water, produced water or aquifer water.

27.   A process as claimed in claim 25 or claim 26, wherein the injection water comprises sodium chloride at a concentration of at least 0.03 mol%.

28.   A process as claimed in any of claims 25 to 27, wherein the amount of microgel particles dispersed into the injection water is in the range of 500 to 10,000 ppm wt/v, preferably 1,000 to 6,000 ppm wt/v, in particular 2,000 to 5,500 ppm wt/v.

29.   A process as claimed in any of claims 25 to 28, wherein the dispersion is injected continuously into the formation for up to 4 weeks, preferably for 5 to 15 days.

30.   A process as claimed in any of claims 25 to 29, wherein the dried and/or concentrated microgel particles are dispersed in a low salinity injection water having a total dissolved solids content of from 3,000 to 8,000 ppm wt/v and having a multivalent cation content less than the multivalent cation content of the connate water of the subterranean hydrocarbon-bearing rock formation.

31.   A process as claimed in any of claims 25 to 30, wherein the threshold temperature for flocculation of the microgel particles is from 25 to 100°C, preferably from 35 to 80°C.

32.   A process as claimed in any one of claims 25 to 31 wherein the dried temperature sensitive, water swellable microgel particles are in the form of disintegratable granules or tablets.

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Intellectual Property Office

Application No: GB1402950.8	**Examiner:** Dr Jonathan Corden
Claims searched: 1-24	**Date of search:** 17 October 2014

Patents Act 1977: Search Report under Section 17

Documents considered to be relevant:

Category	Relevant to claims	Identity of document and passage or figure of particular relevance
A	-	US2010/256298 A1 (CHAMPION TECHNOLOGY INC) see whole document
A	-	WO2013/040178 A1 (LUBRIZOL ADVANCED MAT INC) see paragraph [0165] and whole document
A	-	US4282928 A (DOW CHEMICAL CO) see whole document
A	-	EP0114478 A1 (CELANESE CORP) see whole document

Categories:

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Field of Search:

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C08F; C09K

The following online and other databases have been used in the preparation of this search report

WPI, EPODOC, TXTAU1, TXTCA1, TXTCNT, TXTCNS, TXTEP1, TXTGB1, TXTJPS, txtjpq, TXTJPT, TXTKRT, TXTSG1, TXTUS0-5, TXTWO1, TXTWOT

Intellectual Property Office

International Classification:

Subclass	Subgroup	Valid From
C09K	0008/512	01/01/2006
C08F	0002/14	01/01/2006
C09K	0008/035	01/01/2006
C09K	0008/68	01/01/2006