



- (51) **International Patent Classification:**
C09K 8/60 (2006.01) *E21B 43/25* (2006.01)
- (21) **International Application Number:**
PCT/EP2015/071260
- (22) **International Filing Date:**
16 September 2015 (16.09.2015)
- (25) **Filing Language:** English
- (26) **Publication Language:** English
- (30) **Priority Data:**
14186452.0 25 September 2014 (25.09.2014) EP
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- (81) **Designated States** (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

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- (54) **Title:** PROCESS FOR REDUCING THE PERMEABILITY TO WATER OF A THIEF ZONE OF A SUBTERRANEAN HYDROCARBON RESERVOIR

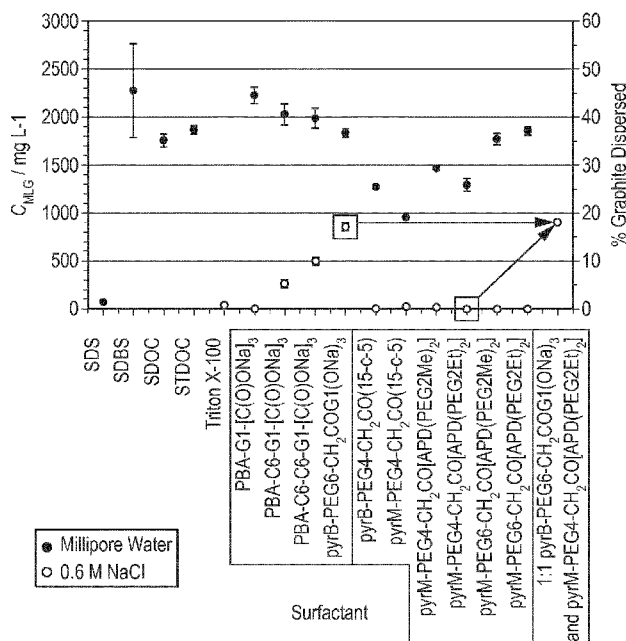


FIG. 3

- (57) **Abstract:** A process for reducing the permeability to water of a thief zone of a subterranean hydrocarbon reservoir, said process comprising injecting an injection fluid down a well and into a thief zone. The injection fluid comprises a dispersion of particles in water, which particles are capable of flocculating at a critical flocculation temperature (CFT) which is at or below the maximum temperature encountered in the thief zone and greater than the maximum temperature encountered in the well, and which particles comprise a carbon allotrope selected from graphene, carbon nanotubes, fullerenes and graphite, having adsorbed at its surface: (a) a non-ionic surfactant, and/or (b) a two-headed surfactant, and (c) optionally an ionic surfactant. The particles flocculate in the thief zone so as to reduce the permeability of the thief zone to water.



(84) **Designated States** (*unless otherwise indicated, for every kind of regional protection available*): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

- *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*
- *of inventorship (Rule 4.17(iv))*

Published:

- *with international search report (Art. 21(3))*

**PROCESS FOR REDUCING THE PERMEABILITY TO WATER OF A
THIEF ZONE OF A SUBTERRANEAN HYDROCARBON
RESERVOIR**

This invention relates to a method of modifying the permeability of a thief zone of a subterranean hydrocarbon reservoir to water.

5 The invention also relates to injection fluid for use in a method of modifying the permeability to water of a thief zone of a subterranean hydrocarbon reservoir, the injection fluid comprising a temperature-sensitive dispersion of particles in water.

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

Hydrocarbons may be recovered from a subterranean reservoir via natural pressure in the reservoir forcing hydrocarbon fluids towards production wells where they can flow or are pumped to a surface production facility (referred to as "primary recovery"). However, reservoir pressure is generally sufficient only to recover around 10 to 20 per cent of the
15 total hydrocarbon present in a subterranean reservoir. Accordingly "secondary recovery" techniques are applied to recover hydrocarbon from subterranean reservoirs in which the hydrocarbon fluids no longer flow by natural forces.

Secondary recovery techniques rely on the supply of external energy to maintain the pressure in a subterranean reservoir and to sweep oil towards a production well. One such
20 technique involves the injection of water (such as aquifer water, river water, seawater or produced water) or a gas (such as carbon dioxide, flue gas, or produced gas) into the subterranean reservoir via one or more 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. The injection of gas during secondary recovery
25 is commonly referred to as gas flooding.

The person skilled in the art will understand that in tertiary recovery, injection of the original fluid is stopped and a different fluid is injected into the subterranean reservoir for enhanced oil recovery.

Enhanced Oil Recovery (EOR) processes involve injecting a fluid into an oil
30 reservoir that increases oil recovery over that which would be achieved by water or gas injection alone. Once ranked as a third stage of oil recovery that was carried out after secondary recovery, the processes employed during enhanced oil recovery can actually be

initiated at any time during the productive life of an oil reservoir. The purpose of EOR is not only to restore reservoir pressure and to sweep oil towards a production well, but also to improve oil displacement or fluid flow in the reservoir.

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. Natural variation in the permeability of different zones (layers or areas) of a subterranean reservoir means that the injection fluid tends to travel most easily in, and therefore preferentially sweeps, the highest permeability zones (i.e. the injected fluid follows the lowest resistance path from the injection well to the production well), thereby potentially by-passing much of the oil present in lower permeability zones of the formation. Once the highest permeability zones are thoroughly swept they tend to accept most of the injected fluid and act as “thief zones”. In such cases the injected fluid does not effectively sweep the hydrocarbon from neighbouring, lower permeability zones of the reservoir.

Herein, the term ‘thief zone’ refers to any region of high permeability relative to the permeabilities of the surrounding rock, such that a high proportion of injected fluid flows through these regions. Such thief zones typically cannot be characterized by absolute values of permeability as the problem arises as a result of heterogeneity in the permeability of the reservoir rock and not absolute values; thus a thief zone may simply be a region of higher permeability than the majority of the reservoir rock that can be contacted by a fluid injected into an injection well.

In order to improve sweep efficiency, these ‘thief zones’ can be partially or totally blocked deep in the reservoir, generating a new pressure gradient and diverting flow of injected fluid into lower permeability zones (layers or areas) of the formation with high oil saturation. Herein, sweep efficiency is taken to mean a measure of the effectiveness of a secondary or tertiary oil recovery process that depends on the proportion of the volume of the formation contacted by the injection fluid.

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

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, 6,729,402, 6,984,705 and 7,300,973. The suspension of microparticles 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. However, a feature of these expandable microparticles is that the block is permanent. In other words, the particles have no ability to shrink back to their original size and move to another location in the reservoir matrix rock and then re-expand to form a further block.

GB 2 262 117A describes certain latex particles that are temperature sensitive and reversibly flocculate, shrink and harden at higher temperatures, and disperse, expand and soften at lower temperatures and that these can form effective blocking agents in the presence of an ionic compound, in a petroleum reservoir. An advantage of the latex particles of GB 2 262 117A is that the block is reversible. This is because the particles deflocculate as the reservoir matrix cools in the vicinity of the original block such that the deflocculated particles become redispersed in the injection water and the resulting dispersion can propagate through the formation to set up a subsequent block deeper within the formation where the temperature is sufficiently high to promote reflocculation, shrinkage and hardening of the latex particles. However, a problem with the dispersions of GB 2 262 117A is that they are produced at the desired particle concentration for the fluid that is to be injected into the reservoir. Accordingly, a large amount of the dispersion of GB 2262117 would be required for the treatment and the cost of handling and shipping the large amount of dispersion renders the treatment uneconomic. Accordingly, the method of GB 2 262 117A has yet to be commercially deployed.

It is an object of the present invention to provide a method which overcomes or at least mitigates the disadvantages associated with conventional methods for reducing the permeability of a thief zone and in particular to increase or improve the recovery of hydrocarbons.

5 Graphene is an allotrope of carbon which consists of sheets of sp^2 -bonded carbon atoms packed in a two-dimensional honeycomb crystal lattice, with each carbon atom found at the intersection of three adjacent hexagonal six-membered rings. Graphite consists of a plurality of layers of graphene stacked to form a three-dimensional lattice. Graphite is available in various forms, for example graphite may be available in lump form
10 or in a processed particulate form. Fullerenes are carbon allotropes having a closed cage structure consisting entirely of three-coordinate carbon atoms. Fullerenes are similar in structure to graphene and graphite, however the presence of pentagonal (in addition to hexagonal) rings induces a spheroidal arrangement of atoms. Carbon nanotubes are allotropes of carbon having a cylindrical nanostructure with walls comprising or consisting
15 of graphene. Single-walled nanotubes contain a single cylinder, whereas multi-walled nanotubes may comprise a concentric arrangement of two or more cylinders. The ends of nanotube cylinders may be capped with fullerene hemispheres which form part of the nanotube structure. Alternative multi-walled morphologies, such as “bamboo” and “herringbone” nanotubes have also been observed (see Masheter et al., Journal of Materials
20 Chemistry, 2007, volume 17, page 2616).

The solubility or dispersibility of fullerenes, carbon nanotubes, graphene and/or graphite particles in polar protic solvents such as water, alcohols (for example, methanol, ethanol, n-propanol, isopropanol, and n-butanol) and mixtures thereof is extremely low.

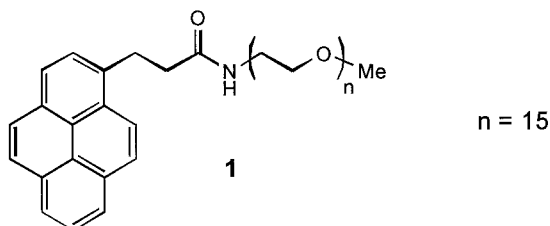
Carbon nanotubes are particularly difficult to solubilise or disperse due to strong
25 inter-tube Van der Waals forces which make them essentially insoluble in most organic solvents and water.

In order to improve the processability of carbon nanotubes, there have been some attempts to functionalise the nanotube surface by means of covalent or non-covalent modifications. In many cases, non-covalent modifications are preferred since this has a
30 minimal effect on the electronic properties of the nanotubes. In particular, there have been a number of reports of the use of π - π -stacking interactions between carbon nanotubes and polycyclic aromatic compounds to functionalise the outer surface of the nanotubes.

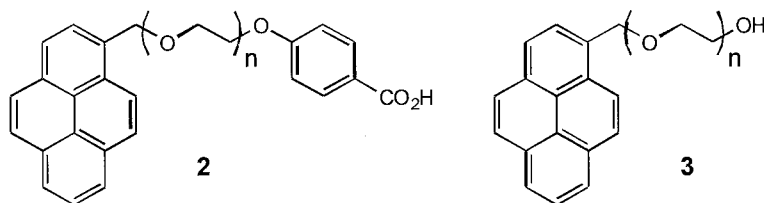
Functionalisation in this manner has only a minimal effect on the electronic properties of carbon nanotubes.

Zhang *et al.* (Nano Letters, 2004, vol. 3, 403-407) have examined the binding of anthracene and anthracenes substituted by bromo, hydroxy or cyano groups to single-walled carbon nanotubes. Hedderman *et al.* (J. Phys. Chem. B, 2006, vol. 110, 3895-3901) have described the interaction of single-walled carbon nanotubes with anthracene and *p*-terphenyl to produce stable suspensions of single-walled carbon nanotubes in toluene. Tomonari *et al.* (Chem. Eur. J., 2006, vol. 12, 4027-4034) disclose that an ammonium-substituted phenanthrene amphiphile [trimethyl-(2-oxo-2-phenanthren-9-yl-ethyl)-ammonium bromide] may be used to dissolve/disperse single-walled carbon nanotubes in water.

Liu *et al.* (New J. Chem., 2009, vol. 33, 1017-1024) have reported the use of pyrene derivative **1** to functionalise multi-walled carbon nanotubes (MWNTs) through π -stacking interactions. The functionalised MWNTs are reported to form stable aqueous suspensions.



Zhang *et al.* (Langmuir, 2007, vol. 23, 7911-7915) have reported the use of pyrene derivative **2** to probe the π - π interaction between pyrene and graphite in an aqueous medium by atomic force microscopy (AFM). The $-\text{CO}_2\text{H}$ moiety of pyrene derivative **2** is used to form a bond to an AFM tip. Also disclosed by Zhang *et al.* is the pyrene derivative **3**, which is a synthetic precursor of **2**. Pyrene derivative **3** is prepared from bromomethyl pyrene and polyethylene glycol having molecular weight of 6600 g mol^{-1} .



S. Bailey *et al.* (J. Chem. Phys., 2014, 140, 054708) report the binding energies of anthracene and pyrene derivatives adsorbed onto graphene. It was found that all the

selected derivatives functionalized with either electron donating or electron accepting substituents bind more strongly to graphene than the parent non-functionalized anthracene or pyrene.

Further consideration of carbon allotropes is required before they may be used in a process for reducing the permeability of a thief zone of a subterranean hydrocarbon reservoir.

According to the present invention there is provided a process for reducing the permeability to water of a thief zone of a subterranean hydrocarbon reservoir, said process comprising injecting an injection fluid down a well and into a thief zone, wherein the injection fluid comprises a dispersion of particles in water, which particles are capable of flocculating at a critical flocculation temperature (CFT) which is at or below the maximum temperature encountered in the thief zone and greater than the maximum temperature encountered in the well, and which particles comprise a carbon allotrope selected from graphene, carbon nanotubes, fullerenes and graphite, having adsorbed at its surface a surfactant selected from the group consisting of:

(a) non-ionic surfactants comprising:

- (i) a hydrophobic unit having a sheet-like structure and including one or more aromatic rings,
- (ii) a head unit which comprises a non-ionic hydrophilic moiety, and
- (iii) a linker unit linking the head unit to the hydrophobic unit, said linker unit comprising from 2 to 16 alkylene glycol units in the form of an oligoether, from 2 to 16 amide units in the form of an oligoamide, or from 2 to 16 units of a combination of alkylene glycol units and amide units in the form of an oligoether-amide;

(b) two-headed surfactants comprising:

- (i) a hydrophobic unit having a sheet-like structure and including one or more aromatic rings,
- (ii) a head unit which comprises a non-ionic hydrophilic moiety (hereinafter "non-ionic head unit"),
- (iii) a head unit which comprises an ionic hydrophilic moiety (hereinafter "ionic head group"), and
- (iv) at least one linker unit linking the non-ionic head unit and the ionic head

unit to the hydrophobic unit, said linker unit comprising from 2 to 16
alkylene glycol units in the form of an oligoether, from 2 to 16 amide units
in the form of an oligoamide, or from 2 to 16 units of a combination of
alkylene glycol units and amide units in the form of an oligoether-amide;
5 and

(c) optionally ionic surfactants comprising:

(i) a hydrophobic unit having a sheet-like structure and including one or more
aromatic rings,

(ii) a head unit which comprises an ionic hydrophilic moiety; and

10 (iii) a linker unit linking the head unit to the hydrophobic unit, said linker unit
comprising from 2 to 16 alkylene glycol units in the form of an oligoether,
from 2 to 16 amide units in the form of an oligoamide, or from 2 to 16 units
of a combination of alkylene glycol units and amide units in the form of an
oligoether-amide;

15 wherein the particles flocculate in the thief zone so as to reduce the permeability of the
thief zone to water.

In preferred embodiments, the process incorporates use of particles comprising a
carbon allotrope having adsorbed at its surface a non-ionic surfactant (a) and optionally an
ionic surfactant (c) as defined previously, in which case a two headed surfactant (b) is
20 preferably not present.

In some embodiments, the process incorporates use of particles comprising a carbon
allotrope having adsorbed at its surface a two-headed surfactant (b) as defined previously ,
in which case a non-ionic surfactant (a) and an ionic surfactant (c) are preferably not
present.

25 By “not present” it is meant that the defined surfactant is not adsorbed at the surface
of the particles.

Also according to another aspect of the present invention, there is provided an
injection fluid for use in a process for reducing the permeability to water of a thief zone of
a subterranean hydrocarbon reservoir, wherein the injection fluid comprises a dispersion of
30 particles in water, which particles are capable of flocculating at a critical flocculation
temperature (CFT) which is at or below the maximum temperature encountered in the thief
zone, and which particles comprise a carbon allotrope selected from graphene, carbon

nanotubes, fullerenes and graphite, having adsorbed at its surface a surfactant selected from the group consisting of:

(a) non-ionic surfactants comprising:

- (i) a hydrophobic unit having a sheet-like structure and including one or more aromatic rings,
- (ii) a head unit which comprises a non-ionic hydrophilic moiety, and
- (iii) a linker unit linking the head unit to the hydrophobic unit, said linker unit comprising from 2 to 16 alkylene glycol units in the form of an oligoether, from 2 to 16 amide units in the form of an oligoamide, or from 2 to 16 units of a combination of alkylene glycol units and amide units in the form of an oligoether-amide;

(b) two-headed surfactants comprising:

- (i) a hydrophobic unit having a sheet-like structure and including one or more aromatic rings,
- (ii) a non-ionic head unit which comprises a non-ionic hydrophilic moiety,
- (iii) an ionic head unit which comprises an ionic hydrophilic moiety, and
- (iv) at least one linker unit linking the non-ionic head unit and the ionic head unit to the hydrophobic unit, said linker unit comprising from 2 to 16 alkylene glycol units in the form of an oligoether, from 2 to 16 amide units in the form of an oligoamide, or from 2 to 16 units of a combination of alkylene glycol units and amide units in the form of an oligoether-amide; and

(c) optionally ionic surfactants comprising:

- (i) a hydrophobic unit having a sheet-like structure and including one or more aromatic rings,
- (ii) a head unit which comprises an ionic hydrophilic moiety; and
- (iii) a linker unit linking the head unit to the hydrophobic unit, said linker unit comprising 2 to 16 alkylene glycol units in the form of an oligoether, 2 to 16 amide units in the form of an oligoamide; or from 2 to 16 units of a combination of alkylene glycol units and amide units in the form of an oligoether-amide.

In preferred embodiments, the injection fluid includes particles comprising a carbon

allotrope having adsorbed at its surface a non-ionic surfactant (a) and optionally an ionic surfactant (c) as defined previously, in which case a two headed surfactant (b) is preferably not present.

5 In some embodiments, the injection fluid includes particles comprising a carbon allotrope having adsorbed at its surface a two-headed surfactant (b) as defined previously, in which case a non-ionic surfactant (a) and an ionic surfactant (c) are preferably not present.

10 It will be understood by the skilled person that the term "water" as used herein is intended to mean any aqueous solution suitable for use in a water flooding process in secondary or tertiary oil recovery, for example, seawater, estuarine water, brackish water, lake water, river water, desalinated water, produced water, aquifer water or mixtures thereof.

The present invention solves the technical problems defined above. Without wishing to be bound by theory, it is believed that the non-ionic and/or two-headed and optional 15 ionic surfactants of the invention are adsorbed at the surface of the carbon allotrope via the hydrophobic units. In particular, it is believed that the hydrophobic units of the non-ionic, and/or two-headed and optional ionic surfactants of the invention bind to the carbon allotrope surface, whilst the hydrophilic head units extend away from the carbon allotrope. Further, it is believed that at temperatures below the CFT the head group and linker unit of 20 the non-ionic, and/or two-headed and optional ionic surfactants of the invention may provide steric stability and hydrophilicity to the carbon allotrope when the particles are dispersed in water. At or above the CFT of the particles, which is at or below the maximum temperature encountered in the thief zone, the ability of the non-ionic, and/or two-headed, and optional ionic surfactants of the invention to stabilise the dispersion is 25 lost. The non-ionic, and/or two-headed and optional ionic surfactants may therefore be considered temperature sensitive surfactants, *i.e.* they impart temperature sensitivity to the particles such that at temperatures at or above the CFT they flocculate.

30 In the method of the present invention, most of the injection fluid will enter the thief zone of the reservoir since the injection fluid will follow the most permeable and/or lowest pressure route or routes from the injection well to an associated production well. When the particles flocculate in the thief zone, they form a block to water. Thus, the permeability of water through the block of flocculated particles is lower than the permeability of water

through neighbouring zones of the reservoir such that subsequently injected water (water injected into the reservoir after the injection fluid of the present invention) is largely diverted out of the thief zone and into neighbouring zones.

Advantageously, the particles may reversibly flocculate such that cooling of the thief zone in the location of the block to a temperature below the CFT results in deflocculation of the particles. Such cooling of the thief zone in the location of the block may occur due to subsequently injected water flowing through neighbouring zones of the reservoir. Accordingly, the deflocculated particles become redispersed in water and the resulting dispersion permeates through the thief zone until it reaches another location where the temperature is at or above the CFT where the particles again reversibly flocculate. These steps of flocculation, redispersion and reflocculation may occur a plurality of times within the thief zone, thereby allowing a greater volume of the reservoir to be swept by subsequently injected water.

In an embodiment of the invention, the dispersion may contain a non-ionic surfactant (a) and an optional ionic surfactant (c), adsorbed at the surface of the particles (*i.e.*, present in the particles), particularly when the water of the injection fluid is a brine. The ionic surfactant promotes the formation of a dispersion of the particles in water at temperatures below the CFT.

In a further embodiment of the invention, the dispersion may contain a two-headed surfactant (b), adsorbed at the surface of the particles, particularly when the water of the injection fluid is a brine. The ionic head unit of the two-headed surfactant promotes the formation of a dispersion of the particles in water at temperatures below the CFT.

The carbon allotrope which is used in the particles is selected from graphene, carbon nanotubes, fullerenes and graphite. The carbon nanotubes (CNTs) may be a single-walled nanotube (SWNT) or a multi-walled carbon nanotube (MWNT). The particles may comprise a single carbon allotrope, or a mixture of different carbon allotropes. Preferably, the particles comprise CNTs (in particular, MWNTs) or graphite.

The particles are preferably present in the injection fluid in an amount of from 30 to 150,000 mg/L, preferably 50 to 7,500 mg/L, most preferably 100 to 5,000 mg/L. The amount of particles employed depends in part on the composition of the injection fluid. For instance, greater amounts of particles may be dispersed in lower salinity brine than higher salinity brine. Reference herein to a "lower salinity brine" corresponds to a brine

having a total dissolved solids content (TDS) of less than 10,000 ppm wt/v, preferably in the range of from 300 to 10,000 ppm wt/v, more preferably in the range of 1,000 to 8,000 ppm wt/v. Reference herein to a “higher salinity brine” corresponds to a brine having a total dissolved solids content (TDS) of greater than 10,000 ppm wt/v, preferably greater than 12,000 ppm wt/v, more preferably greater than 14,000 ppm wt/v.

When the injection fluid is exposed to a temperature at or above the CFT, the dispersed particles flocculate. The skilled person would understand that ‘flocculation’ occurs when the dispersed particles aggregate in the form of a floc.

The non-ionic, two-headed and optional ionic surfactants used in the present invention each comprise a hydrophobic unit having a sheet-like structure and including one or more aromatic rings; a head unit which comprises a non-ionic hydrophilic moiety (in the case of the non-ionic surfactant and the two-headed surfactant) or an ionic hydrophilic moiety (in the case of the ionic surfactant and the two-headed surfactant); and a linker unit linking the head unit to the hydrophobic unit, which comprises an oligoether, an oligoamide, or an oligoether-amide.

Each hydrophobic unit having a sheet-like structure preferably includes two or more aromatic rings, more preferably three or more aromatic rings, and most preferably four or more aromatic rings.

The one or more aromatic rings may independently be carbocyclic or heterocyclic, and are preferably carbocyclic.

Where each hydrophobic unit contains two or more aromatic rings, the rings may be joined by a single or double bond, or may be fused rings. Where there are two or more aromatic rings, each hydrophobic unit preferably comprises at least two fused aromatic rings. Preferably, all of the aromatic rings are fused.

Each hydrophobic unit having a sheet-like structure and including one or more aromatic rings is preferably selected from:

- (a) polycarbocyclic aromatic hydrocarbon groups; and
- (b) polycyclic aromatic hydrocarbon groups including at least one heteroaromatic ring.

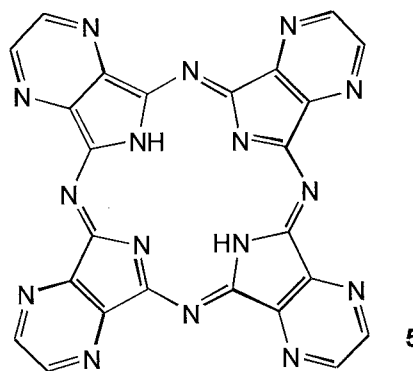
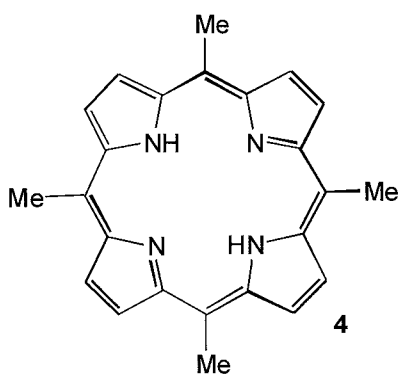
Each hydrophobic unit is preferably a polycarbocyclic aromatic hydrocarbon group containing at least three fused aromatic rings.

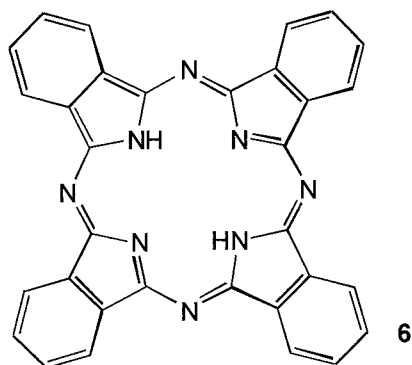
Preferred polycarbocyclic aromatic hydrocarbon groups include naphthalene,

anthracene, tetracene, pentacene, phenanthrene, pyrene, chrysene, triphenylene, perylene, coronene, corannulene, benzo[a]pyrene, fluorene and fluoranthene. Pyrene is particularly preferred. It is believed that polycarbocyclic aromatic hydrocarbon groups with fused aromatic ring systems bind particularly effectively via π - π stacking interactions with the surface of the carbon allotrope (i.e. interactions between π -orbitals of the fused aromatic ring system and π -orbitals at the surface of the allotrope).

Polycyclic aromatic hydrocarbon groups which include at least one heteroaromatic ring preferably have a fused polyaromatic ring structure with at least one heteroatom located within one of the fused heterocyclic rings. In preferred embodiments, the polycyclic aromatic hydrocarbon group may have a ring structure analogous to the polycarbocyclic aromatic hydrocarbon groups named above, wherein one or more carbocyclic aromatic rings are replaced by a pyridyl, pyridazyl, pyrimidyl or pyrazinyl ring. Alternatively, the polycyclic aromatic hydrocarbon group may comprise one or more heterocyclic rings selected from furan, pyrrole, pyrazole, imidazole, oxazole, isoxazole and thiophene fused to a benzene ring or to one of the polycarbocyclic aromatic hydrocarbon groups named above. Examples of polycyclic aromatic hydrocarbon groups that include at least one heterocyclic ring include benzofuran, indole, benzothiophene, quinoline, isoquinoline, and carbazole.

A further category of preferred polycyclic aromatic hydrocarbon groups that include at least one heterocyclic ring includes those having a macrocyclic structure, for example a porphyrins, phthalocyanines or porphyrazines (and derivatives thereof). Examples of suitable structures include the tetramethyl porphyrin (**4**) and the two porphyrazine derivatives (**5** and **6**).





Metallo-complexes may also be used, such as metallo-porphyrin, metallo-phthalocyanine metallo-porphyrine. The metallo-porphyrin, metallo-phthalocyanine and metallo-porphyrines are typically complexed with divalent or trivalent metal ions, typically a transition metal ion, for example, iron, copper, cobalt, or zinc.

The hydrophobic groups described above have the common feature of a sheet-like structure which can lie over the surface of graphite, carbon nanotubes, graphene and fullerenes. By sheet-like structure, it is meant that all carbon atoms and heteroatoms that are present in the hydrophobic unit are sp^2 -hybridised, or at least attached to a sp^2 -hybridised centre. It will be understood that a degree of buckling may be observed in the sheet-like structure. Preferably, only hydrogen atoms will extend out of the plane of the sheet-like hydrophobic unit.

It is believed that the presence of aromatic rings in the sheet-like hydrophobic unit provides π -orbitals which are available to interact with π -orbitals on the surface of the carbon allotrope (π - π stacking interactions) thereby binding the surfactant to the surface of the carbon allotrope. For example, in the case of carbon nanotubes, it is believed that the hydrophobic unit(s) lie over the outer surface of the nanotubes. By careful selection of the hydrophobic unit(s), it is possible to control the binding characteristics of the surfactant; in particular, the binding energy and the separation of the hydrophobic unit from the graphite, graphene, carbon nanotube or fullerene surface.

The use of a linker unit comprising an oligoether, oligoamide or oligoether-amide in the non-ionic, two-headed and optional ionic surfactants of the invention is advantageous as it may encourage dispersion of the particles in water. It provides flexibility to increase or decrease the distance between the hydrophobic unit and the hydrophilic moiety of the head unit in order to modify the properties of the surfactant. In addition, depending on its

structure, the oligoether, oligoamide or oligoether-amide linker can contribute to the hydrophilicity or hydrophobicity of the surfactant.

In preferred examples, the non-ionic and optional ionic surfactants have a structure of formula (I):



wherein:

Ar represents the hydrophobic unit;

A may be present or absent in the linker unit and represents a C₁ to C₆ substituted or unsubstituted alkylene group;

10 L represents the oligoether, oligoamide or oligoether-amide of the linker unit; and
Z represents the head unit of the non-ionic surfactant or the head unit of the ionic surfactant.

Ar is preferably attached to the rest of the surfactant via a ring carbon atom.

In examples, the two-headed surfactant has a structure of formula (Ia):



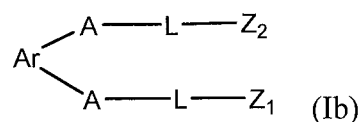
wherein:

Ar, A and L are as defined previously;

Z₁ represents a non-ionic head unit comprising a non-ionic hydrophilic moiety; and

Z₂ represents an ionic head unit comprising an ionic hydrophilic moiety.

20 In examples, the two-headed surfactant has a structure of formula (Ib):



wherein:

Ar, A and L are as defined previously;

25 Z₁ represents a non-ionic head unit comprising a non-ionic hydrophilic moiety; and

Z₂ represents a ionic-head unit comprising the ionic hydrophilic moiety. Groups A and L separately attached to head groups Z₁ and Z₂ in these examples may be the same or different.

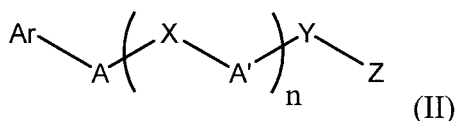
In embodiments where the hydrophobic unit comprises a heterocyclic ring, Ar may be attached to the rest of the surfactant via a ring nitrogen atom, for instance a nitrogen atom of a pyrrolic or piperidinic ring or a nitrogen atom of a cyclic imide ring.

Preferably, A represents a C₁ to C₄ alkylene group. In other instances, A is absent so that the hydrophobic unit is bonded directly to the oligoether, oligoamide or oligoether-amide linker unit. The length of the alkylene chain A in the non-ionic surfactant may influence the CFT of the particles, with longer alkylene chains decreasing the CFT.

The non-ionic and optional ionic surfactants of the invention preferably contain a linear linker unit, though they may alternatively contain a branched linker unit.

The two-headed surfactants (Ia) of the invention preferably contain a branched linker unit. The two-headed surfactants (Ib) of the invention preferably contain a linear linker unit, though they may alternatively contain a branched linker unit.

In a preferred embodiment, the ionic and non-ionic surfactants have a structure of formula (II):



wherein:

X represents -O- or -C(O)NH-, wherein X in each of the n repeat units, -X-A'-, may be the same or different;

A' represents a C₁ to C₆ substituted or unsubstituted alkylene group;

n is an integer of from 2 to 16;

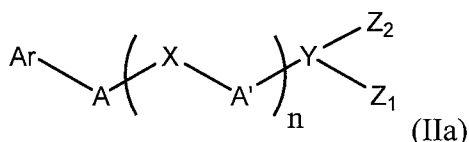
Y may be present or absent in the linker unit and represents -OR¹-, where R¹ is a C₁ to C₄ alkylene group; and

Ar, A and Z are as defined previously.

A' preferably represents a C₂ to C₄ alkylene group.

X preferably represents -O-.

In an embodiment, the two-headed surfactant has a structure of formula (IIa):

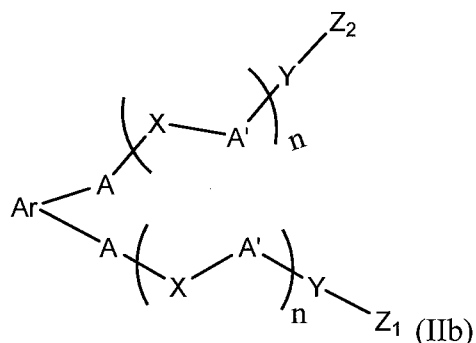


wherein X, A', n, Y, Ar, A, Z₁ and Z₂ are as defined previously.

A' preferably represents a C₂ to C₄ alkylene group.

X preferably represents -O-.

In an embodiment, the two-headed surfactant has a structure of formula (IIb):



wherein X, A', n, Y, Ar, A, Z₁ and Z₂ are as defined previously, wherein each of X and A' in each of the n repeat units, -X-A'-, may be the same or different. Groups A, X, A' and Y which are separately attached to head groups Z₁ and Z₂ in these examples may also be the same or different.

A' preferably represents a C₂ to C₄ alkylene group.

X preferably represents -O-.

Preferably the linker unit comprises an oligoethylene glycol, an oligopropylene glycol, or a random, alternate or block oligomer of ethylene oxide and propylene oxide units. More preferably, the linker unit comprises an oligoethylene glycol. In this embodiment, X is -O- and A' is a C₂ alkylene group.

The integer n is preferably from 2 to 12, and more preferably 4 to 8. An integer of 4 to 8 is particularly preferred where the linker comprises an oligoethylene glycol as such linker units contribute to the hydrophilicity of the surfactant and may therefore promote dispersion of the particles in water at temperatures below the CFT.

A linker group which encourages the formation of a dispersion below the CFT is particularly important for the two-headed surfactant or for the optional ionic surfactant. In particular, the use of a linker unit comprising an oligoether in the ionic surfactant or two-headed surfactant provides for good dispersibility in both fresh water and brine. For the ionic surfactant or two-headed surfactant, dispersibility in brine increases as the number of repeating units in the oligoether, oligoamide or oligoether-amide increases. However, the ability of longer linker units (e.g. linker units comprising greater than 16 alkylene glycol or amide units) to contribute to the dispersion ability of the surfactant may be limited by

chain-folding effects.

The length of the linker units in the non-ionic surfactant may be varied to vary the CFT of the particles. In general, the longer linker units defined above provide particles with an increased CFT. However, the ability of longer linker units (e.g. linker units comprising greater than 16 alkylene glycol or amide units) to contribute to the CFT, may be limited by chain-folding effects.

A linker unit which promotes the formation of a dispersion of the particles in water is also beneficial in the non-ionic surfactant though it is less important for the non-ionic surfactant to promote formation of the dispersion if accompanied by an ionic-surfactant or two-headed surfactant. As with the ionic surfactant, a linker unit comprising an oligoether is preferred.

When the linker unit of the non-ionic surfactant, two-headed surfactant or the optional ionic surfactant comprises an oligoether, Y preferably represents $-OR^1-$ and R^1 preferably represents a C_1 or C_2 alkylene group. When the linker unit comprises an oligoamide, Y is preferably absent.

In preferred examples:

Ar represents a polycarbocyclic aromatic hydrocarbon group which contains at least three fused aromatic rings;

A represents a C_1 to C_4 alkylene group;

X represents $-O-$;

A' represents a C_2 to C_4 alkylene group;

n is an integer of from 4 to 8; and

Y represents $-OR^1-$, and R^1 represents a C_1 or C_2 alkylene group.

The alkylene groups A and A' may be independently substituted or unsubstituted.

Preferred substituents are C_1 to C_4 alkyl groups, fluorine atoms, or hydrophilic substituents, for example, $-NH_2$ and $-OH$ groups. Other hydrophilic substituents are also within the scope of the invention. Preferably each A and A' is independently unsubstituted or substituted by one or more methyl, ethyl, or hydroxyl groups. More preferably, each A and A' is independently unsubstituted or substituted by one or more hydroxyl groups.

Most preferably each A and A' is unsubstituted.

The person skilled in the art will recognize that the physical properties of the particles, for example, their dispersibility and CFT, can be tailored by varying the

molecular weight, the degree of branching and the nature of the A, A' and Y groups of the linker unit.

The head unit of the non-ionic surfactant comprises a non-ionic hydrophilic moiety. The two-headed surfactant also comprises a non-ionic head unit which incorporates a non-ionic hydrophilic moiety. It is believed that the hydrophilic, yet non-ionic, moiety imparts temperature sensitivity to the particles (i.e. causes them to flocculate at or above the CFT), though it will be understood that other portions of the non-ionic surfactant or two-headed surfactant (for example, the linker unit) may also contribute to temperature sensitivity. In embodiments, the head unit of the non-ionic surfactant or the non-ionic head unit of the two-headed surfactant may comprise a plurality of non-ionic hydrophilic moieties, such as from 2 to 20 hydrophilic moieties, more preferably from 2 to 15 hydrophilic moieties and most preferably from 2 to 9 hydrophilic moieties.

The non-ionic hydrophilic moiety may be selected from alkoxy ($-\text{OR}^2$), ester ($-\text{C}(\text{O})\text{OR}^2$) or ($-\text{OC}(\text{O})\text{R}^2$), amide ($-\text{C}(\text{O})\text{NR}^3\text{R}^4$), and crown ethers, wherein: R^2 represents a C_1 to C_3 alkyl group, and more preferably methyl or ethyl; and R^3 and R^4 are independently selected from H and a C_1 to C_3 alkyl group, more preferably H, methyl and ethyl. Most preferably R^3 and R^4 are H. Where the non-ionic surfactant or the two-headed surfactant comprises a plurality of non-ionic hydrophilic moieties, each hydrophilic moiety may be the same or different, though preferably the same.

More preferably, the non-ionic hydrophilic moiety is selected from alkoxy ($-\text{OR}^2$), ester ($-\text{C}(\text{O})\text{OR}^2$) or ($-\text{OC}(\text{O})\text{R}^2$), and crown ethers. Still more preferably, the hydrophilic moiety is independently selected from alkoxy ($-\text{OR}^2$) and crown ethers.

Preferred crown ethers include cyclic oligomers of alkylene oxides, such as cyclic oligomers of ethylene oxide and/or propylene oxide. The cyclic oligomers preferably consist of from 3 to 8 monomeric units. Most preferred are crown ethers including cyclic oligomers of ethylene oxide consisting of from 4 to 6 repeating units.

The nature and number of non-ionic hydrophilic moieties on the head unit of the non-ionic surfactant or the non-ionic head unit of the two-headed surfactant can be varied such that the physical properties of the non-ionic surfactant or the two-headed surfactant can be tailored to a specific application. In particular, reducing the hydrophilicity of the head unit in the non-ionic surfactant or non-ionic head unit in the two-headed surfactant reduces the temperature at which the non-ionic surfactant or the two-headed surfactant imparts

temperature-sensitivity onto the particles (i.e. reduces the CFT). This can be achieved by using fewer non-ionic hydrophilic moieties in the head unit or by modifying the non-ionic hydrophilic moieties (*e.g.* a reduction in the CFT of the particles may be seen on replacing the non-ionic hydrophilic moiety -OMe with the less hydrophilic moiety -OEt).

5 The head unit of the ionic surfactant comprises an ionic hydrophilic moiety. The two-headed surfactant comprises an ionic head unit which also incorporates an ionic hydrophilic moiety. It is believed that the ionic hydrophilic moiety promotes the formation of a dispersion of the particles. The head unit of the ionic surfactant or the ionic head unit of the two-headed surfactant may comprise a single ionic moiety. Alternatively, the head
10 unit of the ionic surfactant or the ionic head unit of the two-headed surfactant may comprise a plurality of ionic hydrophilic moieties, such as from 2 to 20 ionic hydrophilic moieties, more preferably from 2 to 15 ionic hydrophilic moieties and most preferably from 2 to 9 ionic hydrophilic moieties.

 The ionic hydrophilic moiety may be selected from carboxylate anion ($-\text{CO}_2^-$),
15 sulfonate anion ($-\text{SO}_3^-$), sulfate anion ($-\text{O}-\text{SO}_3^-$), phosphonate anion ($-\text{PO}_3^{2-}$), phosphate anion ($-\text{O}-\text{PO}_3^{2-}$), and ammonium cation ($-\text{NR}^5\text{R}^6\text{R}^7+$) wherein R^5 , R^6 and R^7 are independently selected from H and a C_{1-3} alkyl group, more preferably H, methyl and ethyl. Most preferably R^5 , R^6 and R^7 of the ammonium cation are H. Where the ionic surfactant or the two-headed surfactant comprises a plurality of ionic hydrophilic moieties,
20 each ionic moiety may be the same or different, though preferably the same.

 More preferably, the ionic hydrophilic moiety is selected from anionic moieties, such as carboxylate anion ($-\text{CO}_2^-$), sulfonate anion ($-\text{SO}_3^-$) and phosphonate anion ($-\text{PO}_3^{2-}$). Still more preferably, the ionic moiety is a carboxylate anion ($-\text{CO}_2^-$).

 The ionic hydrophilic moiety may be paired with any suitable counter-ion, for
25 instance alkali metal cations (such as Li^+ , Na^+ or K^+ , most preferably Na^+), alkaline earth metal cations (such as Mg^{2+} or Ca^{2+}) or ammonium cations (such as NR_4^+ , wherein each R^8 is independently selected from H and a C_{1-4} alkyl group, most preferably NH_4^+). Optionally, a plurality of singly-charged cations (such as alkali metal or ammonium cations) or a multiply-charged cation (for instance Mg^{2+}) may be paired with a
30 phosphonate or a phosphate anion, or with two or more carboxylate, sulfonate or sulfate anion moieties. Preferably, the ionic hydrophilic moiety is an anionic moiety which is paired with alkali metal cations.

Carboxylate, sulfonate or sulfate anion moieties on the head unit may also be paired with ammonium cation moieties on the head unit, forming zwitterionic surfactants.

The nature and number of ionic hydrophilic moieties on the head unit can be varied such that the physical properties of the ionic surfactant or the two-headed surfactant, such as its hydrophilicity, can be tailored to a specific application.

The head unit of the non-ionic surfactant, either of the non-ionic or ionic head units of the two-headed surfactant and the head unit of the optional ionic surfactant preferably independently have the formula $-O-V(-Z')_p$, $-C(O)-O-V(-Z')_p$ or $-C(O)-NH_q[V(-Z')_p]_{2-q}$, wherein V represents a linking group to which the Z' groups are attached, each Z' independently represents a non-ionic hydrophilic moiety as defined above (in the case of a non-ionic surfactant or a two-headed surfactant) or each Z' independently represents an ionic hydrophilic moiety as defined above (in the case of an ionic surfactant or a two-headed surfactant), and p represents an integer of from 2 to 20, more preferably 2 to 15 and most preferably 2 to 9, and q is 0 or 1, preferably 1.

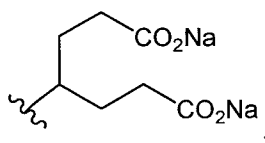
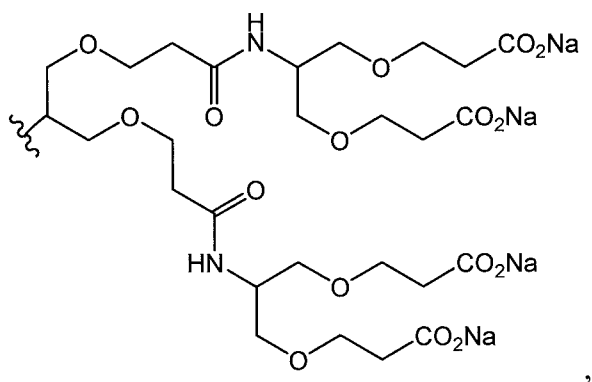
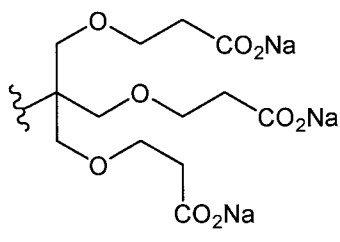
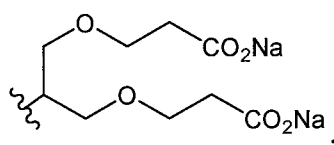
Most preferably, each head unit has the formula $-C(O)-NH_q[V(-Z')_p]_{2-q}$. In one embodiment, V may represent a C_2 to C_{60} hydrocarbyl group, preferably a saturated aliphatic hydrocarbyl group, in which one or more of the carbon atoms is optionally replaced with $-O-$ and one or more of the carbon atoms is optionally replaced with $-C(O)NH-$. In some examples, no carbon atoms are replaced with $-O-$ or with $-C(O)NH-$. Where one or more of the carbon atoms is replaced with $-O-$, from 5% to 35 % of the carbon atoms are preferably replaced with $-O-$. Where one or more of the carbon atoms is replaced with $-C(O)NH-$, from 2% to 15% of the carbon atoms are preferably replaced with $-C(O)NH-$. Preferably the number of carbon atoms in the hydrocarbyl group is greater than p, and no two groups Z' which are bonded through oxygen or nitrogen (e.g. where Z' is $-OH$, OR^2 , $-OC(O)R^2$, $-C(O)NR^3R^4$, $-NR^5R^6R^{7+}$, $-O-SO_3H$, $-O-SO_3^-$, $-O-PO_3H_2$ or $-O-PO_3^{2-}$) are bonded to the same carbon atom of the hydrocarbyl group.

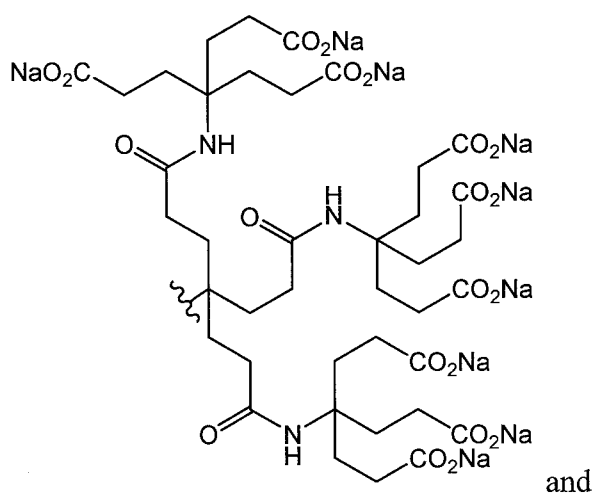
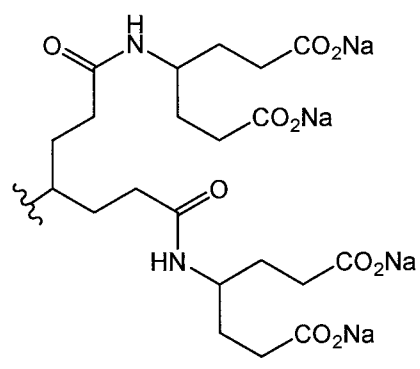
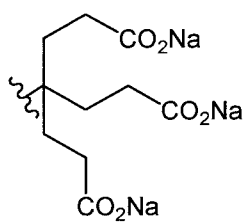
In the above formulae, V may be a branched or straight chain linking group. Where the head unit has the formula $-C(O)-NH_q[V(-Z')_p]_{2-q}$, each V may be independently branched or unbranched. Where V is branched, each branch of the linking group is preferably terminated with Z' . The linking group may have more than one branch point and thus may comprise 3 or more non-ionic hydrophilic units (in the case of the non-ionic surfactant or the two-headed surfactant) or 3 or more ionic hydrophilic units (in the case of

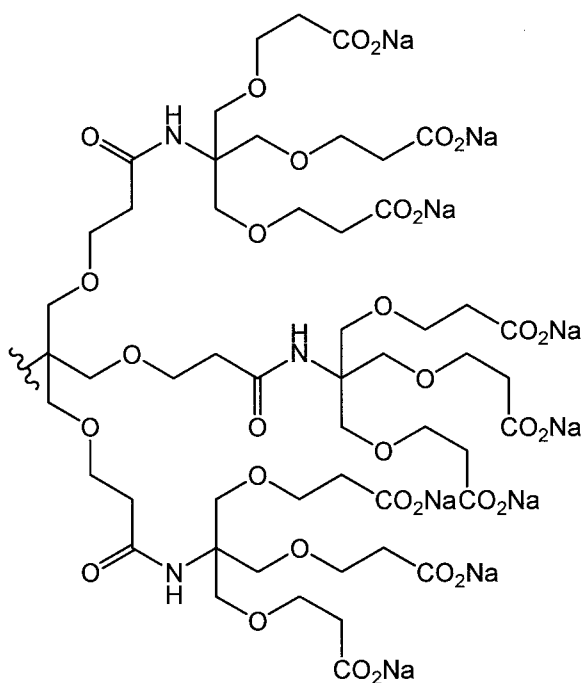
the ionic surfactant or the two-headed surfactant). Preferably, V is branched in the ionic surfactant or the ionic head unit of the two-headed surfactant. Branching in the head unit is believed to encourage the dispersion of the particles in water. More preferably, V is branched in the non-ionic surfactant, or the non-ionic head unit of the two-headed

5 surfactant and V is branched in the ionic surfactant.

In the ionic surfactant and the ionic head unit of the two-headed surfactant, the moiety $-V(-Z')_p$ preferably has a structure selected from:

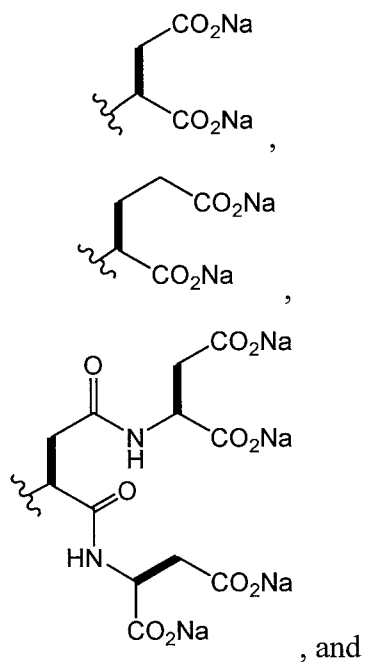


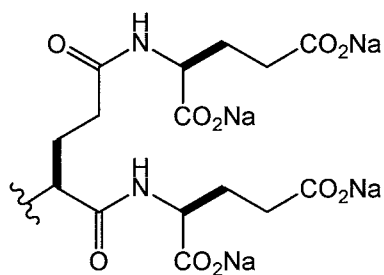




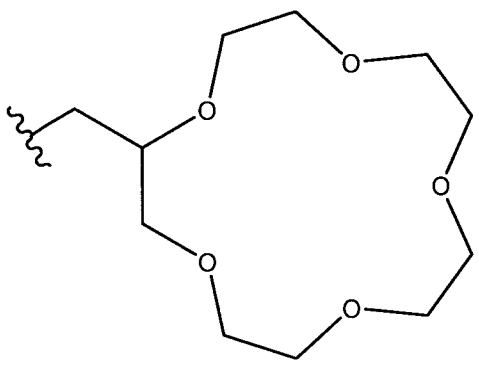
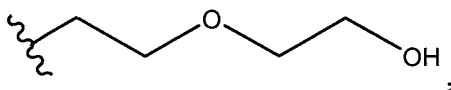
In a further embodiment, the ionic surfactant or the ionic-head unit of the two-headed surfactant may have a moiety $-\text{V}(-\text{Z}')_p$ which is obtained from aspartic acid and/or glutamic acid. For instance, the moiety $-\text{V}(-\text{Z})_p$ may have a structure selected from:

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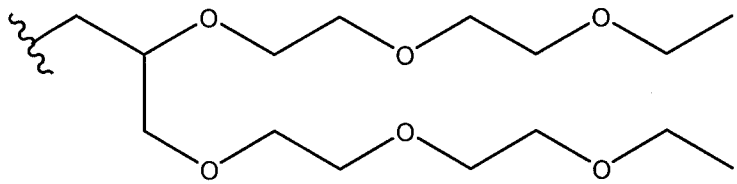
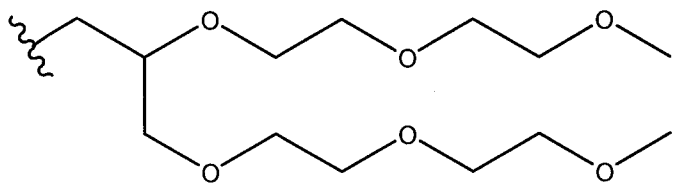


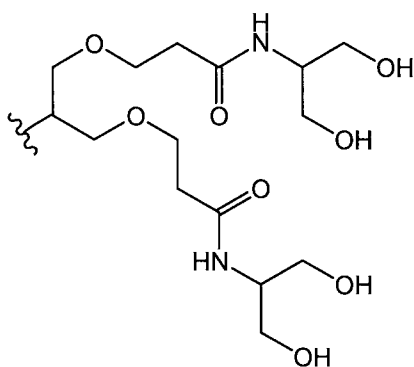
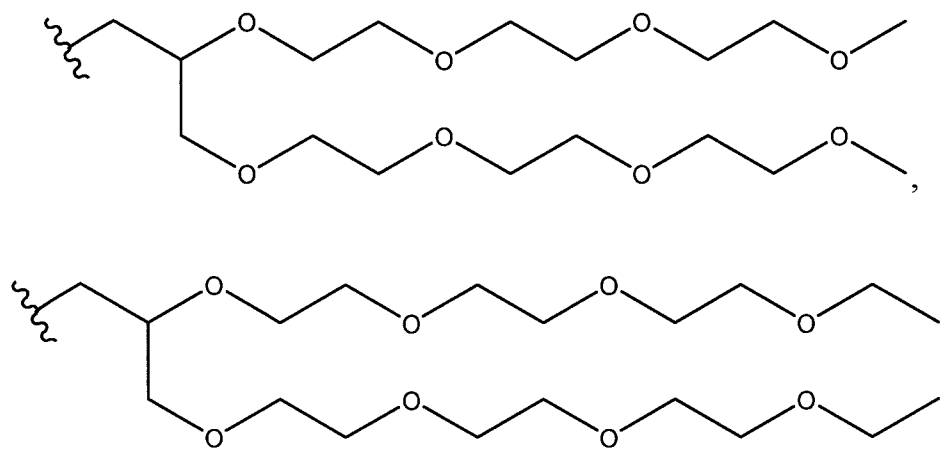


In the non-ionic surfactant and the non-ionic head unit of the two-headed surfactant,
 5 the moiety $-V(-Z')_p$ may have a structure selected from:



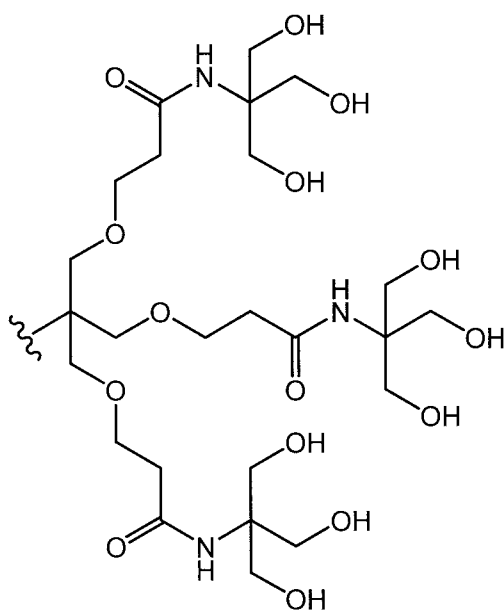
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and



As the skilled person would appreciate, two moieties $-V(-Z')_p$ may be attached to the nitrogen in the head group having the formula $C(O)-NH_q[V(-Z')_p]_{2-q}$.

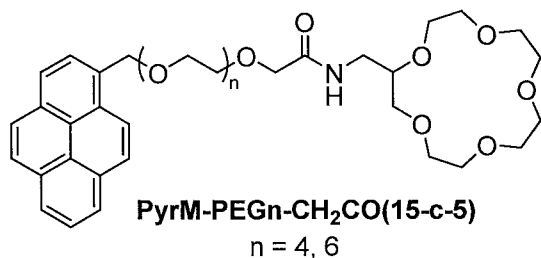
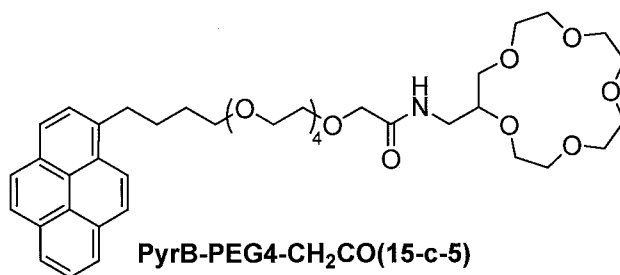
In a further embodiment of the present invention, the non-ionic and optional ionic surfactants may comprise one or more additional linker units linking one or more additional head units to the hydrophobic unit. In this embodiment, there is preferably one additional linker unit linking one or more additional head units to the hydrophobic unit.

- 5 The one or more additional linker units may be bonded to the hydrophobic unit as described above.

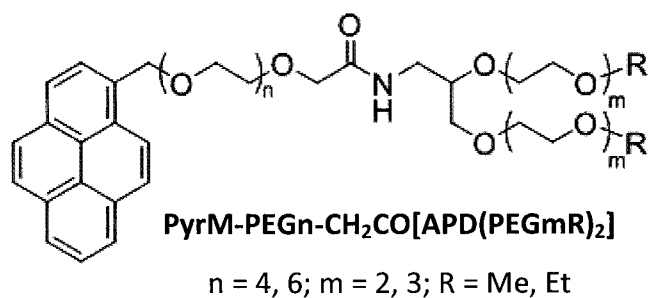
In accordance with the present invention, the non-ionic surfactant and optionally the ionic surfactant preferably comprise no more than three head units as described above, more preferably no more than two head units as described above. Preferably, the non-ionic
10 surfactant and optional ionic surfactant have just one head group.

In a further embodiment of the present invention, the two-headed surfactant may comprise two or more non-ionic head groups and two or more ionic head units. Thus, the term “two-headed surfactant” refers to the presence of both non-ionic and ionic head units in the surfactant. For example, the two-headed surfactant of formula (IIa) may be modified
15 to include more than one $-A-(X-A')_nYZ_1YZ_2$ group attached to the hydrophobic unit, and the two-headed surfactant of formula (IIb) may be modified to include more than one $-A-(X-A')_nYZ_1$ and more than $-A-(X-A')_nYZ_2$ group attached to the hydrophobic unit.

Non-ionic surfactants that may be used in the present invention include:

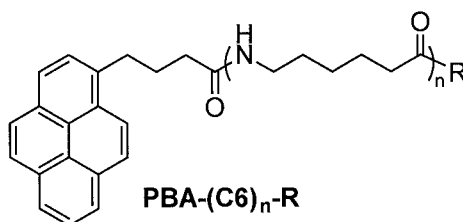


, and



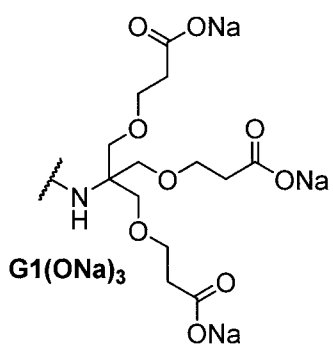
As used herein, “PyrB” refers to a moiety deriving from pyrene butanol, “PyrM” refers to a moiety deriving from pyrene methanol, “PEG” refers to an ethylene glycol oligomer, the number of ethylene glycol units therein being indicated by the number directly following the “PEG” or by the defined values of n, “15-c-5” refers to a crown ether moiety comprising a cyclic oligoether having 15 atoms, 5 of which are oxygen atoms, “APD” refers to a moiety deriving from 3-amino-1,2-propane diol, “Me” refers to a methyl group and “Et” refers to an ethyl group.

Ionic surfactants that may be used in the present invention include:



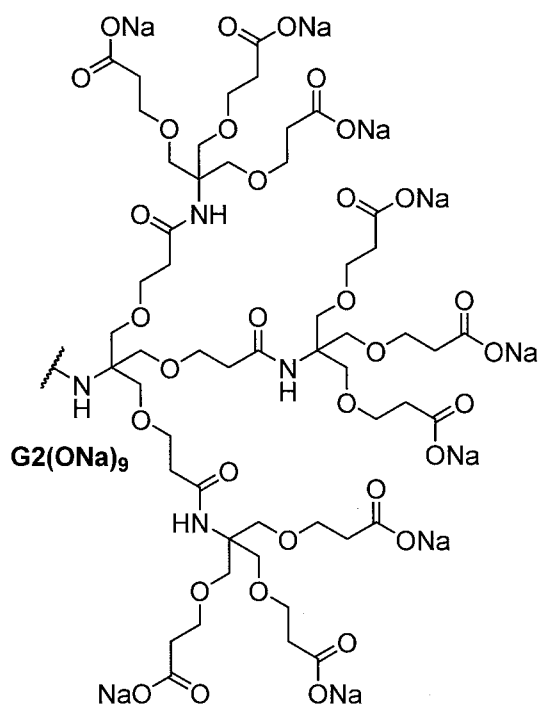
Surfactant	n	R
PBA-C6-G1(ONa) ₃	1	G1(ONa) ₃
PBA-C6-G2(ONa) ₉	1	G2(ONa) ₉
PBA-(C6) ₂ -G1(ONa) ₃	2	G1(ONa) ₃
PBA-(C6) ₂ -G2(ONa) ₉	2	G2(ONa) ₉

where “PBA” refers to a moiety deriving from pyrene butyric acid, “C6” refers to a $-(CH_2)_5C(O)-$ unit, and $G1(ONa)_3$ is:



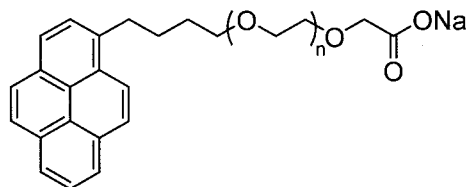
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and $G2(ONa)_9$ is:



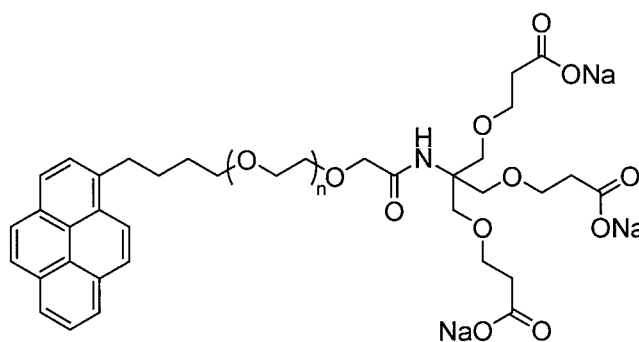
10

;

**PyrB-PEG_n-CH₂COONa**

(n = 2, 4, 6, 12)

, and

**PyrB-PEG_n-CH₂COG1(ONa)₃**

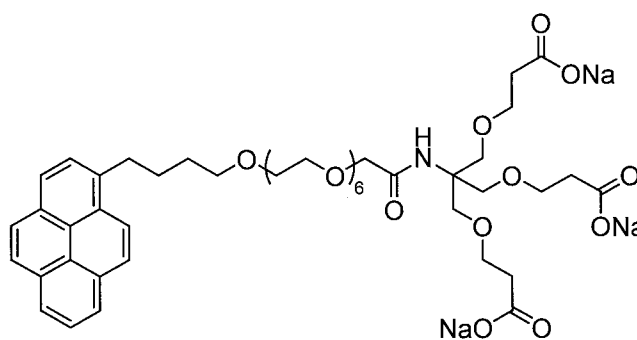
(n = 2, 4, 6)

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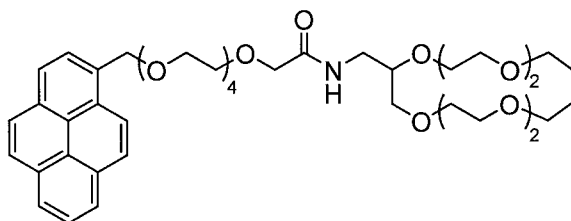
where “PyrB”, “PEG” and G1(ONa)₃ are as defined above.

A single non-ionic surfactant or a plurality of non-ionic surfactants may be adsorbed at the surface of the particles (*i.e.*, present in the particles). A single two-headed surfactant or a plurality of two-headed surfactants may be adsorbed at the surface of the particles (*i.e.*, present in the particles). The non-ionic surfactant may be used in combination with a single ionic surfactant or a plurality of ionic surfactants and/or in combination with a single two-headed surfactant or a plurality of two-headed surfactants.

A particularly preferred combination of ionic surfactant and non-ionic surfactant is:

**PyrB-PEG₆-CH₂COG1(ONa)₃**

and



PyrM-PEG4-CH₂CO[APD(PEG2Et)₂]

The ionic, two-headed and non-ionic surfactants that are used in the present invention may be prepared by a method comprising:

(i) forming a linkage between a hydrophobic unit having a sheet-like structure and including one or more aromatic rings and an oligoether, an oligoamide or an oligoether-amide to form a oligoether-, oligoamide- or oligoether-amide- substituted hydrophobic unit; and

(ii) forming a linkage between the oligoether-, oligoamide- or oligoether-amide-substituted hydrophobic unit and a head unit comprising a non-ionic hydrophilic moiety (in the case of a non-ionic surfactant) or an ionic hydrophilic moiety (in the case of an ionic surfactant); or forming linkages between the oligoether-, oligoamide- or oligoether-amide-substituted hydrophobic unit and both a non-ionic head unit and an ionic head group (in the case of a two-headed surfactant)

As the skilled person will appreciate, the method steps may be carried out in the order recited above, or they may be carried out with step (ii) coming before step (i).

The particles used in the present invention may be prepared by the addition of carbon allotrope to an aqueous surfactant solution. For example, carbon allotrope may be added to an aqueous surfactant solution comprising non-ionic and/or two-headed and optionally ionic surfactants wherein the carbon allotrope is added in an amount of from 10 to 60,000 ppm, preferably from 100 to 10,000 ppm and more preferably from 300 to 3,000 ppm by weight. Where the aqueous surfactant solution comprises the non-ionic and optional ionic surfactant, the molar ratio of non-ionic surfactant to ionic surfactant in the aqueous surfactant solution may be from 10:1 to 1:10, preferably from 1:5 to 5:1 and more preferably from 1:2 to 2:1.

The ratio of carbon allotrope to surfactants in the particles will depend on the type of

carbon allotrope employed, the desired CFT and the amount of non-ionic, and/or two-headed and optional ionic surfactants that are required to provide dispersibility of the particles in water at temperatures below the CFT. The appropriate ratio could be determined by the skilled person.

5 The injection fluid is preferably injected in an amount that is suitable to reduce the permeability of a thief zone to water. The skilled person could determine a suitable amount. As the skilled person will appreciate, the amount of fluid that is required may be varied depending on the concentration of the particles in the injection fluid.

10 The injection fluid may be prepared by dispersing the particles in water at a temperature below the CFT of the particles, thereby forming a dispersion of the particles in water. Agitation means, for example sonication, may be used to promote the formation of a stable dispersion. As the skilled person will appreciate, the injection fluid may also be prepared by separately adding the surfactant(s) and particles comprising carbon allotrope into water. In that case, the surfactant(s) are typically added to the water first, prior to
15 addition of the particles comprising carbon allotrope.

 The injection fluid may also be prepared from a concentrate comprising the particles in a higher concentration in water than is intended for the injection fluid. The concentrate may then be dosed into injection water, for instance injection water located at the injection site, in order to prepare the injection fluid.

20 According to the process of the present invention, the injection fluid is injected down an injection well and into a thief zone so as to reduce the permeability of the thief zone to water. Flocculation of the particles may occur in a single location in a thief zone or at a plurality of locations. For instance, different forms or grades of particles may be present in a single injection fluid, for example by using particles comprising different surfactant(s)
25 adsorbed at the surface thereof. These different grades of particles may undergo flocculation at different temperatures. In turn, flocculation of particles may occur in the thief zone at different locations having different temperatures, thereby reducing the permeability of the thief zone to water at a plurality of locations. In an embodiment, the injection fluid may be used to reduce the permeability of a plurality of thief zones.

30 The well into which the injection fluid is injected may be an injection well or a production well. Where the injection fluid is injected into a production well, the well is taken off production prior to injection of the injection fluid.

The CFT of the particles must be greater than the maximum temperature encountered in the well. It will be understood that by using particles having a CFT which is greater than the maximum temperature encountered in the well, flocculation of the particles before they enter the thief zone can be avoided. The maximum temperature encountered in a particular well could be readily determined by the skilled person.

The CFT of the particles must also be at or below the maximum temperature encountered in the thief zone such that the particles flocculate within the thief zone of the reservoir. The person skilled in the art will understand that the temperature of the thief zone of the reservoir may vary with increasing radial distance from the well. For example, in reservoirs where a waterflood has already taken place, the injection of cold water produces a temperature gradient across the reservoir, i.e. the injection of cold water has a cooling effect in the vicinity of the injection well and for some distance beyond it. Thus, although the initial temperature of the reservoir may be in the range of 80 to 140°C, substantial cooling of the reservoir, and hence the thief zone or zones, may have occurred during a waterflood. Accordingly, the temperature at which flocculation of the dispersed particles is induced (*i.e.* the CFT) 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 85°C. The person skilled in the art will understand that the extent of any cooling of the thief zone in the near wellbore region of a production well is likely to be less than the extent of any cooling of the thief zone in the near wellbore region of an injection well. Preferably, the CFT is at or slightly below (*e.g.* less than 30 °C below, preferably less than 20 °C below and more preferably less than 10 °C below) the maximum temperature encountered in the thief zone, so that the particles flocculate only once they have propagated deep into the thief zone.

The CFT of the particles employed in the process of the present invention may be readily determined by the person skilled in the art. The CFT may be adjusted by appropriate selection of non-ionic surfactant and, if used, by appropriate selection of the ionic surfactant or two-headed surfactant. Accordingly, dispersions of particles may be prepared which have an appropriate CFT for the temperatures encountered within the thief zone where it is desired to form a block, or multiple blocks of flocculated particles.

Once flocculation is triggered, it is believed that flocs of the particles block the pore throats of a region of the thief zone and the flow of subsequently injected water is

largely diverted into neighbouring, previously unswept zones of the reservoir. The flocs of particles that form at the CFT are sufficiently large to bridge the pore throats of the thief zone. After a period of time, the subsequently injected water flowing through neighbouring zones of the reservoir acts to cool the blocked region of the thief zone to below the CFT, resulting in the particles becoming redispersed in water. The resulting particle dispersion then flows on through the thief zone before forming a subsequent block once a further region of the thief zone having a temperature at or above the CFT is reached. In this way, the present invention allows for the formation of multiple, successive blocks within a thief zone such that a greater volume of the reservoir may be swept by subsequently injected water. The net result is that more water passes through the previously unswept zones, with more oil being swept towards the production well, i.e. sweep efficiency is improved.

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

The thief zone of the reservoir may be a layer of reservoir rock having a permeability greater than the permeability of adjacent hydrocarbon-bearing layers of the reservoir, for example at least 50% greater. For example, 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-passed layers of the reservoir.

Alternatively, the thief zone of the reservoir may 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 the particles may penetrate a significant distance into a fracture, for example, to the fracture tip, before encountering the threshold temperature at which the particles flocculate and block the fracture.

The size of the particles employed in the method of the present invention should be such that, prior to encountering a temperature at or greater than the CFT, efficient

propagation of the injection fluid through the pore structure of the reservoir rock, such as sandstone or carbonate, can be achieved. Preferably, prior to flocculation, the particles have a volume average particle size diameter of from about 0.1 to about 1 μm . The size of the particles may be adjusted by appropriate selection of carbon allotrope and non-ionic surfactant and/or two-headed surfactant and optional ionic surfactant, as would be evident to the skilled person.

In at least some examples of the process for modifying the permeability to water of a thief zone, the injection fluid comprises a dispersion of the particles in 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 reservoir or in any other process.

The injection fluid may comprise a dispersion of the particles in water, which water has a total dissolved solids (TDS) concentration in the range of 200 to 250,000 ppm (on a weight by volume basis).

Preferably, the injection fluid comprises a dispersion of the particles in seawater.

Alternatively, the injection fluid comprises a dispersion of the particles in a low salinity injection water having a total dissolved solids content of from 300 to 10,000 ppm wt/v, preferably, 1,000 to 8,000 ppm wt/v and having a multivalent cation content less than the multivalent cation content of the connate water of the reservoir.

Optionally, the injection fluid employed in the method of the present invention may further comprise one or more conventional additives used in enhanced oil recovery, such as viscosifiers, polymers and/or pH adjusters.

Owing to the difference in permeability between thief zones and adjacent hydrocarbon-bearing zones of the reservoir, in the process of the present invention, most of the injection fluid enters the thief zone. However, if desired, the hydrocarbon-bearing zones of the reservoir may be isolated from the well, for example, packers may be arranged in the well, above and below a thief zone, in order to mitigate the risk of the injection fluid entering adjacent hydrocarbon-bearing zones of the reservoir.

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

The invention will now be demonstrated by reference to the following Examples and

Figures, in which:

Figure 1 shows results of turbidimetry and dynamic light scattering (DLS) experiments used to determine the lower critical solution temperature (LCST) of non-ionic surfactants;

5 Figure 2 shows results of studies of MWNT particle dispersions; and

Figure 3 shows results of studies of multilayer graphite particle dispersions.

Examples

The surfactants set out in Table 1 were employed in the Examples discussed below

Table 1:

	<u>Surfactant</u>	<u>Ionic/Non-ionic</u>
A	PyrB-PEG4-CH ₂ CO(15-c-5)	Non-ionic
B	PyrM-PEG4-CH ₂ CO(15-c-5)	Non-ionic
C	PyrM-PEG6-CH ₂ CO(15-c-5)	Non-ionic
D	PyrM-PEG4-CH ₂ CO[APD(PEG2Et) ₂]	Non-ionic
E	PyrM-PEG6-CH ₂ CO[APD(PEG2Et) ₂]	Non-ionic
F	PyrM-PEG4-CH ₂ CO[APD(PEG2Me) ₂]	Non-ionic
G	PyrM-PEG6-CH ₂ CO[APD(PEG2Me) ₂]	Non-ionic
H	PyrM-PEG4-CH ₂ CO[APD(PEG3Et) ₂]	Non-ionic
I	PyrM-PEG6-CH ₂ CO[APD(PEG3Et) ₂]	Non-ionic
J	PyrM-PEG4-CH ₂ CO[APD(PEG3Me) ₂]	Non-ionic
K	PyrM-PEG6-CH ₂ CO[APD(PEG3Me) ₂]	Non-ionic
L	PyrB-PEG2-CH ₂ COONa	Ionic
M	PyrB-PEG4-CH ₂ COONa	Ionic
N	PyrB-PEG6-CH ₂ COONa	Ionic
O	PyrB-PEG2-CH ₂ COG1(ONa) ₃	Ionic
P	PyrB-PEG4-CH ₂ COG1(ONa) ₃	Ionic
Q	PyrB-PEG6-CH ₂ COG1(ONa) ₃	Ionic
R	PBA-G1(ONa) ₃	Ionic
S	PBA-C6-G1(ONa) ₃	Ionic
T	PBA-(C6) ₂ -G1(ONa) ₃	Ionic
U	SDS (sodium dodecyl sulphate)	Ionic

V	SDBS (sodium dodecylbenzenesulphonate)	Ionic
W	SC (sodium cholate)	Ionic
X	SDOC (sodium deoxycholate)	Ionic
Y	SPB (sodium pyrenebutyrate)	Ionic
Z	Triton X-100	Non-ionic

Lower Critical Solution Temperature (LCST) determination

The LCSTs of non-ionic surfactants A to K in deionised water were determined using turbidimetry and dynamic light scattering (DLS). The LCST of a surfactant is the lowest temperature at which the surfactant is no longer miscible with water. Thus, the LCST may provide an indication of the temperature at which particles comprising the surfactant and a carbon allotrope might flocculate in water. For the turbidimetry experiments, the absorbance of surfactant solutions in deionised water was measured at different temperatures. The dynamic light scattering experiments measured the size of particles present in the mixtures at different temperatures. The results of the LCST studies are shown in Figure 1. The turbidimetry results are shown on the left hand side of Figure 1, and the DLS results are shown on the right hand side of Figure 1.

It can be seen from Figure 1 that the LCST of the non-ionic surfactant (and hence the CFT of carbon allotrope particles comprising the surfactant) can be tailored by varying the length of the linker unit and the nature of the head unit.

Example 1 – MWNT Particle Dispersions

Dispersions comprising particles of MWNT having a surfactant adsorbed at its surface were prepared as follows. 1 mg MWNT was added to a 1mM solution of surfactant in either deionised (Millipore) water or in a 0.6M NaCl aqueous solution and the mixture ultrasonicated. Suspended aggregates were removed from the resulting dispersion of particles. The concentration of MWNTs, C_{MWNT} , in each of the prepared dispersions was calculated using the Beer-Lambert Law and the percentage of MWNT that became dispersed was determined. The percentage of dispersed MWNT for each dispersion is shown in Figure 2 (error bars are based on the standard deviations of at least 3 results). Control experiments using deionised water with no surfactant showed no MWNT dispersion.

It can be seen from Figure 2 that both non-ionic and ionic surfactants may

individually be used to disperse MWNTs in deionised water and in 0.6 M NaCl solution. However, it can also be seen from Figure 2 that whilst non-ionic surfactants provide good dispersibility of MWNTs in deionised water, dispersion in salt water is much lower.

The temperature response (i.e. the triggering of particle flocculation on heating to the CFT) of dispersions (both in deionised water and 0.6M NaCl solution) comprising MWNT and ionic surfactants N, R, S and T and of dispersions comprising MWNT and non-ionic surfactants A and D was assessed using UV-visible spectroscopy and visual inspection whilst the dispersions were heated. No temperature response was observed for any of the dispersions of MWNTs with ionic surfactants up to 80°C. For the dispersions of MWNTs with non-ionic surfactants A and D, changes in the UV spectrum were observed for both dispersions at temperatures above the LCST of each surfactant. Further, flocculation of particles was visually observed at temperatures above the LCST for the surfactant. On cooling and gentle agitation, re-dispersion of the particles was visually observed, demonstrating that particle flocculation is reversible.

These results demonstrate that stable dispersions of carbon allotrope particles in water can be achieved when either non-ionic or ionic surfactants are individually employed, although ionic surfactants provide better dispersion in salt water. Further, these results show that the use of a non-ionic surfactant in the absence of an ionic surfactant can achieve temperature triggered particle flocculation, whereas, the use of an ionic surfactant in the absence of a non-ionic surfactant does not achieve such particle flocculation.

Example 2 – Multilayer Graphite Particle Dispersions

Dispersions comprising particles of multilayer graphite (MLG) having a surfactant adsorbed at its surface were prepared as follows. 15 mg MLG was added to 3ml of a 1mM solution of a surfactant in either deionised (Millipore) water or in a 0.6M NaCl aqueous solution and the mixture was ultrasonicated. Suspended aggregates were removed from the resulting dispersion of particles. The concentration of MLG, C_{MLG} , in each of the resulting dispersions was calculated using the Beer-Lambert Law and the percentage of MLG that became dispersed determined. The percentage of dispersed MLG is shown in Figure 3 (error bars are based on the standard deviations of at least 3 results). Control experiments using deionised water with no surfactant showed no MLG dispersion.

Further, a dispersion of particles comprising MLG, a non-ionic surfactant (surfactant D) and an ionic surfactant (surfactant Q) was prepared in the same manner described

above, except that the surfactant solution comprised a mixture of non-ionic and ionic surfactant in a 1:1 molar ratio. The concentration of MLG, C_{MLG} , in the resulting dispersions was calculated using the Beer-Lambert Law and the percentage of MLG that became dispersed determined (also shown in Figure 3).

5 These results demonstrate that stable dispersions of particles comprising MLG in deionised water can be achieved when either non-ionic or ionic surfactant are employed, however, the use of non-ionic surfactants alone provided no dispersion in salt water. Further, these results show that the use of a combination of non-ionic and ionic surfactants provides a level of dispersion in salt water comparable to that provided by the use of the
10 ionic surfactant (surfactant Q) alone.

 A sandpack experiment was carried out using the dispersion of particles comprising MLG and the combination of non-ionic surfactant D and an ionic surfactant Q. A sandpack is a laboratory-prepared sample designed to simulate reservoir rock. The sandpack comprised a 10mm diameter column containing a 90:10 mixture of sand:silica at a depth of
15 15cm. 15ml of the dispersion was loaded dropwise onto the column and the headspace of the column filled with 0.6M NaCl eluent solution. The sandpack was evaluated for evidence of permeability reduction by measuring the flow rate of droplets exiting the bottom of the column at different temperatures, ranging from room temperature to 80 °C. At room temperature the flow rate of one droplet every 5 seconds was observed. At 60°C
20 the flow rate reduced to one droplet every 50 seconds, suggesting that flocculation of the particles had occurred and the permeability of the sandpack to water had been reduced. On cooling, the flow rate rapidly increased to one droplet every 6 seconds suggesting that the particles had re-dispersed. No permeability reduction was observed in a control
25 experiment in which a solution comprising the combination of surfactants without graphite was loaded onto the column.

 These results demonstrate that the method of the present may be employed to reduce the permeability to water of a thief zone of a subterranean hydrocarbon reservoir. These results also demonstrate that the permeability reduction (blocking) provided is reversible.

Claims:

1. A process for reducing the permeability to water of a thief zone of a subterranean hydrocarbon reservoir, said process comprising injecting an injection fluid down a well and into a thief zone, wherein the injection fluid comprises a dispersion of particles in water, which particles are capable of flocculating at a critical flocculation temperature (CFT) which is at or below the maximum temperature encountered in the thief zone and greater than the maximum temperature encountered in the well, and which particles comprise a carbon allotrope selected from graphene, carbon nanotubes, fullerenes and graphite, having adsorbed at its surface a surfactant selected from the groups consisting of:

(a) non-ionic surfactants comprising:

(i) a hydrophobic unit having a sheet-like structure and including one or more aromatic rings,

(ii) a head unit which comprises a non-ionic hydrophilic moiety, and

(iii) a linker unit linking the head unit to the hydrophobic unit, said linker

unit comprising from 2 to 16 alkylene glycol units in the form of an

oligoether, from 2 to 16 amide units in the form of an oligoamide, or from 2 to 16 units of a combination of alkylene glycol units and amide units in the form of an oligoether-amide;

(b) two-headed surfactants comprising:

(i) a hydrophobic unit having a sheet-like structure and including one or more aromatic rings,

(ii) a head unit which comprises a non-ionic hydrophilic moiety ("non-ionic head group"),

(iii) a head unit which comprises an ionic hydrophilic moiety ("ionic head group"), and

(iv) at least one linker unit linking the unit, said linker unit comprising from 2 to 16 alkylene glycol units in the form of an oligoether, from 2 to 16 amide units in the form of an oligoamide, or from 2 to 16 units of a combination of alkylene glycol units and amide units in the form of an oligoether-amide; and

(c) optionally ionic surfactants comprising:

(i) a hydrophobic unit having a sheet-like structure and including one or

more aromatic rings,

(ii) a head unit which comprises an ionic hydrophilic moiety; and

(iii) a linker unit linking the head unit to the hydrophobic unit, said linker unit comprising from 2 to 16 alkylene glycol units in the form of an

5 oligoether, from 2 to 16 amide units in the form of an oligoamide, or from 2 to 16 units of a combination of alkylene glycol units and amide units in the form of an oligoether-amide;

wherein the particles flocculate in the thief zone so as to reduce the permeability of the thief zone to water.

10 2. A process as claimed in claim 1 wherein the particles are present in the injection fluid in an amount of from 30 to 150,000 mg/L, preferably 50 to 7,500 mg/L, most preferably 100 to 5,000 mg/L.

3. A process as claimed in any preceding claim wherein the hydrophobic unit of the non-ionic surfactant and/or the two-headed surfactant includes two or more aromatic rings,
15 more preferably three or more aromatic rings, and most preferably four or more aromatic rings.

4. A process as claimed in any preceding claim wherein the particles comprise the ionic surfactant and wherein the hydrophobic unit of the ionic surfactant includes two or more aromatic rings, more preferably three or more aromatic rings, and most preferably four or
20 more aromatic rings.

5. A process as claimed in claims 3 or 4 wherein each hydrophobic unit contains at least two fused aromatic rings.

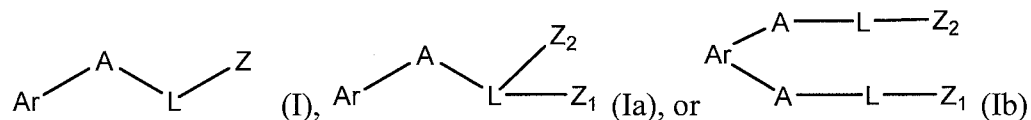
6. A process as claimed in any of claims 3 to 5 wherein each hydrophobic unit is selected from:

25 (a) polycarbocyclic aromatic hydrocarbon groups; and
(b) polycyclic aromatic hydrocarbon groups including at least one heteroaromatic ring.

7. A process as claimed in claim 6 wherein each hydrophobic unit is a polycarbocyclic aromatic hydrocarbon group selected from naphthalene, anthracene, tetracene, pentacene,
30 phenanthrene, pyrene, chrysene, triphenylene, perylene, coronene, corannulene, benzo[a]pyrene, fluorene and fluoranthene.

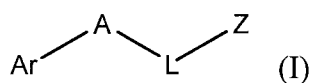
8. A process as claimed in any preceding claim wherein the non-ionic surfactant has a

structure of formula (I); and/or the two-headed surfactant has a structure of formula (Ia) or (Ib):



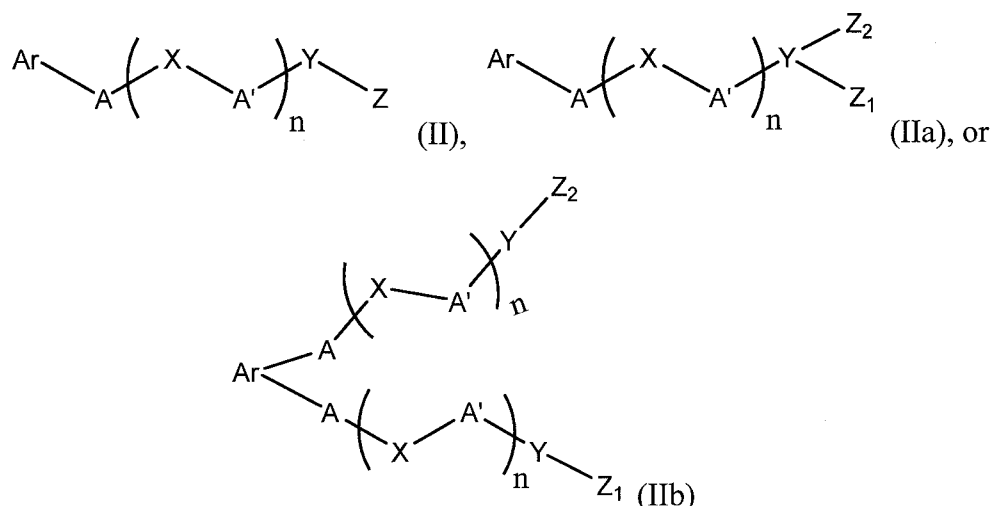
wherein:

- 5 Ar represents the hydrophobic unit;
 A may be present or absent in the linker unit and represents a C₁ to C₆ substituted or unsubstituted alkylene group;
 L represents the oligoether, oligoamide or oligoether-amide of the linker unit;
 Z represents the head unit;
 10 Z₁ represents the non-ionic head unit; and
 Z₂ represents the ionic head unit.
9. A process as claimed in any preceding claim wherein the particles comprise the ionic surfactant and wherein the ionic surfactant has a structure of formula (I):



15 wherein:

- Ar represents the hydrophobic unit;
 A may be present or absent in the linker unit and represents a C₁ to C₆ substituted or unsubstituted alkylene group;
 L represents the oligoether, oligoamide or oligoether-amide of the linker unit; and
 20 Z represents the head unit.
10. A process as claimed in claims 8 or 9 wherein the non-ionic surfactant or the ionic surfactant has a structure of formula (II); and/or the two-headed surfactant has a structure of formula (IIa) or (IIb):



wherein:

X represents -O- or -C(O)NH-, wherein each of X and A' in each of the n repeat units, -X-A'-, may be the same or different;

A' represents a C₁ to C₆ substituted or unsubstituted alkylene group;

n is an integer of from 2 to 16; and

Y may be present or absent in the linker unit and represents -OR¹-, where R¹ is a C₁ to C₄ alkylene group.

11. A process as claimed in claim 10 wherein X is -O- and A' is a C₂ alkylene group.

12. A process as claimed in any preceding claim wherein the head unit of the non-ionic surfactant and/or the non-ionic head unit of the two-headed surfactant comprises a plurality of non-ionic hydrophilic moieties, such as from 2 to 20 hydrophilic moieties, more preferably from 2 to 15 hydrophilic moieties and most preferably from 2 to 9 hydrophilic moieties.

13. A process as claimed in any preceding claim wherein the non-ionic hydrophilic moiety is selected from hydroxyl (-OH), alkoxy (-OR²), ester (-CO₂R²) or (-OC(O)R²), amide (-C(O)NR³R⁴) and crown ethers, wherein: R² represents a C₁ to C₃ alkyl group; and R³ and R⁴ are independently selected from H and a C₁₋₃ alkyl group.

14. A process as claimed in any preceding claim wherein the particles comprise the ionic surfactant and/or the two-headed surfactant and wherein the head unit of the ionic surfactant or the ionic head unit of the two-headed surfactant comprises a plurality of ionic hydrophilic moieties, such as from 2 to 20 ionic hydrophilic moieties, more preferably

from 2 to 15 ionic hydrophilic moieties and most preferably from 2 to 9 ionic hydrophilic moieties.

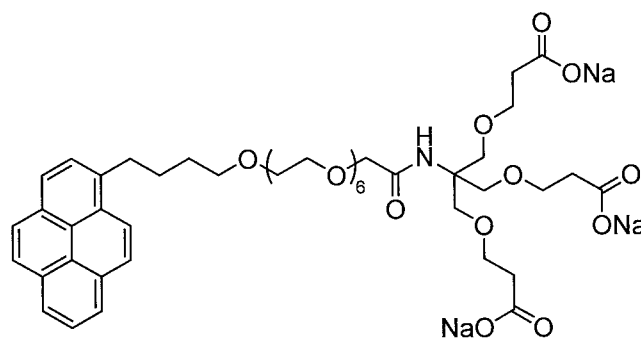
15. A process as claimed in any preceding claim wherein the particles comprise the ionic surfactant and/or the two-headed surfactant and wherein the head unit of the ionic surfactant or the ionic head unit of the two-headed surfactant comprises an ionic hydrophilic moiety selected from ammonium cation ($-\text{NR}^5\text{R}^6\text{R}^{7+}$), carboxylate anion ($-\text{CO}_2^-$), sulfonate anion ($-\text{SO}_3^-$), sulfate anion ($-\text{O}-\text{SO}_3^-$), phosphonate anion ($-\text{PO}_3^{2-}$), and phosphate anion ($-\text{O}-\text{PO}_3^{2-}$), wherein R^5 , R^6 and R^7 are independently selected from H and a C_{1-3} alkyl group.

16. A process as claimed in any preceding claim wherein the head unit of the non-ionic surfactant or the ionic head unit of the two-headed surfactant has the formula $-\text{O}-\text{V}(-\text{Z}')_p$, $-\text{C}(\text{O})-\text{O}-\text{V}(-\text{Z}')_p$ or $-\text{C}(\text{O})-\text{NH}_q[\text{V}(-\text{Z}')_p]_{2-q}$, wherein V represents a linking group to which the Z' groups are attached, each Z' independently represents a non-ionic hydrophilic moiety, and p represents an integer of from 2 to 20.

17. A process as claimed in any preceding claim wherein the particles comprise the ionic surfactant and/or the two-headed surfactant and wherein the head unit of the ionic surfactant or the ionic head unit of the two-headed surfactant has the formula $-\text{O}-\text{V}(-\text{Z}')_p$, $-\text{C}(\text{O})-\text{O}-\text{V}(-\text{Z}')_p$ or $-\text{C}(\text{O})-\text{NH}_q[\text{V}(-\text{Z}')_p]_{2-q}$, wherein V represents a linking group to which the Z' groups are attached, each Z' independently represents an ionic hydrophilic moiety, and p represents an integer of from 2 to 20.

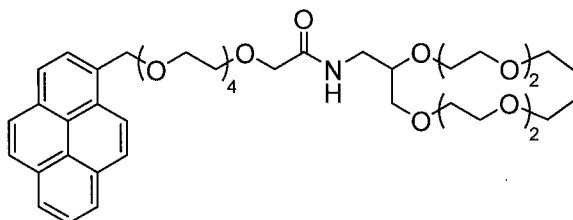
18. A process as claimed in claims 16 or 17 wherein V is a branched linking group.

19. A process as claimed in any preceding claim wherein the particles comprise the ionic surfactant and wherein the ionic surfactant is



PyrB-PEG6-CH₂COG1(ONa)₃

and the non-ionic surfactant is



PyrM-PEG4-CH₂CO[APD(PEG2Et)₂]

20. A process as claimed in any preceding claim wherein the particles have a volume average particle size diameter of from about 0.1 to about 1 μm .

21. An injection fluid for use in a process for reducing the permeability to water of a thief zone of a subterranean hydrocarbon reservoir, wherein the injection fluid comprises a dispersion of particles in water, which particles are capable of flocculating at a critical flocculation temperature (CFT) which is at or below the maximum temperature encountered in the thief zone, and which particles comprise a carbon allotrope selected from graphene, carbon nanotubes, fullerenes and graphite, having adsorbed at its surface a surfactant selected from the group consisting of:

(a) non-ionic surfactants comprising:

- (i) a hydrophobic unit having a sheet-like structure and including one or more aromatic rings,
- (ii) a head unit which comprises a non-ionic hydrophilic moiety, and
- (iii) a linker unit linking the head unit to the hydrophobic unit, said linker unit comprising from 2 to 16 alkylene glycol units in the form of an oligoether, from 2 to 16 amide units in the form of an oligoamide, or from 2 to 16 units of a combination of alkylene glycol units and amide units in the form of an oligoether-amide; and/or

(b) two-headed surfactants comprising:

- (i) a hydrophobic unit having a sheet-like structure and including one or more aromatic rings,
- (ii) a head unit which comprises a non-ionic hydrophilic moiety ("non-ionic head unit"),
- (iii) a head unit which comprises an ionic hydrophilic moiety ("ionic head unit"), and

(iv) at least one linker unit linking the non-ionic head unit and the ionic head unit to the hydrophobic unit, said linker unit comprising from 2 to 16 alkylene glycol units in the form of an oligoether, from 2 to 16 amide units in the form of an oligoamide, or from 2 to 16 units of a combination of alkylene glycol units and amide units in the form of an oligoether-amide; and

(c) optionally an ionic surfactant comprising:

(i) a hydrophobic unit having a sheet-like structure and including one or more aromatic rings,

(ii) a head unit which comprises an ionic hydrophilic moiety; and

(iii) a linker unit linking the head unit to the hydrophobic unit, said linker unit comprising 2 to 16 alkylene glycol units in the form of an oligoether, 2 to 16 amide units in the form of an oligoamide, or from 2 to 16 units of a combination of alkylene glycol units and amide units in the form of an oligoether-amide.

1 / 3

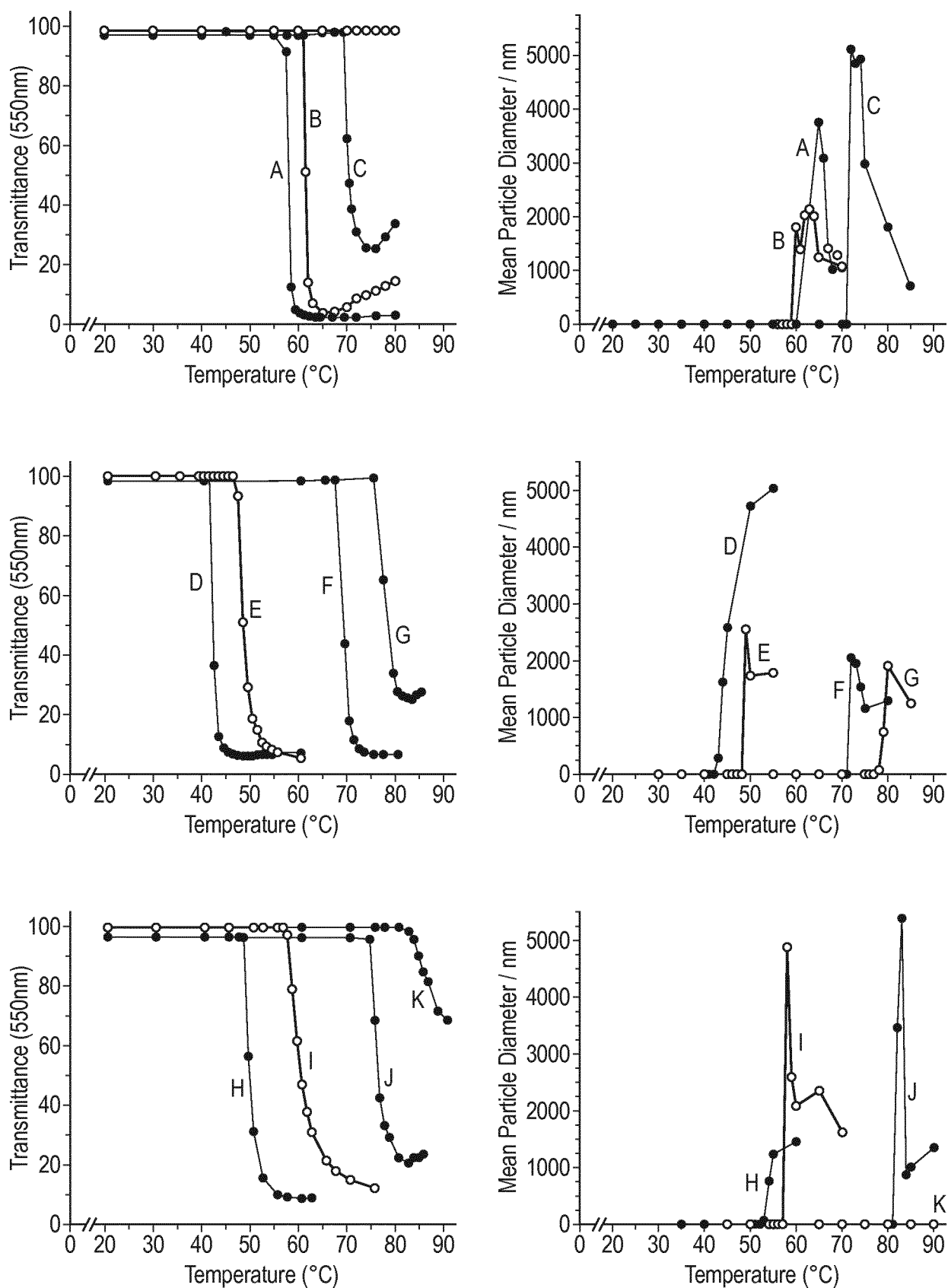


FIG. 1

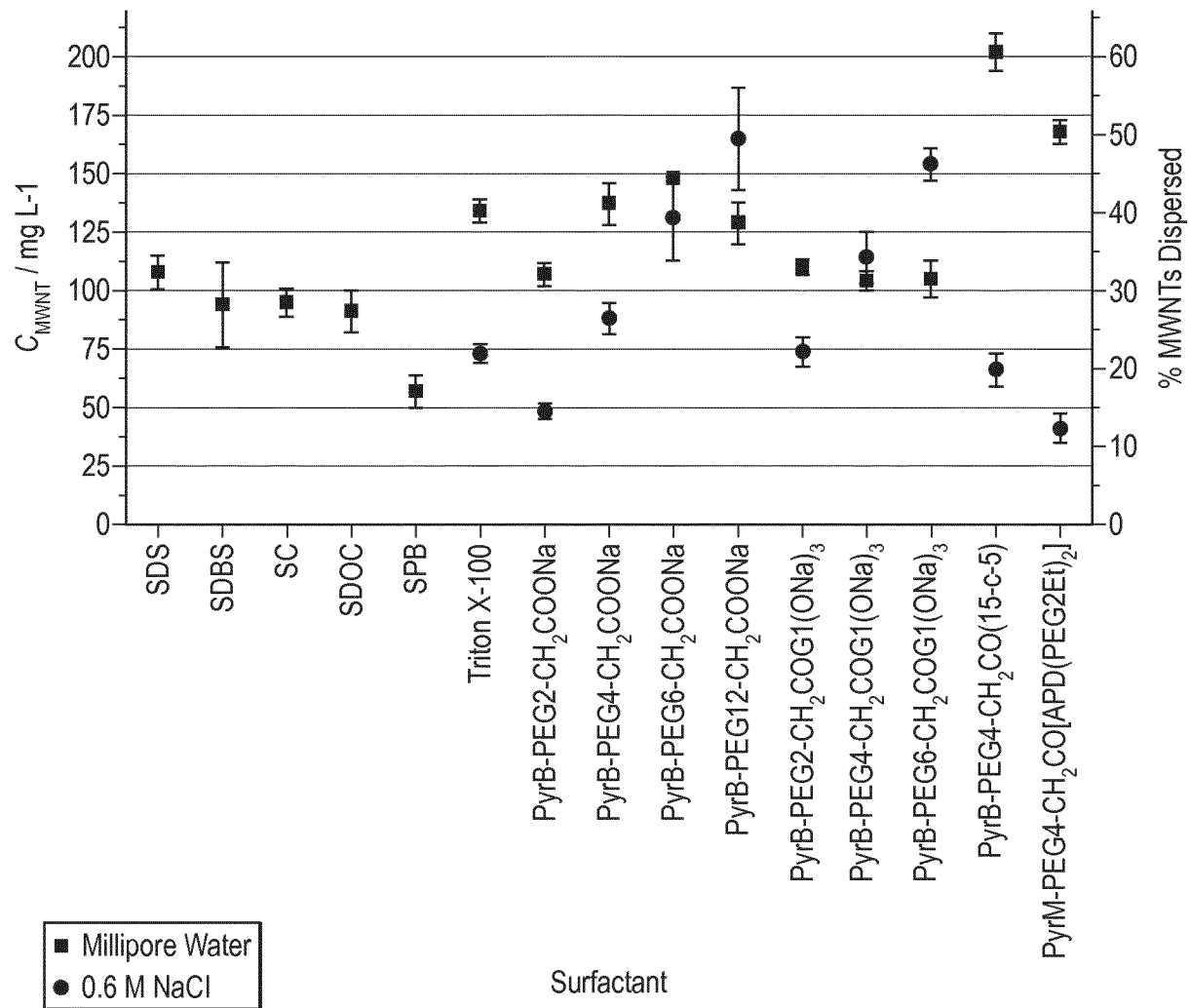


FIG. 2

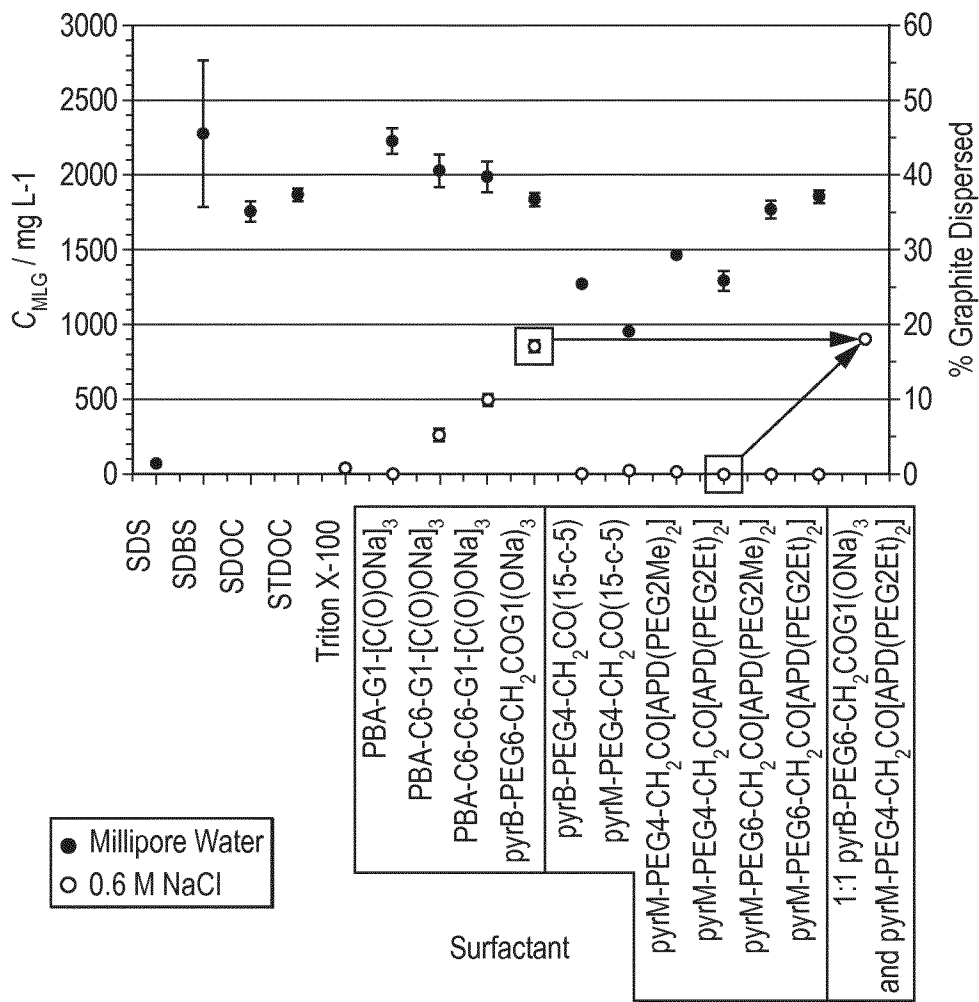


FIG. 3

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2015/071260

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09K8/60 E21B43/25
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C09K E21B

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

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

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2012/150428 A1 (HALLIBURTON ENERGY SERV INC [US]; EOFF LARRY STEVEN [US]; TODD BRADLEY) 8 November 2012 (2012-11-08) the whole document	1-21
A	GB 2 443 824 A (PETROLEO BRASILEIRO SA [BR] PETRA LEO BRASILEIRO S A PETROBRAS [BR]) 21 May 2008 (2008-05-21) the whole document	1-21
A	US 4 572 295 A (WALLEY DAVID [US]) 25 February 1986 (1986-02-25) the whole document	1-21
A	US 3 353 601 A (DOLLARHIDE FRANCIS E ET AL) 21 November 1967 (1967-11-21) the whole document	1-21
	-/--	



Further documents are listed in the continuation of Box C.



See patent family annex.

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"&" document member of the same patent family

Date of the actual completion of the international search

6 November 2015

Date of mailing of the international search report

17/11/2015

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INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2015/071260

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2008/135247 A1 (HUTCHINS RICHARD D [US]) 12 June 2008 (2008-06-12) the whole document -----	1-21

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2015/071260

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