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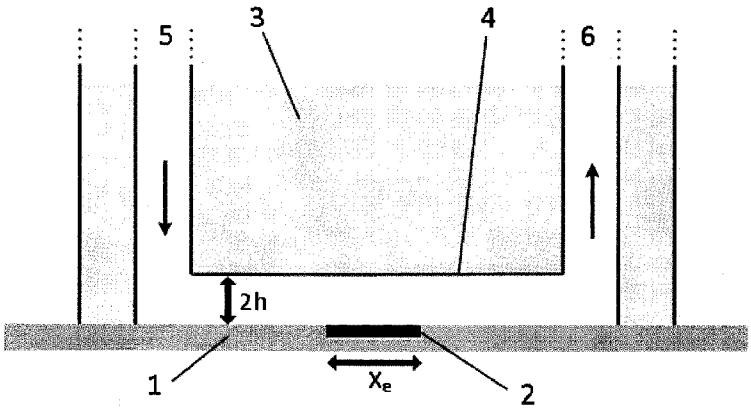
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(54) **Title**: TAGGED SCALE INHIBITING POLYMERS

Figure 1



(57) **Abstract**: A method of controlling scale formation in an oil production operation, the method comprising the steps of: (a) introducing a solution or dispersion of a scale inhibiting polymer comprising: (i) a plurality of polymer units including a scale inhibiting moiety, and (ii) at least one polymer unit including a tagging moiety, wherein the tagging moiety can be detected electrochemically, into an oil-bearing formation; (b) producing oil and aqueous fluids from the oil-bearing formation; (c) periodically or continuously measuring the concentration of scale inhibiting polymer in the produced aqueous fluids by electrochemical detection of the tagging moiety of the scale inhibiting polymer; and (d) introducing further scale inhibiting polymer into the oil-bearing formation when the measured concentration of scale inhibiting polymer in step (c) falls below a pre-determined minimum value.

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TAGGED SCALE INHIBITING POLYMERS

This invention relates to methods of using scale inhibiting polymers in oil and gas production operations. More specifically, the invention relates to methods for controlling scale formation in oil and gas production operations using scale inhibiting polymers that are tagged with redox active groups, the methods comprising detecting the scale inhibiting polymers by electrochemical techniques. The invention also provides novel scale inhibiting polymers that comprise redox active groups. The invention further provides methods of preparing the novel scale inhibiting polymers of the invention and compositions comprising the novel scale inhibiting polymers of the invention.

In the context of the present invention, the term "scale" refers to the solid precipitates that form in aqueous systems when, due to changes in the physical or chemical environment of the system, the solubility limits of certain compounds are exceeded. For example, changes in the pH, temperature, pressure and composition of an aqueous system can lead to the deposition of scale.

The formation of scale presents a problem in many industrial operations involving aqueous fluids, for instance oil and gas industry applications, mineral ore extraction, paper manufacture and geothermal power generation. In the oil and gas industry in particular, scale deposition on equipment surfaces may cause obstructions or blockages, leading to costly interruptions in production and serious safety risks from unforeseen pressure build-up. In oil and gas wells, the formation of scale is largely due to the mixing of incompatible aqueous fluids in subterranean formations. For instance, when seawater is used as an injection fluid to drive oil through a subterranean formation towards a production well, differences in the ionic content of the injected seawater and the ionic content of the connate water of the formation can lead to the precipitation of inorganic salts. The salts that may precipitate include (i) carbonate salts such as calcium carbonate ($CaCO_3$); (ii) sulfate salts such as barium sulfate ($BaSO_4$), strontium sulfate ($SrSO_4$), and calcium sulfate ($CaSO_4$); and (iii) phosphate salts such as calcium phosphate ($CaPO_4$). In the absence of suitable treatment, the precipitated salts form a scale which obstructs the flow of oil towards production wells and accumulates on production equipment, leading ultimately to the blockage of the production well.

Scale inhibitors are widely used in the oil and gas industry. Problems of scaling on equipment surfaces may be addressed by the continuous injection of scale inhibitors into the equipment. To prevent the formation of scale within oil/gas-bearing formations, two techniques are generally used. In one approach, a scale inhibitor may be included in a fluid (typically an aqueous fluid) to be injected into the formation via one or more injection wells, e,g, to flush oil towards a production well (water flooding treatment). In another approach, known as a "squeeze treatment", a fluid containing a scale inhibitor (again typically an aqueous fluid) can be introduced into a production well (after production is stopped) so as to "squeeze" the scale inhibitor into the rock formation surrounding the production well. In this way, scale inhibitors are delivered to the formation rock so as to prevent the formation of scale deposits both in the formation itself (pore blockage) and subsequently in downstream production apparatus.

Scale formation can be controlled only if a scale inhibitor is provided in sufficient quantity. In the case of "squeeze treatment", the concentration of scale inhibitor will reduce over time until a repeat treatment of the scale inhibitor is required (a "re-squeeze" treatment). It would therefore be very useful to be able to analyse the fluid produced from a production well in order to ensure that the concentration of scale inhibitor is always maintained at a level at which scale formation is sufficiently inhibited. By analysing the level of scale inhibitor in produced fluids, the depletion of scale inhibitor concentration can be monitored, and thus the need for repeat treatments of scale inhibitors can be determined. It is desirable that the level of scale inhibitors can be determined accurately, so as to avoid the need to carry out re-squeeze treatments more often than is strictly necessary, as a precautionary measure against the risk of scale deposit and consequent loss of production. Providing more scale inhibitor than is required is undesirable both due to the cost of excess scale inhibitor and due to the interruption of production that is required each time a re-squeeze treatment is carried out.

In modern oil production fields, it is increasingly common for produced fluids from a number of production wells to be combined and transported to a production facility in a single pipeline. In particular, in subsea production, it is common for the fluids from a number of production wells to be combined on the seabed, for example in a manifold, and piped to the nearest production platform, which may be many miles away. There is therefore a need for a means of analysing the level of scale inhibitor in the produced fluids

from each individual well in order to ensure that individual wells do not lose production due to scale build-up. Currently, this analysis can be done in two different ways. Firstly, by turning off the flows from all but one well, the level of scale inhibitor in the one remaining well may be determined. However, this approach is not commercially viable due to the significant loss in production entailed as each individual well is tested. Furthermore, hydraulic limitations may hinder production from a single well back to a test facility. The second approach involves using different scale inhibitors in each production well, such that the level of each may be determined by analysis of the commingled flow. However, not all scale inhibitors are equally effective and, since the number of scale inhibitors required is the same as the number of wells, a situation is rapidly reached where less than optimal scale inhibitors must be used in some wells simply to ensure that each well has a different scale inhibitor. This leads to poorer scale inhibition in certain wells and therefore a requirement for more interventions in those wells than might otherwise be the case could more effective scale inhibitors be used.

It has been proposed to prepare scale inhibiting polymers which differ from one another in that they include a small number of tagging moieties, the tagging moieties of each polymer being different from the tagging moiety of the other polymers. It is expected that, because the tagging moiety is included in the polymer in relatively small numbers, the scale inhibiting properties of the polymer will be largely unchanged from a polymer with no such tagging moieties. In this way, more than one well can be treated with an effective scale inhibitor whilst still permitting identification of the scale inhibitor in the commingled produced flow.

WO 2005/000747 discloses tagged scale inhibiting polymers, compositions comprising the tagged scale inhibiting polymers and a method of preventing or controlling scale formation in systems comprising said fluids. The tagging moieties are derived from a monomer having the formula $X_2C=CYY'$, wherein X, which is identical or different, is a hydrogen atom, or a C_1-C_4 alkyl group, Y is a hydrogen atom or a C_1-C_4 alkyl group, Y' is a group having formula –L-Arom, wherein L is a covalent bound or a divalent organic linking group optionally comprising heteroatoms, and -Arom is a group comprising at least two conjugated aromatic rings, preferably at least three, such as a naphthalene, anthracene, pyrene or phenanthrene moiety. The group -Arom may be detected by fluorimetry.

WO 2005/001241 discloses a method for stimulating an oilfield by injecting an inflow stream of a fluid into an oil producing well linked to the oilfield, displacing the oil and recovering an outflow stream of fluid comprising the oil, wherein at least two streams are injected into at least two production zones of an oil well or are injected into at least two different oil producing wells from which at least two outflow streams from the two zones or wells are combined before recovering, with a scale inhibitor having detectable moieties being introduced into the oilfield(s) and/or into the fluid, characterised in that two different scale inhibitors are used, dedicated to the two zones or wells, said different scale inhibitors having different detectable moieties (tagging moieties) that can be distinguished by analysis.

This document teaches seven groups of tagging moieties, the groups being detectable using different analytical techniques.

WO 2005/001241 also provides background information concerning the water flooding process, scale inhibiting polymers and squeeze treatments.

However, despite the above-mentioned proposals, currently there are no tagged scale inhibitors available commercially.

Further, it is not unusual to combine fluids produced from at least four different wells. Applying the teaching of WO 2005/001241 in such a situation would mean making at least four different tagged scale inhibitors, one for each of the wells. This would require the use of tagging moieties from at least two of the different groups taught therein. Since the different groups are based on different chemicals, different methods are required to prepare the tagging moieties, and thus different methods of preparing the different tagged scale inhibitors are required. This adds to the complications and therefore costs of manufacturing the tagged scale inhibitors. It would also likely be necessary to use two or more analytical techniques to detect the different tagging moieties. Accordingly, implementing the teaching of WO 2005/001241 can be complex in situations involving several wells.

Further still, there are disadvantages associated with the various tagging moieties taught in WO 2005/001241. Some of the tagging moieties must be reacted with another chemical before they can be analysed, thereby adding to the complexity of the analytical method. For other tagging moieties, the absorption/fluorescence signal of some of the tagging moieties is weak or is in the same range as background signals from other species

in the produced fluid, and so the signal cannot be identified. For instance, boron or silicon are typically present in the produced fluid in greater quantities than is proposed to be incorporated into the polymer, so the signal from the polymer cannot be distinguished from the background signal. Polymers including other tagging moieties disclosed by WO 2005/001241 are difficult to synthesise due to poor water solubility or the presence of bulky groups which would be difficult to polymerise or graft onto a polymer. Accordingly, polymers including such tagging moieties would be expensive to produce.

The present invention aims to address one or more of the above-mentioned drawbacks of the scale inhibition procedures proposed in the prior art.

In a first aspect, the present invention provides a method of controlling scale formation in an oil production operation, the method comprising the steps of:

(a) introducing an aqueous solution or dispersion of a scale inhibiting polymer comprising: (i) a plurality of polymer units including a scale inhibiting moiety, and (ii) at least one polymer unit including a tagging moiety, wherein the tagging moiety can be detected electrochemically, into an oil-bearing formation;

(b) producing oil and aqueous fluids from the oil-bearing formation;

(c) periodically or continuously measuring the concentration of scale inhibiting polymer in the produced aqueous fluids by electrochemical detection of the tagging moiety of the scale inhibiting polymer; and

(d) introducing further scale inhibiting polymer into the oil-bearing formation when the measured concentration of scale inhibiting polymer in step (c) falls below a pre-determined minimum value.

As used herein, the term "polymer unit" is used to refer to the portion of a polymeric molecule which is derived from a constituent monomer of the polymer.

The scale inhibiting polymer may have any suitable chemical backbone to which the scale inhibiting moieties and tagging moieties are attached. For instance, the backbone of the scale inhibiting polymer may suitably be selected from polyolefin, polyether, polyester, polyamide, polyimide and polyurethane chemical backbones. However, the scale inhibiting polymer preferably has a polyolefin backbone.

The plurality of scale inhibiting moieties may comprise in principle, any functional group which is capable of preventing or inhibiting scale formation, for instance by binding the metal cations that can form inorganic scales. Examples of functional groups which

provide scale inhibiting properties include carboxylic acids and salts thereof, sulfonic acids and salts thereof, phosphonic acids and salts thereof, hydroxyl groups, amide groups, nitrile groups and halogen groups, among many others which are well-known in the art. Particularly preferred scale inhibiting moieties in accordance with the present invention are carboxylic acid groups, carboxylate salts, sulfonate salts and phosphonate salts. Most preferred are carboxylic acid groups, carboxylate salts, and sulfonate salts. Preferred counterions for salts are alkali metal cations, preferably Na^+ and K^+, and NH_4^+.

The tagging moiety may comprise in principle, any chemical moiety which is capable of undergoing oxidation or reduction under an applied electrical potential so as to enable electrochemical detection of the scale inhibiting polymer.

In some embodiments, the tagging moiety may be an inorganic moiety that is capable of being oxidized or reduced at an electrode. Preferably, the inorganic moiety comprises a metal complex containing at least one metal centre which can be oxidised or reduced at an electrode and ligands coordinated to the metal centre. Preferred metal complexes include transition metal complexes. Preferably, the transition metal complex contains a transition metal selected from Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Ru, Cd and Ir, and most preferably the transition metal complex contains a transition metal selected from Ti, V, Cr, Mn, Fe, Co, Ni and Cu. Other preferred metal complexes include those containing Sn and Se.

The metal complex is preferably an organometallic complex comprising at least one organic ligand. Preferably the metal complex comprises at least one cyclic polyenyl ligand selected from cyclobutadienyl, cyclopentadienyl, cycloocta-1,5-dienyl, benzenyl, pyridyl, and bipyridylligands, which may optionally be substituted with one or more alkyl groups, such as methyl or ethyl groups. More preferably, the metal complex comprises at least one ligand selected from cyclopentadienyl, cycloocta-1,5-dienyl, and benzenyl ligands, and most preferably the metal complex comprises at least one cyclopentadienyl ligand.

The metal complex may further comprise one or more additional ligands, for instance carbonyl (CO), phosphine or amine ligands or anions. Examples of suitable phosphine and amine ligands include trimethylphosphine, triethylphosphine, triphenylphosphine, trimethylamine, triethylamine, tributylamine and diisopropylethylamine. Examples of suitable anions include halide anions, in particular, chloride,

In preferred embodiments, the metal complex may be selected from bis-η5-cyclopentadienyl iron(II) (ferrocenyl), η5-cyclopentadienyl-η6-benzenyl ruthenium(II),

bis-η5-cyclopentadienyl chromium(II), bis-η5-cyclopentadienyl cobalt(II) (cobaltocene), bis-η5-cyclopentadienyl nickel(II) (nickelocene), bis-η5-cyclopentadienyl manganese(II), bis-η6-benzenyl chromium(0), bis-η5-cyclopentadienyl titanium (IV) dichloride, cyclopentadienylcopper (I) triethylphosphine, and bis-η5-cyclopentadienyltitanium(II) (titanocene).

The metal complex may be attached to the backbone of the scale inhibiting polymer by any suitable chemical linking moiety. In a preferred embodiment, the metal complex is attached to the backbone of the scale inhibiting polymer by a linking group of the formula -X-Z-, wherein X is attached to the polymer backbone and represents a covalent bond, a C_1 to C_{10} alkylene chain, a C_6 arylene group or a C_6 to C_{10} alkylarylene group, and Z is attached to the metal complex and represents -O-, -C(O)O- or -C(O)NH-, thus enabling the metal complex to be attached to the scale inhibiting polymer by way of an ether, ester or amide bond respectively. Where Z represents an ester or amide linkage, the ester or amide linkage may be orientated in either direction.

In some embodiments, Z may be attached directly to a ring carbon atom of a cyclobutadienyl, cyclopentadienyl, cycloocta-1,5-dienyl, benzenyl, pyridyl, or bipyridyl ligand of the metal complex. Alternatively, the metal complex may comprise an alkylene chain through which it is bonded to Z. Preferably the alkylene chain has the formula $-(CH_2)_n-$, wherein n represents an integer of from 1 to 10, preferably 1 to 4, and wherein the alkylene moiety having the formula $-(CH_2)_n-$ is attached to a ring carbon atom of a cyclobutadienyl, cyclopentadienyl, cycloocta-1,5-dienyl, benzenyl, pyridyl, or bipyridyl ligand at one end and to the linking moiety Z at the other end.

Alternatively, the metal complex may be attached directly to the backbone of the scale inhibiting polymer via a simple alkylene chain, for instance having the formula $-(CH_2)_m-$, wherein m represents an integer of from 1 to 10.

In other embodiments, the tagging moiety may be an organic moiety that is capable of being oxidized or reduced at an electrode. Preferably, the tagging moiety is an organic moiety comprising at least one aromatic ring, preferably at least one benzene ring, wherein the at least one aromatic ring is substituted with two or more functional groups selected from hydroxyl, alkoxy, aryloxy, amino, thiol, phosphino, halo, formyl, acyl, alkenyl, carboxy, ester, amide, acyloxy, acylamino, nitro or azide groups.

As used herein:

the term "alkoxy" preferably refers to the group of the formula $-OR^1$ wherein R^1 represents a C_1-C_{10} alkyl group;

the term "aryloxy" preferably refers to a group having the formula $-OR^2$, wherein R^2 represents a C_6 to C_{10} aryl group or a C_6 to C_{10} alkaryl group;

the term "amino" preferably refers to $-NR^3_2$, wherein each R^3 independently represents H, a C_1-C_{10} alkyl group, a C_6-C_{10} aryl group or a C_6-C_{10} alkaryl group;

the term "phosphino" preferably refers to $-PR^3_2$, wherein R^3 is as defined above;

the term "halo" refers to -F, -Cl, -Br or -I;

the term "formyl" refers to -C(O)H;

the term "acyl" refers to $-C(O)R^1$ or $-C(O)R^2$, wherein R^1 and R^2 are as defined above;

the term "carboxy" refers to $-CO_2H$;

the term "ester" refers to $-CO_2R^1$ or $-CO_2R^2$, wherein R^1 and R^2 are as defined above;

the term "amide" refers to $-CONR^3_2$, wherein R^3 is as defined above;

the term "alkenyl" refers to $-CR^3=CR^3_2$ or $-CR^3=CR^3R^4$, wherein R^3 is as defined above and R^4 represents an acyl, carboxy or ester group as defined above.

the term "acyloxy" refers to $-OC(O)R^1$ or $-OC(O)R^2$, wherein R^1 and R^2 are as defined above; and

the term "acylamino" preferably refers to $-NHC(O)R^1$ or $-NHC(O)R^2$, wherein R^1 and R^2 are as defined above.

Preferably, the at least one aromatic ring is substituted by at least one hydroxyl or amino group.

Preferably, the at least one aromatic ring is substituted in a 1,2- or 1-4- configuration. In this way, electronic conjugation between the functional groups facilitates oxidation of the aromatic ring.

The at least one aromatic ring may optionally be fused to at least one other ring, which may be aliphatic or aromatic and is preferably aromatic. For instance, the organic moiety may contain a naphthalenic or anthracenic moiety.

In preferred embodiments, the organic moiety may be selected from: phenols, hydroquinones, aromatic amines, aromatic thiols, and aromatic nitros.

Examples of suitable tagging moieties in this category include:

(i) diphenol groups, for instance a benzene-1,2-diol group, a benzene-1,4-diol group, naphthalene-1,4-diol, naphthalene-1,2-diol, anthracene-9,10-diol;

(ii) aminophenol groups, for instance a 4-aminophenol group;

(iii) acetaminophenol groups, for instance a 4-acetaminophenol (paracetamol) group;

(iv) phenolic aldehyde or phenolic ketone groups, such as a vanillyl group;

(v) hydroxybenzoic acids and esters thereof, for instance a 2-hydroxybenzoic acid group or a 4-hydroxybenzoic acid group;

(vi) aminobenzoic acids and esters thereof, for instance anthranilic acid (2-aminobenzoic acid) or 4-aminobenzoic acid; and

(vii) β-(hydroxyphenyl)acrylic acids and esters thereof, for instance β-(4-hydroxyphenyl)acrylic acid (coumaric acid).

Particularly preferred organic moieties in this category are diphenol groups and aminophenol groups.

In another preferred embodiment, the organic moiety may comprise an oxidisable or reducible heterocyclic moiety, such as a phenothiazine, an indole, an ascorbic acid group, or a 4,4-bipyridinium dication, for instance N,N'-dimethyl-4,4'-bipyridinium cations (e.g. as the dichloride salt).

In further embodiments, the organic moiety may be an aromatic or aliphatic organic moiety comprising an oxidisable or reducible functional group, such as a peroxide group, a thioamide group, a nitrosamide group, a nitro group, or an azide group. For example, the organic moiety may comprise an azobenzene moiety (-(C_6H_4)-N=N-Ph).

The organic moiety may be attached to the backbone of the scale inhibiting polymer by any suitable chemical linking moiety.

In a preferred embodiment, the backbone of the scale inhibiting polymer may be substituted with a linking group of the formula -X-Z-, wherein X is attached to the polymer backbone and represents a covalent bond, a C_1 to C_{10} alkylene chain, a C_6 arylene group or a C_6 to C_{10} alkylarylene group, and Z is attached to the organic moiety and represents -O-, -C(O)O- or -C(O)NH-. In this way, the organic moiety may be attached to the scale inhibiting polymer by way of an ether, ester or amide bond respectively. Where Z represents an ester or amide linkage, the ester or amide linkage may be orientated in either direction.

In some embodiments, Z may be attached directly to an aromatic ring of the organic moiety. In such cases, Z may form an alkoxy, acyloxy, ester, acylamino or amide substituent of the aromatic ring as specified above. Alternatively, the organic moiety may comprise an exocyclic alkylene chain through which it is bonded to Z. Preferably the alkylene chain has the formula $-(CH_2)_n-$, wherein n represents an integer of from 1 to 10, preferably 1 to 4, and wherein the alkylene moiety having the formula $-(CH_2)_n-$ is attached to an aromatic ring of the organic moiety.

In a further alternative, where the organic moiety comprises an aromatic ring which is substituted with a group selected from amino, phosphino, acyl, or alkenyl, the organic moiety may be bonded to the backbone of the scale inhibiting polymer or to Z, via an alkyl, aryl or alkylaryl portion of said substituents (i.e. via the alkylene, arylene or alkylarylene analogs of groups R^1 to R^3 as defined above).

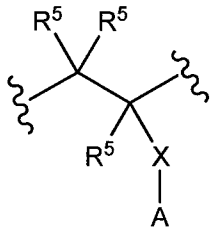
In some instances, the oxidation or reduction of the tagging moieties described above is reversible. In such instances, the tagging moieties suitable for use according to the present invention shall be taken to include the redox counterparts of the tagging moieties described above. For instance, a benzene-1,4-diol (hydroquinone) moiety is reversibly oxidisable to a 1,4-quinone moiety.

The scale inhibiting polymer is preferably a polyolefin obtained by the addition polymerisation of a plurality of olefinically unsaturated monomer units. Preferably the scale inhibiting polymer comprises (i) a plurality of polymer units including a scale inhibiting moiety, and (ii) at least one polymer unit including at least one tagging moiety as defined above. Preferably the ratio of polymer units of type (i) to polymer units of type (ii) is at least 2:1, more preferably at least 5:1. Preferably the ratio of polymer units of type (i) to polymer units of type (ii) is less than 1000:1. Thus, in preferred embodiments of the invention, the ratio of polymer units of type (i) to polymer units of type (ii) is preferably in the range of from 2:1 to 500:1, more preferably from 5:1 to 200:1, still more preferably from 10:1 to 100:1, still more preferably from 20:1 to 100:1, and most preferably from 40:1 to 70:1.

The scale inhibiting polymer may be a random, block, or alternating copolymer.

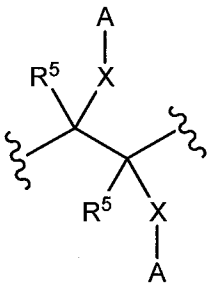
Polymer units of type (i) which form the scale inhibiting polymers are preferably obtained by the polymerisation of olefinically unsaturated monomers bearing one or more carboxylate, sulfonate, phosphonate, amide, hydroxyl, nitrile and halogen groups, or a

precursor of such a group. Preferably, at least a portion of the polymer units of type (i) have the general formula:

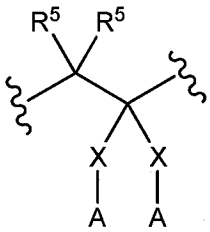


wherein each R^5 is independently selected from hydrogen, or a C_1 to C_4 alkyl group; X represents a covalent bond, a C_1 to C_{10} alkylene chain, a C_6 arylene group or a C_6 to C_{10} alkylarylene group; and A represents a group selected from $-CO_2H$, $-CO_2^-M^+$, $-CO_2R^6$, $-CONH_2$, $-CONR^6_2$, $-SO_3H$, $-SO_3^-M^+$, $-PO_3H_2$, $-PO_3^{2-}M^{2+}$, -CN, -Cl, -Br, -I, and -OH; wherein each R^6 independently represents a C_1 to C_4 alkyl group, optionally substituted by one or more of -CN, -F, -Cl, -Br, -I, and -OH, or wherein two adjacent carbon atoms of said C_1 to C_4 alkyl group together with an oxygen atom to form a three-membered cyclic ether (oxirane), and wherein M^+ and M^{2+} represent any suitable cation or combination of cations that provides charge balance. For instance, M^+ may be Li^+, Na^+, K^+ or NH_4^+. Preferably X represents a C_1 to C_4 alkylene chain. Preferably, at least one R^5 is H. More preferably, each R^5 is H.

Also in accordance with the present invention, the scale inhibiting polymer may comprise polymer units derived from an olefinic monomer bearing two functional groups. Thus, the scale inhibiting polymer may also include polymer units of type (i) having the general formula:



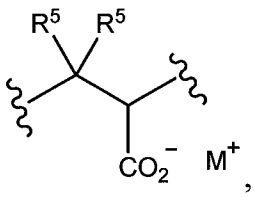
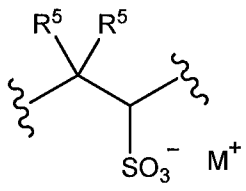
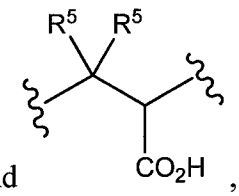
or the general formula:



wherein each R^5, each X and each A is independently as defined above.

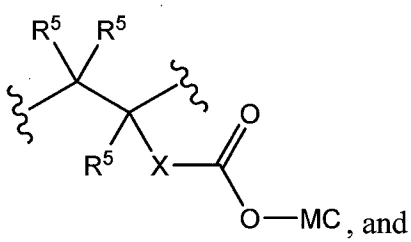
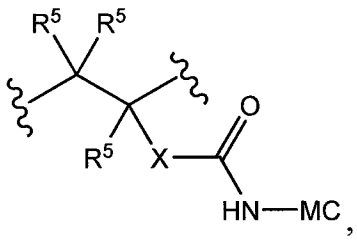
Examples of olefinically unsaturated monomers from which the polymer units of type (i) may be obtained include: vinyl sulfonates, allyl sulfonates, styrene sulphonates, vinyl phosphonates, methyl methacrylate, ethyl methacrylate, propyl methacrylate (all isomers), butyl methacrylate (all isomers), methyl acrylate, ethyl acrylate, propyl acrylate (all isomers), butyl acrylate (all isomers), alkyl acrylates (alkyl = C_nH_{2n+1}) alkyl methacrylates. Other suitable monomers include functionalised methacrylates and acrylates including glycidyl methacrylate, trimethoxysilyl propyl methacrylate, allyl methacrylate, hydroxyethyl methacrylate, hydroxypropyl methacrylate, dialkylaminoalkyl methacrylates, fluoroalkyl(meth)acrylates, methacrylic acid, acrylic acid, fumaric acid (and esters), itaconic acid (and esters), maleic anhydride, styrene, α-methyl styrene, vinyl halides such as vinyl chloride and vinyl fluoride, acrylonitrile, methacrylonitrile, acrylamide and methacrylamide.

In particularly preferred embodiments, the polymer units of type (i) may be selected from:

, , and ,

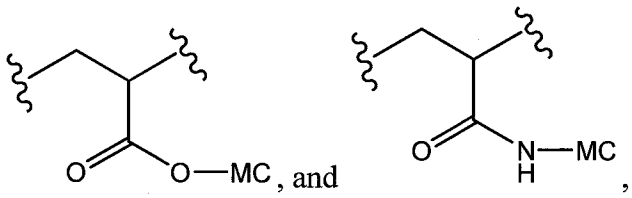
wherein R^5 and M^+ are as defined above. Preferably at least one R^5 is H, and more preferably each R^5 is H. M^+ is preferably Na^+.

Where the tagging moiety is a metal complex, the polymer unit of type (ii) preferably has a formula selected from:

, and ,

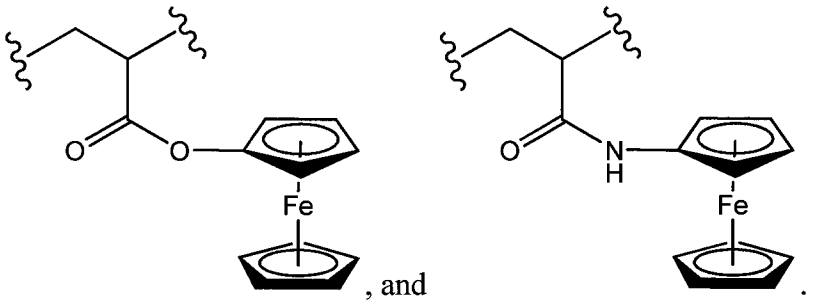
wherein R^5 and X are as defined above, and MC represent the metal complex. Preferably, at least one R^5 is H. More preferably, each R^5 is H.

More preferably the polymer unit of type (ii) has a formula selected from:

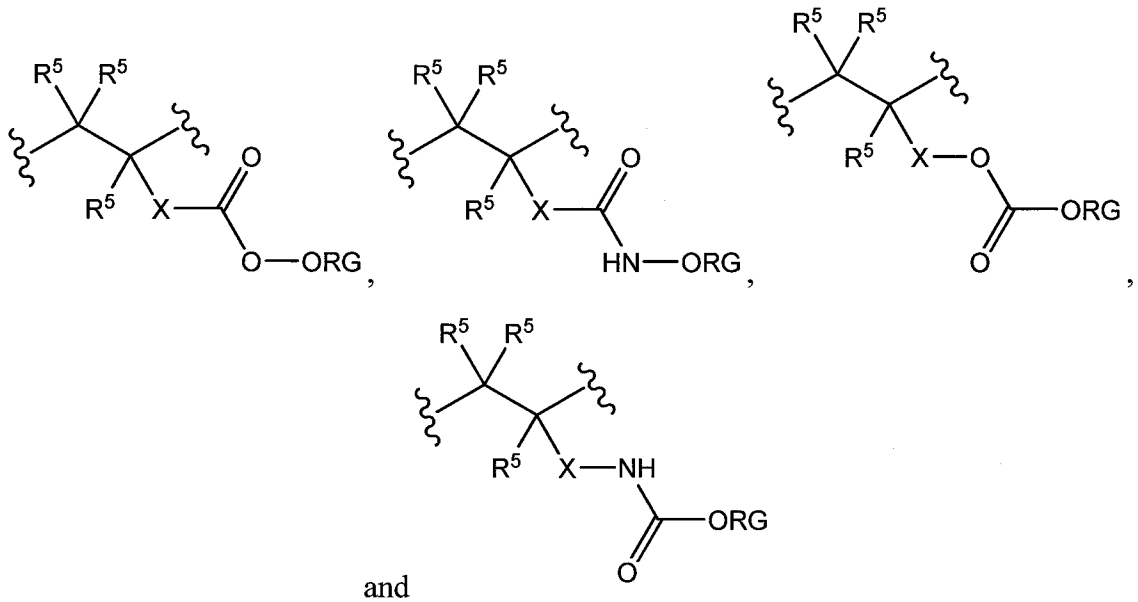


wherein MC represents the metal complex, optionally including an alkylene linking group.

Still more preferably, the polymer unit of type (ii) has a formula selected from:



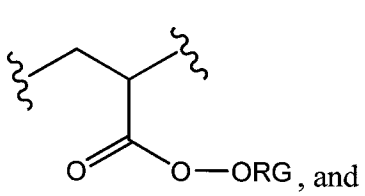
Where the tagging moiety is an organic moiety, the polymer unit of type (ii) preferably has a formula selected from:



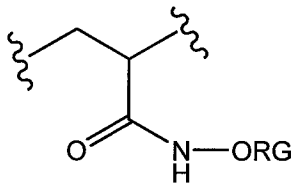
and

wherein R^5 and X are as defined above, and ORG represent the organic moiety, optionally including an alkylene linking group. Preferably, at least one R^5 is H. More preferably, each R^5 is H.

More preferably the polymer unit of type (ii) has a formula selected from:



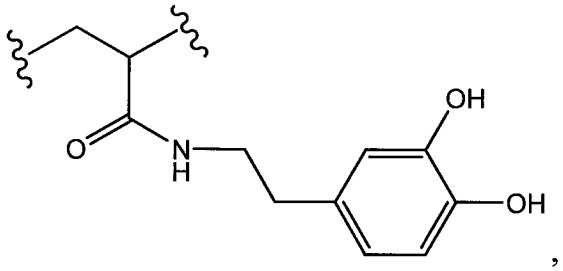
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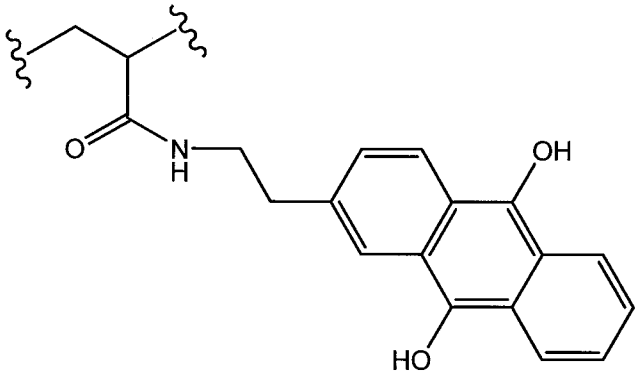
,

wherein ORG represent the organic moiety, optionally including an alkylene linking group.

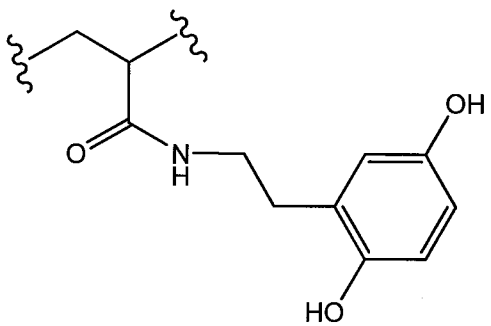
Non-limiting examples of suitable polymer units of type (ii) in accordance with the present invention include:



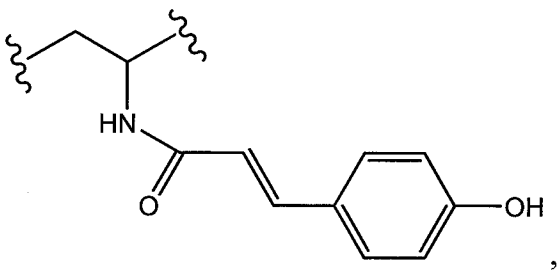
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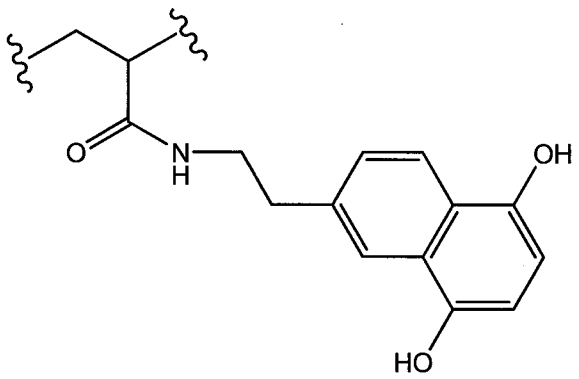
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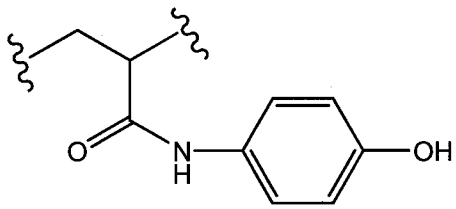
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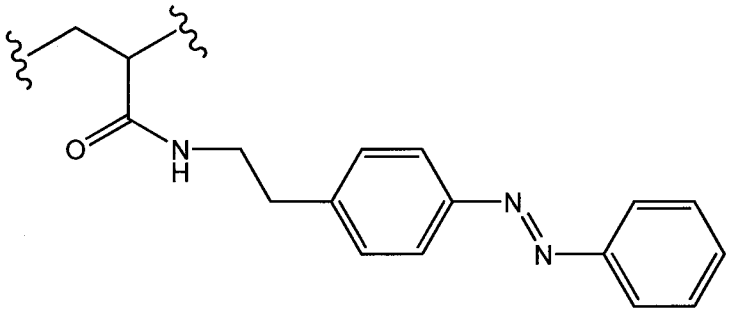
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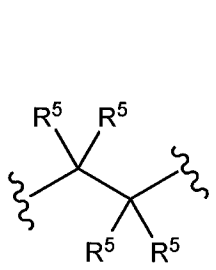


, and

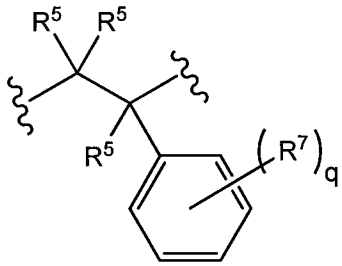


.

In accordance with the present invention, the polymer backbone may comprise additional polymer units, such as non-functionalised polymer units derived from ethylene or other unsubstituted olefins (e.g. propene, isobutene, butadiene, or styrene). For instance, the non-functionalised polymer units may have a formula selected from:



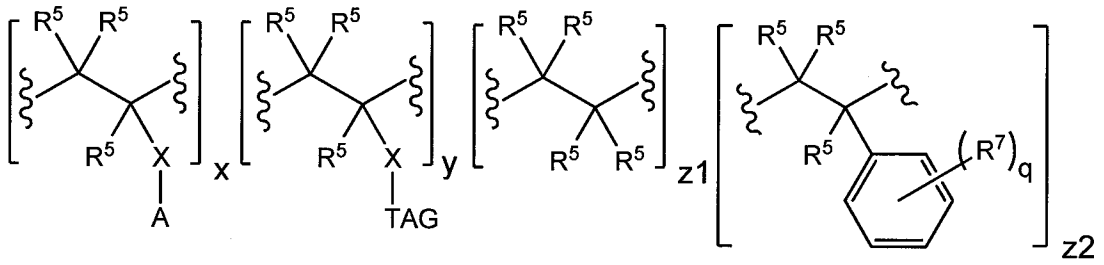
and



wherein each R^5 is independently as defined above, R^7 represents a C_1-C_4 alkyl group, and q is an integer of from 0 to 5. Preferably, at least one R^5 is H. More preferably, each R^5 is H. Preferably, q is an integer of from 0 to 2, more preferably q is 0 or 1, and most preferably q is 0. Where present, R^7 is preferably methyl or ethyl.

The polymer may further comprise end-capping groups (preferably H) or other end groups resulting from a polymerisation initiator.

Preferred scale inhibiting polymers may be represented by the empirical formula:



wherein R^5, X and A are as defined above, and each A may be the same or different, TAG represents the tagging moiety as described above, and x, y, z1 and z2 are integers defining the stoichiometric amounts of each polymer unit in the scale inhibiting polymer. As noted above, the ratio of x:y is preferably at least 2:1, and more preferably at least 5:1. Preferably the ratio x:y is less than 1000:1. In particularly preferred embodiments of the invention, the ratio of x:y is preferably in the range of from 2:1 to 500:1, more preferably from 5:1 to 200:1, still more preferably from 10:1 to 100:1, still more preferably from 20:1 to 100:1, and most preferably from 40:1 to 70:1.

Preferably each TAG is the same.

The ratio of x:(z1+z2) is preferably in the range of from 1:0 to 1:2, more preferably in the range from 1:0 to 1:1, more preferably in the range from 1:0 to 1:0.5, and most preferably in the range of from 1:0 to 1:0.2.

Preferably z2 is 0.

The scale inhibiting polymers preferably have a weight average molecular weight in the range of from 1000 to 100,000 g/mol, more preferably from 1000 to 50,000, g/mol, still more preferably from 2000 to 20,000 g/mol and most preferably from 5,000 to 15,000 g/mol or from 10,000 to 20,000 g/mol. The weight average molecular weight of the polymer can be determined by known techniques, for instance size exclusion chromatography.

The scale inhibiting polymer may be dissolved or dispersed in any suitable aqueous fluid, for instance brine (e.g. seawater) or aqueous fluids produced from the oil-bearing formation.

In accordance with this aspect of the invention, the scale inhibiting polymer may be introduced in the oil-bearing formation by shutting in a production oil well and introducing the scale inhibitor via the production well so as to "squeeze" the scale inhibitor into the rock formation surrounding the production well. Alternatively, the scale inhibiting

polymer may be introduced via an injection well as part of an injection fluid used to flush oil towards a production well (water flooding treatment).

In a preferred embodiment, the method of the invention comprises the steps of:

(a1) introducing a solution or dispersion of a first scale inhibiting polymer as defined above in an aqueous fluid into a first oil-bearing formation;

(a2) introducing a solution or dispersion of a second scale inhibiting polymer as defined above in an aqueous fluid into a second oil-bearing formation, wherein the first and second scale inhibiting polymers comprise different tagging moieties;

(b) co-producing oil and aqueous fluids from the first and second oil-bearing formations as a combined stream;

(c) periodically or continuously measuring the concentration of the first and second scale inhibiting polymers in the co-produced aqueous fluids by electrochemical detection of the tagging moieties of the first and second scale inhibiting polymers;

(d1) introducing further first scale inhibiting polymer into the first oil-bearing formation when the measured concentration of the first scale inhibiting polymer in step (c) falls below a pre-determined minimum value; and

(d2) introducing further second scale inhibiting polymer into the second oil-bearing formation when the measured concentration of the second scale inhibiting polymer in step (c) falls below a pre-determined minimum value.

In accordance with this aspect of the invention, the terms "first oil-bearing formation" and "second oil-bearing formation" may relate to different oil-bearing formations or to different regions within a single oil-bearing formation.

The present inventors have found that the method of the invention provides a significant benefit over known methods for detecting scale inhibitors, since the use of electrochemical detection enables the concentration of scale inhibitor to be determined with a high degree of accuracy and down to very low detection limits. Furthermore, the electrochemical detection of tagged scale inhibitors does not suffer from interfering signals from other components of the produced aqueous fluids, in particular from dissolved salts. Furthermore, the use of a number of different tagging moieties having different redox potentials provides an effective solution to the problem of determining levels of scale inhibitors in multiple wells from a combined production stream. The methods of the

present invention enable different tagged scale inhibitors to be individually identified and quantified with a high degree of accuracy.

The electrochemical detection of the tagged polymer in step (c) may be carried out using a potential sweep or step electrochemical technique. When a stream of a solution passes across an electrode and the electrode is swept or held at a potential within a predetermined range (referred to herein as the solvent window) in which the molecules in the solution are non-electroactive, the current measured is called the background current. When a molecule which is electroactive within the solvent window, such as a polymer having an electroactive tag, is introduced into the solution and the electrode is swept or held at a potential greater than that required for a redox transformation of the molecule to take place (more positive for oxidation, more negative for reduction), the measured current is greater than the background current. By plotting current against potential, the presence of different electrochemical tags can be identified by changes in current at characteristic potentials.

In a preferred embodiment, the electrochemical detection step of the present invention uses a carbon-based band electrode with low background currents within a hydrodynamically well defined laminar flow cell in order to achieve high detection sensitivities. Still more preferably, the electrode material used is a single walled carbon nanotube (SWNT) network electrode. Electrodes of this type have been found to provide detection sensitivities in the nanomolar range. The electrochemical detection may be coupled with flow injection analysis (FIA) to further improve the response and experimental timescale.

In further preferred embodiments of the present invention, the electrochemical detection of the scale inhibiting polymers may be carried out by continuously passing a side-stream of aqueous fluids produced from one or more oil-bearing formation(s) to a continuous flow electrochemical cell.

In another aspect, the present invention provides a scale inhibiting polymer as defined above, wherein the tagging moiety is selected from:

(a) an inorganic moiety comprising a metal complex containing at least one metal centre which can be oxidised or reduced;

(b) an organic moiety comprising at least one aromatic ring, wherein the at least one aromatic ring is substituted with two or more functional groups selected from

hydroxyl, alkoxy, aryloxy, amino, thiol, phosphino, halo, formyl, acyl, alkenyl, carboxy, ester, amide, acyloxy, acylamino, nitro or azide groups;

(c) an organic moiety comprising an oxidisable or reducible heterocyclic group, selected from a phenothiazine group, an indole group, an ascorbic acid group, or a 4,4-bipyridinium dication group; or

(d) an organic moiety comprising an oxidisable or reducible functional group selected from a peroxide group, a thioamide group, a nitrosamide group, a nitro group, or an azide group.

In a further aspect, the present invention provides scale inhibiting compositions comprising a suspension or solution of a scale inhibiting polymer as defined above in a fluid, wherein the tagging moiety of the scale inhibiting polymer is selected from:

(a) an inorganic moiety comprising a metal complex containing at least one metal centre which can be oxidised or reduced;

(b) an organic moiety comprising at least one aromatic ring, wherein the at least one aromatic ring is substituted with two or more functional groups selected from hydroxyl, alkoxy, aryloxy, amino, thiol, phosphino, halo, formyl, acyl, alkenyl, carboxy, ester, amide, acyloxy, acylamino, nitro or azide groups;

(c) an organic moiety comprising an oxidisable or reducible heteroaromatic group, selected from a phenothiazine group, an indole group, or a 4,4-bipyridinium dication group; or

(d) an organic moiety comprising an oxidisable or reducible functional group selected from a peroxide group, a thioamide group, a nitrosamide group, a nitro group, or an azide group.

In a preferred embodiment, the fluid is an aqueous fluid, such as water or brine. In the context of oil or gas production operations, it will be appreciated that the fluid is intended as a carrier medium to transport the scale inhibiting polymer to the oil-bearing formation during a "squeeze" treatment. Alternatively, in a water-flooding operation, the composition comprising a scale inhibiting polymer of the invention may be used as an injection fluid.

In a further aspect, the present invention provides a method of preparing a scale inhibiting polymer as defined above, the method comprising copolymerising (i) at least one olefinically unsaturated monomer including at least one scale inhibiting group and (ii) an

olefinically unsaturated monomer including a tagging moiety, wherein the tagging moiety is selected from:

(a) an inorganic moiety comprising a metal complex containing at least one metal centre which can be oxidised or reduced;

(b) an organic moiety comprising at least one aromatic ring, wherein the at least one aromatic ring is substituted with two or more functional groups selected from hydroxyl, alkoxy, aryloxy, amino, thiol, phosphino, halo, formyl, acyl, alkenyl, carboxy, ester, amide, acyloxy, acylamino, nitro or azide groups;

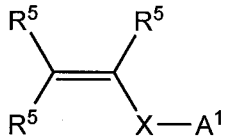
(c) an organic moiety comprising an oxidisable or reducible heteroaromatic group, selected from a phenothiazine group, an indole group, or a 4,4-bipyridinium dication group; or

(d) an organic moiety comprising an oxidisable or reducible functional group selected from a peroxide group, a thioamide group, a nitrosamide group, a nitro group, or an azide group.

Preferably the ratio of monomers of type (i) to monomers of type (ii) is at least 2:1, more preferably at least 5:1. Preferably the ratio of monomers of type (i) to monomers of type (ii) is less than 1000:1. Thus, in preferred embodiments of the invention, the ratio of monomers of type (i) to monomers of type (ii) is preferably in the range of from 2:1 to 500:1, more preferably from 5:1 to 200:1, still more preferably from 10:1 to 100:1, still more preferably from 20:1 to 100:1, and most preferably from 40:1 to 70:1.

Preferably, the monomers of type (i) may include monomers selected from olefinically unsaturated monomers bearing one or more carbonate, sulfonate, phosphonate, hydroxyl, amide, nitrile, halogen groups or a precursor of such a group.

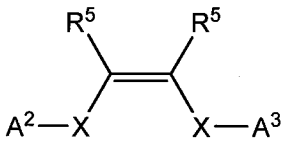
Preferably, the monomer units of type (i) may include monomers having the general formula:



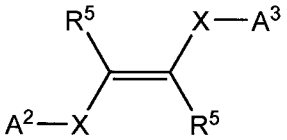
wherein R^5 and X are as defined above, and A^1 represents a group selected from $-CO_2H$, $-CO_2^-M^+$, $-CO_2R^4$, $-CONH_2$, $-CONR^4_2$, $-SO_3H$, $-SO_3^-M^+$, $-PO_3H_2$, $-PO_3^{2-}M^{2+}$, -CN, -Cl, -Br, -I, and -OC(O)Me, wherein M^+ and R^4 are as defined above.

For the avoidance of doubt, olefinic monomer units are depicted herein as both the *cis*- and *trans*- isomers. Where an olefinic monomer may exist as *cis*- and *trans*- isomers, either or both may be used to prepare the scale inhibiting polymers of the invention.

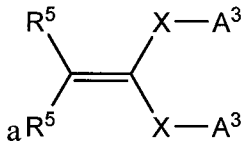
Alternatively, or in addition, the monomer units of type (i) may include monomers having the general formula:



or the general formula:



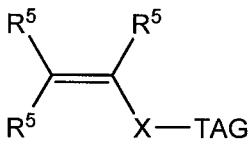
or the general formula:



wherein R^1, R^3, and X are as defined above, and A^1 and A^2 each independently represent a group selected from $-CO_2H$, $-CO_2^-M^+$, $-CO_2R^6$, $-CONH_2$, $-CONR^6{}_2$, $-SO_3H$, $-SO_3^-M^+$, $-PO_3H_2$, $-PO_3^{2-}M^{2+}$, -CN, -Cl, -Br, -I, and -OC(O)Me, wherein M^+ and R^6 are as defined above, or A^2 and A^3 may together form an anhydride group of the formula -C(O)-O-(O)C-.

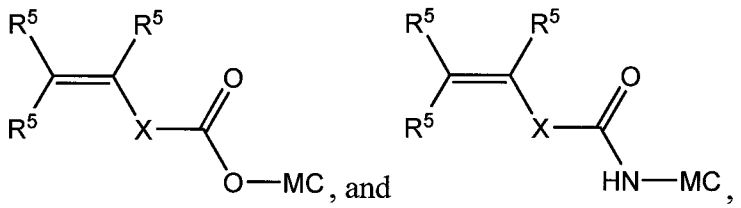
Examples of suitable olefinically unsaturated monomers of type (i) are provided above.

The monomer of type (ii) preferably has the formula:



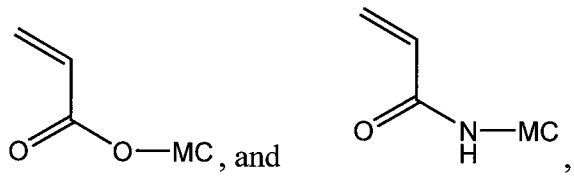
wherein R^5 and X are as defined above, and TAG represents a tagging moiety which is capable of undergoing an oxidation or reduction reaction under an applied electrical potential.

Preferred monomers of type (ii) include:



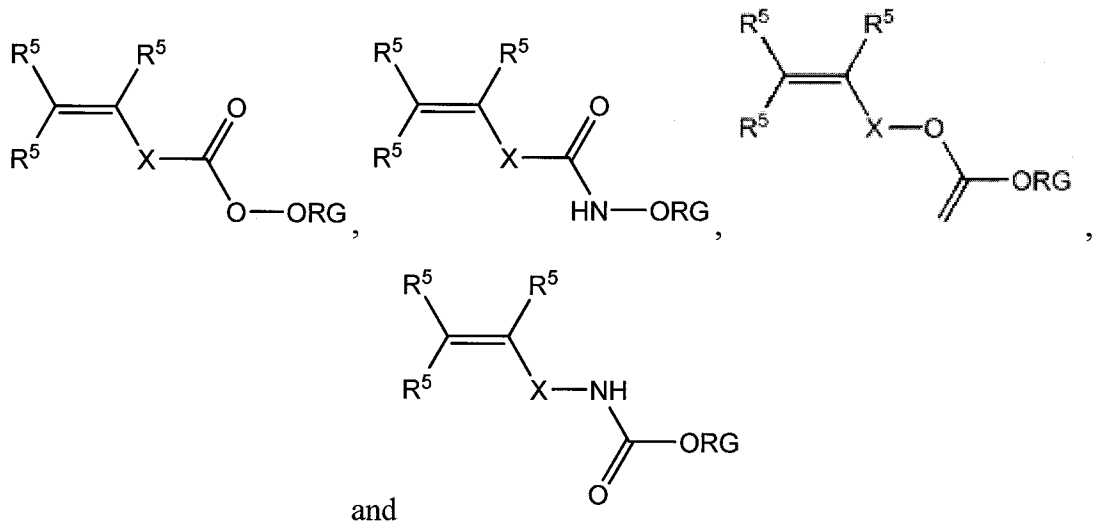
wherein R^5 and X are as defined above, and MC represents a metal complex as defined above.

More preferably the monomer of type (ii) has a formula selected from:



wherein MC represents the metal complex.

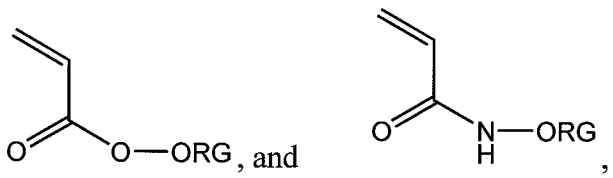
Further preferred monomers of type (ii) include:



and

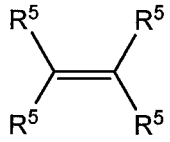
wherein R^5, X and ORG are as defined above.

More preferably the monomer unit of type (ii) has a formula selected from:

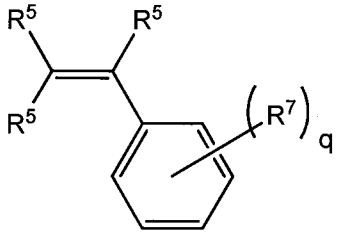


wherein ORG is as defined above.

In accordance with this aspect of the invention, the method of the invention may further comprise copolymerising (iii) at least one monomer of the formula:



or the formula:



wherein R^5, R^7 and q are as defined above.

It will be appreciated that methods of polymerising olefinically unsaturated compounds are well-known to persons of skill in the art. The scale inhibiting polymers of the present invention may be formed using any appropriate method of polymerising olefinically unsaturated compounds.

The polymerisation reaction may take place with or without the presence of a solvent. Suitable solvents include water, and organic solvents including propionitrile, hexane, heptane, dimethoxyethane, diethoxyethane, tetrahydrofuran, ethyl acetate, *N,N*-dimethylformamide, anisole, acetonitrile, diphenylether, methylisobutyrate, butan-2-one, water, alcohols (e.g. methanol, ethanol, isopropanol), acetone, DMSO, DMF, NMP, xylene(s) and toluene. Especially preferred solvents are xylene(s) and toluene. The concentration of solvents is preferably at least 10% by weight.

The reaction may be carried out in solution, bulk, suspension, emulsion, mini-emulsion or in a dispersion.

Optionally, the polymerisation reaction may be carried out under an inert atmosphere such as nitrogen or argon.

The scale inhibiting polymers of the present invention can be incorporated into scale inhibiting treatments in any manner known in the art for conventional scale inhibiting polymers.

The invention will now be illustrated with reference to the following Examples and the accompanying Figures, in which:

Figure 1 shows a schematic view of an electrochemical channel flow cell used for electrochemical detection of tagged polymers. Figures 2 to 6 show the detector response

during the detection of electrochemically tagged polymers according to the present invention. Current is plotted as a function of time.

Figures 7 to 10 are plots of mean peak height vs. concentration of electrochemically tagged polymers corresponding to Figures 2 to 5, respectively.

Examples

Example 1 - Electrochemical Detection Cell

The electrochemical cell used in the following Examples is represented schematically in Figure 1. The cell consists of a planar surface (1) that contains the working electrode (2), and a one piece flow unit (3) positioned on top of the surface (1) defining a flow channel (4) having an inlet (5) and outlet (6). The flow unit was fabricated using microstereolithography (MSL) [Snowden et al, Anal. Chem. 2010, 82, 3124] and has a channel width of 4 mm, a length of 6 mm, and a height ($2h$) of 50 μm. The channel flow unit and planar electrode substrate are held together tightly and can withstand high flow rates (> 2 mL min^{-1}) without leaking. This set-up was used to study the electroactive tagged polymers in a continuous flow regime or in a flow injection analysis (FIA) arrangement. In the latter method, the tagged polymer was injected in μL volumes (dependent on the injection loop used; herein 50 μL) in a continuous stream of non-electroactive mobile phase (0.1 M KNO_3) at a flow rate of 1.0 mL min^{-1}.

Two different working electrodes were employed herein to oxidise the electroactive tags under investigation: (a) a lithographically fabricated gold (Au) band electrode with a width defined by the width of the channel (4 mm) and a thickness (x_e) of 0.3 mm; and (b) a single walled nanotube (SWNT) network band electrode (1.5 mm wide, 0.5 mm thick) defined by an S1818 photoresist mask. To complete the electrochemical cell, a platinum counter electrode (not shown) and a quasi-reference electrode (Ag|AgCl wire, also not shown) were positioned downstream of the working electrode. Electrochemical measurements were carried out with a portable Ivium potentiostat (CompactStat, Alvatek Ltd, UK) which was operated in either a potential sweep or potential step mode.

Example 2 - Electrochemical Testing

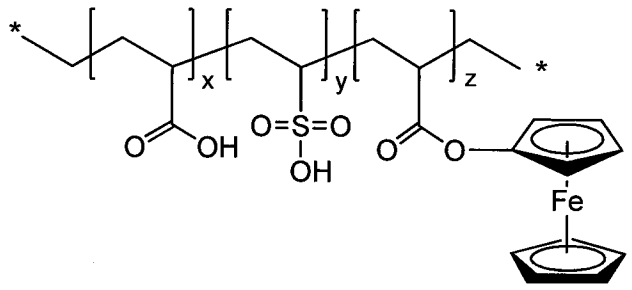
A series of stock solutions containing 1000 ppm (mg L^{-1} weight) of the following polymers were used in 0.1 M KNO_3 supporting electrolyte:

(A) polyacrylic acid (PAA) polymer;

(B) acrylic acid & vinyl sulfonic acid co-polymer (PAA_x-$PVSA_y$);

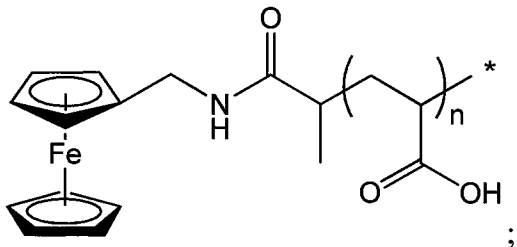
(C) polyethylene glycol (PEG);

(D) a co-polymer of acrylic acid, vinyl sulfonic acid (PSVA), and ferrocene carboxylic acid electroactive tag(s) – scale inhibitor-like polymer (PAA_x-$PVSA_y$-$FcCOO_z$):



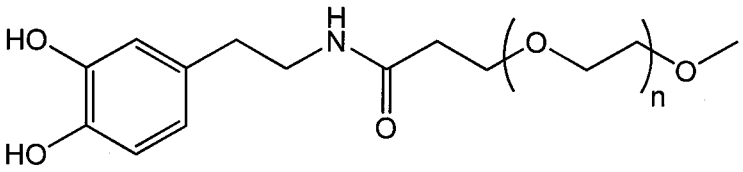
;

(E) PAA-polymer containing a single ferrocene-methylamidecarbonyl ($FcCH_2NHCO$-) electroactive tag ($FcCH_2NHCO$-PAA):



; and

(F) PEG-polymer containing a single dopamine electroactive tag (Dop-PEG).



Polymer stock solutions were subsequently diluted and tested in order to access the current measured by the electrode with respect to varying tagged and untagged (controls) polymer concentrations. Samples (A - C) did not contain an electroactive tag. They were injected in the system as controls (blank sample) in order to derive the limits of detection (L.O.D.s; 3x s_b) of each polymer using the described setup.

FIA electrochemical detection signal ($E_{applied}$ = 0.4 V) using a Au microband electrode for 5x repeated injections of 100 ppm PAA_x-$PVSA_y$ and 100 ppm PAA_x-$PVSA_y$-$FcCOO_z$ in 0.1 M KNO_3 mobile phase is shown in Figure 2.

FIA electrochemical detection signal ($E_{applied}$ = 0.4 V) using a CNT microband electrode for 5x repeated injections of 0.5 ppm PAA_x-$PVSA_y$-$FcCOO_z$ in 0.1 M KNO_3 mobile phase is shown in Figure 3.

FIA electrochemical detection signal ($E_{applied}$ = 0.6 V) using a CNT microband electrode for 5x repeated injections of 250 ppm and 100 ppm $FcCH_2NHCO$-PAA in 0.1 M KNO_3 mobile phase is shown in Figure 4.

FIA electrochemical detection signal ($E_{applied}$ = 0.6 V) using a CNT microband electrode for 4x repeated injections of 1 ppm $FcCH_2NHCO$-PAA in 0.1 M KNO_3 mobile phase is shown in Figure 5.

FIA electrochemical detection signal ($E_{applied}$ = 0.65 V) using a CNT microband electrode for 7x repeated injections of 100 ppm Dop-PEG in 10 mM phosphate buffer saline mobile phase is shown in Figure 6.

A plot of mean peak height vs. concentration of PAA_x-$PVSA_y$-$FcCOO_z$ polymer (Sensitivity = 0.2 pA ppm^{-1}; L.O.D. = 9.1 ppm) is shown in Figure 7.

A plot of mean peak height vs. concentration of PAA_x-$PVSA_y$-$FcCOO_z$ polymer (Sensitivity = 30 pA ppm^{-1}; L.O.D. = 0.3 ppm) is shown in Figure 8.

A plot of mean peak height vs. concentration of $FcCH_2NHCO$-PAA polymer (Sensitivity = 4.2 pA ppm^{-1}; L.O.D. = 0.85 ppm) is shown in Figure 9.

A plot of mean peak height vs. concentration of Dop-PEG polymer (Sensitivity = 30 pA ppm^{-1}; L.O.D. = 0.3 ppm) is shown in Figure 10.

Sensitivity and Limit of Detection Results for each of polymers D, E and F using a single walled carbon nanotube network electrode are summarised in Table 1.

Table 1

Polymer	Sensitivity ($pA \cdot ppm^{-1}$)	Limit of detection (ppm)
D (PAA_x-$PVSA_y$-$FcCOO_z$)	30	0.3
E ($FcCH_2NHCO$-PAA)	4.2	0.85
F (Dop-PEG)	6.3	0.9

CLAIMS

1. A method of controlling scale formation in an oil production operation, the method comprising the steps of:

(a) introducing a solution or dispersion of a scale inhibiting polymer comprising: (i) a plurality of polymer units including a scale inhibiting moiety, and (ii) at least one polymer unit including a tagging moiety, wherein the tagging moiety can be detected electrochemically, into an oil-bearing formation;

(b) producing oil and aqueous fluids from the oil-bearing formation;

(c) periodically or continuously measuring the concentration of scale inhibiting polymer in the produced aqueous fluids by electrochemical detection of the tagging moiety of the scale inhibiting polymer; and

(d) introducing further scale inhibiting polymer into the oil-bearing formation when the measured concentration of scale inhibiting polymer in step (c) falls below a pre-determined minimum value.

2. A method according to Claim 1, wherein the scale inhibiting moieties of the scale inhibiting polymer comprise one or more functional groups selected from carboxylic acids and salts thereof, sulfonic acids and salts thereof, phosphonic acids and salts thereof, hydroxyl groups, amide groups, nitrile groups and halogen groups.

3. A method according to Claim 1 or Claim 2, wherein the tagging moiety is an inorganic moiety comprising a metal complex containing at least one metal centre which can be oxidised or reduced.

4. A method according to Claim 3, wherein the metal complex is a transition metal complex.

5. A method according to Claim 4, wherein the transition metal complex contains a transition metal selected from Ti, V, Cr, Fe, Co, Ni, Cu, Ru, Cd and Ir.

6. A method according to Claim 3, wherein the metal complex comprises at least one metal selected from Sn and Se.

7. A method according to any one of Claims 3 to 6, wherein the metal complex is an organometallic complex comprising at least one organic ligand.

8. A method according to Claim 7, wherein the organometallic complex comprises at least one organic ligand selected from cyclobutadienyl, cyclopentadienyl, cycloocta-1,5-dienyl, benzenyl, pyridyl and bipyridyl.

9. A method according to Claim 8, wherein the organometallic complex is selected from bis-η5-cyclopentadienyl iron(II) (ferrocenyl), η5-cyclopentadienyl-η6-benzenyl ruthenium(II), bis-η5-cyclopentadienyl chromium(II), bis-η5-cyclopentadienyl cobalt(II) (cobaltocene), bis-η5-cyclopentadienyl nickel(II) (nickelocene), bis-η5-cyclopentadienyl manganese(II), bis-η6-benzenyl chromium(0), bis-η5-cyclopentadienyl titanium (IV) dichloride, cyclopentadienylcopper (I) triethylphosphine, and bis-η5-cyclopentadienyltitanium(II) (titanocenyl).

10. A method according to Claim 1 or Claim 2, wherein the tagging moiety is an organic moiety that can be oxidised or reduced at an electrode.

11. A method according to Claim 10, wherein the organic moiety comprises at least one aromatic ring, preferably at least one benzene ring, wherein the at least one aromatic ring is substituted with two or more functional groups selected from hydroxyl, alkoxy, aryloxy, amino, thiol, phosphino, halo, formyl, acyl, alkenyl, carboxy, ester, amide, acyloxy, acylamino, nitro or azide groups.

12. A method according to Claim 11, wherein the organic moiety is selected from diphenol groups, aminophenol groups, acetaminophenol groups, phenolic aldehyde groups, phenolic ketone groups, hydroxybenzoic acid groups, aminobenzoic acids, azidobenzenes, and β-(hydroxyphenyl)acrylic acids.

13. A method according to Claim 12, wherein the organic moiety is selected from a benzene-1,2-diol group, a benzene-1,4-diol group, a naphthalene-1,2-diol group, a naphthalene-1,4-diol group, an anthracene-9,10-diol group, a 4-aminophenol group, a 4-acetaminophenol group; a vanillyl group; a 2-hydroxybenzoic acid group, a 4-hydroxybenzoic acid group, an anthranilic acid group, a 4-aminobenzoic acid group, or a β-(4-hydroxyphenyl)acrylic acid group.

14. A method according to Claim 10, wherein the organic moiety comprises an oxidisable or reducible heterocyclic moiety, such as a phenothiazine group, an indole group, an ascorbic acid group, or a 4,4-bipyridinium dication group.

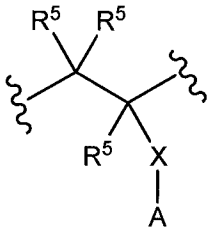
15. A method according to Claim 10, wherein the organic moiety comprises an oxidisable or reducible functional group, such as a peroxide group, a thioamide group, a nitrosamide group, a nitro group, or an azide group.

16. A method according to any one of the preceding claims, wherein the ratio of polymer units of type (i) to polymer units of type (ii) in the scale inhibiting polymer is at least 2:1, more preferably at least 5:1.

17. A method according to any one of the preceding claims, wherein the ratio of polymer units of type (i) to polymer units of type (ii) in the scale inhibiting polymer is less than 1000:1.

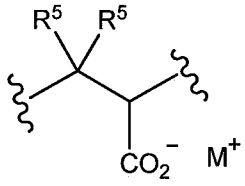
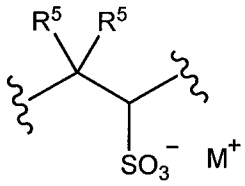
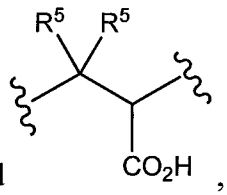
18. A method according to any one of the preceding claims, wherein the scale inhibiting polymer is a polyolefin obtained by the addition polymerisation of a plurality of olefinically unsaturated monomer units.

19. A method according to Claim 18, wherein at least a portion of the polymer units of type (i) in the scale inhibiting polymer have the general formula:



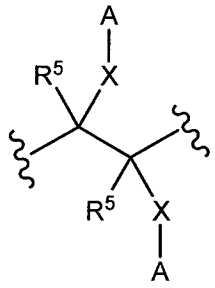
wherein each R^5 is independently selected from hydrogen, or a C_1 to C_4 alkyl group; X represents a covalent bond, a C_1 to C_4 alkylene chain, a C_6 arylene group or a C_6 to C_{10} alkylarylene group; and A represents a group selected from $-CO_2H$, $-CO_2^-M^+$, $-CO_2R^4$, $-CONH_2$, $-CONR^4{}_2$, $-SO_3H$, $-SO_3^-M^+$, $-PO_3H_2$, $-PO_3^{2-}M^{2+}$, -CN, -Cl, -Br, -I, and -OH; wherein each R^4 independently represents a C_1 to C_4 alkyl group, optionally substituted by one or more of -CN, -F, -Cl, -Br, -I, and -OH, or wherein two adjacent carbon atoms of R^4 together with an oxygen atom form a three-membered cyclic ether (oxirane), and wherein M^+ and M^{2+} represent any suitable cation or combination of cations that provides charge balance.

20. A method according to Claim 19, wherein at least a portion of the polymer units of type (i) in the scale inhibiting polymer are selected from:

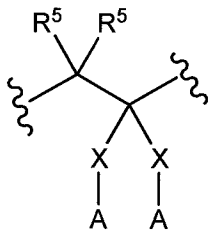
, , and ,

wherein R^5 and M^+ are as defined in Claim 19.

21. A method according to any one of Claims 18 to 20, wherein at least a portion of the polymer units of type (i) in the scale inhibiting polymer have the general formula:

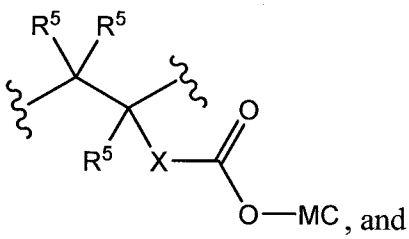


or the general formula:

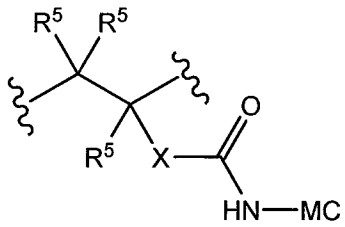


wherein each R^5, each X and each A is independently as defined in Claim 19.

22. A method according to any one of Claims 18 to 21, wherein the at least one polymer unit of type (ii) in the scale inhibiting polymer has a formula selected from:

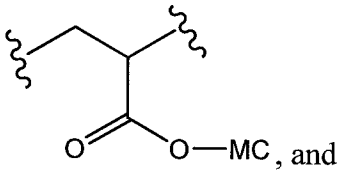


and

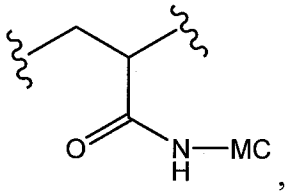


wherein R^5 and X are as defined in Claim 17, and MC represent a metal complex as defined in any one of Claims 5 to 11, optionally including an alkylene linking group.

23. A method according to Claim 22, wherein the at least one polymer unit of type (ii) in the scale inhibiting polymer has a formula selected from:

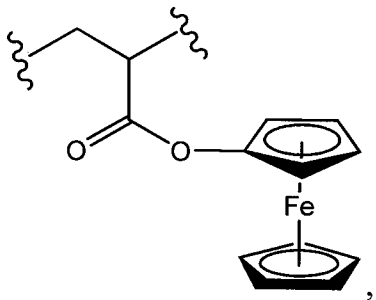


and

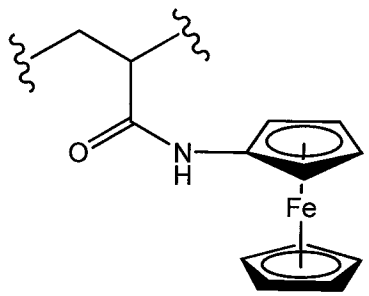


wherein MC represents a metal complex as defined in any one of Claims 5 to 11, optionally including an alkylene linking group.

24. A method according to Claim 23, wherein the at least one polymer unit of type (ii) in the scale inhibiting polymer has a formula selected from:

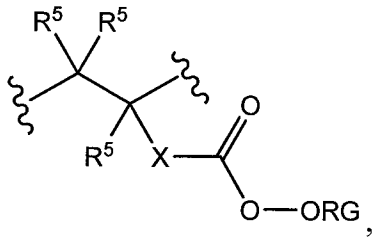


, and

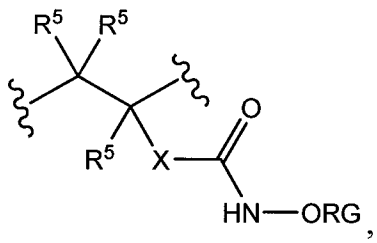


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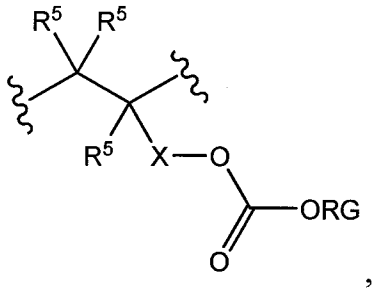
25. A method according to any one of Claims 18 to 21, wherein the polymer unit of type (ii) in the scale inhibiting polymer has a formula selected from:



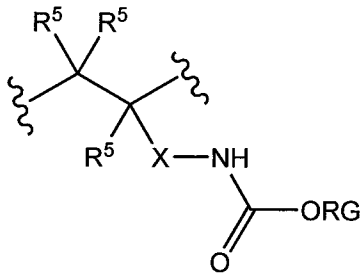
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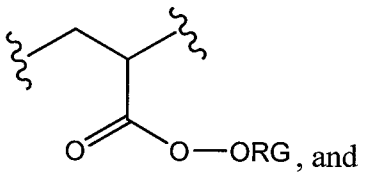
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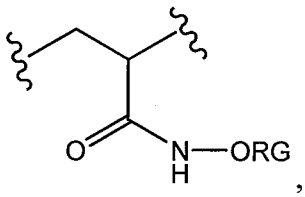
and

wherein R^5 and X are as defined in Claim 19, and ORG represents an organic moiety as defined in any one of Claims 12 to 15.

26. A method according to Claim 25, wherein the polymer unit of type (ii) in the scale inhibiting polymer has a formula selected from:



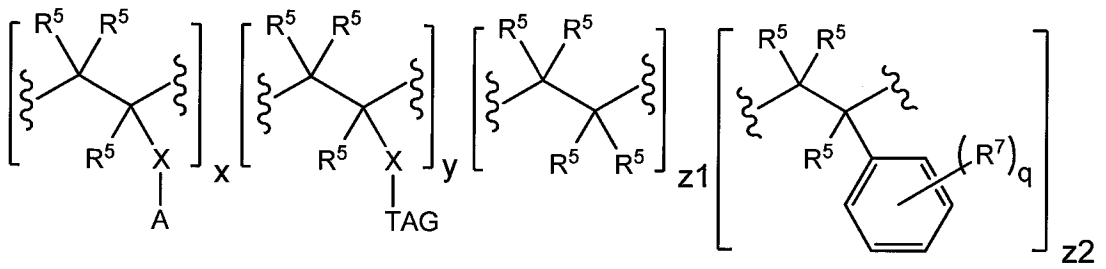
, and



,

wherein ORG represents an organic moiety as defined in any one of Claims 12 to 15.

27. A method according to any one of Claims 18 to 26, wherein the scale inhibiting polymer has the empirical formula:



wherein each R^5, each X and each A are independently as defined in Claim 19, TAG represents a tagging moiety as defined in any one of Claims 3 to 15, and x, y, z1 and z2 are integers defining the stoichiometric amounts of each unit in the scale inhibiting polymer, wherein the ratio of x:y is preferably at least 2:1 and less than 1000:1, and the ratio of x:(z1+z2) is preferably in the range of from 1:0 to 1:2.

28. A method according to any one of the preceding claims, wherein the scale inhibiting polymer has a weight average molecular weight in the range of from 1000 to 100,000 g/mol.

29. A method according to any one of the preceding claims, wherein the scale inhibiting polymer is dissolved or dispersed in brine or aqueous fluids produced from the oil-bearing formation.

30. A method according to any one of the preceding claims, comprising the steps of:

(a1) introducing a solution or dispersion of a first scale inhibiting polymer as defined in any one of Claims 1 to 28 in an aqueous fluid into a first oil-bearing formation;

(a2) introducing a solution or a dispersion of a second scale inhibiting polymer as defined in any one of Claims 1 to 28 in an aqueous fluid into a second oil-bearing formation, wherein the first and second scale inhibiting polymers comprise different tagging moieties;

(b) co-producing oil and aqueous fluids from the first and second oil-bearing formations as a combined stream;

(c) periodically or continuously measuring the concentration of the first and second scale inhibiting polymers in the co-produced aqueous fluids by electrochemical detection of the tagging moieties of the first and second scale inhibiting polymers;

(d1) introducing further first scale inhibiting polymer into the first oil-bearing formation when the measured concentration of the first scale inhibiting polymer in step (c) falls below a pre-determined minimum value; and

(d2) introducing further second scale inhibiting polymer into the second oil-bearing formation when the measured concentration of the second scale inhibiting polymer in step (c) falls below a pre-determined minimum value.

Figure 1

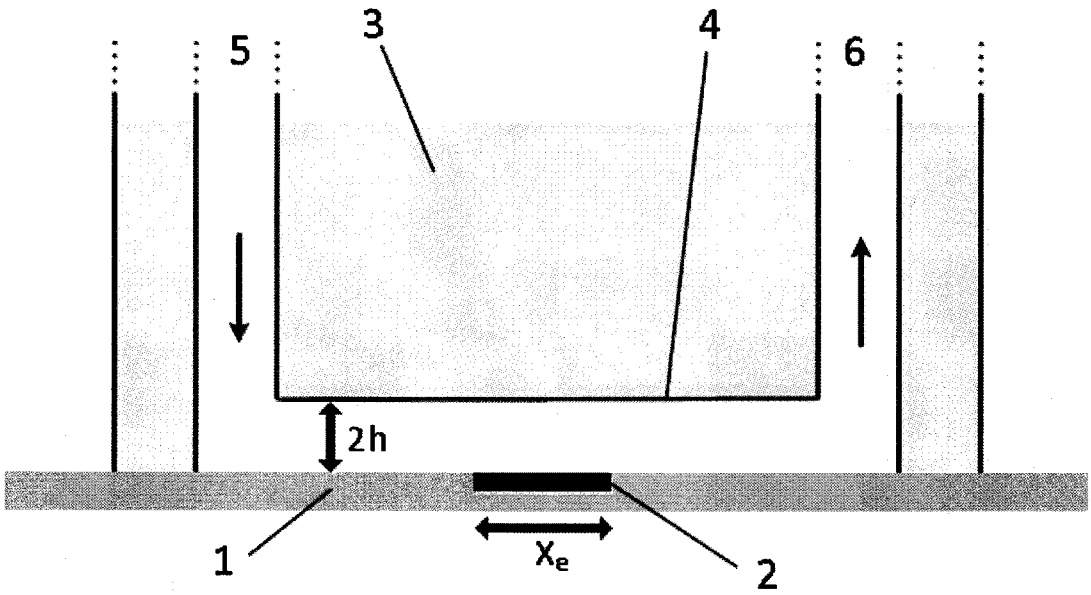


Figure 2

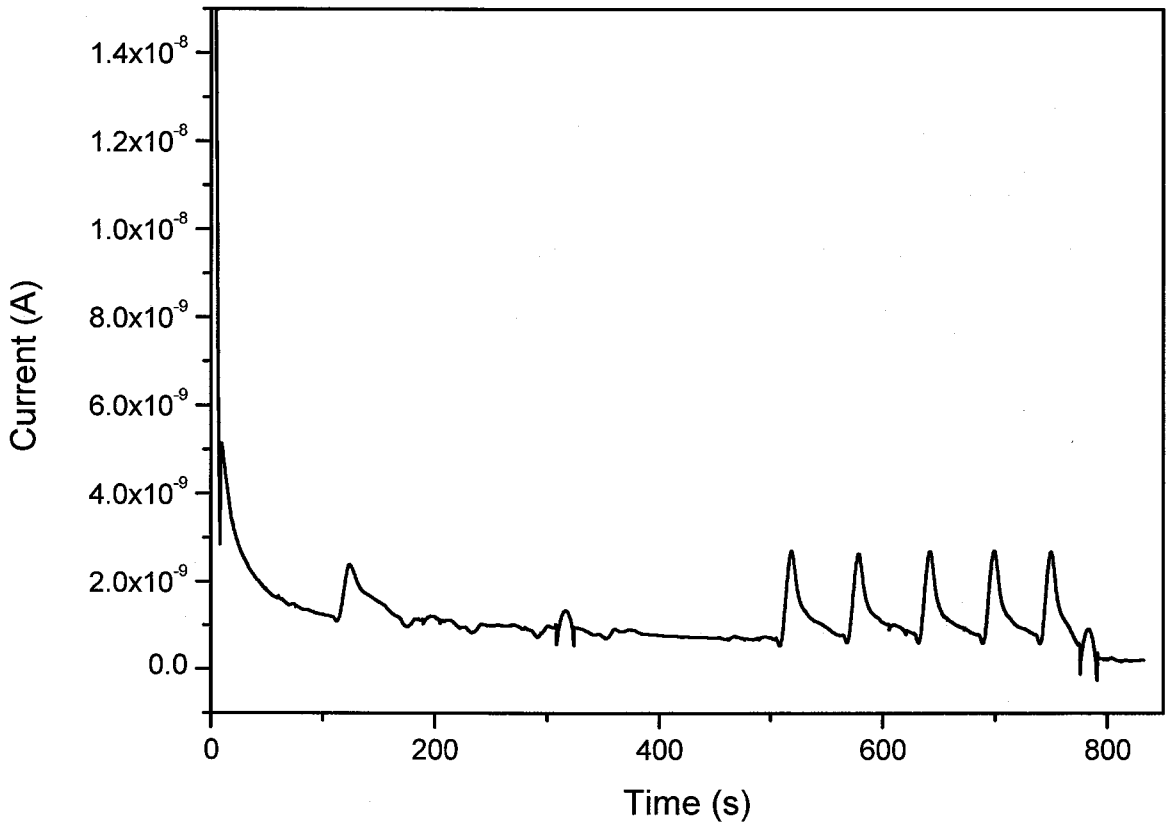


Figure 3

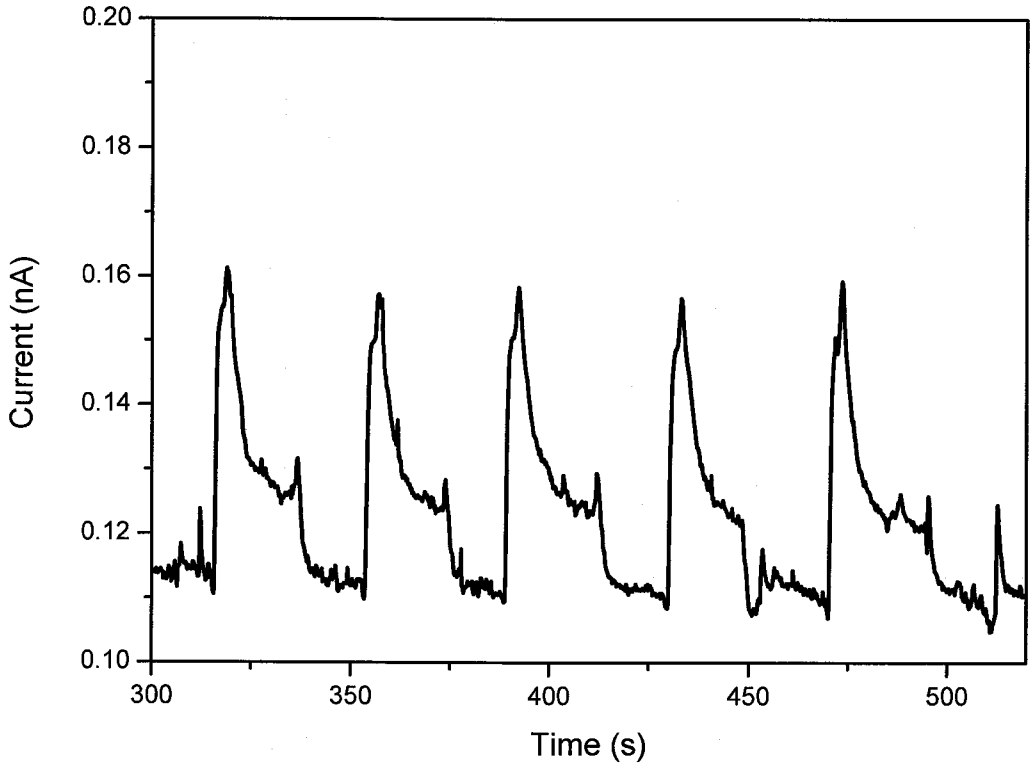


Figure 4

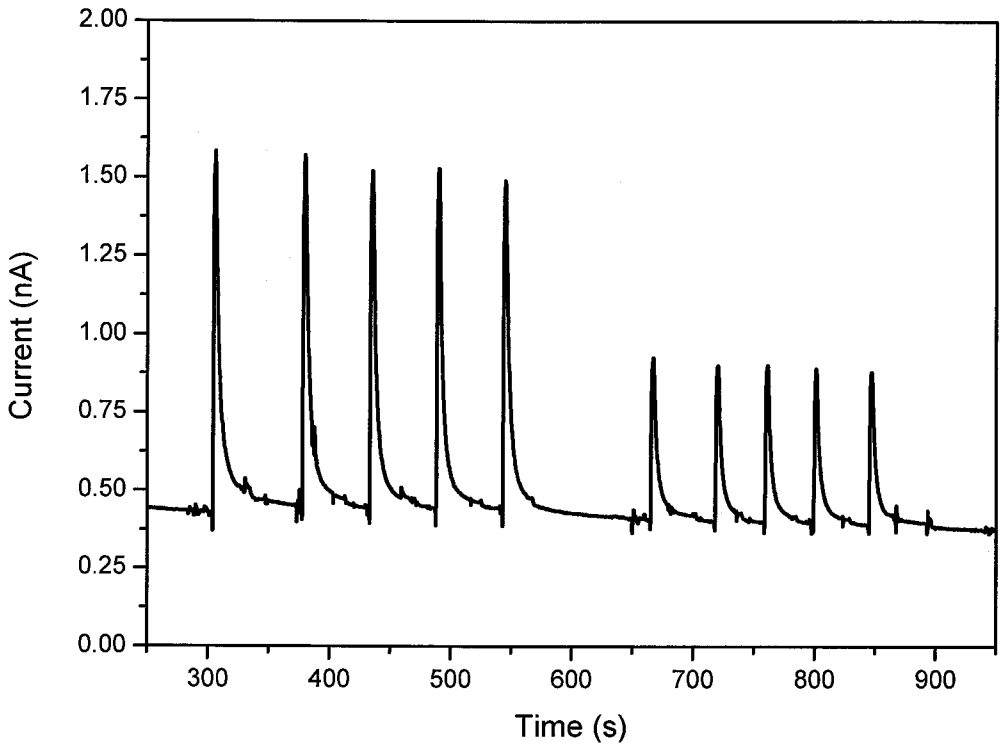


Figure 5

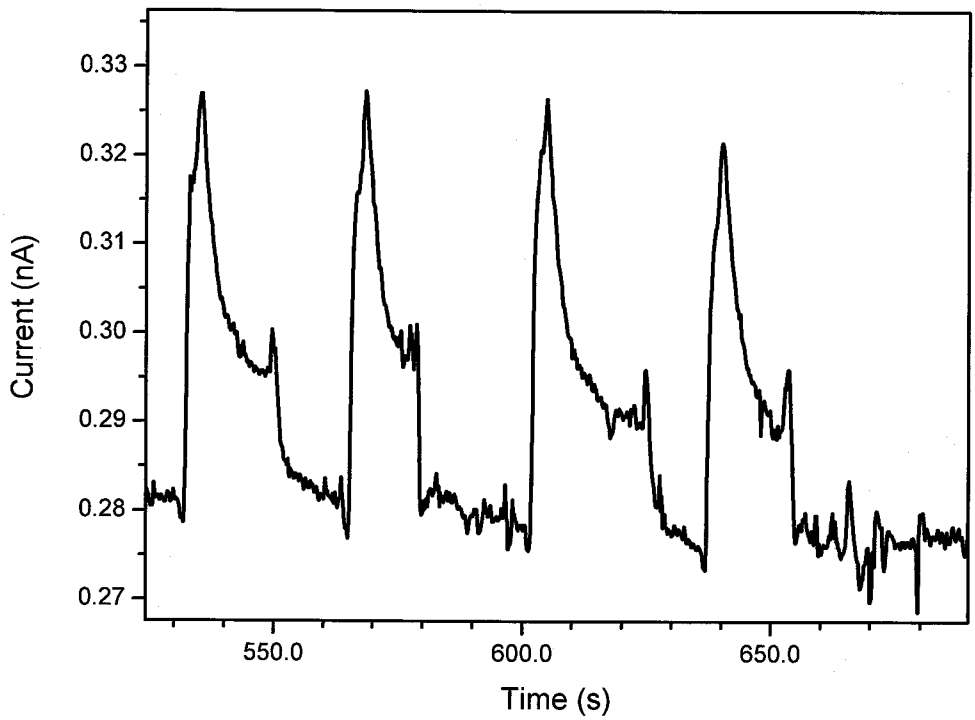
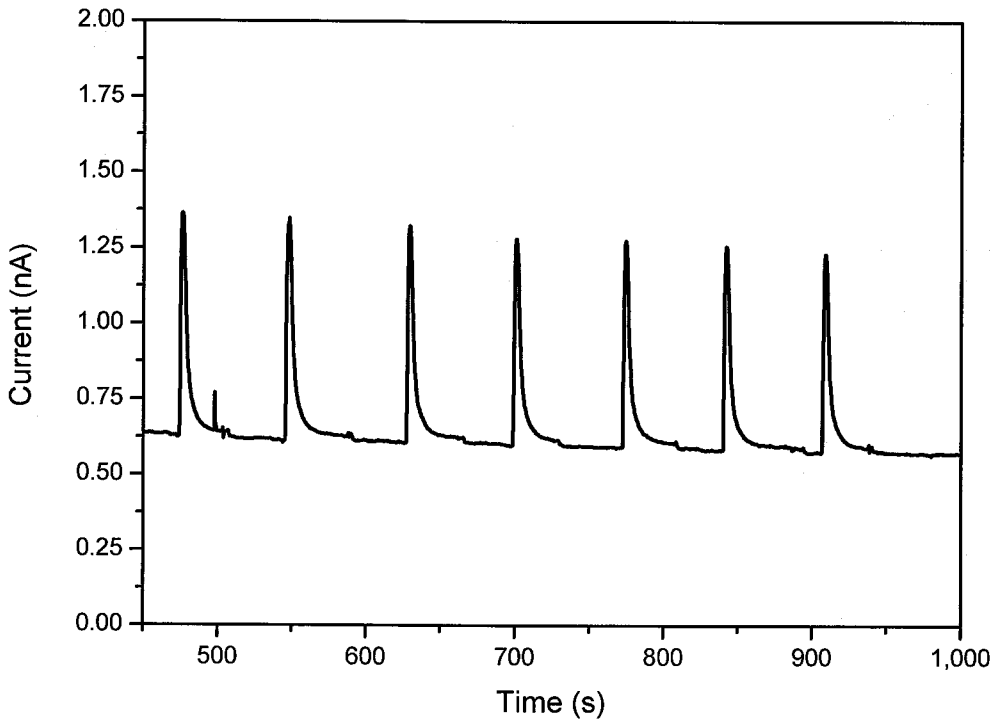
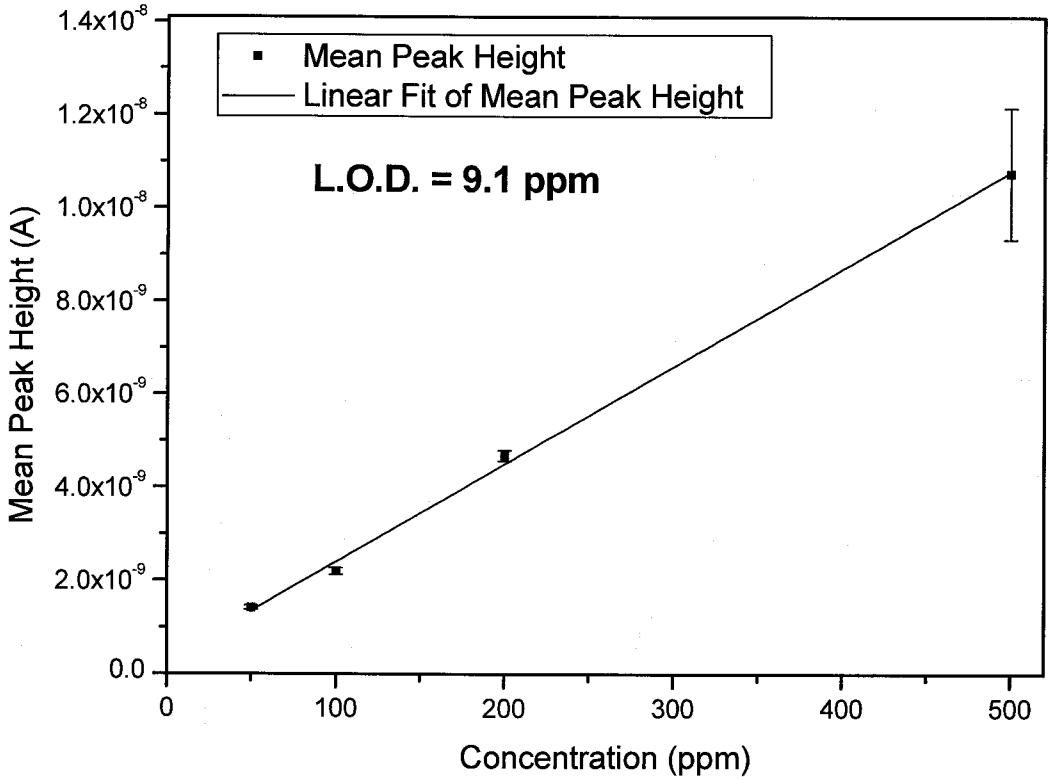


Figure 6



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Figure 7



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Figure 8

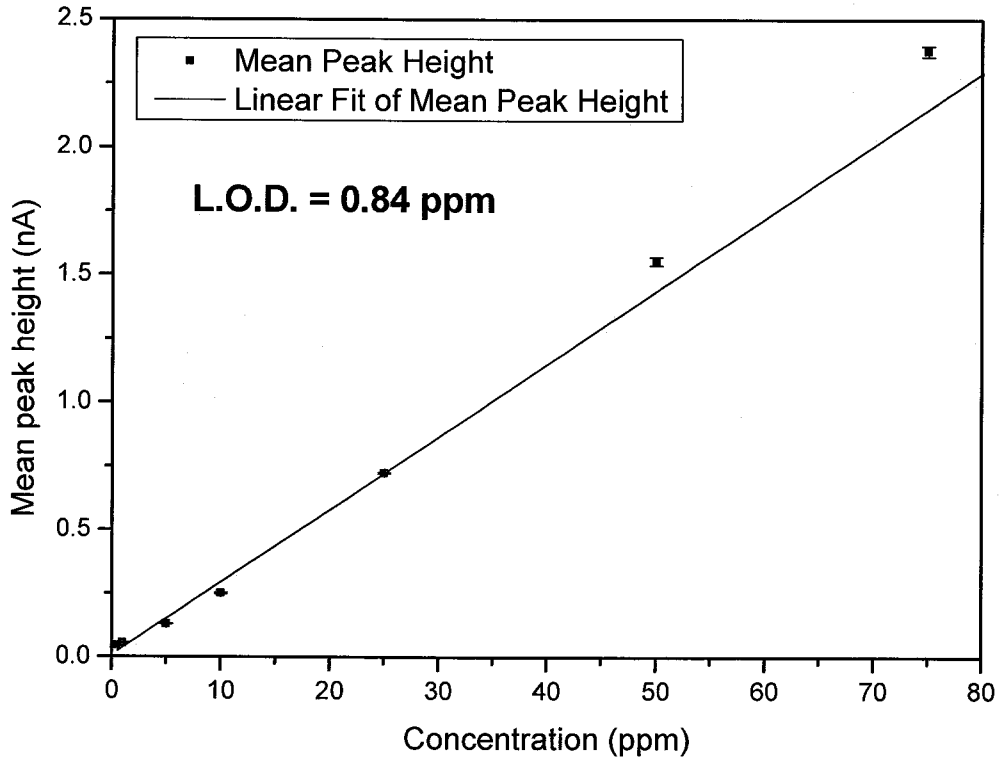


Figure 9

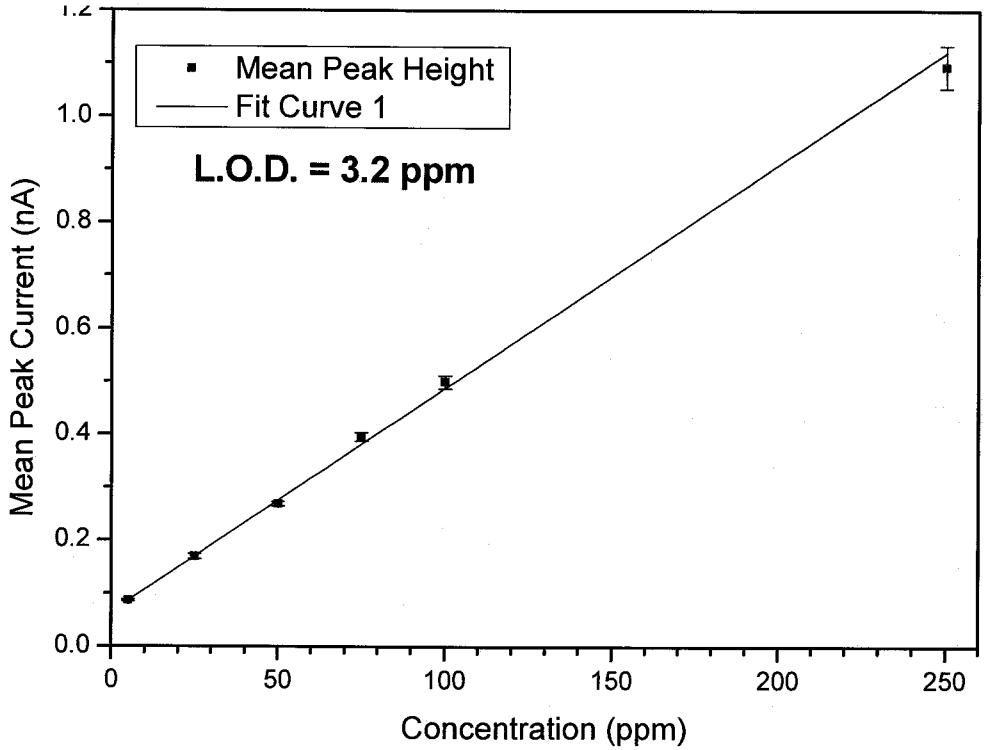
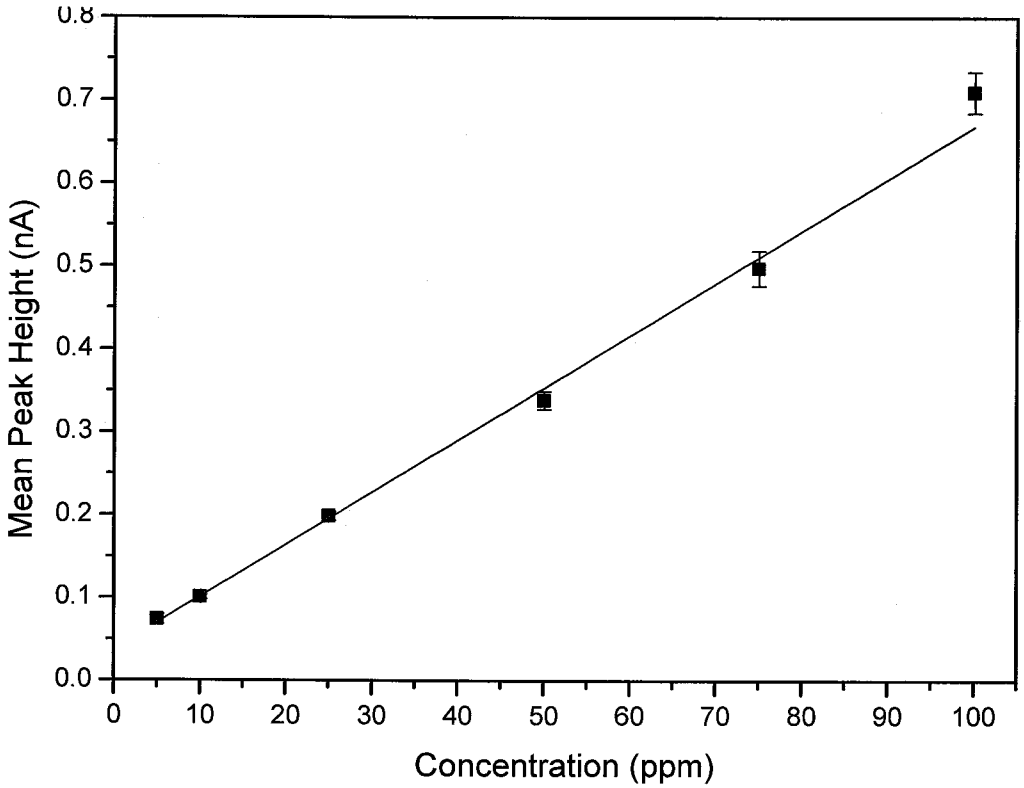


Figure 10



INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2013/070138

A. CLASSIFICATION OF SUBJECT MATTER
INV. C02F5/14 C02F5/12 C02F1/00
ADD. C02F1/68 C02F103/10

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)
C02F

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	WO 2005/000747 A2 (RHONE POULENC CHIMIE [FR]; HILLS EMMA [GB]; CHAPON PASCAL [FR]) 6 January 2005 (2005-01-06) page 15, lines 21-32	1-29
A	US 5 411 889 A (HOOTS JOHN E [US] ET AL) 2 May 1995 (1995-05-02) the whole document	1-29

☐ 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

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

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"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

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

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
27 February 2014	11/03/2014

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Serra, Renato

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2013/070138

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