



(51) International Patent Classification:

C09K 8/516 (2006.01)

C09K 8/588 (2006.01)

C08F 2/16 (2006.01)

C09K 8/594 (2006.01)

(21) International Application Number:

PCT/EP2017/058626

(22) International Filing Date:

11 April 2017 (11.04.2017)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

1607910.5

06 May 2016 (06.05.2016)

GB

(71) Applicant: BP EXPLORATION OPERATING COMPANY LIMITED [GB/GB]; Chertsey Road, Sunbury on Thames Middlesex TW16 7BP (GB).

(72) Inventors: BENNISON, Michael John; University of Liverpool, Foundation Building, 765 Brownlow Hill, Liverpool Lancashire L69 7ZX (GB). CHAPPELL, David; Chertsey Road, Sunbury on Thames Middlesex TW16 7LN (GB). COOPER, Andrew; University of Liverpool, Foundation Building, 765 Brownlow Hill, Liverpool Lancashire L69 7ZX (GB). FRAMPTON, Harry; Chertsey Road, Sunbury on Thames Middlesex TW16 7LN (GB). SATHERLEY, John; University of Liverpool, Foundation Building, 765 Brownlow Hill, Liverpool Lancashire L69 7ZX (GB). VIJAYARAGHAVAN, Meera; University of Liverpool, Foundation Building, 765 Brownlow Hill, Liverpool Lancashire L69 7ZX (GB).

(74) Agent: COLLINS, Frances Mary; BP INTERNATIONAL LIMITED, Global Patents & Technology Law, Chertsey Road, Sunbury on Thames Middlesex TW16 7LN (GB).

(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, DJ, 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, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC,

SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

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

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))

(54) Title: MICROPARTICLES AND COMPOSITION

(57) Abstract: The present invention provides microparticles having an average particle diameter in the range 0.05 to 10 microns and comprising a polymeric network of cross-linked co- polymers, which co-polymers comprise: a) a polymer backbone including structural units derived from a monomer having a CO₂-philic functional group, one or more cross-linking structural units derived from a hydrolytically labile cross-linking monomer and one or more cross-linking structural units derived from a non-labile cross-linking monomer; and b) one or more oligomer chains including structural units derived from a monomer having a CO₂-philic functional group, which oligomer chains are pendant from the polymer backbone and/or are grafted onto an end group of the polymer backbone. Also provided is a composition comprising said microparticles dispersed in a continuous phase comprising dense carbon dioxide. Such a composition may be injected into a subterranean oil-bearing formation where the microparticles are modified under the conditions of the formation so as to improve oil recovery from the formation..



MICROPARTICLES AND COMPOSITION

The present invention relates to cross-linked polymeric microparticles and a composition comprising a dispersion of said polymeric microparticles dispersed in a continuous phase comprising dense carbon dioxide. The composition of the present invention may be injected into a subterranean oil-bearing formation where the polymeric microparticles are modified under the conditions of the subterranean formation so as to improve oil recovery from the formation.

Oil may be recovered from a subterranean formation via natural pressure in the formation forcing oil towards production wells where it can flow or be pumped to a surface production facility (referred to as “primary recovery”). However, formation pressure is generally sufficient only to recover around 10 to 20 per cent of the total oil present in a subterranean formation. Accordingly “secondary recovery” techniques may be applied to recover oil from subterranean formations in which the oil no longer flows by natural forces.

Secondary recovery techniques rely on the supply of external energy to maintain the pressure in a subterranean formation and to sweep oil towards a production well. One such 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 formation via one or more injection wells to drive the oil towards one or more production wells. The injection of water during secondary recovery is commonly referred to as waterflooding. The injection of gas during secondary recovery is commonly referred to as gasflooding.

Enhanced Oil Recovery (EOR) processes often involve injecting a fluid into an oil formation 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 (often referred to as “tertiary 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-bearing formation. The purpose of EOR is not only to restore formation pressure and to sweep oil towards a production well, but also to improve oil displacement or fluid flow in the formation.

Enhanced oil recovery techniques include miscible gas injection, wherein a gas is

injected into a subterranean formation and, under favorable pressure and temperature conditions, is or gradually becomes miscible with the oil present in the formation; thereby allowing the oil and injected gas to mix and form a single phase. The resulting single phase has an increased volume and a decreased viscosity and a decreased surface tension compared to the oil; thus, the ability of the oil to flow out of the formation is improved.

In miscible gas injection, the injected gas may be a gaseous hydrocarbon, carbon dioxide (CO₂) or nitrogen or mixtures thereof. Where the injected gas comprises carbon dioxide, typically the pressure of a subterranean formation will be greater than the critical pressure of carbon dioxide (72.9atm) and hence the carbon dioxide injected into the formation will be in either a liquid or supercritical state (hereinafter referred to as “dense carbon dioxide”).

Dense carbon dioxide injection may also be employed in oil recovery where the temperature and pressure conditions within the formation are not such that the injected carbon dioxide and the oil in the formation can become miscible (known as “immiscible carbon dioxide injection”). In immiscible carbon dioxide injection the main function of the injected carbon dioxide is to raise and maintain formation pressure.

The use of carbon dioxide in enhanced oil recovery is discussed in “E. Tizimas, A. Georgakaki, C. Garcia Cortes and S. D. Peteves, ENHANCED OIL RECOVERY USING CARBON DIOXIDE IN THE EUROPEAN ENERGY SYSTEM, DG JRC, Institute for Energy, Petten, The Netherlands, December 2005.

Dense carbon dioxide may be co-injected with one or more other gases in EOR processes, for example, dense carbon dioxide may be co-injected with methane, ethane, n-propane, iso-propane or mixtures thereof. In particular, dense carbon dioxide may be co-injected with a produced gas (defined herein as “gas separated from the fluids produced from an oil-bearing formation”).

The efficiency of carbon dioxide injection techniques depends on a number of variables, including the viscosity of the oil in the formation and the permeability of the formation.

One problem associated with oil recovery processes involving carbon dioxide injection is that, since the injected carbon dioxide has a low viscosity relative to that of the oil, the carbon dioxide has a higher mobility than the oil present in the formation. Mobility, M , is a measure of the flow of fluid through a permeable formation. It is defined

herein as the ratio of the relative permeability of the fluid moving through a porous medium divided by the apparent viscosity of the fluid. Mobility ratio is defined as the mobility of an injection fluid divided by the mobility of the oil it is displacing. As a general principal, at a mobility ratio of 1, the fluid front moves almost in a “plug flow” manner and the sweep of the formation is good. When the mobility of the injection fluid is substantially higher than the oil (e.g. ten times higher) viscous instabilities, known as fingering, develop and the sweep of the formation is poor.

It has been recognised that increasing the viscosity of the injected, dense carbon dioxide by addition of viscosifying agents would improve sweep of the formation by lowering the mobility ratio between the dense carbon dioxide and the oil. It is understood that viscosifying agents should increase the viscosity of the carbon dioxide by a factor of 2 to 100, and should be non-damaging to the subterranean formation (*Enick, R.M. “A Literature Review of Attempts to Increase the Viscosity of Dense Carbon Dioxide”*).

Various substances have been considered for use as “direct thickeners” for dense carbon dioxide, i.e. additives which dissolve or disperse in the dense carbon dioxide and increase its viscosity. In particular, high molecular weight polymers have been considered as direct thickeners for dense carbon dioxide. For example, Harris et al. disclose that polysiloxanes and polyvinyl ethers may be used to viscosify carbon dioxide (US Patent Nos. 4,913, 235 and 5,045,220). However, these compounds tend to be either insoluble or sparingly soluble in dense carbon dioxide. Consequently, large amounts (such as greater than 10wt%, for example, 20wt%) of co-solvent are typically mixed with the dense carbon dioxide in order to increase the solubility of these additives. Handling of such large amounts of co-solvent at the injection site can be difficult. Further, there may be restrictions on the types of co-solvent that can be injected into a subterranean formation (for example, for toxicology and/or flammability reasons).

A further disadvantage of employing direct thickeners is that the rate at which the resulting viscosified dense carbon dioxide can be injected into a subterranean formation (the injectivity) is reduced compared to non-viscosified dense carbon dioxide. Such reduced injectivity may require the drilling of additional injection wells in order for voidage replacement to be maintained (i.e. replacing the volume of fluids produced from the formation by injected fluids).

A second problem associated with oil recovery processes involving carbon dioxide

injection relates to the heterogeneity of the formation rock strata. Natural variation in the permeability of different zones (layers and/or areas) of a subterranean formation means that the carbon dioxide tends to travel most easily in, and therefore preferentially sweep, 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 carbon dioxide and act as “thief zones”. Where the carbon dioxide is re-cycled (i.e. is separated from the produced oil and re-injected) this can lead to carbon dioxide cycling through the thief zone with little EOR benefit and at great cost in terms of operating the facility for the separation and injection of carbon dioxide. The oil in the less permeable zones is recovered much slower, if at all, because the proportion of injected carbon dioxide entering the lower permeability zones is small.

Herein, the term ‘thief zone’ refers to any zone (also referred to as “region”) of high permeability relative to the permeabilities of the surrounding rock, such that a high proportion of injected fluid flows through these zones. 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 formation rock between different zones of the formation; thus a thief zone may simply be a region of higher permeability than the majority of the formation 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, preferably, deep within the formation, thereby generating a new pressure gradient and forcing injected fluid into lower permeability, poorly swept areas of the formation of high oil saturation. Herein, “sweep efficiency” is taken to mean a measure of the effectiveness of an enhanced oil recovery process that depends on the proportion of the volume of the formation contacted by the injection fluid.

Various physical and chemical treatments have been used to divert injected fluids out of thief zones and thereby increase formation sweep efficiency. By reducing the permeability of the thief zones, loss of subsequently injected fluids to these thief zones is reduced, e.g. during secondary and/or tertiary recovery. Accordingly, the sweep efficiency associated with subsequent secondary and/or tertiary recovery processes is improved, as

compared with prior to the treatment.

Emulsions (sometimes referred to as “foams”) have been employed to divert injected fluids out of thief zones in oil recovery processes that use carbon dioxide injection. Such emulsions typically comprise droplets of dense carbon dioxide (the discontinuous phase) dispersed in a continuous phase (for example, brine), which emulsion is stabilized by a surfactant. Typical use of emulsions employs alternating injection of low pore volume amounts (e.g. pore volumes of less than 0.1PV) of a surfactant solution and carbon dioxide. On mixing within the formation, the surfactant solution and the carbon dioxide will form an emulsion in situ. Such carbon dioxide emulsions have very low mobility and consequently they travel very slowly through flow paths within the zone of the subterranean formation into which it is injected, thus, reduced fluid conductivity of thief-zones may temporarily be achieved, allowing the diversion of subsequently injected, higher mobility fluids to be diverted into other zones of the formation. However, high amounts of surfactant are required to produce carbon dioxide emulsions with sufficiently low mobility to achieve flow diversion. Further, a problem associated with the use of such carbon dioxide emulsions is that they will eventually be produced from the formation. The production of such low mobility emulsions may give rise to problems in the operation of a production plant. Furthermore, there are environmental hazards associated with the handling and disposal of surfactant rich fluids. Still further, the use of carbon dioxide emulsions may cause injectivity problems.

Techniques employing chemical gels have also been developed for permeability reduction in subterranean formations where carbon dioxide injection is employed. However, such chemical gels tend to be multi-component, and one or more of the components may separate out within the formation. A further problem associated with the use of such chemical gels is that they may not propagate very far into the subterranean formation.

Viscosification and permeability reduction in carbon dioxide EOR are discussed in Enick and Olsen, Mobility and Conformance Control for Carbon Dioxide Enhanced Oil Recovery (CO₂-EOR) via Thickeners, Foams and Gels – A Detailed Literature Review of 40 Years of Research, DOE/NETL-2012/1540.

According to the present invention there is provided microparticles having an average particle diameter in the range 0.05 to 10 microns and comprising a polymeric network of

cross-linked co-polymers, which co-polymers comprise:

- a) a polymer backbone having greater than 20 structural units derived from polymerisable monomers, including structural units derived from a monomer having a CO₂-philic functional group, one or more cross-linking structural units derived from a hydrolytically labile cross-linking monomer and one or more cross-linking structural units derived from a non-labile cross-linking monomer; and
- b) one or more oligomer chains having 2 to 20 structural units, and including structural units derived from a monomer having a CO₂-philic functional group, which oligomer chains are pendant from the polymer backbone and/or are grafted onto an end group of the polymer backbone;

wherein the microparticles comprise up to 10mol% of cross-linking structural units derived from a hydrolytically labile cross-linking monomer and up to 10mol% of cross-linking structural units derived from a non-labile cross-linking monomer (based on total structural unit content of the microparticles excluding the structural unit content of the oligomer chains), and wherein cross-linking structural units are substantially absent from the one or more oligomer chains.

According to a further aspect of the present invention, there is provided a composition comprising microparticles as defined above dispersed in a continuous phase comprising dense carbon dioxide.

As used herein, the term "average particle diameter" refers to an arithmetic mean of particle diameters as would be determined using scanning electron microscopy (SEM) techniques. As would be understood by the skilled person, in such techniques, a sample of particles is deposited onto a planar surface (for example graphite) and is coated with a thin conductive layer (for example gold). A focused electron beam is scanned over the coated sample. Secondary effects caused by interaction of the electrons with the sample, such as back-scattering, can be detected and the information received converted into an enlarged image of the sample. The image may then be analyzed to determine the diameter of individual particles either by using known particle size characterization software or by manual measurement. In cases where particles are non-spherical, particle diameter is taken to be the average of the two lengths measured across the longest and shortest axes of a given particle.

As used herein, the term “structural unit” refers to a structural unit derived from a polymerisable allylic, vinylic or acrylic monomer having at least one site of ethylenic unsaturation. Preferred monomers are vinylic or acrylic compounds, and particularly preferred monomers are acrylic compounds.

5 As used herein, “CO₂-philic functional group” means a functional group which has a tendency to exhibit a positive thermodynamic intermolecular interaction with CO₂ such that the functional group may be solvated by CO₂.

As used herein the term “polymer backbone” includes both linear and branched polymer backbones. By “branched polymer backbone” is meant a polymer chain having at
10 least one branch point connected to three or four chain segments wherein each of the chain segments include structural units derived from a monomer having a CO₂-philic functional group, one or more cross-linking structural units derived from a hydrolytically labile cross-linking monomer and one or more of cross-linking structural units derived from a non-labile cross-linking monomer. Where the polymer backbone is branched, preferably the
15 branched polymer backbone comprises a main chain and one or more shorter branch chains connected to the main chain at the branch point(s). The oligomer chains may be pendant from or grafted onto an end group of either or both of the main chain and branch chain(s) of a branched polymer backbone. Preferably, the polymer backbone is linear.

As used herein, the term “cross-linking structural unit” refers to a structural unit
20 which forms a covalent cross-link between the polymer backbones of two co-polymers or between different regions of the polymer backbone of an individual co-polymer. A cross-linking structural unit is derived from a “cross-linking monomer” containing at least two sites of ethylenic unsaturation. Cross-linking structural units are included in the microparticles of the invention to constrain the microparticle conformation. Preferably, the
25 sites of ethylenic unsaturation in the cross-linking monomer are located at terminal positions in the cross-linking monomer.

As used herein, the term “hydrolytically labile cross-linking structural unit” refers to a cross-linking structural unit which contains hydrolysable functional groups which can be hydrolytically degraded under specific conditions to cleave the cross-links between co-
30 polymers or, if present, the cross-links between different regions of the polymer backbone of an individual co-polymer. A hydrolytically labile, cross-linking structural unit is a cross-linking structural unit which is derived from a hydrolytically labile cross-linking

monomer. Typically, the hydrolysable functional groups of the hydrolytically labile cross-linking structural unit degrade at specific temperature and/or pH conditions.

As used herein the term “non-labile cross-linking structural units” refers to a cross-linking structural unit which is not readily chemically degraded under the conditions which cause the chemical degradation of the hydrolytically labile, cross-linking structural units. A non-labile cross-linking structural units is a cross-linking structural unit which is derived from a non-labile cross-linking monomer.

As used herein the term “oligomer chains” refers to oligomer chains derived from an oligomeric monomer. Typically, the oligomeric monomer is formed by dehydration of an oligomer that includes structural units derived from a monomer having a CO₂-philic functional group wherein the dehydration reaction generates a site of ethylenic unsaturation in the oligomer via elimination of one molecule of water.

Advantageously, the microparticles of the present invention are capable of forming a stable dispersion in dense carbon dioxide. By “stable dispersion” it is meant a system in which the microparticles are dispersed in a continuous phase comprising dense carbon dioxide, and wherein the microparticles remain dispersed in the continuous phase, without aggregation for up to several months. Without wishing to be bound by theory, it is believed that the presence of the oligomer chains provides steric stability to the microparticles of the present invention when dispersed in a continuous phase comprising dense carbon dioxide; that is, it is believed that steric repulsion between oligomer chains of discrete microparticles prevents agglomeration of the microparticles.

Thus, a composition comprising a dispersion of the microparticles of the present invention dispersed in a continuous phase comprising dense carbon dioxide may be injected into an oil-bearing subterranean formation as a relatively low-viscosity, stable dispersion. The microparticle properties, such as particle size distribution, can be designed such that efficient propagation of the microparticle dispersion through the pore structure of the formation rock (for example, sandstone) can be achieved. In order to achieve efficient propagation of the microparticle dispersion, the microparticles of the dispersion may, for example, have an average particle diameter that is less than one tenth of the smallest pore throat size of the formation rock of the zone into which the dispersion is to be injected.

When the microparticles encounter specific formation conditions, at least some of the hydrolytically labile cross-linking structural units react with water present in the

subterranean formation (connate water and any previously injected water, hereinafter referred to as "formation water") and cleave. On cleavage of these hydrolytically labile cross-linking structural units, the particles absorb surrounding dense carbon dioxide, causing them to expand (i.e. increase in volume).

5 The properties of the expanded microparticles, such as particle size distribution and rheology, may be designed to suit the desired effect, for example, by suitable selection of the number of structural units in the polymer backbone or the degree of labile and non-labile crosslinking introduced into the particles during manufacture.

10 In particular, where the desired effect is to increase the viscosity of dense carbon dioxide injected into a subterranean formation, the microparticles may be designed such that they comprise a relatively low degree of non-labile cross-linking, for example, the microparticles may comprise less than 0.25mol% of cross-linking structural units derived from a non-labile cross-linking monomer (based on total structural unit content of the microparticles excluding the structural units content of the oligomer chains). Without
15 wishing to be bound by any theory, it is believed that on hydrolysis of the labile cross-linking structural units, such microparticles expand and become a loosely linked network of co-polymer chains having a low degree of non-labile cross-links. The expanded microparticles are solvated by the dense carbon dioxide to form a homogenous fluid of increased viscosity, and hence reduced mobility, compared to that of the injected fluid.
20 Thus, the increased viscosity/reduced mobility fluid may provide a more uniform sweep of the formation compared to non-viscosified dense carbon dioxide.

 Alternatively, where the desired effect is to reduce the permeability of a thief-zone, the microparticles may be designed such that they comprise a relatively high degree of non-labile cross-linking, for example, the microparticles may comprise at least 0.25mol%
25 of cross-linking structural units derived from a non-labile cross-linking monomer (based on total structural unit content of the microparticles excluding the structural unit content of the oligomer chains). On hydrolysis of the hydrolytically labile cross-linking structural units, such microparticles retain a constrained conformation but expand to a size which is sufficient to effect blockage of pore throats of a thief zone of the formation. Thus, where a
30 dispersion of such microparticles in dense carbon dioxide is injected into a thief zone of a formation, when the microparticles encounter specific formation conditions they expand so as to reduce the permeability of the thief zone, thereby allowing the flow of subsequently

injected fluid to be largely diverted into neighbouring, previously unswept zones of the formation.

As would be understood by the skilled person, the exact amount of non-labile cross-linking that is required to provide the desired effect will depend on a number of factors, for example, the nature of the polymer backbone and the oligomer chain, and the conditions of the particular subterranean formation, such as temperature, pH of the formation water and the transit time of the injection fluid.

The microparticles of the present invention provide the particular advantage that hydrolysis of the labile cross-linking structural units so as to cause the microparticles to expand can be controlled so as to take place only once the microparticles are exposed to certain conditions. More specifically, the microparticles of the present invention have a chemical composition such that hydrolysis is temperature-dependent. For example, hydrolytic degradation of the labile cross-linking structural units may be substantially retarded at temperatures below that of the zone of the formation where expansion of the microparticles would be desirable and greatly accelerated at and above that temperature. Further specific conditions may accelerate hydrolytic cleavage of labile cross-linking structural units. For example, hydrolysis of labile cross-linking structural units may accelerate under acidic or basic conditions, in particular, at a pH of less than 5 or at a pH of greater than 9. Thus, where the composition of the present invention is injected into a subterranean formation, expansion of the microparticles will only take place once they encounter specific formation conditions. Since the expansion of the microparticles is delayed, the disadvantages associated with the reduced injectivity of viscous fluids may be avoided.

The microparticles of the present invention have an unexpanded average particle diameter in the range 0.05 to 10 microns. In preferred embodiments, the microparticles of the present invention have an unexpanded average particle diameter of from about 0.1 to about 3 microns, more preferably from about 0.2 to about 1 microns, still more preferably 0.3 to 0.8 microns.

Preferably, at least a major portion of the structural units of the polymer backbone of the microparticles are derived from a monomer having a CO₂-philic functional group. For example, microparticles may comprise from about 75 to about 99.9 mol% of structural units deriving from monomers having a CO₂-philic functional group, preferably from about

80 mol% to about 99 mol%, more preferably from about 90 mol% to about 99 mol% (based on the total structural unit content of the microparticles excluding the structural unit content of the oligomer chains).

Suitable hydrolytically labile cross-linking structural units may be derived from hydrolytically labile cross-linking monomers including diacrylamides and methacrylamides of diamines such as the diacrylamide of piperazine; acrylate or methacrylate esters of di, tri, tetra hydroxy compounds including ethyleneglycol diacrylate, polyethyleneglycol diacrylate, trimethylpropane trimethacrylate, ethoxylated trimethylol triacrylate, ethoxylated pentaerythritol tetracrylate, and the like; diacrylamides and methacrylamides of dialdehydes, such as the diacrylamide of glyoxal; divinyl or diallyl compounds separated by an azo such as the diallylamide of 2,2'-Azobis (isbutyric acid), or separated by a carbonate, such as diallyl carbonate; the vinyl or allyl esters of di or tri functional acids; and polycaprolactones. Preferred hydrolytically labile cross linking monomers include diallyl carbonate, ethylene glycol dimethacrylate and dicumyldiacetate.

In preferred embodiments, the microparticles of the present invention comprise from 0.1 to 10mol% of cross-linking structural units derived from a hydrolytically labile cross-linking monomer, more preferably from 0.5 to 7.5mol% of cross-linking structural units derived from a hydrolytically labile cross-linking monomer, most preferably from 1 to 5mol% of cross-linking structural units derived from a hydrolytically labile cross-linking monomer (based on the total structural unit content of the microparticles excluding the structural unit content of the oligomer chains).

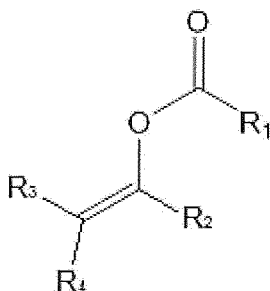
The temperature at which the hydrolytically labile cross-linking structural units of the microparticle undergo hydrolysis and cleave may be controlled such that it falls within the range of temperatures encountered in oil-bearing subterranean formations, for instance in the range of from 20 to 150 °C. Preferably, the temperature at which the hydrolytically labile cross-linking structural units of the microparticle undergo hydrolysis is in the range 40 to 80°C, more preferably 50 to 70°C.

Suitable non-labile cross-linking structural units may be derived from cross-linking monomers including methylene bisacrylamide, divinyl adipate, diallylamine, triallylamine, divinyl sulfone, diethyleneglycol diallyl ether, and the like. Preferred non-labile cross linking monomers are methylene bisacrylamide and divinyl adipate.

The microparticles comprise up to 10mol%, preferably from about 0.01mol% to

about 10mol%, preferably 0.1 to 5mol% of cross-linking structural units derived from a non-labile cross-linking monomer (based in total structural unit content of the microparticles excluding the structural unit content of the oligomer chains). Where it is intended to employ the particles to increase the viscosity of dense carbon dioxide injected into a subterranean formation, the microparticles may comprise less than 0.25mol%, preferably less than 0.2mol% of cross-linking structural units derived from a non-labile cross-linking monomer (based on total structural unit content of the microparticles excluding the structural unit content of the oligomer chains). Where it is intended to employ the particles to reduce the permeability of a thief-zone, the microparticles may comprise from 0.25mol% to 10mol%, preferably from 0.25mol% to 5mol% of cross-linking structural units derived from a non-labile cross-linking monomer (based on total structural unit content of the microparticles excluding the structural units content of the oligomer chains).

In accordance with the present invention, the polymer backbone includes structural units derived from a monomer having a CO₂-philic functional group. Monomers having a CO₂-philic functional group include vinyl esters, such as vinyl acetate and/or vinyl pivalate, isopropyl esters, such as isopropyl acetate and isopropyl pivalate, and dimethylsiloxane. Preferably, the polymer backbone comprises structural units derived from a vinyl ester monomer having the following formula (Formula 1):



where R₁ is an alkyl group and R₂, R₃ and R₄ are independently H or a C₁ to C₂ alkyl group.

R_1 is preferably a C_1 to C_{10} alkyl group, and more preferably a C_1 to C_5 alkyl group. The alkyl group may be straight chain or branched. Preferably, the structural units deriving from monomers having a CO_2 -philic functional group are derived from vinyl acetate, in which R_1 is a methyl group, and/or vinyl pivalate, in which R_1 is a t-butyl group.

5 Preferably, R_2 , R_3 and R_4 are independently H.

Preferably, all of the structural units of the polymer backbone which are not cross-linking structural units are derived from vinyl acetate and/or vinyl pivalate.

Preferably, the polymer backbone has a weight average molecular weight, M_w , in the range 2,500 Da to 1 MDa (megadaltons).

10 In the co-polymers of the microparticles of the present invention, the one or more oligomer chains are pendant from the polymer backbone and/or are grafted onto an end group of the polymer backbone.

In accordance with the present invention, the one or more oligomer chains include structural units derived from a monomer having a CO_2 -philic functional group. Preferably, 15 the one or more oligomer chains comprise structural units deriving from vinyl esters of Formula 1. Most preferably, the one or more oligomer chains include structural units deriving from vinyl acetate and/or vinyl pivalate.

In one embodiment of the present invention, substantially all of the structural units, such as at least 91mol%, preferably, at least 95 mol%, most preferably, at least 99 mol% of 20 the structural units of the one or more oligomer chains are derived from monomers having a CO_2 -philic functional group, preferably vinyl acetate and/or vinyl pivalate.

In the microparticles of the present invention, cross-linking structural units are substantially absent from the one or more oligomer chains. Preferably, each oligomer chain comprises less than 0.1mol% of cross-linking structural units.

25 The one or more oligomer chains may individually have a weight average molecular weight, M_w , of 500 to 4000 Da, preferably 800 to 3,000Da, most preferably 900 to 2,000 Da.

The one or more oligomer chains may individually have a number average molecular weight, M_n , of 400 to 6000, though it is preferably in the range 750-1000.

30 The oligomer chain preferably has a polydispersity index (M_w/M_n) value of less than 2.5, more preferably less than 2, and most preferably less than 1.5.

The one or more oligomer chains may be present in the microparticles of the present

invention in an amount of up to 2mol%, preferably in the range 0.1 to 1.5mol%, more preferably in the range 0.2 to 1mol%.

The microparticles of the present invention may be prepared by polymerization of monomers including one or more monomers having a CO₂-philic functional group in the presence of one or more hydrolytically labile cross-linking monomers, one or more non-labile cross-linking monomers, a pre-formed dehydrated oligomer and a polymerisation initiator.

The pre-formed oligomer may be prepared by oligomerisation of monomers including one or more monomers having a CO₂-philic functional group in the presence of an oligomerisation initiator. The oligomerisation may be carried out, for example, via a solution oligomerisation process, where the reaction mixture contains solvent, initiator and monomers. Alternatively, the oligomer may be prepared by an emulsion or suspension oligomerisation process.

Any suitable initiator may be used in the oligomerisation reaction. For example, a free-radical initiator may be employed. Preferred initiators for such a reaction include azo compounds such as azobisisobutyronitrile (AIBN) and 4,4'-azobis(4-cyanovaleric acid) (ACVA); organic peroxides such as dibutyl peroxide; inorganic compounds, such as potassium persulfate; and, redox couples, such as benzoyl peroxide/dimethylaminopyridine and potassium persulfate/sodium metabisulfite.

Once oligomerisation has been initiated, the oligomer chain grows until termination occurs.

Termination of the oligomerisation reaction may occur by chain transfer in which the activity of the growing oligomer is transferred to another molecule thereby limiting the average molecular weight of the final oligomer chain. In particular, termination of the oligomerisation reaction may occur by chain transfer to a solvent that acts as a chain transfer agent (referred to hereinafter as "chain transfer solvent"). By using a large amount of chain transfer solvent, it is possible to limit the chain length of the resulting oligomer (i.e. to prevent the formation of a polymer having greater than 20 structural units rather than an oligomer having 2 to 20 structural units). Suitable chain transfer solvents which may be employed in the oligomerisation include propan-2-ol, tert-butanol, methyl ethyl ketone and p-xylene.

Preferably, the molar ratio of monomer to initiator in the oligomerisation reaction is

in the range of from 200:1 to 10:1, preferably from 100:1 to 20:1, such as 40:1.

The oligomerisation reaction may be conducted at elevated temperature, for instance a temperature of from 50 to 140 °C, more preferably from 60 to 120 °C, such as from 70 to 90 °C; and by carrying out the reaction for a time period of from 12 to 30 hours, such as from 12 to 24 hours.

The skilled person would recognise that a suitable oligomerisation reaction can be conducted under conditions other than those mentioned. As an example, a higher temperature may be used in connection with a lower reaction time. However, shorter reaction times can be harder to monitor or control and so are not preferred for the present invention.

The oligomerisation reaction is preferably carried out under an inert atmosphere, for instance under a nitrogen atmosphere. The reaction mixture is preferably stirred.

On completion of the oligomerisation reaction, the resulting oligomer may be isolated from the reaction mixture, for example, via reduced pressure solvent evaporation, filtration or centrifugation.

The isolated oligomer may be dried and stored for use in forming the particles at a later date. Suitable methods of drying include drying under vacuum and drying in a low temperature oven. The low temperature oven may dry the oligomers at a temperature of from 40 to 80 °C.

Prior to a polymerization reaction for production of the microparticles of the present invention, the pre-formed oligomer may be dehydrated by a dehydration reaction that involves the elimination of a molecule of water from the oligomer. Typically, the pre-formed oligomer has a terminal hydroxyl functional group and the dehydration reaction generates a site of ethylenic unsaturation via elimination of one molecule of water. The oligomer may be dehydrated by techniques that would be known to the skilled person, for example, by acid catalysed dehydration.

In accordance with preferred embodiments of the invention, the microparticles are prepared by an emulsion polymerisation process, whereby monomers having a CO₂-philic functional group, hydrolytically labile cross-linking monomers, non-labile cross-linking monomers and pre-formed dehydrated oligomers are contacted with a polymerisation initiator in a suitable dispersion medium, such as methanol.

Suitably, a portion of the pre-formed dehydrated oligomer may be added to the

polymerisation reaction mixture at the start of the polymerisation reaction and one or more further portions of the pre-formed dehydrated oligomer may be added periodically to the reaction mixture. The portions of pre-formed dehydrated oligomer that are added to the polymerisation reaction mixture may be the same or different, preferably, the same. The intervals of time between the addition of successive portions of the pre-formed dehydrated oligomer may be the same or different. Typically, the time interval between the addition of successive portions of the pre-formed dehydrated oligomers may be in the range of 0.25 to 1.5 hours, preferably 0.5 to 1.25 hours, more preferably about 1 hour. It is also envisaged that the pre-formed dehydrated oligomer may be continuously added to the reaction mixture.

The emulsion polymerization process may be initiated using a conventional thermal or redox free-radical initiator. Suitable initiators include azo compounds, such as azobisisobutyronitrile (AIBN) and 4,4'-azobis(4-cyanovaleric acid) (ACVA); peroxides, such as di-t-butyl peroxide; inorganic compounds, such as potassium persulfate; and, redox couples, such as benzoyl peroxide/dimethylaminopyridine and potassium persulfate/tetramethylethylenediamine.

In addition to the monomers having CO₂-philic functional groups, hydrolytically labile cross-linking monomers, non-labile cross-linking monomers, pre-formed dehydrated oligomers and polymerization initiator the emulsion may also contain other conventional additives, for instance pH adjusters.

The person skilled in the art will understand that the mol% of cross-linking structural units derived from the hydrolytically labile cross-linking monomer and the mol% of structural units derived from the non-labile cross-linking monomer (based on the total structural unit content of the microparticles excluding the structural unit content of the oligomer chains) corresponds to the mol% of hydrolytically labile cross-linking monomer and the mol% of non-labile cross-linking monomer (based on the total moles of monomers in the polymerisation reaction mixture excluding the moles of pre-formed dehydrated oligomer (i.e. the moles of oligomeric monomer).

The molar ratio of monomer having a CO₂-philic functional group to the dehydrated oligomer that is used to prepare the particles may be in the range of from 20:1 to 100:1, preferably from 25:1 to 50:1.

The molar ratio of monomer having CO₂-philic functional groups to polymerisation

initiator may be in the range of from 150:1 to 1:1, from 65:1 to 5:1, such as about 20:1.

The molar ratio of monomer having CO₂-philic functional groups to hydrolytically labile cross-linking monomer is preferably in the range of from 1000:1 to 10:1, preferably from 500:1 to 50:1.

5 Where it is intended to employ the particles to increase the viscosity of dense carbon dioxide injected into a subterranean formation, the molar ratio of monomer having CO₂-philic functional groups to non-labile cross-linking monomer is preferably in the range of from 10,000:1 to 400:1. Where it is intended to employ the particles to reduce the permeability of a thief-zone, the molar ratio of monomer having CO₂-philic functional
10 groups to non-labile cross-linking monomer is preferably in the range of from 2000:1 to 20:1, preferably from 400:1 to 50:1.

 The polymerization reaction may be conducted at elevated temperature, for example, at a temperature of from 30 to 120°C, more preferably from 50 to 100°C, for example 60°C; and by carrying the reaction out for a time period of from 30 minutes to 5
15 hours, such as from 1 to 3 hours.

 The polymerisation reaction is preferably carried out under an inert atmosphere, for instance under a nitrogen atmosphere. The reaction mixture is preferably agitated.

 The skilled person would recognise that a suitable polymerisation reaction may be conducted under conditions other than those mentioned.

20 The polymeric microparticles of the invention may be obtained in dry form by separating the microparticles from the emulsion using a suitable solvent, such as isopropanol, acetone, isopropanol/acetone or methanol/acetone or other solvents or solvent mixtures that are miscible with both the dispersion medium and water. The microparticles may then be isolated from the supernatant by centrifugation, dialysis and/or filtration and
25 dried by conventional procedures.

 The composition of the present invention may be formed by dosing the microparticles into a continuous phase comprising dense carbon dioxide in an amount from 0.01 to 2wt% based on the total weight of the composition, more preferably in an amount of from 0.05 to 1.5wt% based on the total weight of the composition, and most preferably
30 from 0.15 to 0.75wt% based on the total weight of the composition.

 Where the composition is formed by dispersing dried microparticles in a continuous phase comprising dense carbon dioxide, the microparticles are preferably dispersed in an

organic solvent which is miscible with the continuous phase comprising dense carbon dioxide (hereinafter the organic solvent is termed "carbon dioxide miscible solvent") to form a concentrated dispersion of the microparticles in the organic solvent which is subsequently added into the continuous phase comprising dense carbon dioxide. Suitable carbon dioxide miscible solvents include methanol and hexane. Suitably, the amount of carbon dioxide-miscible solvent used to form the concentrated dispersion is in the range of 2 to 200 litres, preferably, 10 to 50 litres per kilogram of dried polymeric microparticles. Where the composition is to be used as an injection fluid in an EOR process, such a concentrated dispersion of microparticles may be dosed into the continuous phase comprising dense carbon dioxide, for example, using a metered pump system at the injection site.

Alternatively, the composition may be formed by dosing the microparticles in powder form into the continuous phase comprising dense carbon dioxide. Where the composition is to be employed as an injection fluid in an EOR process, such a powder may be dosed into the continuous phase comprising dense carbon dioxide, for example, by using a metered hopper system at the injection site. Preferably, the powder is stored under a blanket of dry inert gas in order to mitigate risks associated with powder handling.

Suitably the amount of powder or of the concentrated dispersion that is dosed into the continuous phase comprising dense carbon dioxide may be controlled, for example, to maintain the concentration of microparticles in the continuous phase comprising dense carbon dioxide at or near a target concentration, for example within $\pm 10\%$ of a target concentration. The dosing of the powder or concentrated dispersion is preferably automated, for example, using a metering system that is controlled via a computer. Preferably, the powder or concentrated dispersion is dosed into an injection well head at an injection site or down hole in an injection well.

The present invention will now be illustrated by reference to the following Examples.

Example 1 - Synthesis of Vinyl Pivalate Oligomer

A dried two-neck round-bottomed flask was equipped with a condenser and a magnetic follower before being sealed. The internal atmosphere of the flask was exchanged for nitrogen *via* repeated evacuation-refill cycles using an attached Schlenk line. 57.2 mg (0.35 mmol) of purified 2,2'-azobis(2-methylpropionitrile) was dissolved in 14.89 g, (116.16 mmol) vinyl pivalate. 2 g of the resulting solution was then added to the

round-bottomed flask. 71.1 ml (929.26 mmol) of propan-2-ol was subsequently charged to the flask *via* syringe. The flask was then heated to 80 °C. The remaining vinyl pivalate/2,2'-azobis(2-methylpropionitrile) solution was then added to the flask via syringe at a rate of 0.92 ml h⁻¹ over 14 hours. On completion of this addition, the reaction was
5 stopped by removing the heat source and allowing the reaction mixture to cool to room temperature. Solvent and any residual monomer were then removed under reduced pressure at 40 °C yielding 11.54g of a viscous colourless material (the oligomer).

Example 2 – Dehydration of Vinyl Pivalate Oligomer

2g of the oligomer prepared in Example 1 was charged to a dried, open round-
10 bottomed flask equipped with a magnetic follower. 10 ml glacial acetic was added to the flask and the mixture agitated for several hours. 1ml of sulfuric acid was subsequently added to the flask. On addition of the sulphuric acid the mixture turned from a transparent, colourless solution to a transparent, dark brown reaction mixture. The flask was fitted with a condenser and then heated to 50 °C and maintained at that temperature for three hours.
15 The reaction mixture was then cooled to room temperature and diluted with 100 ml toluene before being washed with deionised water (5 x 100 mL), leaving a pale orange solution. The toluene solution was isolated by phase separation, dried over anhydrous magnesium sulfate and filtered. The solvent was then removed under reduced pressure to yield 1.92 g of highly viscous dark orange material (the dehydrated oligomer). The dehydrated
20 oligomer was found to have a number average molecular weight of 1000 Daltons.

Example 3 – Microparticle Synthesis

A dried two-neck round-bottomed flask was fitted with a condenser and magnetic follower before being sealed. The internal atmosphere of the flask was exchanged for nitrogen *via* repeated evacuation-refill cycles using an attached Schlenk line. 17.5 mL
25 methanol was added to the flask followed by 8.029 ml (54.25 mmol) vinyl pivalate. The resulting solution was agitated and the following reactants added: 173.8 mg (0.174 µmol) of the dehydrated oligomer prepared in Example 2, 53.8 mg (0.271 mmol) divinyl adipate, 154.2mg (1.085mmol) diallyl carbonate and 25ml deionised water. The agitated reaction mixture was then heated to 60°C. 44.0 mg (0.163 mmol) potassium persulfate in 2.5 mL
30 deionised water was then added to the reaction mixture. The flask was sealed and the reaction mixture agitated for 1 hour before the addition of a further 173.8 mg (0.174 µmol) of the dehydrated oligomer prepared in Example 2. The flask was resealed and the

reaction mixture was heated at a temperature of 60°C with agitation until microparticles were visually determined to have formed (approx. 2 hours total reaction time). The reaction mixture was then cooled to room temperature before being filtered through a loose plug of glass wool to remove any coagulum. The remaining dispersion of microparticles was transferred to a regenerated cellulose dialysis membrane having a nominal molecular weight cut off of 12-14kDa. The membrane was sealed, placed in methanol and agitated. The methanol was replaced with fresh methanol every two hours for a total of eight hours. This dialysis removed any unreacted monomer and any other contaminants from the dispersion of microparticles.

10 **Example 4 – Particle diameter determination**

A droplet of the microparticle dispersion prepared in Example 3 was deposited onto a graphite substrate and the methanol allowed to evaporate overnight. The resulting sample of dried microparticles was then coated with a thin layer of gold via a plasma coupling method (at a current of 10mA for 2 minutes).

15 The coated sample was analysed by scanning electron microscopy (SEM) carried out under vacuum at 19°C using a Hitachi S4800 Scanning Electron Microscope.

The resulting SEM image showed that the particles were spherical. Microparticle diameters were determined using post-analysis software MeasureIT (from Olympus Soft Imaging Solutions) and the average particle diameter calculated. The average particle diameter of the microparticles was approximately 0.53 microns.

20 **Example 5 – Dispersibility of the microparticles in dense CO₂**

A 5wt% dispersion of microparticles, as prepared in Example 3, in methanol was prepared and 1ml of this dispersion was charged to a high pressure vessel having two optically transparent sapphire windows and an internal volume of 35ml. Carbon dioxide was charged to the vessel at room temperature until the pressure within the vessel was in the range 50-60 bar (5000-6000 kPa) – under such conditions carbon dioxide is in the gaseous state. The contents of the vessel were agitated using a magnetically driven anchor type impellor at 300 rpm. It was visually observed through the sapphire window that under these conditions the microparticles settled at the bottom of the vessel, i.e. they did not form a stable dispersion in the gaseous carbon dioxide.

30 The high pressure vessel was then heated to 36°C and further carbon dioxide added until the pressure reached 140 bar (14000 kPa) – under such temperature and pressure

conditions carbon dioxide is in the supercritical state. It was visually observed through the sapphire window that the microparticles formed a stable dispersion in the supercritical (i.e. dense) carbon dioxide. The dispersion remained stable (i.e. no settling of the microparticles was observed) for several hours after agitation was stopped.

5 This example demonstrates that the microparticles of the present invention are capable of forming a stable dispersion in dense carbon dioxide.

Example 6 – Delayed hydrolysis of labile cross-linking structural units

Four samples (A, B, C and D) each comprising 25mg of diallyl carbonate in 0.8ml of deuterated methanol were prepared. 4μl of hydrochloric acid (36mol%) was added to
10 samples A and B. The samples were incubated at the temperatures indicated in Table 1 for 72 hours.

Samples A to D were analyzed by ¹H NMR spectroscopy at 19°C on a 400MHz spectrometer (Bruker DPX-400) both before and after the incubation. Comparison of the NMR spectra of samples prior to and after the incubation allowed the degree of
15 degradation of the diallyl carbonate which had taken place to be determined. The results are shown in Table 1.

Table 1

Sample	HCl present	Temperature (°C)	Amount of degradation (%)
A	Yes	50	16.7
B	Yes	20	3.7
C	No	50	8.2
D	No	20	2.3

As can be seen from the results shown in Table 1, the degradation of diallyl
20 carbonate is accelerated at increased temperature and increased acidity. Thus, these results demonstrate that appropriate choice of cross-linking monomer will allow cleavage of the cross-linking structural units of the microparticles to be delayed until the desired temperature and/or pH conditions are encountered.

Claims

1. Microparticles having an average particle diameter in the range 0.05 to 10 microns and comprising a polymeric network of cross-linked co-polymers, which co-polymers comprise:

- 5 a) a polymer backbone having greater than 20 structural units derived from polymerisable monomers, including structural units derived from a monomer having a CO₂-philic functional group, one or more cross-linking structural units derived from a hydrolytically labile cross-linking monomer and one or more cross-linking structural units
10 derived from a non-labile cross-linking monomer; and
- b) one or more oligomer chains having 2 to 20 structural units, and including structural units derived from a monomer having a CO₂-philic functional group, which oligomer chains are pendant from the polymer backbone and/or are grafted onto an end group of the
15 polymer backbone;

wherein the microparticles comprise up to 10mol% of cross-linking structural units derived from a hydrolytically labile cross-linking monomer and up to 10mol% of cross-linking structural units derived from a non-labile cross-linking monomer (based on the total structural unit content of the microparticles excluding the structural unit content of the
20 oligomer chains), and wherein cross-linking structural units are substantially absent from the one or more oligomer chains.

2. Microparticles as claimed in claim 1 wherein the microparticles comprise from about 75 to about 99.9 mol%, preferably from about 80 mol% to about 99 mol%, more preferably from about 90 mol% to about 99 mol% of structural units derived from
25 monomers having a CO₂-philic functional group (based on the total structural unit content of the microparticles excluding the structural unit content of the oligomer chains).

3. Microparticles as claimed in any preceding claim wherein the cross-linking structural units derived from a hydrolytically labile cross-linking monomer are derived from hydrolytically labile cross-linking monomers selected from diacrylamides and
30 methacrylamides of diamines; acrylate or methacrylate esters of di, tri, tetra hydroxy compounds; diacrylamides and methacrylamides of dialdehydes; divinyl or diallyl compounds separated by an azo or separated by a carbonate; vinyl or allyl esters of di or tri

functional acids; polycaprolactones and mixtures thereof.

4. Microparticles as claimed in claim 3 wherein the cross-linking structural units derived from a hydrolytically labile cross-linking monomer are derived from diallyl carbonate.

5. Microparticles as claimed in any preceding claim wherein the microparticles comprise from 0.1 to 10mol%, preferably from 0.5 to 7.5mol%, more preferably from 1 to 5mol%, of cross-linking structural units derived from a hydrolytically labile cross-linking monomer (based on the total structural unit content of the microparticles excluding the structural unit content of the oligomer chains).

6. Microparticles as claimed in any preceding claim wherein the cross-linking structural units derived from a non-labile cross-linking monomer are derived from non-labile cross-linking monomers selected from methylene bisacrylamide, divinyl adipate, diallylamine, triallylamine, divinyl sulfone, diethyleneglycol diallyl ether, and mixtures thereof.

7. Microparticles as claimed in claim 6 wherein the non-labile cross linking monomers are selected from methylene bisacrylamide, divinyl adipate and mixtures thereof.

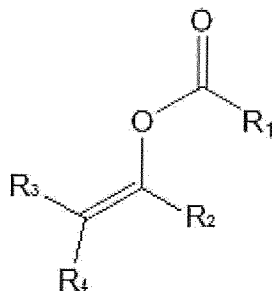
8. Microparticles as claimed in any preceding claim wherein wherein the microparticles comprise from 0.01mol% to 10mol%, preferably 0.1 to 5mol% of cross-linking structural units derived from a non-labile cross-linking monomer (based on the total structural unit content of the microparticles excluding the structural unit content of the oligomer chains).

9. Microparticles as claimed in claim 8 wherein the microparticles comprise less than 0.25mol%, preferably less than 0.2mol%, of cross-linking structural units derived from a non-labile cross-linking monomer (based on the total structural unit content of the microparticles excluding the structural unit content of the oligomer chains).

10. Microparticles as claimed in claim 8 wherein the microparticles comprise from 0.25mol% to 10mol%, preferably from 0.25mol% to 5mol%, of cross-linking structural units derived from a non-labile cross-linking monomer (based on the total structural unit content of the microparticles excluding the structural unit content of the oligomer chains).

11. Microparticles as claimed in any preceding claim wherein the structural units of the polymer backbone which derive from a monomer having a CO₂-philic functional group are

derived from a vinyl ester monomer having the following formula (Formula 1):



where R_1 is an alkyl group and R_2 , R_3 and R_4 are independently H or a C_1 to C_2 alkyl group.

12. Microparticles as claimed in claim 11 wherein R_1 is a C_1 to C_{10} alkyl group, preferably a C_1 to C_5 alkyl group.

13. Microparticles as claimed in claim 11 or 12 wherein the structural units of the polymer backbone which derive from a monomer having a CO_2 -philic functional group are derived from vinyl acetate and/or vinyl pivalate.

14. Microparticles as claimed in any of claims 11 to 13 wherein R_2 , R_3 and R_4 are independently H.

15. Microparticles as claimed in any preceding claim wherein all of the structural units of the polymer backbone which are not cross-linking structural units are derived from vinyl acetate and/or vinyl pivalate.

16. Microparticles as claimed in any preceding claim wherein at least 91mol%, preferably at least 95 mol%, more preferably at least 99 mol% of the structural units of the one or more oligomer chains are derived from a monomer having a CO_2 -philic functional group.

17. Microparticles as claimed in claim 16 wherein the structural units of the one or more oligomer chains which derive from a monomer having a CO_2 -philic functional group are derived from vinyl acetate and/or vinyl pivalate.

18. Microparticles as claimed in any preceding claim wherein the one or more oligomer chains each comprise less than 0.1mol% of cross-linking structural units.

19. Microparticles as claimed in any preceding claim wherein the one or more oligomer chains are present in an amount of up to 2mol%, preferably in the range 0.1 to 1.5mol%, more preferably in the range 0.2 to 1mol% (based on total structural unit content of the microparticles).

- 5 20. A composition comprising microparticles as defined in any preceding claim dispersed in a continuous phase comprising dense carbon dioxide.

10

15

20

25

30

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2017/058626

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09K8/516 C08F2/16 C09K8/588 C09K8/594
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 C08F C08G

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

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

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2015/322333 A1 (KURIAN PIOUS V [US] ET AL) 12 November 2015 (2015-11-12)	1-10,16, 18-20
Y	claims 1,7,10,12; figure 1; example 1; tables 1,2; compounds 4,17	11-15,17
X	WO 2015/059024 A1 (BP EXPLORATION OPERATING [GB]; CHAPPELL DAVID [GB]; FRAMPTON HARRY [GB]) 30 April 2015 (2015-04-30) claim 1; example 3	1-3,5, 8-10,16, 18,19
X	US 2011/046329 A1 (GOTOU AKIHIRO [JP] ET AL) 24 February 2011 (2011-02-24)	1-3,5, 8-10,16, 18,19
	paragraph [0110]; claims 1,6; examples prod 1,1	
	-/-	



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

9 June 2017

Date of mailing of the international search report

21/06/2017

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer

Redecker, Michael

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2017/058626

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	NATASHA A. BIRKIN ET AL: "Synthesis and application of new CO₂-soluble vinyl pivalate hydrocarbon stabilisers via RAFT polymerisation", POLYMER CHEMISTRY, vol. 2, no. 6, 1 January 2011 (2011-01-01) , page 1293, XP55379298, GB ISSN: 1759-9954, DOI: 10.1039/c1py00062d abstract page 1293 - page 1294 -----	11-15,17

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2017/058626

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2015322333	A1	12-11-2015	AR 089816 A1 17-09-2014
		AU 2013212130 A1 19-06-2014	
		AU 2016204046 A1 30-06-2016	
		CA 2858435 A1 01-08-2013	
		CN 104053743 A 17-09-2014	
		CN 106221689 A 14-12-2016	
		EP 2807228 A1 03-12-2014	
		NZ 625655 A 29-04-2016	
		RU 2014134878 A 20-03-2016	
		US 2013192826 A1 01-08-2013	
		US 2015322333 A1 12-11-2015	
		WO 2013112664 A1 01-08-2013	

WO 2015059024	A1	30-04-2015	AR 098139 A1 04-05-2016
		UY 35791 A 30-04-2015	
		WO 2015059024 A1 30-04-2015	

US 2011046329	A1	24-02-2011	EP 2239280 A1 13-10-2010
		JP 5499711 B2 21-05-2014	
		US 2011046329 A1 24-02-2011	
		WO 2009096300 A1 06-08-2009	
