

FOULING CONTROL COATING COMPOSITION

Technical Field

- 5 This invention relates to a fouling control coating composition, to a substrate or article coated with such a fouling control coating composition, and to a method for controlling aquatic biofouling on man-made objects using such a coating.

Background Art

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Fouling of ship hulls and other water-borne objects by aquatic organisms is a continuing problem. Fouling can increase frictional resistance of boats in the water, increasing fuel costs. On static structures, for example on drilling rigs, it can alter the water flow around the supporting legs, risking unpredictable and increased stresses. Fouling can also
15 make inspections more difficult by obscuring defects and cracks. It can further reduce the cross-sectional area of pipework such as cooling water or ballast tank intakes, leading to reduced flow rates.

Coatings can be used to reduce fouling. Such coatings can contain a biocide to control
20 the growth of aquatic organisms on the surface. These fall typically into two broad categories, namely "hard" antifouling coatings, where biocide gradually leaches from the coating over time, and "eroding" antifouling coatings (sometimes called self-polishing coatings), where the coating gradually erodes to release the biocide. However, biocides can carry environmental risks, particularly in areas with heavy shipping activity. They
25 are therefore the subject of increasingly stringent environmental legislation.

Biocide-free coatings are available, which include so-called "fouling release" coatings, which have a "low surface energy" surface that inhibits adherence of fouling organisms, and also causes them to be more easily washed from the surface. The fouling control
30 effects can be enhanced by including non-biocidal adhesion reducing fluids in the formulation. Biocide-free self-polishing coatings can also be used, so-called surface active self-polishing coatings, where the gradual wear or dissolution continually presents a new, clean surface that is designed to prevent biofouling settlement and growth, and which promotes its release. Examples are described in WO2004/081121 and
35 WO2009/011332.

Fouling control coatings can comprise rosins or rosin derivatives, as described for example in CN103881576, EP0877061, EP1036786, EP1479737, EP2368949, EP2489710, EP2489711, JP3368618, JP3774310, JP2006077095, KR101115200, 5 KR101137563, KR101970431, US2003/0225184, US2009/0042042, US5116407, US5236493, US5298061, US10487216, WO91/15546, WO96/04341 and WO2015/150249. Other fouling control coatings can include acrylate-based polymers modified with polysiloxanes, such as those described in CN102702914, EP3604394, JP2001072869, JP2006077095, KR20190129735, US2020/0010697, US2020/0017617 10 and WO2017/065172.

However, there remains a need for further types of fouling control coatings with improved properties. In particular, there is a need for fouling control coatings that can avoid the need for biocides and also avoid the need for toxic catalysts.

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Summary of Invention

The present invention is a fouling control coating composition comprising an anionic polymer and one or more amine cations, the anionic polymer also having one or more 20 covalently attached siloxane moieties. The amount of water in the coating composition is no more than 5 wt%. The amine cation is a protonated amine compound. The amine compound (before protonation) has a molecular weight of at least 70 and a boiling point at atmospheric pressure of at least 100 °C.

25 The present invention is also directed to a method for controlling aquatic biofouling on a man-made object, comprising applying the above coating composition onto the surface of a man-made structure. The man-made structure is one that is intended to be permanently or intermittently immersed in water, e.g. sea water, fresh water or brackish water.

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The invention is further directed to a substrate or article coated with the above-mentioned fouling control coating composition, both before and after drying and/or curing.

The invention is additionally directed to the use of such a coating composition for 35 controlling aquatic biofouling of a man-made structure.

Terminology

In the discussion below, reference to quantities of components in the coating composition as a whole are to the uncured or undried composition, unless otherwise stated. Also, unless otherwise stated, concentrations given are in wt% of the coating composition as a whole. Where a coating composition is provided in separate parts (e.g. a binder-containing part and a curing agent-containing part) the amount of a component in the coating composition as a whole is based on the total amount of components in all the different parts combined.

References to “terminal” groups in a resin, polymer or oligomer are to groups bound to the oligomer/polymer chain or “backbone” at the end (terminal) positions. References to “pendant” groups are to groups attached to the oligomer/polymer chain at positions other than terminal positions.

References to “aliphatic hydrocarbyl” groups or substituents include saturated and unsaturated hydrocarbyl groups (e.g. alkyl or alkenyl groups), which can be cyclic, linear or branched, or comprise a mixture of cyclic and non-cyclic portions. Similarly, references to “alkyl” or “alkenyl” groups or substituents includes cyclic, linear or branched groups, or groups comprising a mixture of cyclic and non-cyclic portions. Unsaturated groups, for example alkenyl groups, have a minimum of two carbon atoms.

References to “aryl” are to aromatic hydrocarbon groups that can comprise one or more aromatic rings. References to “heteroaryl” are to aromatic groups that comprise one or more heteroatoms in the aromatic ring, typically selected from oxygen, nitrogen and sulfur.

The monomer (or monomer unit) content of a polymer or oligomer, expressed in either weight% or molar%, can be calculated from, respectively, the weight fraction or the mole fraction of monomer used to make the polymer or oligomer.

The term “monomer unit” refers to a constituent monomer of a polymer, i.e. to the moiety derived from the monomer after being incorporated into a polymer.

Atmospheric pressure is defined as 1.013 bar-a, where bar-a represents bar-absolute as opposed to bar-gauge.

The term "saturated carbon atom" refers to a carbon atom that has four single covalent
5 bonds to other atoms, and no double or triple covalent bonds to other atoms.

Description of Embodiments

[Anionic polymer]

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The coating composition comprises one or more binder resins, at least one of which is a
anionic polymer comprising one or more amine cations. The anionic polymer is formed
from at least one monomer with an anionic functionality, in which one or more amine
cations are used to balance the negative charge. In embodiments, it is a thermoplastic
15 polymer.

Examples of anionic polymers include those having an anionic moiety selected from
phosphyl, phosphonyl, sulfyl, sulfonyl, carboxyl and carbonate. In embodiments, the
anionic moiety, or at least one anionic moiety, is carboxyl.

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The anionic polymer is typically formed from polymerisation of mixture of unsaturated
monomers, at least one of which comprises an anionic moiety. In embodiments, such
an anionic monomer is an acrylate-based anionic monomer, as described in more detail
below.

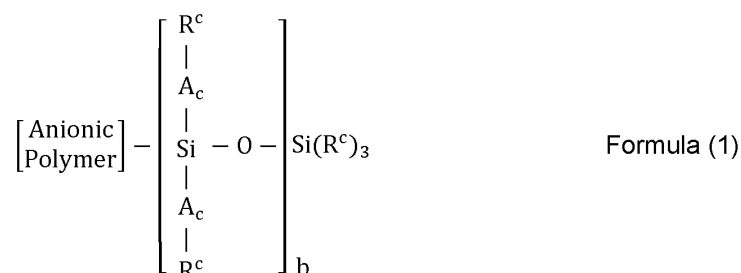
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The amounts of anionic polymer in the coating composition will typically be in the range
of from 20 to 80 wt%, for example 20 to 75 wt%, from 25 to 70 wt% or from 25 to 60 wt%.

[Siloxane moiety]

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The anionic polymer comprises a covalently bound siloxane moiety. The siloxane moiety
can be linear, branched or cyclic, or can comprise a mixture of cyclic and non-cyclic
portions or regions. In embodiments, the siloxane moiety comprises from 4 to 150 silicon
atoms. In embodiments, the siloxane moiety attached to the anionic polymer can be
35 represented by Formula (1):



In embodiments the siloxane moiety is bound to the anionic polymer via an oxygen or a carbon atom. Typically, it is bonded to a carbon atom. B is in the range of from 3 to 150, for example in the range of from 3 to 100 or from 8 to 80, and c is in the range of from 0 to 20, for example from 0 to 10, from 0 to 5 or from 0 to 3. In embodiments, c is 0.

Each A is $[\text{Osi}(\text{R}^c)_2]$.

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Each R^c is independently selected from optionally substituted C_{1-20} aliphatic hydrocarbyl groups, optionally substituted C_{6-12} aryl groups, and optionally substituted C_{6-12} aryl groups having one or more C_{1-6} alkyl groups. Optional substituents are defined further below.

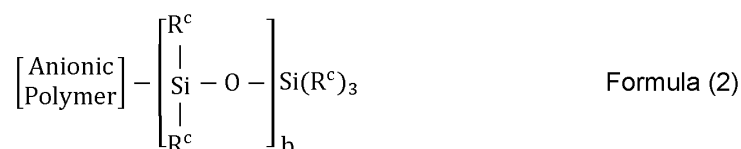
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Any alkyl groups can be cyclic or non-cyclic, or can comprise cyclic and non-cyclic portions. Non-cyclic alkyl groups or substituents can be linear or branched.

Each R^t is independently selected from H, C_{1-6} alkyl and C_{1-6} haloalkyl.

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In embodiments, the siloxane moiety can be represented by Formula (2):



25 In embodiments, in any of Formulae (1) and (2), there are no halides or halide-containing substituents. In further embodiments of Formulae (1) and (2), there are no optional substituents on any R^c group.

In embodiments, the siloxane moiety is a non-functional dimethylpolysiloxane or methylphenylpolysiloxane, where in Formula (2) each R^c is unsubstituted methyl or phenyl.

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The molecular weight of the polysiloxane moiety can be in the range of from 800 to 6000, for example from 1000 to 5000, or from 1400 to 3500.

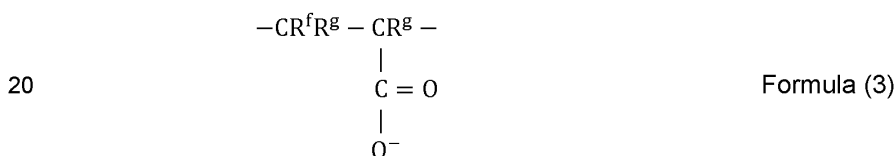
[Monomer units of the anionic polymer]

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The anionic polymer is, in embodiments, an acrylate-based polymer or co-polymer. Such polymers or copolymers are obtainable by polymerisation of a mixture of monomers comprising one or more acrylate-based monomers. An acrylate-based monomer is a monomer having a moiety in which a C=C double bond is directly bonded to a carboxyl, carboxylate or amide group.

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In embodiments, the acrylate-based polymer comprises one or more carboxylate-containing acrylate-based monomer units represented by Formula (3):



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Each R^f is selected from H, C₁₋₂₀ aliphatic hydrocarbyl, C₆₋₁₂ aryl, and C₆₋₁₂ aryl with one or more substituents selected from C₁₋₆ alkyl, C(O)O⁻ and C(O)OR^t.

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Each R^g is independently selected from H and C₁₋₂₀ aliphatic hydrocarbyl (e.g. alkyl), C₆₋₁₂ aryl and C₆₋₁₂ aryl substituted with one or more (e.g. 1 to 4) C₁₋₆ aliphatic hydrocarbyl groups.

Each aliphatic hydrocarbyl substituent, aliphatic hydrocarbyl group and aryl group in R^f and R^g can also optionally be substituted as described further below.

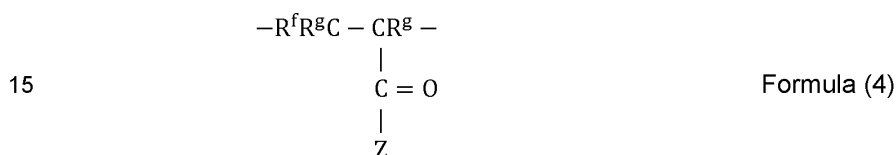
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In embodiments, the C₁₋₂₀ aliphatic hydrocarbyl can be selected from C₁₋₁₀ or C₁₋₆ aliphatic hydrocarbyl groups, such as C₁₋₁₀ or C₁₋₆ alkyl groups. In embodiments, each R^g is selected from hydrogen and methyl.

- 5 In embodiments, the R^g groups are selected independently from H and unsubstituted C₁₋₆ alkyl, for example H and C₁₋₄ alkyl, such as H and methyl. In embodiments, R^f is selected from H, -C(O)O⁻, -C(O)OR^t, and C₁₋₆ alkyl optionally substituted with one or more groups selected from -C(O)O⁻ and -C(O)OR^t. In embodiments, where R^f is an optionally substituted C₁₋₆ alkyl group, there is only one optional -C(O)O⁻ or -C(O)OR^t substituent.

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In embodiments, the acrylate-based polymer is a co-polymer comprising one or more additional monomer units. In one embodiment, one or more additional monomer units can be selected from those represented by Formula (4):



R^f and R^g are as defined above. Z is selected from -OR^h, and -N(R^h)₂.

In embodiments, group Z is selected from OR^h, for example OR^t.

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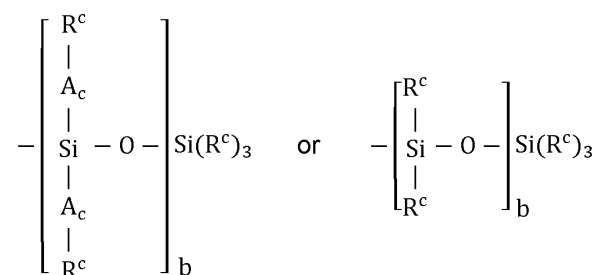
In embodiments, where Z is N(R^h)₂, none of R^f and R^g contain any carbonyl-containing moieties, i.e. -C(O)O⁻, -C(O)OR^t or -C(O)NR^t₂.

- Each R^h is independently selected from H and C₁₋₂₀ alkyl, optionally substituted as set out
 25 further below. In embodiments, the C₁₋₂₀ alkyl is C₁₋₁₀ or C₁₋₆ alkyl.

- In embodiments, the monomer(s) of Formula (3) can be based on acrylate, methacrylate, itaconate, maleate, or crotonate. These also apply for monomer(s) of Formula (4), but they can also include acrylamide and methacrylamide. In embodiments, monomers of
 30 Formula (3) are based on acrylate or methacrylate, and those of Formula (4) are based on acrylate, methacrylate, acrylamide or methacrylamide.

In embodiments, there is at least one monomer unit of Formula (4) comprising a siloxane moiety as a substituent on an R^h group, e.g. where Z is OR^h , and where the siloxane moiety can be:

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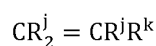


In such embodiments, the R^h can be selected from C_{1-6} alkyl, and A , R^c , b and c are as defined above.

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Other types of co-monomer (i.e. non acrylate-based monomers) that can form part of the anionic polymer include those having polymerizable unsaturated carbon-carbon bonds, for example those represented by Formula (5):

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Formula (5)

Each R^j is independently selected from H, halide (e.g. selected from F and Cl), and C_{1-6} alkyl. R^k can be selected from R^j , C_{2-6} alkenyl, C_{6-12} aryl and C_{6-12} aryl substituted with one or more C_{1-6} aliphatic hydrocarbyl groups. In embodiments, only one of R^j and R^k can be a halide or comprise a halide-containing substituent. In embodiments R^k comprises C_{6-12} aryl. In embodiments, the co-monomer can comprise one or more optional substituents, as set out below for R^h and R^g .

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The average number of monomer units in the acrylate-based anionic polymer can be in the range of from 5 to 500, for example from 10 to 300.

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In embodiments, an optionally substituted group can comprise from 1 to 4 substituents, for example 1 or 2 substituents.

In embodiments, the viscosity of the siloxane-modified anionic polymer is in the range of from 3 to 100 Poise, for example from 5 to 50 Poise, when measured at 25 °C.

- 5 In embodiments, the amine cation-containing siloxane-modified anionic polymer is made using anionic monomers in their acidic, i.e protonated form, e.g. where the monomer units are of Formula (4) where Z is OH, and adding amine, which undergoes an acid-base reaction to form the amine cation.

- 10 When making the siloxane-modified anionic polymer, the proportion of the anionic monomers (or protonated forms of the anionic monomers) in the mixture of monomers is typically in the range of from 0.5 to 20 wt%, for example from 1 to 12 wt%, such as from 2 to 10 wt%.

- 15 In embodiments, on a molar basis, the anionic monomer is an acrylate-based anionic monomer comprising at least 80 % on a molar basis of monomer units according to Formulae (3) and (4). In further embodiments this amount is at least 90 % or at least 95 % on a molar basis. In still further embodiments, all monomer units are according to Formula (3) and (4).

- 20 In embodiments, in the anionic polymer, the amount of amine cations to anionic monomer units in the polymer is at least 80 mol%, for example at least 90 mol% or at least 95 mol%. In this sense, a monomer unit containing acidic groups, e.g. monomer units of Formula (4) where Z is -OH, is considered to be an anionic monomer unit.

- 25 In embodiments, anionic monomer units that are not charge-balanced by amine cations can be charge-balanced by other cations, such as protons or metallic cations. In embodiments, substantially all anionic monomer units are charge balanced by amine cations.

- 30 [Amine cation]

The anionic polymer comprises one or more amine cations that ionically associate with the anionic polymer. The amine should be chosen such that the salt it forms with the anionic polymer is not too water-soluble, as otherwise the polymer degrades too quickly

when in use. Conversely, it should not be completely insoluble, as otherwise it would have poor efficacy as a self-polishing fouling control coating.

5 The amine cations are protonated versions of an amine compound, where the proton can derive from a protonated form of anionic monomer units in the anionic polymer (e.g. monomer units of Formula (4) above where Z is OH). The amine compound (before protonation) has a molecular weight of at least 70, for example in the range of from 70 to 10 000 or from 70 to 1000, such as from 70 to 500. In embodiments, the molecular weight is at least 100, for example at least 200 or at least 250.

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The neutral amine compound (i.e. before protonation) has a boiling point at atmospheric pressure of at least 100 °C, for example at least 200 °C, or at least 250 °C.

15 In embodiments, the amine cation has a formula of $[H_{(4-w)}NR^n]^+$.

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w is an integer in the range of from 1 to 3. However, in preferred embodiments w is 1 or 2, or w is 1.

20 R^n is selected from groups having from 2 to 60 carbon atoms selected from optionally substituted aliphatic hydrocarbyl groups, optionally substituted aryl groups, and optionally substituted aryl groups having one or more aliphatic groups. Optional substituents are defined further below. Aliphatic groups can be saturated or unsaturated, and can be cyclic, non-cyclic or comprise both cyclic and non-cyclic portions.

25 Typically, the amine cation in total will have from 4 to 60 carbon atoms, for example from 6 to 60 carbon atoms or from 10 to 60 carbon atoms. In embodiments, the amine will comprise at least one aromatic or aliphatic ring. Where there is more than one ring, the rings can be aliphatic, aromatic or a mixture of aromatic and aliphatic. Rings can be fused or unfused. The aliphatic ring(s) can be saturated or unsaturated. In embodiments, there
30 can be a mixture of aromatic and non-aromatic rings.

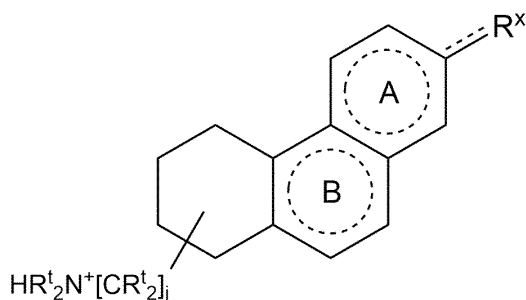
In embodiments, the amine cation (or at least one of the amine cations) is a rosin amine cation based on a rosin amine, for example being a protonated rosin amine. Rosin amines are commercially available. They are typically derived from an acidic rosin, i.e.
35 comprising one or more carboxyl groups, which are then converted into amine by suitable

reactions, e.g. via reaction with ammonia or an amine to form a corresponding amide, and subsequent conversion to amine via reduction or Hoffmann rearrangement.

In embodiments the rosin amine cation comprises a diterpenoid “skeleton”, for example comprising three fused rings. The rings can be saturated, unsaturated or aromatic, or any mixture thereof.

In embodiments, there are no halides or halide-containing substituents on the amine compound or amine cation.

In embodiments the rosin amine cation is of Formula (6). In further embodiments, where there is more than one rosin amine cation, all are of Formula (6):



Formula (6)

Ring A is an alicyclic C_6 ring or an aromatic C_6 ring. The alicyclic C_6 ring comprises zero, one or two $C=C$ double bonds.

Ring B is an alicyclic C_6 ring that has zero or one $C=C$ double bond.

The bond between Ring A and group R^x can be a single or double bond.

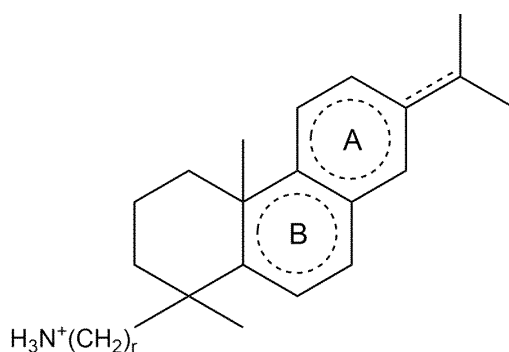
Each R^t is as defined above, and j is in the range of from 1 to 6.

R^x is selected from C_{1-20} aliphatic hydrocarbyl, which can optionally be substituted with one or more substituents selected from halide (typically from F and Cl), $-OR^t$ and $-N(R^t)_2$. In embodiments, R^x is a $-C(R^t)_3$ group or a $=C(R^t)_2$ group where each R^t is H or C_{1-6} alkyl.

In group $\text{HR}^t_2\text{N}^+[\text{CR}^t_2]_j^-$, R^t and j are as defined above. In embodiments, j is 2, and in further embodiments R^t in each case is H.

Optionally, the rings of Formula (6) can have one or more substituents selected from halide (typically selected from F and Cl), OR^t , $\text{N}(\text{R}^t)_2$ and R^x . In embodiments, the compound of Formula (6) has no halide or halide-containing substituents. In embodiments, the C_{1-20} aliphatic hydrocarbyl group is an optionally substituted C_{1-6} alkyl or C_{1-6} alkenyl group.

10 In embodiments, the rosin amine cation (or at least one such rosin amine cation) is of Formula (7). In further embodiments, where there is more than one such rosin amine cation, all are of Formula (7):



Formula (7)

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In Formula (7), r can be from 1 to 6, for example from 1 to 2, and in embodiments it is 1.

In embodiments, the rosin amine cation (or at least one such cation) is selected from those in Figure 1. In further embodiments (where there is more than one such cation) at least 50% on a molar basis are selected from those in Figure 1, for example at least 75% on a molar basis.

One or more amine cations can be included in the anionic polymer. For example, commercial sources of rosin amines often comprise more than one type of amine moiety which, after protonation, are of Formula (6) or (7). In embodiments, the rosin amine cation is derived from abietylamine or dehydroabietylamine.

The amine cation can be added to the coating composition in the form of a salt, e.g. with a corresponding anion such as a carboxylate or carbonate. However, in a preferred embodiment, it is added in the form of the corresponding amine compound, together with the anionic polymer in an acid (protonated) form. The amine cation then forms from an acid-base interaction, by taking a proton from the corresponding acidic group on the anionic polymer.

[Optional substituents]

Optional substituents for R^c can be selected from halide, $-OR^t$ and $-N(R^t)_2$.

Optional substituents for R^h and R^g can be selected from halide, $-OR^t$, $-N(R^t)_2$, siloxane moieties as defined above, $-OC(O)R^t$, $-C(O)N(R^t)_2$, and $-OC(O)N(R^t)_2$. Additional optional substituents include polyether, polyamine and polyether/amine groups selected from $-([CR^t_2]_jE-)_pR^t$ and $-E-([CR^t_2]_jE-)_pR^t$. Each E is independently selected from O and NR^t . j can be from 1 to 6, such as from 2 to 4. and p can be from 1 to 20. For R^f , the same optional substituents apply, with further optional substituents being selected from $-C(O)O^-$ and $-C(O)OR^t$.

Optional substituents for R^n can be selected from halide, $-OR^t$, $-N(R^t)_2$, and groups selected from $-([CR^t_2]_jE-)_pR^t$ and $-E-([CR^t_2]_jE-)_pR^t$ as defined above, although typically in such groups E is NR^t .

Any halide substituents or any halides in any of the substituents are typically selected from F and Cl.

[Additional components]

The coating composition may optionally also contain other components, for example one or more substance selected from curable resins, crosslinking agents, reactive diluents, anti-corrosion additives, pigments, gloss additives, waxes, rosins, fillers, thixotropic agents, plasticizers, inorganic and organic dehydrators (stabilizers), UV stabilizers, defoamers, and any combination thereof. These components are well-known to the skilled person.

The total amount of such further optional components can be in the range of from 0 to 65 wt% based on the total content of the coating composition, typically no more than 50 wt%, for example no more than 35 wt% of the coating composition.

- 5 Except for organic solvents, marine biocides, pigments, fillers and anticorrosive agents, which are discussed further below, the coating composition can comprise less than 5 wt% or less than 3 wt% in total of further optional components.

- 10 Further, the coatings compositions can have low amounts of non-volatile and non-reactive fluids (e.g. polysiloxane oils or fluoropolymers such as perfluoropolyethers), or hydrocarbon wax or oil mixtures (e.g. petrolatum), or even no such non-volatile and non-reactive fluids. For example, their content can be 5 wt% or less, such as 3 wt% or less, 1 wt% or less or 0.1 wt% or less.

- 15 [Organic solvents]

- 20 The composition can comprise one or more organic solvents. These are typically organic liquids that have a boiling point of 250 °C or lower at atmospheric pressure (i.e. 101.3 kPa or 1.013 bar-a), and evaporate from the coating composition during the drying and curing process.

They can be selected from hydrocarbon compounds and heteroatom-containing organic compounds, where heteroatoms are selected from O, S and N, for example O.

- 25 Examples of organic solvents include alkyl aromatic hydrocarbons (such as xylene, toluene and trimethyl benzene), aliphatic hydrocarbons (such as cyclic and acyclic hydrocarbons selected from C₄₋₂₀ alkanes, or mixtures of any two or more thereof), alcohols (such as benzyl alcohol, octyl phenol, resorcinol, n-butanol, isobutanol and isopropanol), ethers (such as methoxypropanol), ketones (such as methyl ethyl ketone, 30 methyl isobutyl ketone and methyl isopentyl ketone), and esters (such as butyl acetate). In embodiments, the organic solvent comprises from 2 to 20 carbon atoms, for example from 3 to 15 carbon atoms. Mixtures of any two or more organic solvents can be used.

- 35 The total amount of organic solvent can constitute up to 65 wt% of the total weight of the coating composition, for example up to 50 wt%, 30wt%, 20wt% or 10wt% of the coating

composition as a whole. In embodiments, it is in the range of from 1 to 65 wt% or from 1 to 50 wt%, for example from 5 to 45 wt%. In other embodiments, the concentration of organic solvent in the coating composition is from 15 to 40 wt%.

- 5 The organic solvent content is separate to the water content. The coating composition is a non-aqueous composition, comprising no more than 5 wt%, for example no more than 1 wt% water.

[Marine biocides]

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The coating composition can, in embodiments, comprise one or more marine biocides. These are chemical substances known to have chemical or biological biocidal activity against marine or freshwater organisms.

- 15 Although the coating compositions described herein do not require any additional marine biocides, they can be incorporated if desired. In embodiments, where marine biocide is present, it can be included at concentrations of up to 10 wt%. However, in embodiments, there are limited quantities of marine biocide, for example 1 wt% or less, such as 0.5 wt% or less, or 0.1 wt% or less based on the entire coating composition. In
20 embodiments, the coating composition is free of marine biocide.

If used, examples of suitable marine biocides are well-known in the art and include inorganic, organometallic, metal-organic or organic biocides.

- 25 Examples of inorganic biocides include copper compounds such as copper oxide, copper thiocyanate, copper bronze, copper carbonate, copper chloride, copper nickel alloys, and silver salts such as silver chloride or nitrate.

- Organometallic and metal-organic biocides include zinc pyrithione (the zinc salt of 2-pyridinethiol-1-oxide), copper pyrithione, bis (N-cyclohexyl-diazenium dioxy) copper, zinc
30 ethylene-bis(dithiocarbamate) (i.e. zineb), zinc dimethyl dithiocarbamate (ziram), and manganese ethylene-bis(dithiocarbamate) complexed with zinc salt (i.e. mancozeb).

- Organic biocides include formaldehyde, dodecylguanidine monohydrochloride,
35 thiabendazole, medetomidine, N-trihalomethyl thiophthalimides, trihalomethyl

thiosulphamides, N-aryl maleimides such as N-(2,4,6-trichlorophenyl) maleimide, 3-(3,4-dichlorophenyl)-1,1-dimethylurea (diuron), 2,3,5,6-tetrachloro-4-(methylsulphonyl) pyridine, 2-methylthio-4-butylamino-6-cyclopopylamino-s-triazine, 3-benzo[b]thien-yl-5,6-dihydro-1,4,2-oxathiazine 4-oxide, 4,5-dichloro-2-(n-octyl)-3(2H)-isothiazolone, 2,4,5,6-tetrachloroisophthalonitrile, tolylfluanid, dichlofluanid, diiodomethyl-p-tosylsulphone, capsaicin and substituted capsaicins, N-cyclopropyl-N'-(1,1-dimethylethyl)-6-(methylthio)-1,3,5-triazine-2, 4-diamine, 3-iodo-2-propynylbutyl carbamate, medetomidine, 1,4-dithiaanthraquinone-2,3-dicarbonitrile (dithianon), boranes such as pyridine triphenylborane, 2-trihalogenomethyl-3-halogeno-4-cyano pyrrole derivatives substituted in position 5 and optionally in position 1, such as 2-(p-chlorophenyl)-3-cyano-4-bromo-5-trifluoromethyl pyrrole (tralopyril), furanones such as 3-butyl-5-(dibromomethylidene)-2(5H)-furanone, macrocyclic lactones such as avermectins, for example avermectin B1, ivermectin, doramectin, abamectin, amamectin and selamectin, and quaternary ammonium salts such as didecyldimethylammonium chloride and an alkyl dimethylbenzylammonium chloride.

The biocide can, in embodiments, be wholly or partially encapsulated, adsorbed, entrapped, supported or bound. Certain biocides are difficult or hazardous to handle and are advantageously used in an encapsulated, entrapped, absorbed, supported, or bound form. Encapsulation, entrapment, absorption, support or binding of the biocide can provide a secondary mechanism for controlling biocide leaching from the coating system in order to achieve an even more gradual release and long-lasting effect. The method of encapsulation, entrapment, adsorption, support or binding of the biocide is not particularly limited. Examples include the use of mono and dual walled amino-formaldehyde or hydrolysed polyvinyl acetate-phenolic resin capsules or microcapsules as described in WO2006/032019. An example of a suitable encapsulated biocide is encapsulated 4,5-dichloro-2-(n-octyl)-3(2H)-isothiazolone marketed by Dow Microbial Control as Sea-Nine CR2 Marine Antifouling Agent. Examples of ways in which an absorbed or supported or bound biocide may be prepared include the use of host-guest complexes such as clathrates as described in EP0709358, phenolic resins as described in EP0880892, carbon-based adsorbents such as those described in EP1142477, or inorganic microporous carriers such as the amorphous silicas, amorphous aluminas, pseudoboehmites or zeolites described in WO00/11949.

[Pigments, fillers and anticorrosive agents]

In embodiments, one or more pigments, fillers and/or anticorrosive agents can be included in the coating composition.

5

Examples of suitable fillers include zinc oxide, barium sulphate, calcium sulphate, calcium carbonate, silicas or silicates (such as talc, feldspar, and china clay), including pyrogenic silica, bentonite and other clays. Some fillers, such as fumed silica, may have a thixotropic effect on the coating composition.

10

The proportion of fillers may be in the range of from 0 to 25 wt%, based on the total weight of the coating composition. If clay is present, it is in an amount of up to 1 wt%, for example 0.1 to 1 wt%, based on the coating composition as a whole. If a thixotrope is present, it is in an amount of up to 5 wt%, for example from 0.1 to 5 wt%, based on the total weight of the coating composition.

15

Examples of pigments include black iron oxide, red iron oxide, yellow iron oxide, titanium dioxide, carbon black, graphite, red molybdate, yellow molybdate, zinc sulfide, antimony oxide, sodium aluminium sulfosilicates, quinacridones, phthalocyanine blue, phthalocyanine green, indanthrone blue, cobalt aluminium oxide, carbazodioxazine, chromium oxide, isoindoline orange, bis-acetoaceto-tolidiole, benzimidazolone, quinaphthalone yellow, isoindoline yellow, tetrachloroisoindolinone, and quinophthalone yellow, and metallic flake materials such as aluminium flakes. Pigments can be present in amounts of from 0 to 25 wt%, based on the total weight of the coating composition.

25

Examples of anticorrosive agents include zinc dust and zinc alloys, and so-called lubricious pigments such as graphite, molybdenum disulfide, tungsten disulphide and boron nitride. If present, they can be in amounts of up to 25 wt% based the coating composition as a whole, for example in the range of from 0.1 to 25 wt%.

30

In embodiments, where any pigments, fillers or anticorrosive agents are included, they can constitute in total up to 50 wt% of the coating composition based on the total weight of the coating composition, for example up to 40 wt%. In embodiments, there is at least 0.1 wt% of these components, for example at least 5 wt%, at least 10 wt%, or at least 20 wt%. Example ranges include from 0.1 to 50 wt%, from 0.1 to 40 wt%, from 5 to 50 wt%,

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from 5 to 40 wt%, from 10 to 50 wt%, from 10 to 40 wt%, from 20 to 50 wt% and from 20 to 40 wt%.

[Properties of the coating composition]

5

The coating composition in embodiments has a non-volatile content of 35wt% or more, based on the entire weight of the coating composition. In further embodiments, the non-volatile content is 50wt% or more, for example 70 wt% or more. In embodiments the non-volatile content is 85 wt% or less. Non-volatile content can be determined according to ASTM D2697, e.g. D2697-03 (2014).

In embodiments, the touch dry time of the coating composition at 23°C and 50% relative humidity is in the range of from 0.1 to 4 hours, for example in the range of from 0.2 to 3 hours. The touch dry time is the time at which slight pressure with a finger reveals no stickiness and leaves no mark in the coating.

In embodiments, the hard dry time is in the range of from 1 to 30 hours at 23°C and 50% relative humidity, for example from 2 to 20 hours. The hard dry time is the time at which no film disruption and no marks occur when a thumb is pressed firmly on the surface and twisted through 180°.

[Preparation of the coating composition]

The coating composition may be prepared by any suitable technique.

25

The coating composition may be prepared by mechanical mixing of the components, which can be carried out using conventional means and devices, including agitation mixers such as anchor, paddle, propellor, turbine and helical mixers.

In embodiments, the composition is prepared and provided in the separate parts, such as 2-pack or 2-component (2K) systems. However, typically, the coating composition is a 1-pack (1K) composition, i.e. the formulation is provided in a single pack, such that no mixing of separate curing and binder components is necessary at the point of application.

The coating compositions manage to achieve highly effective fouling control performance, without the need for marine biocide. In addition, they can also achieve such high performance in the absence of non-functional oligomeric or polymeric fluids, which are often used in biocide-free foul release and self-polishing coatings.

5

In embodiments, the coating is a so-called self-polishing coating, i.e. one that is designed to gradually wear-away or erode with time. Continuous erosion of the surface prevents or at least reduces the duration of attachment of fouling organisms.

10 [Application of the coating composition]

The coating composition can be applied to a substrate by known methods, for example by conventional air-spraying, or by airless- or airmix-spraying equipment. It can alternatively be applied using brush or roller, for example when used as a stripe coat, or
15 for smaller vessels such as yachts. The composition can be applied at ambient conditions without pre-heating the coating composition. In spraying applications, conventional pressures such as 3 to 6 bara (bar-absolute) can be used.

The coating is typically applied so that a total dry film thickness of from 100-1000 μm is
20 obtained, such as 100-500 μm or 150-350 μm . The applied film thickness can vary depending on the nature of substrate being coated and the environment to which it will be exposed.

[Coating systems]

25

The coating composition can be used on its own or can be part of a coating system comprising more than one coating composition. It can be applied directly to a substrate surface or to a previously coated surface. For example, it can be applied on top of a primer, or an intermediate coat such as a tie-coat.

30

A particular benefit of the above-described coating compositions is the ability to combine the desirable attributes of good adhesion to undercoats or tie-coats, while still having highly effective fouling control properties.

In embodiments, the coating composition is applied directly to a primed surface. In further embodiments, the coating composition is applied to a tie-coat layer. The tie-coat can be on top of a primer layer, or directly on the substrate surface.

- 5 In embodiments, the coating composition is applied directly to a bare substrate. In other embodiments, the coating composition is applied to a previously coated substrate, such that it comprises one or more pre-existing and pre-cured and/or dried coating layers.

In embodiments, the coating composition is applied to a primer layer on the substrate.

- 10 The origin of the primer layer is not particularly limited, although in embodiments the primer is an epoxy resin-based primer.

In embodiments, the coating composition is applied to a tie-coat layer on the substrate, in which tie-coat layer is optionally on a primer layer on the substrate.

15

In embodiments, the coating composition forms part of a multi-coat system that additionally comprises a primer and/or a tie-coat.

In embodiments, a tie-coat layer can be applied on top of the primer layer to assist binding of the coating composition with the primer layer. However, in embodiments, no tie-coat is required.

20

[Substrate]

- 25 The substrate to which the coating is applied can be one that is intended to be immersed permanently or intermittently in water when in use. Substrates include metal, concrete, wood or polymeric surfaces.

Polymeric surfaces include polyvinyl chloride (PVC), or composites of fibre-reinforced resins. They also include flexible polymeric carrier foils, e.g. a PVC carrier foil to which the non-coated side is or can be adhered to a different surface.

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In embodiments, the substrate is a submergeable surface of a boat or ship, e.g. selected from one or more of the hull(s) (or at least the draft portion of the hull(s)), the propeller(s), and the rudder(s).

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Examples

The invention will now be described with reference to the following, non-limiting examples.

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[Anionic polymer synthesis]

The amounts of materials (in wt%) used in preparing amine cation-containing siloxane-modified acrylate-based polymers are listed in Table 1.

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Table 1 - Reaction mixtures for anionic polymer synthesis (wt%)

Ingredient	Anionic Polymer 1	Anionic Polymer 2	Anionic Polymer 3
Monomers:			
Acrylic acid	1.63	1.62	1.60
Methacrylic acid	1.86	1.85	1.83
Methacryl-modified PDMS ^[1]	23.26	23.14	22.82
Methyl methacrylate	8.38	10.18	8.21
Ethyl acrylate	6.98	0.00	6.85
Butyl acrylate	0.00	4.86	0.00
Initiators:			
Azobis(isobutyronitrile)	1.16	0.00	1.14
Azobis(methylbutyronitrile)	0.47	1.16	0.46
Peroxide:			
t-butyl peroxy-2-ethylhexanoate	0.23	0.23	0.23
Solvents:			
Xylene	24.43	24.83	23.96
1-methoxypropan-2-ol	17.91	18.21	17.57
Others:			
Rosin amine 90 [2]	13.69	13.93	0.00
Zinc Oxide	0.00	0.00	3.45
Naphthenic Acid	0.00	0.00	11.89

^[1] X-22-174BX – a single end methacryl-modified polydimethylsiloxane from ShinEtsu

^[2] Rosin Amine 90 (min.90% amine content) from Langley-Smith & Co Ltd, UK; CAS 61790-47-4

15 Approximately 75% of the total amount of solvents (by weight) were added to a polymerisation reaction vessel and heated to 100 °C. The monomers and the “azo” initiators were dissolved in 10% of the solvents, and then added dropwise to the

polymerisation vessel under constant stirring over a 5 hour period. A solution of the peroxide in the remaining 15% of the solvents was then added over a 30 minute period. The reaction was maintained for 90 minutes before being allowed to cool to room temperature.

5

The resulting resin solution was then mixed with a rosin amine, or with zinc oxide and naphthenic acid and heated under constant stirring at 105 °C for 10 hours, before being allowed to cool to room temperature.

10 [Coating Compositions]

The solutions containing the anionic polymers were used to prepare coating formulations according to the ingredients listed in Table 2. A further comparative composition was prepared based on a curable polysiloxane resin.

15

Table 2 – Base compositions for coating compositions (wt%)

Component	Example 1	Example 2	Comparative Example 1	Comparative Example 2
Anionic Polymer 1	80.50	0.00	0.00	0.0
Anionic Polymer 2	0.00	80.50	0.00	0.0
Anionic Polymer 3	0.00	0.00	80.50	0.0
HO-PDMS ^[1]	0.00	0.00	0.00	60.0
Aerosil™ R972 ^[2]	3.50	3.50	3.50	1.7
Tioxide™ TR92 ^[3]	15.00	15.00	15.00	0.0
Black Iron Oxide ^[4]	0.00	0.00	0.00	1.1
TEOS ^[5]	0.00	0.00	0.00	2.7
DOTL ^[6]	0.00	0.00	0.00	0.5
2,4-Pentandione	0.00	0.00	0.00	4.3
Xylene	1.00	1.00	1.00	18.7

^[1] Hydroxy-terminated polydimethylsiloxane, with a viscosity of 3678 mPa.s at 25°C

^[2] Dimethyldichlorosilane-treated fumed silica (Evonik)

^[3] Titanium dioxide (Huntsman)

20 ^[4] Bayferrox™ 318M (Lanxess)

^[5] Tetraethylorthosilicate, TES 40 (Wacker)

^[6] Dioctyl tin dilaurate, Tib Kat™ 216 (Tib Chemicals)

- Comparative Example 3 is Intersmooth™ 7640HS from International Paint Ltd, which is a commercially available self-polishing copolymer antifouling coating.
- Comparative Example 4 is Interswift™ 6800 HS from International Paint Ltd, which is another commercially available self-polishing copolymer antifouling coating, based on a copper acrylate copolymer.
- Comparative Example 5 is Intershield™ 1100SR from International Paint Ltd, which is a fluoropolymer-containing foul release coating composition. It is not a self-polishing antifouling coating.

[Polishing rate]

- Substrates used in these experiments were 23cm diameter Perspex discs which had been pre-coated with a layer of Intergard™ 263 epoxy tie-coat. The test coats were applied via a 600 µm drawdown cube, and left to dry under ambient conditions for 2 weeks. 5 replica experiments were carried out for each test coating.
- The substrates were immersed in sea-water and rotated at 700 rpm. The film thickness was measured at periodic intervals using a laser profilometer, and the film loss calculated. Results are shown in Table 3 and graphically illustrated in Figure 2.

Table 3 – Incremental film loss results (µm)

Composition	Days							
	0	6	29	90	133	218	260	324
C.Ex. 1	0	13.62	19.54	33.88	51.85	72.14	169.62	173.63
C.Ex. 3	0	4.87	2.92	11.38	8.82	8.57	7.78	5.30
Ex.1	0	14.79	27.45	36.94	42.16	51.21	54.68	59.74

- These results indicate that the polishing performance of Example 1 is stable over the long-term, significantly more so than Comparative Example 1 where the rate of film loss increases substantially after about 218 days, indicating that the coating film has begun to degrade and lose integrity. The film loss rate of Example 1 more closely matches that of the commercially available material of Comparative Example 3.

[Antifouling Activity]

Coatings were applied in a 6x6 “latin square” arrangement on plywood test panels. The panels were immersed in sea water in Singapore, and periodically checked for bio-fouling. The extent of observed fouling was assigned on a scale of 1 to 10, where 1 is very low and 10 is very high fouling. Two different boards were made, with results given in Tables 4 and 5.

Table 4 – Static fouling results (Board 1)

Material	Time	
	9 weeks	17 weeks
Example 1	2	2
Comparative Example 2	6	10
Comparative Example 4	1	3
Comparative Example 5	2	8

Table 5 – Static fouling results (Board 2)

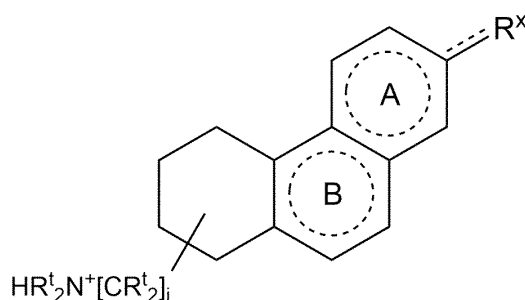
Material	Time	
	9 weeks	17 weeks
Example 1	1	2
Example 2	2	2
Comparative Example 2	5	9
Comparative Example 5	2	7

The results indicated that the Examples have good resistance to fouling, comparable to that of a commercial self-polishing copolymer-containing fouling control coating.

CLAIMS

1. A fouling control coating composition comprising an anionic polymer, an amine cation, and no more than 5 wt% water, the anionic polymer having one or more covalently attached siloxane moieties, wherein the amine cation is a protonated amine compound, and wherein the amine compound (before protonation) has a molecular weight of at least 70 and a boiling point at atmospheric pressure of at least 100 °C.
2. The fouling control coating composition as claimed in claim 1, wherein the amine cation is of formula $[H_{(4-w)}NR^n_w]^+$ and comprises from 4 to 60 carbon atoms in total, in which:
 - w is an integer in the range of from 1 to 3; and
 - each R^n is independently selected from groups having from 2 to 60 carbon atoms selected from optionally substituted aliphatic hydrocarbyl groups, optionally substituted aryl groups, and optionally substituted aryl groups having one or more aliphatic groups; the optional substituents being selected from:
 - halide, $-OR^t$, $-N(R^t)_2$, and groups selected from $-([CR^t_2]_jE-)_pR^t$ and $-E-([CR^t_2]_jE-)_pR^t$;
 - where:
 - each R^t is independently selected from H, C_{1-6} alkyl and C_{1-6} haloalkyl;
 - each E is independently selected from O and NR^t ;
 - each j is independently in the range of from 1 to 6; and
 - each p is independently in the range of from 1 to 20.
3. The fouling control composition as claimed in claim 2, in which w is an integer in the range of from 1 to 2.
4. The fouling control coating composition as claimed in any one of claims 1 to 3, which is a self-polishing fouling control coating composition.
5. The fouling control coating composition as claimed in any one of claims 1 to 4, in which the anionic polymer is a co-polymer made from one or more acrylate-based monomers at least one of which is an acrylate-based anionic monomer and at least one of which comprises a covalently attached siloxane moiety.

6. The fouling control composition as claimed in any one of claims 1 to 5, in which the anionic polymer is a thermoplastic polymer.
7. The fouling control composition as claimed in any one of claims 1 to 6, wherein the amine cation has one or more rings.
8. The fouling control composition as claimed in claim 7, where the amine cation is of formula:



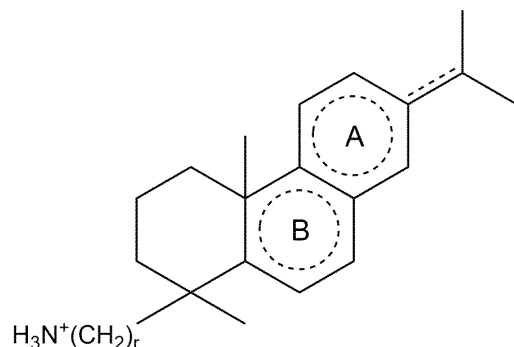
10

where:

- ring A is an alicyclic C_6 ring comprising zero, one or two $\text{C}=\text{C}$ double bonds, or an aromatic C_6 ring;
- ring B is an alicyclic C_6 ring that has zero or one $\text{C}=\text{C}$ double bond;
- 15 the bond between Ring A and R^x is a single or double bond;
- each R^1 is independently selected from H, C_{1-6} alkyl and C_{1-6} haloalkyl;
- R^x is a C_{1-20} aliphatic hydrocarbyl group, which can optionally be substituted with one or more substituents selected from halide, $-\text{OR}^1$ and $-\text{N}(\text{R}^1)_2$; and
- j is in the range of from 1 to 6.

20

9. The fouling control composition as claimed in claim 8, in which the amine cation is of formula:



where r is in the range of from 1 to 6.

10. The fouling control coating composition as claimed in any one of claims 1 to 9,
5 in which the amount of amine cations to anionic monomer units in the anionic polymer is at least 80 mol%.
11. The fouling control coating composition as claimed in any one of claims 1 to 10,
in which the anionic polymer is an acrylate-based anionic polymer comprising at least 80
10 mol% of monomer units selected from those of Formula (3) and Formula (4):



15

where:

each R^f is independently selected from H, C₁₋₂₀ aliphatic hydrocarbyl, C₆₋₁₂ aryl, and C₆₋₁₂ aryl with one or more substituents selected from C₁₋₆ alkyl, C(O)O⁻, and C(O)OR^t;

each R^g is independently selected from H and C₁₋₂₀ aliphatic hydrocarbyl, C₆₋₁₂ aryl and C₆₋₁₂ aryl substituted with one or more C₁₋₆ aliphatic hydrocarbyl groups;
20 each R^t is independently selected from H, C₁₋₆ alkyl and C₁₋₆ haloalkyl;

each aliphatic hydrocarbyl substituent, aliphatic hydrocarbyl group and aryl group in R^g is optionally substituted with one or more substituents selected from halide, $-OR^t$, $-N(R^t)_2$, $-OC(O)R^t$, $-C(O)N(R^t)_2$, $-OC(O)N(R^t)_2$, $-([CR^t_j]E-)_pR^t$ and $-E-([CR^t_j]E-)_pR^t$; each E is independently selected from O and NR^t ;

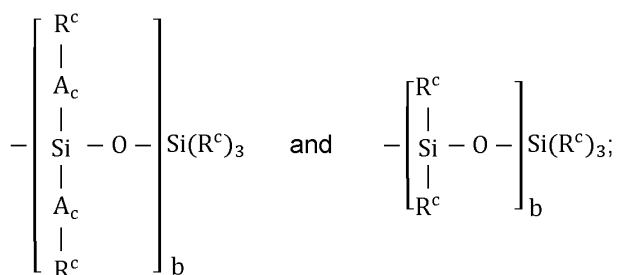
5 j is in the range of from 1 to 6; and

p is in the range of from 1 to 20;

each aliphatic hydrocarbyl substituent, aliphatic hydrocarbyl group and aryl group in R^f is optionally substituted with one or more substituents as set out above for R^g and also from $-C(O)O^-$ and $-C(O)OR^t$;

10 Z is selected from $-OR^h$, and $-N(R^h)_2$;

each R^h is independently selected from H and C_{1-20} alkyl, optionally substituted as set out above for R^g , and also from siloxane moieties of formula:



15

where each A is independently $[OSi(R^c)_2]$;

each R^c is independently selected from optionally substituted C_{1-20} aliphatic hydrocarbyl groups, optionally substituted C_{6-12} aryl groups, and optionally substituted C_{6-12} aryl groups having one or more C_{1-6} alkyl groups, the optional substituents being selected from halide, $-OR^t$ and $-N(R^t)_2$;

20

b is in the range of from 3 to 150; and

c is in the range of from 0 to 20;

wherein there is at least one monomer unit of Formula (4) in which at least one R^h group has a siloxane moiety.

25

12. The fouling control coating composition as claimed in claim 11, in which the siloxane moiety is a non-functional dimethylpolysiloxane or methylphenylpolysiloxane.

13. A method for controlling aquatic biofouling on a man-made object, comprising

30 applying the fouling control coating composition as claimed in any one of claims 1 to 12

onto the surface of a man-made structure, the man-made structure being a structure that is intended to be permanently or intermittently immersed in water.

14. A substrate or article coated with the fouling control coating composition as
5 claimed in any one of claims 1 to 12.

15. Use of the coating composition as claimed in any one of claims 1 to 12 for controlling aquatic biofouling on a man-made structure.