Antifouling Composition

Field of the Invention

The present invention relates to a binder for a marine antifouling coating composition, more specifically to marine antifouling coating compositions comprising a three component binder based on a hydrophilic (meth)acrylate copolymer, a cyclic monocarboxylic acid and a silyl ester or (meth)acrylic polymer. The invention further relates to a method of protecting objects from fouling, and objects coated with the antifouling composition of the invention.

Background of invention

Surfaces that are submerged in seawater are subjected to fouling by marine organisms such as green and brown algae, barnacles, mussels, tube worms and the like. On marine constructions such as vessels, oil platforms, buoys, etc. such fouling is undesired and has economic consequences. The fouling may lead to biological degradation of the surface, increased load and accelerated corrosion. On vessels the fouling will increase the frictional resistance which will cause reduced speed and/or increased fuel consumption. It can also result in reduced manoeuvrability.

To prevent settlement and growth of marine organisms antifouling paints are used. These paints generally comprise a film-forming binder, together with different components such as pigments, fillers, solvents and biologically active substances.

The most successful self-polishing antifouling systems on the market today are based on silyl ester functional (meth)acrylic copolymers. Silyl ester functional (meth)acrylic copolymers are often used together with other binders such as acrylates and rosin or rosin derivatives to adjust the self-polishing properties and the mechanical properties of antifouling coating films.

Whilst marine antifouling paints are designed to operate in sea water, it is also important that these coatings operate in fresh water. In particular, it is important that the coatings do not suffer from excessive water uptake in fresh water.

It may not be immediately obvious why water uptake in freshwater is important for coatings on ships that operate on the seas. However, many vessels will trade in freshwater for some period of time. For example, the Panama Canal contains fresh water. Also, many new builds are outfitted in freshwater rivers in China. In these cases, excessive water uptake can lead to excessive swelling and, in the worst case, breakdown of the paint film.

The ability to resist water uptake in fresh water is also an important indicator for operations in seawater. It is a good indicator that the coatings will have long term stability. In seawater, paint films will take up water but the rate and amount is reduced due to the lower osmotic pressure. Excessive water uptake in freshwater indicates that, long term, the water uptake in seawater will increase.

Antifouling coatings are designed to work for up to 7.5 years in-service. Maintaining a minimal water uptake throughout this period is an important factor in controlling the release of active components from the coating. Within any given type of antifouling technology there is a clear relationship between long term reliable performance and water uptake. Excessive water uptake will lead to higher release rates of active components than desired and a fall in performance over the lifetime of the coating. Depending upon the type of binder system used the increased water uptake can lead to faster hydrolysis and excessive erosion or accelerated leaching of active components, resulting in the formation of a thick depleted layer (leached layer) towards the surface of the coating. In all cases the control of water uptake is a key parameter in designing high performance antifouling coatings such as those for new builds and dry dockings.

The inventors have found that the use of a particular binder in an antifouling paint surprisingly reduces the water uptake in freshwater. The binder is one that comprises three components, a hydrophilic (meth)acrylate copolymer comprising certain hydrophilic monomers, a cyclic monocarboxylic acid component and an acrylic/silyl ester copolymer component. When used together in an antifouling coating composition the binder reduces the amount of water that is taken up by the film. Antifouling coatings comprising the binder of the invention therefore offer extended service intervals.

The literature contains many disclosures of binder polymers for anti-fouling coatings. In particular silyl ester copolymers and acrylate based polymers are well known. There are however few disclosures of binders comprising a blend of three binder components as required in the present invention.

In EP2128208, antifouling coating compositions are prepared comprising silyl ester copolymers, a rosin component and a plasticising resin of very low glass transition temperature. As we have established in the examples, if the hydrophilic (meth)acrylate polymer has a low Tg, the binder will suffer from high water uptake.

WO03070832 describes a coating composition comprising copolymer A (silyl copolymer), polymer B (which is incompatible with copolymer A and may comprise a hydrophilic comonomer) and optionally polymer C (often a non hydrophobic copolymer). None of the paint examples uses a cyclic monocarboxylic acid. The use of such as acid is advantageous as this reduces the viscosity of the coating composition and therefore makes it possible to make coating compositions with lower VOC.

WO2014175246 describes an antifouling coating composition comprising a binder based on a copolymer based on styrene and glycidyl (meth)acrylate and a silyl ester copolymer. Example 15 uses rosin but there is no disclosure of a copolymer (i) as required in the present invention as there is a large excess of styrene present. Copolymers therein such as A-13 have a Tg of considerably less than 0°C.

WO97/44401 describes the use of rosin or rosin equivalents, fibres and a polymeric flexibilizer in an antifouling coating composition. There are no paint examples comprising two types of (meth)acrylic copolymers.

EP1288234 describes a film-forming polymer prepared from binders with a low hydrolysable monomer content. The only hydrophilic comonomers exemplified are vinyl pyrrolidone and methacrylic acid and no examples are based on a combination of acrylic copolymers.

WO2005/005516 describes silyl ester copolymers with low Mw and their use in antifouling coatings. Example 7 describes a coating composition containing a binder based on an unidentified silyl ester copolymer, rosin and Degalan LP 64/12 (a

non-hydrophilic BMA/MMA copolymer). None of the disclosed silyl copolymers have a hydrophilic monomer content above 10 wt%, i.e. the hydrophilic binder component of the present invention is lacking.

WO2011/131721 describes coating composition which is produced by adding the different components in a specific order (e.g. drying agent). In the examples rosin is used together with Neocryl B725 (a non-hydrophilic BMA/MMA copolymer) and Polyace NSP-100 (silyl acrylate). No hydrophilic comonomers are used in Neocryl B725.

WO2014/175140 describes a silyl copolymer with specific end groups.

EP3078715 covers an antifouling coating composition comprising a silyl ester copolymer, tralopyril and a stabilizer. In the examples a triisopropylsilyl methacrylate copolymer, gum rosin and an acrylic polymer are used. The monomer composition or the polymer properties of the acrylic copolymer is not specified.

WO2009/149919 patent covers the use of caprolactone modified comonomers in a silyl copolymer. No additional acrylic polymer is used.

EP2489710 exemplifies antifouling coatings and exemplifies two acrylic acid copolymers T3 and T4. These are combined with rosin and a vinyl chloride-isobutylvinyl ether copolymer).

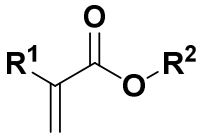
In EP2161316 and the related US2011/0166253, the binder is based on a rosin component and a silyl ester component, i.e. the third binder component of the present invention is lacking.

The combination of components required in the claims is new and offers remarkable results.

Summary

In a first example the disclosure provides a binder for an antifouling coating composition comprising:

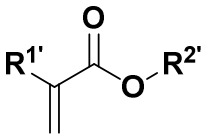
(i) a hydrophilic copolymer having a glass transition temperature of at least 0°C comprising at least 10 wt% of at least one monomer of Formula (I)



(I)

wherein R^1 is H or CH_3, and R^2 is a C3-C18 substituent with at least one oxygen or nitrogen atom, preferably at least one oxygen atom or R^2 is a poly(alkylene glycol) chain;

and at least one monomer of Formula (II),



(II)

wherein $R^{1'}$ is H or CH_3, and $R^{2'}$ is a C1-C20 hydrocarbyl;

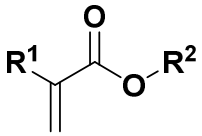
said hydrophilic copolymer comprising less than 15 wt% comonomers other than those of Formula (I) or (II);

(ii) a cyclic monocarboxylic acid such as rosin or a derivative thereof (such as a salt thereof); and

(iii) a silyl ester copolymer comprising at least 15 wt% of silyl ester monomer and/or a non-hydrophilic (meth)acrylic polymer comprising less than 10 wt% of monomer according to Formula (I), preferably less than 5 wt%, most preferably 0 wt% of monomers of Formula (I).

In one aspect, the present disclosure refers to a binder for an antifouling coating composition comprising:

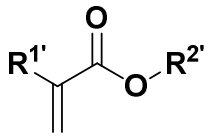
(i) a hydrophilic copolymer having a glass transition temperature of at least 0°C, said hydrophilic copolymer comprising at least 10 wt% of at least one monomer of Formula (I)



(I)

wherein R^1 is H or CH_3, and R^2 is a C3-C18 substituent with at least one oxygen or nitrogen atom, preferably at least one oxygen atom or R^2 is a poly(alkylene glycol) chain;

and at least one monomer of Formula (II),



(II)

wherein $R^{1'}$ is H or CH_3, and $R^{2'}$ is a C1-C20 hydrocarbyl;

wherein said hydrophilic copolymer is free of any metal-ion containing comonomers; and

said hydrophilic copolymer comprising less than 15 wt% comonomers other than those of Formula (I) or (II);

(ii) a cyclic monocarboxylic acid such as rosin or a derivative thereof (such as a salt thereof); and

(iii) a silyl ester copolymer comprising at least 15 wt% of silyl ester monomer and/or a non-hydrophilic (meth)acrylic polymer which comprises less than 10 wt% of a monomer of Formula (I).

The amount of component (i) in the binder is preferably in the range of 20 to 60 wt% (dry solids). The amount of component (ii) in the binder is preferably in the range of 10 to 70 wt% (dry solids). The amount of component (iii) in the binder is preferably in the range of 5 to 70 wt% (dry solids).

The disclosure also provides an antifouling coating composition comprising a binder as described herein, preferably dispersed in a solvent. The antifouling coating may further comprise an antifouling agent, preferably cuprous oxide, zinc ethylenebis(dithiocarbamate) and/or copper pyrithione.

In another aspect, the present disclosure refers to an antifouling coating composition comprising a binder as disclosed herein and at least one antifouling agent.

In another aspect, the present disclosure refers to a process for protecting an object from fouling, said process comprising coating at least a part of said object which is subject to fouling with an antifouling coating composition as disclosed herein.

The disclosure also relates to objects coated with the antifouling coating composition as defined herein or to the use of the antifouling composition of the disclosure to protect a marine surface from fouling.

In another aspect, the present disclosure refers to an object coated with the antifouling coating composition as disclosed herein.

Definitions

The term "marine antifouling coating composition", "antifouling coating composition" or simply "coating composition" refers to a composition which is suitable for use in marine environments. The antifouling coating composition preferably contains an antifouling agent, e.g. a biocide.

The term hydrocarbyl group refers to any group containing C atoms and H atoms only and therefore covers alkyl, alkenyl, aryl, cycloalkyl, arylalkyl groups and so on.

The term "(meth)acrylate" means a methacrylate or acrylate.

The term "poly(alkylene oxide)" refers to a compound comprising –[alkylene-O]- repeat units. Typically the alkylene is ethylene or propylene.

The term "rosin" used in the text which follows is being used to cover "rosin or derivatives thereof".

The term "binder" defines part of the composition which includes the copolymers and cyclic monocarboxylic acid, and any other components which together form a matrix giving substance and strength to the composition. The "binder" includes the polymer components (i) and (iii) along with the cyclic monocarboxylic acid (ii).

The term non-hydrophilic (meth)acrylic polymer defines a polymer that comprises at least one (meth) acrylic acid monomer or at least one (meth)acrylate monomer (or potentially both) but comprises less than 10 wt% of monomer according to Formula (I), preferably less than 5 wt%, most preferred 0 wt% of a monomer of Formula (I). When less than 10 wt% of monomer of Formula (I) is present, this is deemed non-hydrophilic.

Where a wt% of a given monomer is given, the wt% is relative to the sum total (weight) of each monomer present in the copolymer. Thus if 2-methoxyethyl

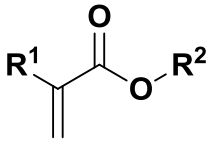
acrylate (MEA) and methyl methacrylate (MMA) are the only monomers in the copolymer component (i), the wt% of MEA is calculated as (MEA (weight) / (MEA (weight) + MMA (weight))) x 100%.

Detailed description of invention

This invention relates to a new binder for marine antifouling coating composition that exhibits remarkably low water uptake in freshwater. These compositions therefore offer an extended service life. The antifouling coating composition of the invention comprises a binder which contains at least three components.

Copolymer component (i)

The invention requires the use of certain hydrophilic (meth)acrylate based copolymers. The term hydrophilic is used herein to imply the presence of at least 10 wt% of at least one monomer of Formula (I). The copolymer component (i) therefore comprises at least one monomer of Formula (I):



(I)

wherein R^1 is H or CH_3, and R^2 is a C3-C18 substituent containing at least one oxygen or nitrogen atom, preferably at least one oxygen atom or R^2 represents a poly(alkylene glycol) group. As used herein, this structure defines “hydrophilic” (meth)acrylate monomers.

As indicated in the above formula, the term “hydrophilic (meth)acrylate” requires the R^2 group in Formula (I) to include at least one oxygen or nitrogen atom, preferably at least one oxygen atom. As explained in detail below, additional non-hydrophilic (meth)acrylate monomers are also present in component (i) of the binder as monomers of Formula (II), in which the $R^{2'}$ unit consists of C and H atoms only.

In an embodiment, the binder copolymer component (i) contains at least one monomer of Formula (I) above in which the R^2 group is of formula $(CH_2CH_2O)_n$-R^3 where R^3 is a C1-C10 hydrocarbyl substituent, preferably a C1-C10 alkyl or C6-C10 aryl substituent, and n is an integer in the range of 1 to 5, preferably 1 to 3. Preferably R^2 is of formula $(CH_2CH_2O)_n$-R^3 where R^3 is a C1-C10 alkyl substituent, preferably CH_3 or CH_2CH_3, and n is an integer in the range of 1 to 3, preferably 1 or 2. Such a monomer might be 2-methoxyethyl acrylate, 2-ethoxyethyl acrylate, 2-butoxyethyl acrylate, 2-(2-methoxyethoxy)ethyl acrylate, 2-(2-ethoxyethoxy)ethyl acrylate, 2-(2-butoxyethoxy)ethyl acrylate, 2-[2-(2-methoxyethoxy)ethoxy]ethyl acrylate, 2-[2-(2-ethoxyethoxy)ethoxy]ethyl acrylate, 2-methoxyethyl methacrylate, 2-ethoxyethyl methacrylate, 2-butoxyethyl methacrylate, 2-(2-methoxyethoxy)ethyl methacrylate, 2-(2-ethoxyethoxy)ethyl methacrylate, 2-(2-butoxyethoxy)ethyl methacrylate, 2-[2-(2-methoxyethoxy)ethoxy]ethyl methacrylate, 2-[2-(2-ethoxyethoxy)ethoxy]ethyl methacrylate.

In an embodiment, the copolymer component (i) includes one or more of 2-methoxyethyl acrylate (MEA), 2-methoxyethyl methacrylate (MEMA), 2-ethoxyethyl methacrylate (EEMA), 2-(2-ethoxyethoxy)ethyl acrylate (EDEGA) or 2-(2-ethoxyethoxy)ethyl methacrylate (EDEGMA).

In another embodiment, the copolymer component (i) contains at least one monomer of Formula (I) above in which the R^2 group is a poly(alkylene glycol) group such as a poly(ethylene glycol) group. Such a group might have a formula $(CH_2CH_2O)_m$-R^{13} or $(CH_2CH(CH_3)O)_m$-R^{13} where R^{13} is a C1-C10 hydrocarbyl substituent, preferably a C1-C10 alkyl or C6-C10 aryl substituent, and m is an integer in the range of 5 to 100, preferably 5 to 20. Such a monomer might be poly(ethylene glycol) methyl ether acrylate, poly(ethylene glycol) ethyl ether acrylate, poly(ethylene glycol) methyl ether methacrylate, poly(ethylene glycol) ethyl ether methacrylate. Preferred such a monomer have a number average molecular weight (Mn) of 300-4000, more preferably 300-1000.

In an embodiment, the copolymer component (i) contains at least one monomer of Formula (I) above in which the R^2 group is a saturated cyclic group containing at least one oxygen or nitrogen atom, preferably at least one oxygen

atom. More preferably, R^2 is a group W-R^{10} wherein R^{10} is a cyclic ether (such as oxolane, oxane, dioxolane, dioxane optionally alkyl substituted) and W is a C1-C4 alkylene. Such a monomer might be furfuryl acrylate, tetrahydrofurfuryl acrylate, (1,3-dioxolan-4-yl)methyl acrylate, furfuryl methacrylate, tetrahydrofurfuryl methacrylate, (2,2-dimethyl-1,3-dioxolan-4-yl)methyl methacrylate. Preferred cyclic ethers should contain at least 4 atoms in the ring. Most preferably in this embodiment, the compound of Formula (I) is tetrahydrofurfuryl acrylate (THFA) and tetrahydrofurfuryl methacrylate (THFMA).

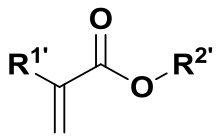
In one embodiment, the hydrophilic copolymer component (i) does not comprises a glycidyl group.

Monomers of Formula (I) preferably form at least 15 wt% of the copolymer (i). Particularly preferred amounts of hydrophilic (meth)acrylate monomer of Formula (I) in the binder component (i) are 15 to 65 wt%, preferably 18 to 62 wt%, such as 20 to 50 wt%. Where a mixture of monomers of Formula (I) are present, these amounts relate to the combined weight fraction of the monomers of Formula (I) in the copolymer.

The monomer of Formula (I) is preferably 2-methoxyethyl acrylate (MEA), 2-methoxyethyl methacrylate (MEMA), 2-ethoxyethyl methacrylate (EEMA), tetrahydrofurfuryl acrylate (THFA), tetrahydrofurfuryl methacrylate (THFMA), 2-(2-ethoxyethoxy)ethyl acrylate (EDEGA) or 2-(2-ethoxyethoxy)ethyl methacrylate (EDEGMA).

Non-hydrophilic (meth)acrylate monomer(s)

The copolymer component (i) of the invention also includes one or more non-hydrophilic (meth)acrylate monomers of Formula (II)



(II)

wherein $R^{1'}$ is H or CH_3, and $R^{2'}$ is a C1-C20 hydrocarbyl substituent, preferably a C1-8 alkyl substituent, most preferably methyl, ethyl, n-propyl, n-butyl or 2-

ethylhexyl. Monomers according to Formula (II) are referred to as "non-hydrophilic" monomers herein.

In all embodiments of the invention, the copolymer component (i) includes at least one non-hydrophilic methacrylate and/or non-hydrophilic acrylate monomer (II) along with at least one monomer of Formula (I). Monomers of Formula (II) preferably form at most 85 wt% of component (i), preferably 35 to 85 wt%, such as 38 to 82 wt%, such as in the range of 40 to 80 wt%. Where a mixture of monomers of Formula (II) are present, these preferred amounts relate to the combined weight fraction of the monomers of Formula (II) in the copolymer.

In a preferred embodiment, the copolymer component (i) consists of monomers of Formula (I) and (II) only.

In a preferred embodiment, there is more monomer by wt of Formula (II) than Formula (I).

Preferred options for monomers of Formula (II) include methyl methacrylate (MMA), n-butyl acrylate (n-BA), n-butyl methacrylate (n-BMA), 2-ethylhexyl acrylate (2-EHA) or 2-ethylhexyl methacrylate (2-EHMA). In all embodiments of the invention it is preferred that methyl methacrylate (MMA) or n-butyl acrylate (n-BA) is included in copolymer component (i).

In an embodiment the copolymer includes one or more of the hydrophilic monomers MEA, EDEGA, EEMA, poly(ethylene glycol) methyl ether methacrylate or THFA and at least one non-hydrophilic (meth)acrylate monomer MMA or n-BA.

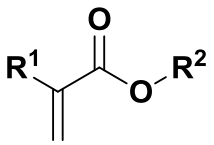
The copolymer component (i) contains less than 15 wt% of any monomer other than the monomers of Formula (I) and (II) above. It is therefore required that copolymer component (i) contains less than 15 wt% of any silyl ester monomers of Formula (III) defined below, preferably less than 10 wt% of any silyl ester monomers of Formula (III) defined below. In some embodiments component (i) may consist of monomers of Formulae (I) and (II) only.

The copolymer component (i) is preferably free of any (meth)acrylic acid comonomers.

The copolymer component (i) is preferably free of any metal-ion containing comonomers.

In a preferred embodiment, the hydrophilic copolymer (i) comprises

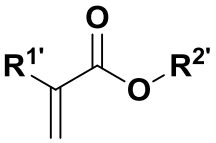
(i) 15 to 65 wt% of at least one monomer of Formula (I)



(I)

wherein R^1 is H or CH_3, and R^2 is a C3-C18 substituent with at least one oxygen or nitrogen atom, preferably at least one oxygen atom or R^2 is a poly(alkylene glycol) chain;

and 35 to 85 wt% of at least one monomer of Formula (II),



(II)

wherein $R^{1'}$ is H or CH_3, and $R^{2'}$ is a C1-C20 hydrocarbyl;

said hydrophilic copolymer comprising less than 15 wt% comonomers other than those of Formula (I) or (II).

Properties of copolymer component (i)

The copolymer preferably has a weight-average molecular weight (Mw) of from 5,000 to 70,000, preferably of from 10,000 to 60,000, especially 15,000 to 40,000. Mw is measured as described in the examples section.

The copolymer preferably has a polydispersity index (PDI) of from 1.5 to 5.0.

The copolymer component (i) preferably has a glass transition temperature (Tg) of at least 0°C. The copolymer preferably has a glass transition temperature (Tg) of at least 5°C, preferably at least 10°C, such as at least 15°C, all values being measured according to the Tg test described in the examples section. Values less than 80°C are preferred, such as less than 75°C, e.g. less than 50°C. Without wishing to be limited by theory, it is believed that the higher Tg contributes to the

reduction in water uptake that we observe in the examples. Where the Tg is below 0°C, water uptake is higher.

The copolymer component (i) preferably is partially or fully incompatible with the blend of the other binder components. By incompatible is meant that the binder components are incompatible according to the test method explained below in the examples section.

The amount of copolymer component (i) in the binder is preferably in the range of 20 to 60 wt%, such as 30 to 50 wt% (dry solids).

The final antifouling coating composition of the invention preferably comprises 0.5 to 45 wt% (dry solids) of the copolymer component (i), such as 1.0 to 30 wt%, in particular 5.0 to 25 wt%.

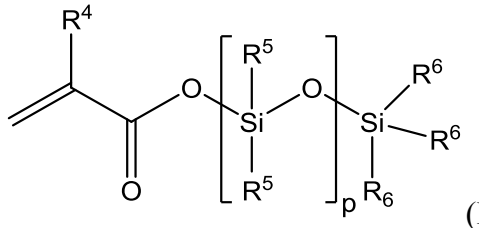
An antifouling coating composition of the invention may optionally comprise a mixture of copolymer components (i) of the invention.

Polymer component (iii)

The binder of the invention additional comprises a polymer component (iii). This component is different from component (i). Component (iii) may be based on a non-hydrophilic (meth)acrylic acid polymer, a non-hydrophilic (meth)acrylate polymer (iii-2) or a silyl ester copolymer comprising at least 15 wt% of silyl ester monomer (iii-1). Component (iii) may be a non-hydrophilic (meth)acrylic polymer (referred to herein as (iii-2)). Component (iii) may also be a mixture of copolymer (iii-1) and polymer (iii-2). Component (iii) is therefore different to component (i).

Silyl ester copolymer component (iii-1)

Component (iii-1) comprises at least one silyl (meth)acrylate monomer. Suitable silyl (meth)acrylate monomers of use in component (iii) are preferably of Formula (III)



(III)

wherein

R^4 is H or CH_3;

R^5 is each independently selected from linear or branched C_{1-4} alkyl groups;

R^6 is each independently selected from the group consisting of linear or branched C1-C20 alkyl groups, C3-C12 cycloalkyl groups, optionally substituted C6-C20 aryl groups and $-OSi(R^7)_3$ groups;

each R^7 is independently a linear or branched C1-C4 alkyl groups,

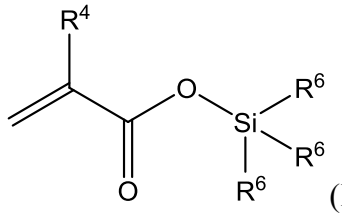
p is an integer from 0 to 5;

The term "alkyl" is intended to cover both linear or branched alkyl groups such as methyl, ethyl, isopropyl, propyl, butyl and tert-butyl. Particularly preferred cycloalkyl groups include cyclohexyl and substituted cyclohexyl.

Examples of the substituted aryl groups include aryl groups substituted with at least one substituent selected from halogens, alkyl groups having 1 to about 8 carbon atoms, acyl groups, or a nitro group. Particularly preferred aryl groups include substituted and unsubstituted phenyl, benzyl, phenalkyl or naphthyl.

Ideally, preferred silyl ester monomers are based on compounds of Formula (III) in which p is 0.

More preferably, silyl ester monomers are of Formula (IV)



(IV)

wherein R^4 is H or CH_3; and

R^6 is each independently selected from the group consisting of linear or branched C1-C10 alkyl groups.

Examples of monomers containing silyl ester functionality are well known. Monomers as defined by the general Formula (III) include:

silyl ester monomers of acrylic acid and methacrylic acid, such as tri-n-propylsilyl (meth)acrylate, triisopropylsilyl (meth)acrylate, tri-n-butylsilyl (meth)acrylate, triisobutylsilyl (meth)acrylate, *tert*-butyldimethylsilyl (meth)acrylate, thexyldimethylsilyl (meth)acrylate, *tert*-butyldiphenylsilyl (meth)acrylate, nonamethyltetrasiloxanyl (meth)acrylate, bis(trimethylsiloxy)methylsilyl (meth)acrylate, tris(trimethylsiloxy)silyl (meth)acrylate.

The use of triisopropylsilyl acrylate (TISA) or triisopropylsilyl methacrylate (TISMA) is preferred.

Preferably, component (iii-1) comprises at least 15 wt% of the silyl ester monomer, preferably 15 to 65 wt%, especially 35 to 60 wt%.

Preferably, as well as the silyl ester monomer(s), the silyl ester copolymer component (iii-1) comprises a second comonomer other than a silyl ester monomer. The second comonomer is preferably of Formula (I) or (II) as herein before defined. Silyl ester copolymer component (iii-1) may also comprise a monomer of Formula (I) and a monomer of Formula (II) as hereinbefore defined.

Preferred monomers of Formula (I) of use in silyl ester copolymer component (iii) are EDEGA, THFA, MEA and MEMA, especially EDEGA and THFA. Preferred hydrophobic comonomers include MMA, n-BA, n-BMA and 2-EHA.

The silyl ester copolymer preferably includes at least the monomers triisopropylsilyl (meth)acrylate, a monomer of Formula (I) and a monomer of Formula (II). Preferred options for Formulae (I) and (II) above apply independently to the component (iii) embodiment. Preferred options for monomers of Formula (II) include methyl methacrylate (MMA), n-butyl acrylate (n-BA), n-butyl methacrylate (n-BMA), 2-ethylhexyl acrylate (2-EHA) or 2-ethylhexyl methacrylate (2-EHMA). In all embodiments of the invention it is preferred that methyl methacrylate (MMA) or butyl acrylate (n-BA) is included in copolymer component (iii).

Preferably, silyl ester copolymer component (iii) comprises at least 15 wt% of the monomer of Formula (II) component, especially 15 to 65 wt%.

Preferably, silyl ester copolymer component (iii) comprises 5 to 30 wt% of the monomer of Formula (I).

The silyl ester copolymer preferably has a glass transition temperature (Tg) of at least 15°C, preferably at least 20°C, such as at least 25°C, all values being measured according to the Tg test described in the examples section. Values less than 80°C are preferred, such as less than 75°C, e.g. less than 50°C.

The silyl ester copolymer component (iii) preferably has a weight-average molecular weight of from 5,000 to 70,000, preferably of from 10,000 to 60,000, especially 20,000 to 50,000. Mw is measured as described in the examples section.

The silyl ester copolymer preferably has PDI of 2 to 6.

The amount of silyl ester component (iii) in the binder is preferably in the range of 10 to 60 wt%, preferably 15 to 50 wt% (dry solids).

(Meth)acrylic polymer component (iii-2)

Alternatively or in addition, the component (iii) comprises a non-hydrophilic (meth)acrylic polymer comprising at least one (meth)acrylic acid monomer or at least one (meth)acrylate monomer (or both) such as one of Formula (II). Component (iii-2) can be a homopolymer or a copolymer, preferably a copolymer. In particular, where a (meth)acrylic acid monomer is present, it is preferred if a second monomer is present to thus form a copolymer. The second monomer in this embodiment is preferably a monomer of Formula (II) as herein defined.

The non-hydrophilic (meth)acrylic polymer comprises less than 10 wt% of any monomers of Formula (I) and is preferably free of any monomers of Formula (I). It is also preferably free of any silyl ester monomers.

Preferably, (meth)acrylic acid is present in the non hydrophilic (meth)acrylic polymer component (iii-2). Preferably, (meth)acrylic acid is present in a non hydrophilic (meth)acrylic copolymer component (iii-2), especially with a second comonomer of formula (II).

Preferred options for combination with (meth)acrylic acid include a monomer of Formula (II) such as MMA, n-BMA and n-BA.

The (meth)acrylic acid content within the copolymer component (iii-2) is preferably in the range of 0.5 to 10 wt%. Monomers of Formula (II) preferably form at least 50 wt% of the (meth)acrylic acid copolymer, such as at least 75 wt%, especially 90 to 99.5 wt%.

Alternatively, the non-hydrophilic (meth)acrylic polymer component (iii-2) can comprise one or more monomers of Formula (II). In one embodiment therefore, non-hydrophilic (meth)acrylic polymer component (iii-2) is a (meth)acrylate homopolymer, e.g. of a monomer of formula (II).

Monomers of Formula (II) preferably form at least 50 wt% of the (meth)acrylic polymer, such as at least 75 wt%, especially 90 to 100 wt% in this embodiment. Preferred options for Formula (II) are those recited above in connection with component (i), such as methyl methacrylate (MMA), n-butyl acrylate (n-BA), n-butyl methacrylate (n-BMA), 2-ethylhexyl acrylate (2-EHA) or 2-ethylhexyl methacrylate (2-EHMA).

In all embodiments of the invention it is preferred that methyl methacrylate (MMA) or n-butyl acrylate (n-BA) is included in polymer component (iii-2).

The (meth)acrylic polymer component (iii-2) preferably has a glass transition temperature (Tg) of less than 0°C, preferably less than -20°C, such as less than -22°C, all values being measured according to the Tg test described in the examples section. Values more than -60°C are preferred, e.g. more than -50°C.

The (meth)acrylic polymer component (iii-2) preferably has a weight-average molecular weight of from 5,000 to 70,000, preferably of from 10,000 to 60,000, especially 15,000 to 35,000. Mw is measured as described in the examples section.

The (meth)acrylic polymer component (iii-2) preferably has PDI of 1.5 to 5.0.

The binder composition of the invention preferably comprises 0.5 to 25 wt% (dry solids) of the (meth)acrylic polymer component (iii-2) if present, such as 1.0 to 22 wt%, in particular 2.0 to 18 wt%.

In general, the amount of component (iii) (combined amounts of (iii-1)+(iii-2)) in the binder is preferably in the range of 5 to 70 wt%, preferably 10 to 60 wt%, preferably 10 to 50 wt%, especially 15 to 50 wt% (dry solids).

It is preferred if (meth)acrylic polymer component (iii-2) is present. If a silyl ester copolymer component (iii-1) is present, it is also preferred if a (meth)acrylic polymer component (iii-2) is present. The weight ratio of these components may be 95 to 50: 50 to 5, preferably 90 to 60: 40 to 10 component (iii-1) to (iii-2). Hence if both (iii-1) and (iii-2) are present it is preferred if there is an excess of component (iii-1).

Antifouling coating compositions of the invention preferably comprise at least 0.5 wt% (dry solids) component (iii), such as at least 1 wt%. The upper limit for component (iii) may be 20 wt%, such as 15 wt%.

Preparation of the copolymer component (i) and polymer component (iii)

The polymers may be prepared using polymerization reactions known in the art. Acrylic polymers are preferably prepared using addition polymerization or chain growth polymerization. Examples of suitable addition polymerization techniques include free-radical polymerization, anionic polymerization and adequate controlled polymerization techniques. The polymer may, for example, be obtained by polymerizing a monomer mixture in the presence of a polymerization initiator and optionally a chain transfer agent by any of various methods such as solution polymerization, bulk polymerization, emulsion polymerization, and suspension polymerization in a conventional way or by controlled polymerization techniques. In preparing a coating composition using this polymer, the polymer is preferably diluted with an organic solvent to give a polymer solution having an appropriate viscosity. From this standpoint, it is desirable to employ solution polymerization.

Examples of polymerization initiators for free-radical polymerization include azo compounds such as dimethyl 2,2’-azobis(2-methylpropionate), 2,2'-azobis(2-methylbutyronitrile), 2,2'-azobis(isobutyronitrile) and 1,1'-azobis(cyanocyclohexane) and peroxides such as *tert*-butyl peroxypivalate, *tert*-butyl peroxy-2-ethylhexanoate, *tert*-butyl peroxydiethylacetate, *tert*-butyl

peroxyisobutyrate, di-*tert*-butyl peroxide, *tert*-butyl peroxybenozate, and *tert*-butyl peroxyisopropylcarbonate, *tert*-amyl peroxypivalate, *tert*-amyl peroxy-2-ethylhexanoate, 1,1-di(*tert*-amyl peroxy)cyclohexane and dibenzoyl peroxide. These compounds are used alone or as a mixture of two or more thereof.

Examples of the organic solvent include aromatic hydrocarbons such as xylene, toluene, mesitylene; ketones such as methyl ethyl ketone, methyl isobutyl ketone, methyl amyl ketone, methyl isoamyl ketone, cyclopentanone, cyclohexanone; esters such as butyl acetate, *tert*-butyl acetate, amyl acetate, ethylene glycol methyl ether acetate, butyl propionate, isobutyl isobutyrate; ethers such as ethylene glycol dimethyl ether, diethylene glycol dimethyl ether, dibutyl ether, dioxane, tetrahydrofuran, alcohols such as n-butanol, isobutanol, benzyl alcohol; ether alcohols such as butoxyethanol, 1-methoxy-2-propanol; cyclic terpenes such as d-limonene; aliphatic hydrocarbons such as white spirit; and optionally a mixture of two or more solvents. These compounds are used alone or as a mixture of two or more thereof. The copolymer components (i) or (iii) are preferably a random copolymers.

Cyclic monocarboxylic acid component (ii)

The binder of the invention comprises at least one cyclic monocarboxylic acid. The cyclic monocarboxylic acid contains a single carboxyl functional group (which may be in its salt form). The cyclic monocarboxylic acid may contain one ring or multiple cyclic rings. In particular, such rings may be fused rings. The cyclic monocarboxylic acid is preferably selected from resin acids, a derivative of resin acids, C6-20 cyclic carboxylic acid and mixtures thereof. Suitable monocarboxylic acids include resin acids such as abietic acid, neoabietic acid, dehydroabietic acid, dihydroabietic acid, tetrahydroabietic acid, palustric acid, levopimaric acid, pimaric acid, isopimaric acid, sandaracopimaric acid, communic acid; naphthenic acids, methyl isohexenyl cyclohexene carboxylic acids, such as 1-methyl-3-(4-methyl-3-pentenyl)-3-cyclohexen-1-yl-carboxylic acid, 1-methyl-4-(4-methyl-3-pentenyl)-4-cyclohexen-1-yl-carboxylic acid, trimethyl isobutenyl cyclohexene carboxylic acids such as 1,4,5-trimethyl-2-(2-methyl-1-propenyl)-3-

cyclohexen-1-yl-carboxylic acid and 1,5,6-trimethyl-3-(2-methyl-1-propenyl)-4-cyclohexen-1-yl-carboxylic acid and mixtures thereof. Ideally, the cyclic monocarboxylic acid is a rosin or derivative thereof.

The monocarboxylic acid can be used to adjust the self-polishing properties and the mechanical properties of the antifouling coating film. The amount of component (ii) in the binder is preferably in the range of 10 to 70 wt% (dry solids), preferably 20 to 50 wt%.

The rosin of use in the invention can be a rosin or derivative thereof such as a salt thereof e.g. as described below. Examples of rosin materials include wood rosin, tall oil rosin and gum rosin; rosin derivatives such as hydrogenated and partially hydrogenated rosin, disproportionated rosin, maleic acid modified rosin, fumaric acid modified rosin; metal salts of rosin and rosin derivatives such as copper resinate, zinc resinate, calcium resinate, magnesium resinate and others as described in WO 97/44401. Preferred are gum rosin and derivatives of gum rosin.

In the present invention, the antifouling composition preferably comprises 0.5 to 25 wt%, preferably 1 to 20 wt% (dry solids) of a cyclic monocarboxylic acid material, preferably 3 to 15 wt% (dry solids).

In one embodiment of the binder of the invention therefore, the amount of component (i) is in the range of 20 to 60 wt% of the binder (dry solids);

the amount of component (ii) is in the range of 10 to 70 wt% of the binder (dry solids); and

the amount component (iii) is in the range of 10 to 60 wt% (dry solids).

The properties of the antifouling coating can be tuned by varying the relative amounts of binder copolymer and rosin components.

Other Binder components

In addition to the component (i) to (iii) described above, an additional binder component can be used to adjust the properties of the antifouling coating film. Examples of binders that can be used include:

esters of rosin and hydrogenated rosin such as methyl esters, glycerol esters, poly(ethylene glycol) esters, pentaerythritol esters, preferred are esters of gum rosin and hydrogenated gum rosin;

dimerised rosin and polymerised rosin;

acid functional polymers of which the acid group is blocked with divalent metals bonded to a monovalent organic residue, or divalent metals bonded to a hydroxyl residue;

hydrophilic copolymers for example (meth)acrylate copolymers for example poly(*N*-vinyl pyrrolidone) copolymers and poly(ethylene glycol) copolymers;

vinyl ether polymers and copolymers, such as poly(methyl vinyl ether), poly(ethyl vinyl ether), poly(isobutyl vinyl ether), poly(vinyl chloride-*co*-isobutyl vinyl ether);

aliphatic polyesters, such as poly(lactic acid), poly(glycolic acid), poly(2-hydroxybutyric acid), poly(3-hydroxybutyric acid), poly(4-hydroxyvaleric acid), polycaprolactone and aliphatic polyester copolymer containing two or more of the units selected from the above mentioned units; and other condensation polymers such as polyoxalates;

alkyd resins and modified alkyd resins;

hydrocarbon resin, such as hydrocarbon resin formed only from the polymerisation of at least one monomer selected from a C5 aliphatic monomer, a C9 aromatic monomer, an indene coumarone monomer, or a terpene or mixtures thereof.

Acyclic monocarboxylic acid

In one embodiment, anti-fouling coatings of the invention may comprise a liquid C12-C24 monocarboxylic acid or a salt thereof, i.e. an acid containing a single -COOH moiety within the molecule or its salt. Such acids contain an acid “head group” and a non-polar “tail group” which is preferably a branched chain of carbon atoms. The monocarboxylic acid preferably contains C, H and O atoms only.

The use of such a material may allow improved control of the leached layer formation (reduced thickness) than a comparative composition not containing the

acid component. Furthermore, compositions containing the acid component should show similar levels of polishing while maintaining or even reducing the viscosity of the paint.

This component may comprise one or more monocarboxylic acids selected from liquid, acyclic, saturated C12-C24 monocarboxylic acids or liquid, acyclic, branched C12-C24 monocarboxylic acids. The acid should not therefore be a linear unsaturated carboxylic acid. It is preferred if the acid is saturated.

The monocarboxylic acid is ideally of formula $R_{11}COOH$ where R_{11} is a C11-23 acyclic, branched alkyl or alkenyl group or a C11-23 acyclic, saturated, linear or branched alkyl group. It is preferred if R_{11} is a C11-23 acyclic, branched alkyl group.

Most preferably, the acyclic monocarboxylic acid is a branched C12-24 fatty acid or mixture thereof.

The acid is preferably a liquid at room temperature and pressure (23°C and 1 atm).

It is preferred if the acid component is branched. A branched acid must contain a tertiary or quaternary carbon atom in its tail group.

It will be appreciated that many of the acids may be derived from natural sources, in which case in isolated form they typically exist as a mixture of acids of differing chain lengths with varying degrees of branching. Where the acid used is a mixture of components, the acid may have a degree of branching of greater than 50%, preferably greater than 70%, greater than 80% or even greater than 90%. The percentage here is wt%. By way of example, a C18 acid component having a degree of branching of at least 50% will contain no more than 50 part by mass of linear C18 acids (n-stearic acid acid, n-oleic acid, n-linoleic acid etc.), with the remainder being branched C18 acids (generically “isostearic acid”, “isooleic acid”, “isolinoleic acid” etc.).

In a preferred aspect the acid is an acyclic C14-C20 monocarboxylic acid, preferably an acyclic C16-C20 monocarboxylic acid, especially acyclic C16-18 monocarboxylic acid. It is preferred if carbon chains contain an even number of

carbon atoms. In a preferred aspect, the acid has a molecular weight of below 350 g/mol, especially below 320 g/mol, and particularly below 300 g/mol.

In a preferred aspect the acid has an acid number below 310, especially below 300, such as below 290 or even below 280. “Acid number” is a well-known parameter, and is the mass of KOH in milligrams that is required to neutralize one gram of the acid (ISO 660:2009).

In a preferred aspect the acid has an iodine number of below 50, such as below 40, below 30, or below 20. In some embodiments the acid may be a saturated acid having an iodine number of 0. “Iodine number” is a well-known parameter, and is the mass of iodine in grams that reacts with 100 grams of the acid (AOCS Tg 1a-64).

Particularly preferred acids for use include one or more selected from the group consisting of: isopalmitic acid or isostearic acid or mixtures thereof. In each case the acid may be natural or synthetic. A blend of isostearic acid and isopalmitic acid is available in a suitable degree of branching under the name Radiacid 0906, Radiacid 0907 and Radiacid 0909 from Oleon. A particularly high grade of branched isostearic acid is the product Fineoxocol Isostearic acid N from Nissan Chemicals.

Particularly preferred acids are isostearic acid and isopalmitic acid, in each case having a degree of branching greater than 70% and an iodine number of below 30. Particularly suitable components are the products Fineoxocol Isostearic acid N from Nissan Chemicals, and Radiacid 0906, Radiacid 0907 or Radiacid 0909 from Oleon.

It will be appreciated that any acid can form a salt if there are metal ions present. Whilst the inventors suggest adding the acid in its acid form, it is also possible to add the acid in its salt form. The acid may also convert into a salt form in the composition. The wt% of acid added in the composition should be calculated assuming that the acid is in its acid form.

If a further binder component is present, this ideally forms less than 10 wt% of the binder, ideally less than 5 wt%. In a preferred embodiment, no additional binder component is present and the binder consists of components (i) to (iii) only.

In a preferred embodiment of the binder the weight ratio (dry solids) of copolymer (i) : component (ii) may be in the range of 20:80 to 80:20, preferably from 30:70 to 70:30, more preferably from 40:60 to 60:40.

In a preferred embodiment of the binder the weight ratio (dry solids) of polymers (i)+(iii) : component (ii) may be in the range of 35:65 to 85:15, preferably from 40:60 to 80:20, more preferably from 45:55 to 75:25.

In one embodiment, component (i) of the binder is partially or fully incompatible, i.e. it does not form a homogeneous mixture with the other binder components present, as determined according to the method in the experimental section (Determination of incompatibility of hydrophilic copolymer (i) in binder mixtures of component (i), (ii) and (iii)).

The binder composition of the invention is ideally incorporated into an antifouling coating composition. An antifouling coating composition of the invention may comprise 15 to 50 wt% of the binder, in particular the antifouling coating composition of the invention comprises 15 to 50 wt% of the binder components (i) to (iii) as defined in claim 1.

Biocide

The antifouling coating preferably additionally comprises a compound capable of preventing or removing marine fouling on or from a surface. The terms antifouling agent, antifoulant, biocide, toxicant are used in the industry to describe known compounds that act to prevent marine fouling on a surface. The antifouling agents of the invention are marine antifouling agents.

The antifouling agent may be inorganic, organometallic or organic. Suitable antifouling agents are commercially available.

Examples of inorganic antifouling agents include copper and copper compounds such as copper oxides, e.g. copper(I) oxide and copper(II) oxide; copper alloys, e.g. copper-nickel alloys; copper salts, e.g. copper(I) thiocyanate and copper sulphide.

Examples of organometallic marine antifouling agents include zinc 2-pyridinethiol-1-oxide [zinc pyrithione]; organocopper compounds such as copper 2-pyridinethiol-1-oxide [copper pyrithione], copper acetate, copper naphthenate,

copper 8-quinolinonate [oxine-copper], copper nonylphenolsulfonate, copper bis(ethylenediamine)bis(dodecylbenzensulfonate) and copper bis(pentachlorophenolate); dithiocarbamate compounds such as zinc bis(dimethyldithiocarbamate) [ziram], zinc ethylenebis(dithiocarbamate) [zineb], manganese ethylenebis(dithiocarbamate) [maneb] and manganese ethylenebis(dithiocarbamate) complexed with zinc salt [mancozeb].

Examples of organic marine antifouling agents include heterocyclic compounds such as 2-(*tert*-butylamino)-4-(cyclopropylamino)-6-(methylthio)-1,3,5-triazine [cybutryne], 4,5-dichloro-2-*n*-octyl-4-isothiazolin-3-one, 1,2-benzisothiazolin-3-one [DCOIT], 2-(thiocyanatomethylthio)-1,3-benzothiazole [benthiazole], 3-benzo[b]thien-2-yl-5,6-dihydro-1,4,2-oxathiazine 4-oxide [bethoxazin] and 2,3,5,6-tetrachloro-4-(methylsulphonyl)pyridine; urea derivatives such as 3-(3,4-dichlorophenyl)-1,1-dimethylurea [diuron]; amides and imides of carboxylic acids, sulphonic acids and sulphenic acids such as *N*-(dichlorofluoromethylthio)phthalimide, *N*-dichlorofluoromethylthio-*N*′,*N*′-dimethyl-*N*-phenylsulfamide [dichlofluanid], *N*-dichlorofluoromethylthio-*N*′,*N*′-dimethyl-*N*-*p*-tolylsulfamide [tolylfluanid] and *N*-(2,4,6-trichlorophenyl)maleimide; other organic compounds such as pyridine triphenylborane, amine triphenylborane, 3-iodo-2-propynyl *N*-butylcarbamate [iodocarb], 2,4,5,6-tetrachloroisophthalonitrile [chlorothalonil], *p*-((diiodomethyl)sulphonyl)toluene and 4-bromo-2-(4-chlorophenyl)-5-(trifluoromethyl)-1H-pyrrole-3-carbonitrile [tralopyril].

Other examples of marine antifouling agents may be tetraalkylphosphonium halogenides, guanidine derivatives; imidazole containing compounds such as 4-[1-(2,3-dimethylphenyl)ethyl]-1H-imidazole [medetomidine] and derivatives; macrocyclic lactones including avermectins and derivatives thereof such as ivermectine; spinosyns and derivatives such as spinosad; capsaicin and derivatives such as phenylcapsaicin; and enzymes such as oxidase, proteolytically, hemicellulolytically, cellulolytically, lipolytically and amylolytically active enzymes.

Traditionally an antifouling coating composition contains copper biocides such as metallic copper, cuprous oxide, copper thiocyanate and the like.

The cuprous oxide material has a typical particle diameter distribution of 0.1-70 μm and an average particle size (d50) of 1-25 μm. The cuprous oxide material may contain a stabilizing agent to prevent surface oxidation and caking. Examples of commercial available cuprous oxide include Nordox Cuprous Oxide Red Paint Grade, Nordox XLT from Nordox AS, Cuprous oxide from Furukawa Chemicals Co., Ltd.; Red Copp 97N, Purple Copp, Lolo Tint 97N, Chemet CDC, Chemet LD from American Chemet Corporation; Cuprous Oxide Red from Spiess-Urania; Cuprous oxide Roast, Cuprous oxide Electrolytic fromTaixing Smelting Plant Co., Ltd.

A series of organic biocides can be used instead of copper biocides such as 4-[1-(2,3-dimethylphenyl)ethyl]-1H-imidazole [medetomidine] and 4-bromo-2-(4-chlorophenyl)-5-(trifluoromethyl)-1H-pyrrole-3-carbonitrile [tralopyril]. Any known biocide can be used in the invention.

Preferred biocides are cuprous oxide, copper thiocyanate, zinc pyrithione, copper pyrithione, zinc ethylenebis(dithiocarbamate) [zineb], 2-(*tert*-butylamino)-4-(cyclopropylamino)-6-(methylthio)-l,3,5-triazine [cubutryne], 4,5-dichloro-2-n-octyl-4-isothiazolin-3-one [DCOIT], N-dichlorofluoromethylthio-N',N'-dimethyl-N-phenylsulfamide [dichlorofluanid], N-dichlorofluoromethylthio-N',N'-dimethyl-N-p-tolylsulfamide [tolylfluanid], 4-[1-(2,3-dimethylphenyl)ethyl]-1H-imidazole [medetomidine], triphenylborane pyridine [TPBP] and 4-bromo-2-(4-chlorophenyl)-5-(trifluoromethyl)-1H-pyrrole-3-carbonitrile [tralopyril].

A mixture of biocides can be used as is known in the art as different biocides operate against different marine fouling organisms. Mixtures of antifouling agents are generally preferred.

In one embodiment the antifouling coating composition comprises cuprous oxide and/or copper thiocyanate and one or more biocides selected from copper pyrithione, zinc ethylenebis(dithiocarbamate), 4,5-dichloro-2-octyl-4-isothiazolin-3-one and medetomidine.

In an alternative embodiment the antifouling coating is free of an inorganic copper biocide. In this embodiment, a preferred biocide combination involves a combination of tralopyril and one or more selected from zinc pyrithione, zinc

ethylenebis(dithiocarbamate), 4,5-dichloro-2-octyl-4-isothiazolin-3-one and medetomidine.

Where present, the combined amount of biocides may form up to 70 wt% of the coating composition, such as 4 to 60 wt%, e.g. 5 to 60 wt%. Where copper is present, a suitable amount of biocide might be 20 to 60 wt% in the coating composition. Where copper is avoided, lower amounts might be used such as 0.1 to 20 wt%, e.g. 0.2 to 15 wt%. It will be appreciated that the amount of biocide will vary depending on the end use and the biocide used.

Some biocides may be encapsulated or adsorbed on an inert carrier or bonded to other materials for controlled release. These percentages refer to the amount of active biocide present and not therefore to any carrier used.

Other components

In addition to the binder and any of the optional components described above, the antifouling coating composition according to the present invention may optionally further comprise one or more components selected among other binders, inorganic or organic pigments, extenders and fillers, additives, solvents and thinners.

Pigments, extenders and fillers

The pigments may be inorganic pigments, organic pigments or a mixture thereof. Inorganic pigments are preferred. Examples of inorganic pigments include titanium dioxide and iron oxides. Examples of organic pigments include phthalocyanine compounds, azo pigments and carbon black.

Examples of extenders and fillers are minerals such as dolomite, plastorite, calcite, quartz, barite, magnesite, aragonite, silica, wollastonite, talc, chlorite, mica, kaolin, ground silica and feldspar; synthetic inorganic compounds such as zinc oxide, zinc phosphate, calcium carbonate, magnesium carbonate, barium sulphate, calcium silicate ground silica and precipitated silica; polymeric and inorganic microspheres such as uncoated or coated hollow and solid glass beads, uncoated or coated hollow and solid ceramic beads, porous and compact beads of polymeric materials such as poly(methyl methacrylate), poly(methyl methacrylate-co-ethylene

glycol dimethacrylate), poly(styrene-co-ethylene glycol dimethacrylate), poly(styrene-co-divinylbenzene), polystyrene, poly(vinyl chloride).

Preferably the total amount of extender, filler and/or pigment present in the compositions of the invention is 0-70 wt%, more preferably 1-60 wt% and still more preferably 2-50 wt%, based on the total weight of the composition. The skilled person will appreciate that the extender and pigment content will vary depending on the other components present and the end use of the coating composition.

Dehydrating agent

The antifouling coating composition of the present invention optionally comprises a dehydrating agent, also referred to as water scavenger or drying agent. Preferably the dehydrating agent is a compound which removes water from the composition in which it is present. Dehydrating agents improve the storage stability of the antifouling coating composition containing water reactive compounds, e.g. silyl ester copolymers, by removing moisture introduced from raw materials, such as pigments and solvents, or water formed by reaction between carboxylic acid compounds and specific compounds, e.g. bivalent metal oxides, in the antifouling coating composition. The dehydrating agents and desiccants that may be used in the antifouling coating compositions include organic and inorganic compounds.

The dehydrating agents can be hygroscopic materials that absorbs water or binds water as crystal water, often referred to as desiccants. Examples of desiccants include calcium sulphate hemihydrate, anhydrous calcium sulphate, anhydrous magnesium sulphate, anhydrous sodium sulphate, anhydrous zinc sulphate, molecular sieves and zeolites.

The dehydrating agent can be a compound that chemically reacts with water. Examples of dehydrating agents that reacts with water include orthoesters such as trimethyl orthoformate, triethyl orthoformate, tripropyl orthoformate, triisopropyl orthoformate, tributyl orthoformate, trimethyl orthoacetate, triethyl orthoacetate, tributyl orthoacetate and triethyl orthopropionate; ketals; acetals; enolethers; orthoborates such as trimethyl borate, triethyl borate, tripropyl borate, triisopropyl borate, tributyl borate and tri-t-butyl borate; organosilanes such as trimethoxymethyl

silane, vinyltrimethoxysilane, phenyltrimethoxysilane, tetraethoxysilane and ethyl polysilicate.

Preferred dehydrating agents are those that chemically react with water. Particularly preferred dehydrating agents are organosilanes.

Preferably the dehydrating agent is present in the compositions of the invention in an amount of 0-5 wt%, more preferably 0.5-2.5 wt% and still more preferably 1.0-2.0 wt%, based on the total weight of the composition.

Solvents and thinners

It is highly preferred if the antifouling composition contains a solvent. This solvent is preferably volatile and is preferably organic. Examples of organic solvents and thinners are aromatic hydrocarbons such as xylene, toluene, mesitylene; ketones such as methyl ethyl ketone, methyl isobutyl ketone, methyl isoamyl ketone, methyl amyl ketone, diisobutyl ketone, methyl propyl ketone, cyclopentanone, cyclohexanone; esters such as butyl acetate, *tert*-butyl acetate, amyl acetate, isoamyl acetate, ethylene glycol methyl ether acetate, propyl propionate, butyl propionate, isobutyl isobutyrate; ethers such as ethylene glycol dimethyl ether, diethylene glycol dimethyl ether, dibutyl ether, dioxane, tetrahydrofuran; alcohols such as *n*-butanol, isobutanol, benzyl alcohol; ether alcohols such as butoxyethanol, 1-methoxy-2-propanol; cyclic terpenes such as d-limonene; aliphatic hydrocarbons such as white spirit; and optionally a mixture of two or more solvents and thinners. Examples of other thinners include water.

Preferred solvents are aromatic solvents and 1-methoxy-2-propanol, especially xylene and mixtures of aromatic hydrocarbons and 1-methoxy-2-propanol.

The amount of solvent is preferably as low as possible. The solvent content may be up to 50 wt% of the composition, preferably up to 45 wt% of the composition, such as up to 40 wt% but may be as low as 15 wt% or less, e.g. 10 wt% or less. Again, the skilled man will appreciate that the solvent content will vary depending on the other components present and the end use of the coating composition.

Alternatively the coating can be dispersed in an organic non-solvent for the film-forming components in the coating composition or in an aqueous dispersion.

The antifouling coating composition of the invention should preferably have solids content above 40 vol%, e.g. above 45 % by volume, such as above 50 vol%, preferably above 55 vol%.

More preferably the antifouling coating composition should have a content of volatile organic compounds (VOC) below 500 g/L, preferably below 400 g/L, e.g. below 390 g/L. VOC content can be calculated (ASTM D5201-01) or measured (US EPA method 24 or ISO 11890-1).

Other additives

Examples of other additives that can be added to an antifouling coating composition are reinforcing agents, thixotropic agents, thickening agents, anti-settling agents, wetting and dispersing agents, plasticizers and stabilizers.

Examples of reinforcing agents are flakes and fibres. Fibres include natural and synthetic inorganic fibres such as silicon-containing fibres, carbon fibres, oxide fibres, carbide fibres, nitride fibres, sulphide fibres, phosphate fibres, mineral fibres; metallic fibres; natural and synthetic organic fibres such as cellulose fibres, rubber fibres, acrylic fibres, polyamide fibres, polyimide, polyester fibres, polyhydrazide fibres, polyvinylchloride fibres, polyethylene fibres and others as described in WO 00/77102. Preferably, the fibres have an average length of 25 to 2,000 μm and an average thickness of 1 to 50 μm with a ratio between the average length and the average thickness of at least 5.

Examples of thixotropic agents, thickening agents and anti-settling agents are silicas such as fumed silicas, organo-modified clays, amide waxes, polyamide waxes, amide derivatives, polyethylene waxes, oxidised polyethylene waxes, hydrogenated castor oil wax, ethyl cellulose, aluminium stearates and mixtures thereof.

Examples of plasticizers are chlorinated paraffins, phthalates, phosphate esters, sulphonamides, adipates and epoxidized vegetable oils.

Examples of stabilizers that contribute to the storage stability of the antifouling coating composition are carbodiimide compounds, such as bis(2,6-diisopropylphenyl)carbodiimide and poly(1,3,5-triisopropylphenylene-2,4-carbodiimide) and others as described in patent EP 2725073.

In general, any of these optional components can be present in an amount ranging from 0.1 to 20 wt%, typically 0.5 to 20 wt%, preferably 0.75 to 15 wt% of the antifouling composition. It will be appreciated that the amount of these optional components will vary depending on the end use.

The antifouling coating composition of the invention can be applied to a whole or part of any object surface which is subject to fouling. The surface may be permanently or intermittently underwater (e.g. through tide movement, different cargo loading or swell). The object surface will typically be the hull of a vessel or surface of a fixed marine object such as an oil platform or buoy. Application of the coating composition can be accomplished by any convenient means, e.g. via painting (e.g. with brush or roller) or spraying the coating onto the object. Typically the surface will need to be separated from the seawater to allow coating. The application of the coating can be achieved as conventionally known in the art.

When applying the antifouling coating to an object (e.g. a ship hull) the surface of the object is typically not protected solely by a single coat of antifouling. Depending on the nature of the surface the antifouling coating can be applied directly to an existing coating system. Such a coating system may comprise several layers of paint of different generic types (e.g. epoxy, polyester, vinyl or acrylic or mixtures thereof). If the surface is a clean and intact antifouling coating from a previous application, the new antifouling paint can be applied directly, typically as one or two coats with more in exceptional cases.

Alternatively, the artisan may start with an uncoated surface (e.g. steel, aluminium, plastic, composite, glass fiber or carbon fiber). To protect such a surface, the full coating system will typically comprise one or two layers of an anticorrosive coating, one layer of tie-coat and one or two layers of antifouling paint. The person skilled in the art will be familiar with these coating layers.

In exceptional cases additional antifouling paint layers may be applied.

In a further embodiment therefore the invention provides a substrate having coated thereon an anticorrosive coating layer such as an epoxy primer, a tie layer and an antifouling coating composition as herein defined.

The invention will now be defined with reference to the following non limiting examples.

Materials and methods

Abbreviations	Name
AMBN	2,2'-Azobis(2-methylbutyronitrile)
BDGMA	2-(2-butoxyethoxy)ethyl methacrylate
EDEGA	2-(2-Ethoxyethoxy)ethyl acrylate
EEMA	2-Ethoxyethyl methacrylate
MEA	2-Methoxyethyl acrylate
MEMA	2-Methoxyethyl methacrylate
MMA	Methyl methacrylate
MPEG-MA 300	Poly(ethylene glycol) methyl ether methacrylate, Mn 300
n-BA	n-Butyl acrylate
PM	1-Methoxy-2-propanol
THFA	Tetrahydrofurfuryl acrylate
TISA	Triisopropylsilyl acrylate
TISMA	Triisopropylsilyl methacrylate

Solvesso 100 was purchased from Brenntag.

<u>Determination of polymer solution viscosity</u>

The viscosity of the polymers was determined in accordance with ASTM D2196-15 Test method A using a Brookfield DV-I viscometer with LV-2 or LV-4 spindle at 12 rpm. The polymers were tempered to 23.0°C ± 0.5°C before the measurements.

<u>Determination of non-volatile matter content of the polymer solutions</u>

The non-volatile matter content of the polymer solutions was determined in accordance with ISO 3251. A test sample of 0.5 g ± 0.1 g was taken out and dried in a ventilated oven at 105°C for 3 hours. The weight of the residual material is considered to be the non-volatile matter (NVM). The non-volatile matter content is expressed in weight percent. The value given is the average of three parallels.

Determination of polymer average molecular weights distribution

The polymers were characterised by Gel Permeation Chromatography (GPC) measurement. The molecular weight distribution (MWD) was determined using a Malvern Omnisec Resolve and Reveal system with two PLgel 5 µm Mixed-D columns from Agilent in series. The columns were calibrated by conventional calibration using narrow polystyrene standards.

Samples were prepared by dissolving an amount of polymer solution corresponding to 25 mg dry polymer in 5 mL THF. The samples were kept for minimum 3 hours at room temperature prior to sampling for the GPC measurements. Before analysis the samples were filtrated through 0.45 µm Nylon filters. The weight-average molecular weight (Mw) and the polydispersity index (PDI), given as Mw/Mn, are reported.

Analysis conditions are given below:

Detector	RI
Cell volume	12 µl
Column Set	Agilent PLgel 5 µm Mixed-D, 2 columns in series
Mobile Phase	THF
Flow rate	1 ml/min
Injection volume	100 µl
Autosampler Temperature	25°C
Column Oven Temperature	35°C
Detector Oven	35°C

Temperature	
Data Processing	Omnisec 5.1
Calibration standards	Agilent Polystyrene Medium EasiVials (4 ml) Red, Yellow and Green

Determination of the glass transition temperature

The glass transition temperature (Tg) is obtained by Differential Scanning Calorimetry (DSC) measurements. The DSC measurements were performed on a TA Instruments DSC Q200. Samples were prepared by drawdown on glass panel with applicator with 100 µm gap size. The glass panels were dried for 24 hour at 23ºC and 24 hours at 50ºC in a ventilated heating cabinet. Approximately 10 mg dry polymer material was collected from the glass panels and transferred to aluminium pans with lid. The measurements were done by a heat-cool-heat procedure (-80ºC to 120ºC) with a heating rate of 10°C/min and cooling rate of 10°C/min. An empty pan is used as reference. The data were processed using Universal Analysis software from TA Instruments. The inflection point of the glass transition range, as defined in ASTM E1356-08, of the second heating is reported as the Tg of the polymers.

Determination of paint viscosity using Cone and Plate viscometer

The viscosity of the antifouling paint compositions was determined according to ISO 2884-1:1999 using a digital Cone and Plate viscometer set at a temperature of 23°C, working at a shear rate of 10000 s^{-1} and providing viscosity measurement range of 0-10 P. The result is given as the average of three measurements. The results are shown in Table 8-13.

Gravimetric water uptake in freshwater/deionized water

The water uptake in the coating films were determined by gravimetric method. The paints were applied on pre-weighed and numbered sandblasted glass panels (5.0 x 7.5 cm) using a film applicator with 300 µm gap size. The films were dried under ambient conditions for at least 1 day, at 50°C overnight and then in a desiccator under vacuum for 24 h. After drying, the coated glass panels were weighed and

placed in containers filled with distilled water. At the time of the reading, the panels and paint surfaces were quickly dried using compressed air. The panels were weighed ($m_{directly}$) and thereafter allowed to dry under ambient conditions for 2 days and then placed in a desiccator under vacuum for 24 hours before they were weighed again (m_{dry}). The difference in weight before and after drying relative to the dry weight of the paint film after exposure is expressed as the water uptake in percentage.

Amount of water uptake = $(m_{directly} - m_{dry})/(m_{dry} - m_{empty\ panel})$

The readings were done after 34 days. The results are shown in Table 8-13.

Calculation of the volatile organic compound (VOC) content of the antifouling coating composition

The volatile organic compound (VOC) content of the antifouling coating composition is calculated in accordance with ASTM D5201.

Determination of incompatibility of hydrophilic copolymer (i) in binder mixtures of component (i), (ii) and (iii).

A mixture of binder components (i), (ii), (iii) and Irgazin Red L 3670 HD were mixed in 10 ml glass vials. The proportions are given in Table 3-7. The vials were mixed for 3 minutes using a Collomix Viba vibrational shaker. The samples were left to stand at room temperature for at least 24 h before the incompatibility was visually evaluated. The copolymer (i) is regarded as incompatible if at least 2 different phases were seen. Irgazin Red L 3670 HD was added to make the phase separation more visually clear. The results are given as incompatible (I) or compatible (C) in Table 3-7. The binder mixtures should have a wt% solid of 52-57. Xylene:PM should be used in a wt ratio of 85:15 to 95:5.

Determination of the polishing of antifouling coating films on rotating disc in seawater

The polishing was determined by measuring the reduction in film thickness of a coating film. For this test PVC discs were used. The coating compositions were applied as radial stripes on the disc using a film applicator. The thicknesses of the dry coating films were measured by a surface profiler. The PVC discs were mounted on a shaft and rotated in a container in which seawater was flowing through. Natural seawater which has been filtered and temperature-adjusted to 25 °C ± 2 °C was used. The speed of the rotated shaft provided an average simulated speed of 16 knots on the disc. The PVC discs were taken out for measuring the film thickness. The discs were rinsed and allowed to dry overnight at room temperature before measuring the film thicknesses. The results were given as film reduction, i.e. the difference between the initial film thickness and the measured thickness at the given time.

General procedure for preparation of copolymer solution P1 to P12 and C1 to C8 (copolymer component (i))

The polymers tested were all produced in the same way by charging 28.84 parts xylene and 6.75 parts PM to a temperature-controlled reaction vessel equipped with a stirrer, a reflux condenser, a nitrogen inlet and a feed inlet. The reaction vessel was heated and maintained at 95°C. A pre-mix of monomers, 6.57 parts xylene, 3.25 part PM and initiator was prepared and charged to the reaction vessel at a constant rate over 2 hours and 30 minutes under a nitrogen atmosphere. After a further 1 hour reaction a post-addition of a boost initiator solution of initiator and 4.6 parts xylene was charged to the reaction vessel at a constant rate over 15 minutes. The reaction vessel was maintained at the reaction temperature for a further 1 hour and then cooled to room temperature. The exception from this was that polymer P4 and P6 had reaction temperatures of 105°C and 85°C, respectively.

Overview of the different polymers synthesised are given in Table 1 and 2. The amount of ingredients are given in parts by weight.

Preparation of acrylic copolymer solution A-1 (polymer component (iii-2))

19.20 parts of xylene and 7.70 parts of 1-methoxy-2-propanol were charged to a temperature-controlled reaction vessel equipped with a stirrer, a reflux condenser, a nitrogen inlet and a feed inlet. The reaction vessel was heated and maintained at 85°C. A pre-mix of 53.80 parts n-butyl acrylate, 3.40 parts n-butyl methacrylate, 2.40 parts methyl methacrylate, 0.40 parts methacrylic acid, 0.93 parts 2,2'-azobis(2-methylbutyronitrile) and 8.00 parts xylene was prepared and charged to the reaction vessel at a constant rate over 2 hours and 30 minutes under a nitrogen atmosphere. After a further 1 hour reaction a post-addition of a boost initiator solution of 0.20 parts 2,2'-azobis(2-methylbutyronitrile) and 4.00 parts xylene was charged to the reaction vessel at a constant rate over 15 minutes. The reaction vessel was maintained at the reaction temperature for a further 1 hour and then cooled to room temperature. The amount of ingredients are given in parts by weight. Copolymer solution A-1 had viscosity of 327 cP, non-volatile content of 61.7 wt%, Mw 36 200, PDI 3.23 and Tg -39°C.

<u>Preparation of silyl ester acrylic copolymer solution A-2 (polymer component (iii-1))</u>

35.00 parts of xylene was charged to a temperature-controlled reaction vessel equipped with a stirrer, a reflux condenser, a nitrogen inlet and a feed inlet. The reaction vessel was heated and maintained at 85°C. A pre-mix of 16.50 parts methyl methacrylate, 3.50 parts 2-methoxyethyl acrylate, 30.00 parts of triisopropylsilyl acrylate, 0.50 parts 2,2'-azobis(2-methylbutyronitrile) and 5.00 parts xylene was prepared and charged to the reaction vessel at a constant rate over 2 hours under a nitrogen atmosphere. After a further 1 hour reaction a post-addition of a boost initiator solution of 0.10 parts 2,2'-azobis(2-methylbutyronitrile) and 5.00 parts xylene was charged to the reaction vessel at a constant rate over 15 minutes. The reaction vessel was maintained at the reaction temperature for a further 2 hour. The temperature of the reaction vessel was increased to 120°C and maintained for 30 minutes and then cooled to room temperature. The amount of ingredients are given in parts by weight.

Copolymer solution A-2 had viscosity of 152 cP, non-volatile content of 50.5 wt%, Mw 28 000, PDI 3.61 and Tg 35°C.

Preparation of silyl ester acrylic copolymer solution A-3 (polymer component (iii-1))

35.50 parts of xylene was charged to a temperature-controlled reaction vessel equipped with a stirrer, a reflux condenser, a nitrogen inlet and a feed inlet. The reaction vessel was heated and maintained at 85°C. A pre-mix of 11.83 parts methyl methacrylate, 2.96 parts n-butyl acrylate, 11.83 parts of tetrahydrofurfuryl acrylate, 32.54 parts of triisopropylsilyl methacrylate and 0.71 parts 2,2'-azobis(2-methylbutyronitrile) was prepared and charged to the reaction vessel at a constant rate over 2 hours under an atmosphere of nitrogen atmosphere. After a further 0,5 hour reaction a post-addition of a boost initiator solution of 0.12 parts 2,2'-azobis(2-methylbutyronitrile) and 4.50 parts xylene was charged to the reaction vessel at a constant rate over 20 minutes. The reaction vessel was maintained at the reaction temperature for a further 2 hour. The temperature of the reaction vessel was increased to 110°C and maintained for 30 minutes and then cooled to room temperature. The amount of ingredients are given in parts by weight.

Copolymer solution A-3 had viscosity of 1275 cP, non-volatile content of 60.2 w%, Mw 31 000, PDI 3.10 and Tg 46°C.

General procedure for preparation of antifouling coating compositions

The components were mixed in the proportions given in Table 8-13. The mixture was dispersed in the presence of glass beads (approx. 2mm in diameter) in a paint can of 250 ml using a vibrational shaker for 15 minutes. The glass beads were filtered of before testing.

Table 1 Overview of polymers according to the invention

Polymer example		**P1**	**P2**	**P3**	**P4**	**P5**	**P6**	**P7**	**P8**	**P9**	**P10**	**P11**	**P12**
wt % Monomers	MEA	19.62	9.80	0	0	0	0	0	0	0	0	0	0
	EDEGA	0	0	9.64	9.80	9.83	19.63	0	0	0	0	0	0
	MMA	29.42	39.19	28.93	29.41	29.50	29.44	31.97	29.40	19.43	39.15	29.41	19.64
	n-BA	0	0	9.64	9.80	9.83	0	5.12	4.90	0	0	0	0
	MPEG-MA 300	0	0	0	0	0	0	11.97	0	0	0	0	0
	EEMA	0	0	0	0	0	0	0	14.70	0	0	0	0
	BDGMA	0	0	0	0	0	0	0	0	29.80	0	0	0
	THFA	0	0	0.00	0	0	0	0	0	0	9.78	19.60	29.46
Wt % Xylene (total)		40.00	40.00	40.00	40.00	40.00	40.00	40.00	40.00	40.00	40.00	40.00	40.00
Wt % PM (total)		10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00
Wt% ABMN (first addition)		0.79	0.82	1.63	0.83	0.66	0.78	0.78	0.83	0.63	0.89	0.82	0.75
Wt% AMBN (boost addition)		0.17	0.18	0.16	0.17	0.17	0.16	0.16	0.17	0.13	0.18	0.16	0.15
Measured NVM:	Wt %	50.2	52.9	49.2	49.5	49.3	48.9	49.7	50.1	49.1	53.0	50.5	49.8
Polymer solution viscosity:	cP	470	1408	125	357	1292	452	655	611	190	1517	595	235
MWD:	Mw	20709	19016	10700	23578	57992	33005	23119	18902	22612	16590	19608	19863
	PDI	2.48	2.23	2.32	2.93	4.04	3.43	2.50	2.25	2.43	2.30	2.68	2.95
Tg	(°C)	30	49	18	23	28	20	42	48	9	52	37	27

Table 2 Overview of comparative polymers

Polymer example		**C1**	**C2**	**C3**	**C4**	**C5**	**C6**	**C7**	**C8**
wt % Monomers	MEA	49.18	39.31	0	0	0	9.84	39.34	0
	EDEGA	0	0	49.43	9.82	29.50	0	0	3.92
	MMA	0	9.83	0	9.82	19.67	0	0	26.45
	n-BA	0	0	0	29.46	0	39.34	9.84	18.62
Wt % Xylene (total)		40.00	40.00	40.00	40.00	40.00	40.00	40.00	40.00
Wt % PM (total)		10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00
Wt% ABMN (first addition)		0.67	0.71	0.46	0.75	0.69	0.68	0.67	0.84
Wt% AMBN (boost addition)		0.15	0.16	0.10	0.15	0.14	0.15	0.15	0.17
Measured NVM:	Wt %	50.1	50.0	48.9	50.0	48.9	50.5	51.2	49.5
Polymer solution viscosity:	cP	42	86	30	55	165	27	30	262
MWD:	Mw	11695	16962	17670	18909	37194	12851	11734	20478
	PDI	2.42	2.68	2.84	3.01	4.03	2.46	2.41	3.03
Tg	(°C)	-36	-21	-54	-34	-16	-47	-39	17

Table 3: Determination of incompatibility (ingredients given in gram)

Example	B1	B2	B3	B4	B5	B6	B7	B8	B9	B10	B11	B12
P1	2.48	-	-	-	-	-	-	-	-	-	-	-
P2	-	2.48	-	-	-	-	-	-	-	-	-	-
P3	-	-	2.48	-	-	-	-	-	-	-	-	-
P4	-	-	-	2.48	-	-	-	-	-	-	-	-
P5	-	-	-	-	2.48	-	-	-	-	-	-	-
P6	-	-	-	-	-	2.48	-	-	-	-	-	-
P7	-	-	-	-	-	-	2.48	-	-	-	-	-
P8	-	-	-	-	-	-	-	2.48	-	-	-	-
P9	-	-	-	-	-	-	-	-	2.48	-	-	-
P10	-	-	-	-	-	-	-	-	-	2.48	-	-
P11	-	-	-	-	-	-	-	-	-	-	2.48	-
P12	-	-	-	-	-	-	-	-	-	-	-	2.48
A1	0.96	0.96	0.96	0.96	0.96	0.96	0.96	0.96	0.96	0.96	0.96	0.96
Gum rosin solution (60 wt% in xylene)	2.56	2.56	2.56	2.56	2.56	2.56	2.56	2.56	2.56	2.56	2.56	2.56
Irgazin Red L 3670 HD	$2*10^{-3}$	$2*10^{-3}$	$2*10^{-3}$	$2*10^{-3}$	$2*10^{-3}$	$2*10^{-3}$	$2*10^{-3}$	$2*10^{-3}$	$2*10^{-3}$	$2*10^{-3}$	$2*10^{-3}$	$2*10^{-3}$
Wt% PM	5.35	5.35	5.35	5.35	5.35	5.35	5.35	5.35	5.35	5.35	5.35	5.35
Wt% Xylene	38.60	38.60	38.60	38.60	38.60	38.60	38.60	38.60	38.60	38.60	38.60	38.60
Wt % solids	56.05	56.05	56.05	56.05	56.05	56.05	56.05	56.05	56.05	56.05	56.05	56.05
Incompatibility	I	I	I	I	I	I	I	I	I	I	I	I

Table 4: Determination of incompatibility (ingredients given in gram)

Example	B13	B14	B15	B16	B17	B18	B19
C1	2.48	-	-	-	-	-	-
C2	-	2.48	-	-	-	-	-
C3	-	-	2.48	-	-	-	-
C4	-	-	-	2.48	-	-	-
C5	-	-	-	-	2.48	-	-
C6	-	-	-	-	-	2.48	-
C7	-	-	-	-	-	-	2.48
A1	0.96	0.96	0.96	0.96	0.96	0.96	0.96
Gum rosin solution (60 wt% in xylene)	2.56	2.56	2.56	2.56	2.56	2.56	2.56
Irgazin Red L 3670 HD	$2*10^{-3}$	$2*10^{-3}$	$2*10^{-3}$	$2*10^{-3}$	$2*10^{-3}$	$2*10^{-3}$	$2*10^{-3}$
Wt% PM	5.35	5.35	5.35	5.35	5.35	5.35	5.35
Wt% Xylene	38.60	38.60	38.60	38.60	38.60	38.60	38.60
Wt % solids	56.05	56.05	56.05	56.05	56.05	56.05	56.05
Incompatibility	I	I	C	C	I	C	I

Table 5: Determination of incompatibility (ingredients given in gram)

Example	B20	B21	B22	B23	B24	B25	B26	B27	B28
P1	1.94	-	-	-	-	-	-	-	-
P2	-	1.94	-	-	-	-	-	-	-
P3	-	-	1.94	-	-	-	-	-	-
P4	-	-	-	1.94	-	-	-	-	-

Example	B20	B21	B22	B23	B24	B25	B26	B27	B28
P5	-	-	-	-	1.94	-	-	-	-
P7	-	-	-	-	-	1.94	-	-	-
P8	-	-	-	-	-	-	1.94	-	-
P10	-	-	-	-	-	-	-	1.94	-
P11	-	-	-	-	-	-	-	-	1.94
A2	2.32	2.32	2.32	2.32	2.32	2.32	2.32	2.32	2.32
A1	0.58	0.58	0.58	0.58	0.58	0.58	0.58	0.58	0.58
Gum rosin solution (60 wt% in xylene)	1.16	1.16	1.16	1.16	1.16	1.16	1.16	1.16	1.16
Irgazin Red L 3670 HD	$2*10^{-3}$	$2*10^{-3}$	$2*10^{-3}$	$2*10^{-3}$	$2*10^{-3}$	$2*10^{-3}$	$2*10^{-3}$	$2*10^{-3}$	$2*10^{-3}$
Wt% PM	3.97	3.97	3.97	3.97	3.97	3.97	3.97	3.97	3.97
Wt% Xylene	43.02	43.02	43.02	43.02	43.02	43.02	43.02	43.02	43.02
Wt % solids	53.01	53.01	53.01	53.01	53.01	53.01	53.01	53.01	53.01
Incompatibility	I	I	I	I	I	I	I	I	I

Table 6: Determination of incompatibility (ingredients given in gram)

Example	B29	B30	B31	B32	323	B34	B35	B36	B37
P1	1.94	-	-	-	-	-	-	-	-
P2	-	1.94	-	-	-	-	-	-	-
P3	-	-	1.94	-	-	-	-	-	-
P4	-	-	-	1.94	-	-	-	-	-

Example	B29	B30	B31	B32	323	B34	B35	B36	B37
P5	-	-	-	-	1.94	-	-	-	-
P7	-	-	-	-	-	1.94	-	-	-
P8	-	-	-	-	-	-	1.94	-	-
P10	-	-	-	-	-	-	-	1.94	-
P11	-	-	-	-	-	-	-	-	1.94
A3	2.32	2.32	2.32	2.32	2.32	2.32	2.32	2.32	2.32
A1	0.58	0.58	0.58	0.58	0.58	0.58	0.58	0.58	0.58
Gum rosin solution (60 wt% in xylene)	1.16	1.16	1.16	1.16	1.16	1.16	1.16	1.16	1.16
Irgazin Red L 3670 HD	$2*10^{-3}$	$2*10^{-3}$	$2*10^{-3}$	$2*10^{-3}$	$2*10^{-3}$	$2*10^{-3}$	$2*10^{-3}$	$2*10^{-3}$	$2*10^{-3}$
Wt% PM	3.97	3.97	3.97	3.97	3.97	3.97	3.97	3.97	3.97
Wt% Xylene	43.02	43.02	43.02	43.02	43.02	43.02	43.02	43.02	43.02
Wt % solids	53.01	53.01	53.01	53.01	53.01	53.01	53.01	53.01	53.01
Incompatibility	I	I	I	I	I	I	I	I	I

Table 7: Determination of incompatibility (ingredients given in gram)

Example	B38	B39	B40	B41	B42	B43	B44
C1	1.94	-	-	-	-	-	-
C2	-	1.94	-	-	-	-	-
C3	-	-	1.94	-	-	-	-
C4	-	-	-	1.94	-	-	-
C5	-	-	-	-	1.94	-	-
C6	-	-	-	-	-	1.94	-

Example	B38	B39	B40	B41	B42	B43	B44
C7	-	-	-	-	-	-	1.94
A2	2.32	2.32	2.32	2.32	2.32	2.32	2.32
A1	0.58	0.58	0.58	0.58	0.58	0.58	0.58
Gum rosin solution (60 wt% in xylene)	1.16	1.16	1.16	1.16	1.16	1.16	1.16
Irgazin Red L 3670 HD	$2*10^{-3}$	$2*10^{-3}$	$2*10^{-3}$	$2*10^{-3}$	$2*10^{-3}$	$2*10^{-3}$	$2*10^{-3}$
Wt% PM	3.97	3.97	3.97	3.97	3.97	3.97	3.97
Wt% Xylene	43.02	43.02	43.02	43.02	43.02	43.02	43.02
Wt % solids	53.01	53.01	53.01	53.01	53.01	53.01	53.01
Incompatibility	I	I	C	C	I	C	I

Table 8: Paint compositions (ingredients given in wt%)

Paint example	M1	M2	M3	M4	M5	M6	M7	M8	M9	M10	M11	M12
P1	15.8	-	-	-	-	-	-	-	-	-	-	-
P2	-	15.8	-	-	-	-	-	-	-	-	-	-
P3	-	-	15.8	-	-	-	-	-	-	-	-	-
P4	-	-	-	15.8	-	-	-	-	-	-	-	-
P5	-	-	-	-	15.8	-	-	-	-	-	-	-
P6	-	-	-	-	-	15.8	-	-	-	-	-	-
P7	-	-	-	-	-	-	15.8	-	-	-	-	-
P8	-	-	-	-	-	-	-	15.8	-	-	-	-
P9	-	-	-	-	-	-	-	-	15.8	-	-	-

Paint example	M1	M2	M3	M4	M5	M6	M7	M8	M9	M10	M11	M12
P10	-	-	-	-	-	-	-	-	-	15.8	-	-
P11	-	-	-	-	-	-	-	-	-	-	15.8	-
P12	-	-	-	-	-	-	-	-	-	-	-	15.8
A1	6.05	6.05	6.05	6.05	6.05	6.05	6.05	6.05	6.05	6.05	6.05	6.05
Gum rosin solution (60 wt% in xylene)	16.66	16.66	16.66	16.66	16.66	16.66	16.66	16.66	16.66	16.66	16.66	16.66
Cuprous oxide	30.23	30.23	30.23	30.23	30.23	30.23	30.23	30.23	30.23	30.23	30.23	30.23
Zineb	7.44	7.44	7.44	7.44	7.44	7.44	7.44	7.44	7.44	7.44	7.44	7.44
Zinc oxide	7.17	7.17	7.17	7.17	7.17	7.17	7.17	7.17	7.17	7.17	7.17	7.17
Iron oxide	2.78	2.78	2.78	2.78	2.78	2.78	2.78	2.78	2.78	2.78	2.78	2.78
Titanium dioxide	2.78	2.78	2.78	2.78	2.78	2.78	2.78	2.78	2.78	2.78	2.78	2.78
Dolomite	2.94	2.94	2.94	2.94	2.94	2.94	2.94	2.94	2.94	2.94	2.94	2.94
Bentone 52	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92
Ethanol	0.45	0.45	0.45	0.45	0.45	0.45	0.45	0.45	0.45	0.45	0.45	0.45
Solvesso 100	2.05	2.05	2.05	2.05	2.05	2.05	2.05	2.05	2.05	2.05	2.05	2.05
Xylene	4.73	4.73	4.73	4.73	4.73	4.73	4.73	4.73	4.73	4.73	4.73	4.73
VOC (g/L)	401	400	399	399	399	400	400	400	400	400	400	400
Vol % solids	54.20	54.20	54.20	54.20	54.20	54.20	54.20	54.20	54.2	54.20	54.20	54.20
Cone & Plate viscosity (cP)	520	520	350	485	820	675	640	260	260	730	640	440
Water uptake (34 days, wt%)	2.6	2.2	2.3	2.3	2.4	2.9	2.2	2.7	2.7	2.4	2.3	2.3
Film thickness reduction (14 weeks, µm)	15	15	11	13	15	14	14	10	22	14	14	14

Table 9: Comparative paint compositions (ingredients given in wt%)

Paint example	CP1	CP2	CP3	CP4	CP5	CP6	CP7	CP18	CP19
C1	15.8	-	-	-	-	-	-	-	32.21
C2	-	15.8	-	-	-	-	-	-	-
C3	-	-	15.8	-	-	-	-	-	-
C4	-	-	-	15.8	-	-	-	-	-
C5	-	-	-	-	15.8	-	-	-	-
C6	-	-	-	-	-	15.8	-	-	-
C7	-	-	-	-	-	-	15.8	-	-
C8								15.8	-
A1	6.05	6.05	6.05	6.05	6.05	6.05	6.05	6.05	-
Gum rosin solution (60 wt% in xylene)	16.66	16.66	16.66	16.66	16.66	16.66	16.66	16.66	2.98
Cuprous oxide	30.23	30.23	30.23	30.23	30.23	30.23	30.23	30.23	30.23
Zineb	7.44	7.44	7.44	7.44	7.44	7.44	7.44	7.44	7.44
Zinc oxide	7.17	7.17	7.17	7.17	7.17	7.17	7.17	7.17	7.17
Iron oxide	2.78	2.78	2.78	2.78	2.78	2.78	2.78	2.78	2.78
Titanium dioxide	2.78	2.78	2.78	2.78	2.78	2.78	2.78	2.78	2.78
Dolomite	2.94	2.94	2.94	2.94	2.94	2.94	2.94	2.94	2.94
Bentone 52	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92
Ethanol	0.45	0.45	0.45	0.45	0.45	0.45	0.45	0.45	0.45
Solvesso 100	2.05	2.05	2.05	2.05	2.05	2.05	2.05	2.05	2.05
Xylene	4.73	4.73	4.73	4.73	4.73	4.73	4.73	4.73	4.73
VOC (g/L)	400	400	398	399	399	395	399	395	434

Paint example	CP1	CP2	CP3	CP4	CP5	CP6	CP7	CP18	CP19
Vol % solids	54.20	54.20	54.68	54.44	54.44	54.20	54.4	54.7	50.20
Cone & Plate viscosity (cP)	210	260	170	245	360	185	210	413	596
Water uptake (34 days, wt%)	4.1	3.9	5.3	5.9	3.9	7.6	5.9	3.5	14.5
Film thickness reduction (14 weeks, µm)	16	10	31	27	13	18	20	8	12

Table 10: Paint compositions (ingredients given in wt%)

Paint example	M13	M14	M15	M16	M17	M18	M19	M20	M21
P1	11.54	-	-	-	-	-	-	-	-
P2	-	11.54	-	-	-	-	-	-	-
P3	-	-	11.54	-	-	-	-	-	-
P4	-	-	-	11.54	-	-	-	-	-
P5	-	-	-	-	11.54	-	-	-	-
P7	-	-	-	-	-	11.54	-	-	-
P8	-	-	-	-	-	-	11.54	-	-
P10	-	-	-	-	-	-	-	11.54	-
P11	-	-	-	-	-	-	-	-	11.54
A2	13.83	13.83	13.83	13.83	13.83	13.83	13.83	13.83	13.83
A1	3.43	3.43	3.43	3.43	3.43	3.43	3.43	3.43	3.43
Gum rosin solution (60 wt% in xylene)	6.91	6.91	6.91	6.91	6.91	6.91	6.91	6.91	6.91

Paint example	M13	M14	M15	M16	M17	M18	M19	M20	M21
Cuprous oxide	32.79	32.79	32.79	32.79	32.79	32.79	32.79	32.79	32.79
Zineb	4.49	4.49	4.49	4.49	4.49	4.49	4.49	4.49	4.49
Copper pyrithione	1.38	1.38	1.38	1.38	1.38	1.38	1.38	1.38	1.38
Zinc oxide	8.63	8.63	8.63	8.63	8.63	8.63	8.63	8.63	8.63
Iron oxide	1.38	1.38	1.38	1.38	1.38	1.38	1.38	1.38	1.38
Titanium dioxide	2.07	2.07	2.07	2.07	2.07	2.07	2.07	2.07	2.07
Dolomite	3.57	3.57	3.57	3.57	3.57	3.57	3.57	3.57	3.57
Disparlon A603-20X	1.04	1.04	1.04	1.04	1.04	1.04	1.04	1.04	1.04
Tetraethoxysilane	0.35	0.35	0.35	0.35	0.35	0.35	0.35	0.35	0.35
Solvesso 100	2.07	2.07	2.07	2.07	2.07	2.07	2.07	2.07	2.07
Xylene	6.54	6.54	6.54	6.54	6.54	6.54	6.54	6.54	6.54
Vol % solids	49.89	49.89	50.25	50.25	50.25	50.25	50.07	50.46	49.88
VOC (g/L)	437	437	435	435	435	435	436	436	436
Cone & Plate viscosity (cP)	270	285	210	250	320	285	290	325	300
Water uptake (34 days, wt%)	3.0	2.1	2.5	3.0	2.6	3.2	1.6	2.3	2.4
Film thickness reduction (14 weeks, µm)	15	12	16	17	16	16	15	10	13

Table 11: Paint compositions (ingredients given in wt%)

Paint example	M22	M23	M24	M25	M26	M27	M28	M29	M30	M31
P1	11.54	-	-	-	-	-	-	-	-	-

Paint example	M22	M23	M24	M25	M26	M27	M28	M29	M30	M31
P2	-	11.54	-	-	-	-	-	-	11.54	-
P3	-	-	11.54	-	-	-	-	-	-	-
P4	-	-	-	11.54	-	-	-	-	-	11.54
P5	-	-	-	-	11.54	-	-	-	-	-
P8	-	-	-	-	-	11.54	-	-	-	-
P10	-	-	-	-	-	-	11.54	-	-	-
P11	-	-	-	-	-	-	-	11.54	-	-
A3	13.83	13.83	13.83	13.83	13.83	13.83	13.83	13.83	13.83	13.83
A1	3.43	3.43	3.43	3.43	3.43	3.43	3.43	3.43	3.43	3.43
Gum rosin solution (60 wt% in xylene)	6.91	6.91	6.91	6.91	6.91	6.91	6.91	6.91	6.91	6.91
Cuprous oxide	32.79	32.79	32.79	32.79	32.79	32.79	32.79	32.79	32.79	32.79
Zineb	4.49	4.49	4.49	4.49	4.49	4.49	4.49	4.49	4.49	4.49
Copper pyrithione	1.38	1.38	1.38	1.38	1.38	1.38	1.38	1.38	1.38	1.38
Selektope (medetomidine)	-	-	-	-	-	-	-	-	0.10	0.10
Zinc oxide	8.63	8.63	8.63	8.63	8.63	8.63	8.63	8.63	8.63	8.63
Iron oxide	1.38	1.38	1.38	1.38	1.38	1.38	1.38	1.38	1.38	1.38
Titanium dioxide	2.07	2.07	2.07	2.07	2.07	2.07	2.07	2.07	2.07	2.07
Dolomite	3.57	3.57	3.57	3.57	3.57	3.57	3.57	3.57	3.57	3.57
Disparlon A603-20X	1.04	1.04	1.04	1.04	1.04	1.04	1.04	1.04	1.04	1.04
Tetraethoxysilane	0.35	0.35	0.35	0.35	0.35	0.35	0.35	0.35	0.35	0.35
Solvesso 100	2.07	2.07	2.07	2.07	2.07	2.07	2.07	2.07	2.07	2.07
Xylene	6.54	6.54	6.54	6.54	6.54	6.54	6.54	6.54	6.54	6.54

Paint example	M22	M23	M24	M25	M26	M27	M28	M29	M30	M31
Vol % solids	52.36	52.36	52.70	52.70	52.70	52.50	52.90	52.30	51.8	52.2
VOC (g/L)	415	415	414	414	414	415	415	415	421	419
Cone & Plate viscosity (cP)	410	340	360	450	610	510	380	450	595	491
Water uptake (34 days, wt%)	3.6	2.1	3.0	2.7	2.8	1.9	2.7	3.3	2.3	2.6
Film thickness reduction (14 weeks, µm)	10	14	17	14	11	13	10	11	12	13

Table 12: Comparative paint compositions (ingredients given in wt%)

Paint example	CP8	CP9	CP10	CP11	CP12	CP13	CP14	CP15	CP16	CP17
C1	11.54	-	-	-	-	11.54	-	-	-	-
C2	-	11.54	-	-	-	-	11.54	-	-	-
C3	-	-	11.54	-	-	-	-	11.54	-	-
C5	-	-	-	11.54	-	-	-	-	11.54	-
C7	-	-	-	-	11.54	-	-	-	-	11.54
A3						13.83	13.83	13.83	13.83	13.83
A2	13.83	13.83	13.83	13.83	13.83	-	-	-	-	-
A1	3.43	3.43	3.43	3.43	3.43	3.43	3.43	3.43	3.43	3.43
Gum rosin solution (60 wt% in xylene)	6.91	6.91	6.91	6.91	6.91	6.91	6.91	6.91	6.91	6.91
Cuprous oxide	32.79	32.79	32.79	32.79	32.79	32.79	32.79	32.79	32.79	32.79
Zineb	4.49	4.49	4.49	4.49	4.49	4.49	4.49	4.49	4.49	4.49
Copper pyrithione	1.38	1.38	1.38	1.38	1.38	1.38	1.38	1.38	1.38	1.38
Zinc oxide	8.63	8.63	8.63	8.63	8.63	8.63	8.63	8.63	8.63	8.63
Iron oxide	1.38	1.38	1.38	1.38	1.38	1.38	1.38	1.38	1.38	1.38
Titanium dioxide	2.07	2.07	2.07	2.07	2.07	2.07	2.07	2.07	2.07	2.07
Dolomite	3.57	3.57	3.57	3.57	3.57	3.57	3.57	3.57	3.57	3.57
Disparlon A603-20X	1.04	1.04	1.04	1.04	1.04	1.04	1.04	1.04	1.04	1.04
Tetraethoxy silane	0.35	0.35	0.35	0.35	0.35	0.35	0.35	0.35	0.35	0.35
Solvesso 100	2.07	2.07	2.07	2.07	2.07	2.07	2.07	2.07	2.07	2.07
Xylene	6.54	6.54	6.54	6.54	6.54	6.54	6.54	6.54	6.54	6.54
Vol % solids	50.0	50.07	50.44	50.25	50.25	52.53	52.53	52.89	52.70	52.70

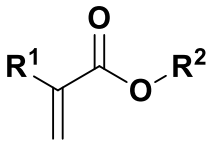
Paint example	CP8	CP9	CP10	CP11	CP12	CP13	CP14	CP15	CP16	CP17
VOC (g/L)	436	436	434	435	435	415	415	413	414	414
Cone & Plate viscosity (cP)	150	195	125	220	140	221	255	183	320	233
Water uptake (34 days, wt%)	5.3	4.6	6.6	4.3	4.2	5.9	4.9	7.6	5.4	4.6
Film thickness reduction (14 weeks, µm)	9	10	16	6	12	9	11	5	8	7

The combination of binder component (i), component (ii) and component (iii) is required to fine tune the hydrophilic/hydrophobic balance of the coating. The balance influences coating properties such as water uptake, polishing rate, cracking resistance and paint viscosity. If there is too little hydrophilic monomer (see comparative example C8) polishing is slow. Where only components (i)+(ii) are used in the binder, (see comparative example CP19) water uptake is high.

Claims

1. A binder for an antifouling coating composition comprising:

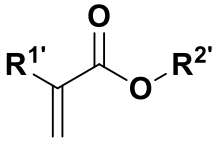
(i) a hydrophilic copolymer having a glass transition temperature of at least 0°C, said hydrophilic copolymer comprising at least 10 wt% of at least one monomer of Formula (I)



(I)

wherein R^1 is H or CH_3, and R^2 is a C3-C18 substituent with at least one oxygen or nitrogen atom, preferably at least one oxygen atom or R^2 is a poly(alkylene glycol) chain;

and at least one monomer of Formula (II),



(II)

wherein $R^{1'}$ is H or CH_3, and $R^{2'}$ is a C1-C20 hydrocarbyl;

wherein said hydrophilic copolymer is free of any metal-ion containing comonomers; and

said hydrophilic copolymer comprising less than 15 wt% comonomers other than those of Formula (I) or (II);

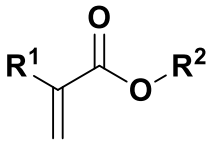
(ii) a cyclic monocarboxylic acid such as rosin or a derivative thereof (such as a salt thereof); and

(iii) a silyl ester (meth)acrylic copolymer comprising at least 15 wt% of silyl ester monomer and/or a non-hydrophilic (meth)acrylic polymer which comprises less than 10 wt% of a monomer of Formula (I).

2. A binder as claimed in claim 1 wherein component (iii) comprises silyl ester (meth)acrylic copolymer in which the monomer is triisopropylsilyl methacrylate (TISMA) or triisopropylsilyl acrylate (TISA).

3. A binder as claimed in any preceding claim wherein the hydrophilic copolymer (i) comprises

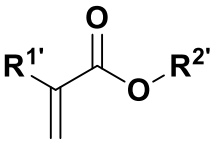
(a) 15 to 65 wt% of at least one monomer of Formula (I)



(I)

wherein R^1 is H or CH_3, and R^2 is a C3-C18 substituent with at least one oxygen or nitrogen atom, preferably at least one oxygen atom or R^2 is a poly(alkylene glycol) chain;

and (b) 85 to 35 wt% of at least one monomer of Formula (II),



(II)

wherein $R^{1'}$ is H or CH_3, and $R^{2'}$ is a C1-C8 hydrocarbyl;

wherein said hydrophilic copolymer is free of any metal-ion containing comonomers; and

said hydrophilic copolymer comprising less than 15 wt% comonomers other than those of Formula (I) or (II).

4. A binder according to any of claims 1 to 3 wherein the amount of component (ii) is in the range of 10 to 70 wt% of the binder (dry solids).

5. A binder as claimed in any preceding claim wherein component (ii) is a rosin or derivative thereof (such as a salt thereof).

6. A binder according to claim 1 to 5 wherein R^2 is a group of formula $(CH_2CH_2O)_n$-R^3 where R^3 is a C1-C10 alkyl or C6-C10 aryl substituent and n is an integer in the range of 1 to 6.

7. A binder as claimed in any preceding claim wherein the amount of component (i) is in the range of 20 to 60 wt% of the binder (dry solids).

8. A binder according to any preceding claim wherein the monomer of Formula (I) is 2-methoxyethyl methacrylate (MEMA), 2-methoxyethyl acrylate (MEA), 2-ethoxyethyl methacrylate (EEMA), 2-(2-ethoxyethoxy)ethyl acrylate (EDEGA) and tetrahydrofurfuryl acrylate (THFA).

9. A binder according to any preceding claim wherein the monomer of Formula (II) is methyl methacrylate (MMA), n-butyl methacrylate (n-BMA), 2-ethylhexyl acrylate (2-EHA) and n-butyl acrylate (n-BA).

10. A binder according to any of claims 1 to 9 comprising (iii) a silyl ester (meth)acrylic copolymer comprising at least 15 wt% of silyl ester monomer and a non-hydrophilic (meth)acrylic polymer which comprises less than 10 wt% of a monomer of Formula (I).

11. A binder according to any of claims 1 to 10 comprising a non-hydrophilic (meth)acrylic acid copolymer (iii-2) which comprises less than 10 wt% of a monomer of Formula (I).

12. A binder according to any of claims 1 to 11 comprising 10 to 60 wt% of component (iii) (dry solids).

13. A binder according to any of claims 1 to 10 wherein the Tg of the non-hydrophilic (meth)acrylic polymer is less than $0^{\circ}C$.

14. An antifouling coating composition comprising a binder according to any of claims 1 to 13 and at least one antifouling agent.

15. An antifouling coating composition according to claim 14, wherein said antifouling agent comprises cuprous oxide and/or copper pyrithione and/or zinc ethylenebis(dithiocarbamate).

16. An antifouling coating composition according to claim 14 or 15, wherein said binder comprises 15 to 50 wt% of the antifouling coating composition.

17. A process for protecting an object from fouling, said process comprising coating at least a part of said object which is subject to fouling with an antifouling coating composition as claimed in any of claims 14 to 16.

18. An object coated with the antifouling coating composition as claimed in any of claims 14 to 16.

19. An object as claimed in claim 17 wherein the object is coated with an anticorrosive coating layer, a tie layer and an antifouling coating composition as claimed in claim 14 to 16.

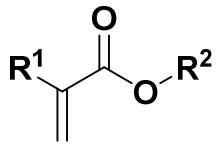
20. An object as claimed in claim 18 wherein the object is coated with an antifouling coating composition as claimed in claims 14 to 16 which covers a pre-existing antifouling coating composition on the substrate.

Abstract

Antifouling Composition

A binder for an antifouling coating composition comprising:

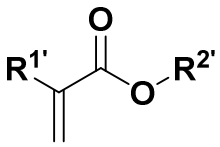
(i) a hydrophilic copolymer having a glass transition temperature of at least 0°C comprising at least 10 wt% of at least one monomer of Formula (I)



(I)

wherein R^1 is H or CH_3, and R^2 is a C3-C18 substituent with at least one oxygen or nitrogen atom, preferably at least one oxygen atom or R^2 is a poly(alkylene glycol) chain;

and at least one monomer of Formula (II),



(II)

wherein $R^{1'}$ is H or CH_3, and $R^{2'}$ is a C1-C20 hydrocarbyl;

said hydrophilic copolymer comprising less than 15 wt% comonomers other than those of Formula (I) or (II);

(ii) a cyclic monocarboxylic acid such as rosin or a derivative thereof

(iii) a silyl ester copolymer comprising at least 15 wt% of silyl ester monomer and/or a non-hydrophilic (meth)acrylic polymer which comprises less than 10 wt% of a monomer of Formula (I).

[No suitable figure]