

Antifouling Composition

Field of the Invention

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The present invention relates to marine antifouling coating compositions, more specifically to antifouling coating compositions comprising biocides in an amount of 10.0 wt% or less, wherein the biocides comprise tralopyril and a copper compound having a copper content of at least 40 wt%. The compositions additionally contain a monocarboxylic acid or a metal salt thereof, a (meth)acrylic silyl ester copolymer and/or a (meth)acrylic polymer and pigments and/or extenders. The invention further relates to a method of protecting objects from fouling, and to objects coated with the antifouling composition of the invention.

15 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.

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, extenders, additives and solvents together with biologically active substances (biocides). Biocides can be broadly divided into those active against soft fouling, such as green and brown algae, grass, slime and those active against hard fouling, such as barnacles, mussels, tube worms etc.

30 The largest product segment for antifouling coating system on merchant vessels is self-polishing antifouling coatings (SPC). The majority of the products are copper based with a relatively high total content of biocides, pigments and extenders. The commercial copper containing products typically contain 20-50 % by

weight of copper(I) oxide, which is known to have good activity against hard fouling, and an additional 1-10 % by weight of organic biocides, which are mainly active against soft fouling, to broaden the antifouling activity spectrum of the products. One of the success factors with SPC products is that the polishing rate can
5 be adjusted to maximise their effectiveness on vessels with different operational speeds and activity.

There is a limited number of biocides approved for use as marine antifouling agents by regulatory bodies. The approved biocides are considered safe to use and without adverse environmental effects. However, it is still important to optimize the
10 effect of the combination of biocides in the coating film to limit their use to a minimum. Restrictions on the use of biocides are increasing and it is likely that in the future the amounts of biocides in antifouling coatings will have to be significantly reduced. When reducing the amounts of biocides there is a challenge in maintaining good long term antifouling performance.

15 Low biocide formulations are generally associated with formulations having a low content of pigments and extenders often in combination with polysiloxane binders or binders having polysiloxane blocks and/or added silicone oils. An example of commercial products are biocidal fouling release coatings (FRC). Reducing the biocide to low levels in conventional self-polishing antifouling
20 coatings will require a full or part replacement of biocides by other components. That will have consequences for the self-polishing properties, mechanical properties and antifouling performance of the coating, unless the formulation is carefully re-designed. There thus remains a need to develop new self-polishing antifouling coating compositions which contain reduced levels of biocides.

25 Tralopyril is a relatively new metal-free, organic marine antifouling agent which has a broad spectrum of activity against hard-shelled and soft-bodied invertebrates such as barnacles, hydroids, mussels, oysters, tube worms and tunicates. Tralopyril is sold under the trade name Econeal and the supplier's product datasheet recommend using between 4 and 6 wt% in antifouling coating
30 compositions. When lower amounts of tralopyril are used as the only biocide active against hard fouling there is a challenge with achieving sufficient antifouling performance.

The present inventors have surprisingly found that combining tralopyril with a copper compound as defined herein, self-polishing antifouling coating compositions with 10 wt% or less total biocides can be prepared. Such coating compositions have unexpectedly attractive antifouling properties.

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Summary of invention

In one aspect, the invention relates to an antifouling coating composition comprising:

- 10 (i) a (meth)acrylic silyl ester copolymer comprising at least 15 wt% silyl ester monomers, relative to the total weight of monomers present in the (meth)acrylic silyl ester copolymer; and/or
- (ii) a (meth)acrylic polymer comprising 10 wt% or less of silyl ester monomers and 5.0 wt% or less of metal ester monomers, relative to the
- 15 total weight of monomers present in the (meth)acrylic polymer;
- (iii) a monocarboxylic acid or a metal salt thereof;
- (iv) biocides comprising:
 - a. tralopyril; and
 - b. one or more copper compounds having a copper content of at least 40
 - 20 wt%, relative to the formula weight of the copper compound, wherein the coating composition as a whole comprises 10.0 wt% or less of biocides; and
- (v) at least 35 wt% of pigments, extenders and biocides combined, relative to
- 25 the total weight of the coating composition as a whole.

In another aspect, the invention relates to an antifouling coating composition comprising:

- (i) a (meth)acrylic silyl ester copolymer comprising at least 15 wt% silyl ester monomers, relative to the total weight of monomers present in the
- 30 (meth)acrylic silyl ester copolymer; and

- (ii) a (meth)acrylic polymer comprising 10 wt% or less of silyl ester monomers and 5.0 wt% or less of metal ester monomers, relative to the total weight of monomers present in the (meth)acrylic polymer;
- (iii) a monocarboxylic acid or a metal salt thereof;
- 5 (iv) biocides comprising:
- a. tralopyril; and
- b. one or more copper compounds having a copper content of at least 40 wt%, relative to the formula weight of the copper compound, wherein the coating composition as a whole comprises 10.0 wt% or less of biocides;
- 10 and
- (v) at least 35 wt% of pigments, extenders and biocides combined, relative to the total weight of the coating composition as a whole.

In another aspect, the invention relates to an antifouling coating composition comprising:

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- (ii) at least one, preferably at least two, (meth)acrylic polymer comprising 10 wt% or less of silyl ester monomers and 5.0 wt% or less of metal ester monomers, relative to the total weight of monomers present in the (meth)acrylic polymer;
- 20 (iii) a monocarboxylic acid or a metal salt thereof;
- (iv) biocides comprising:
- a. tralopyril; and
- b. one or more copper compounds having a copper content of at least 40 wt%, relative to the formula weight of the copper compound, wherein the coating composition as a whole comprises 10.0 wt% or less of biocides;
- 25 and
- (v) at least 35 wt% of pigments, extenders and biocides combined, relative to the total weight of the coating composition as a whole.

30 In a further aspect, the invention relates 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 hereinbefore defined.

In another aspect, the invention relates to an object coated with the antifouling coating composition as hereinbefore defined.

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Definitions

As used herein the terms “marine antifouling coating composition”, “antifouling coating composition” or simply “coating composition” refer to a composition that, when applied to a surface, prevents or minimises growth of marine organisms on the surface.

The antifouling coating compositions of the invention are “self-polishing” coatings. By “self-polishing” or “polishing” we mean that the coating is subject to a reduction in the film thickness due to removal of coating material at the surface of the coating film over time as the result of degradation and/or erosion by the surrounding water medium.

As used herein the term “paint” refers to a composition comprising the antifouling coating composition as herein described and optionally solvent, which is ready for use, e.g. for spraying. Thus, the antifouling coating composition may itself be a paint or the coating composition may be a concentrate to which solvent is added to produce a paint.

As used herein the term “(meth)acrylic polymer” and “(meth)acrylic silyl ester copolymer” refers to polymers comprising repeating units derived from (meth)acrylate monomers. Generally, a (meth)acrylic polymer or a (meth)acrylic silyl ester copolymer will comprise at least 50 wt% of repeating units derived from (meth)acrylate monomers, i.e. acrylate and/or methacrylate monomers.

Where a wt% of a given monomer is given for a polymer, the wt% is relative to the sum total (weight) of monomers present in the copolymer.

As used herein the term “hydrocarbyl group” refers to any group containing C atoms and H atoms only and therefore covers alkyl, aryl, cycloalkyl, arylalkyl groups and so on.

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As used herein the term “alkyl” refers to saturated, straight chained, or branched groups.

As used herein the term “cycloalkyl” refers to a cyclic alkyl group.

As used herein the term “alkylene” refers to a bivalent alkyl group.

5 As used herein the term “aryl” refers to a group comprising at least one aromatic ring. Aryl groups may be substituted or unsubstituted. An example of an aryl group is phenyl, i.e. C₆H₅. Phenyl groups may be substituted or unsubstituted.

As used herein the term “(meth)acrylate” encompasses both methacrylate and acrylate.

10 As used herein the term “volatile organic compound (VOC)” refers to a compound having a boiling point of 250 °C or less at standard atmospheric pressure of 1 atm.

As used herein “antifouling agent” or “biocide” refers to a biologically active compound or mixture of biologically active compounds that prevents or minimises
15 the settlement and/or the growth of marine organisms on a surface.

As used herein the term “monocarboxylic acid” refers to a compound comprising one -COOH group.

The term “binder” defines part of the composition which includes components (i), (ii) and (iii) as defined herein and any other components which
20 together form a matrix giving strength and/or flexibility to the coating film.

The term “T_g” means glass transition temperature.

The term “wt% based on the total weight of the composition” refers to the wt% of a component present in the total coating composition, unless otherwise specified.

25 As used herein the term “wt% based on the total dry weight of the composition” refers to the wt% of a dry component present in the dry weight of the coating composition, i.e. excluding solvents and other volatiles, unless otherwise specified.

30 **Detailed description of invention**

The invention relates to a new antifouling coating composition comprising (i) a (meth)acrylic silyl ester copolymer and/or (ii) a (meth)acrylic polymer; (iii) a monocarboxylic acid or a metal salt thereof; and (iv) biocides comprising tralopyril and a copper compound in an amount of 10.0 wt% or less, together with (v) at least 35 wt% of pigments, extenders and biocides combined, relative to the total weight of the coating composition.

The binder of the invention comprises components (i) to (iii), which ever present. The coating compositions of the present invention comprise (i) a (meth)acrylic silyl ester copolymer and/or (ii) a (meth)acrylic copolymer as herein defined.

In one preferred embodiment the antifouling coating composition of the invention comprises a (meth)acrylic silyl ester copolymer (i) as herein defined.

In a second preferred embodiment the antifouling coating composition of the invention comprises both a (meth)acrylic silyl ester copolymer (i) and a (meth)acrylic polymer (ii) as defined herein.

In a third preferred embodiment the antifouling coating composition of the invention comprises a (meth)acrylic polymer (ii) as herein defined.

In a fourth preferred embodiment the antifouling coating composition of the invention comprises at least two (meth)acrylic polymers (ii), e.g. a (meth)acrylic polymer (ii-a) and a (meth)acrylic polymer (ii-b) wherein the polymers (ii-a) and (ii-b) are different.

(Meth)acrylic silyl ester copolymer (i)

The use of (meth)acrylic silyl ester copolymers in antifouling coating compositions is well known and, in its broadest embodiment, the invention covers any of these well-known copolymers.

The (meth)acrylic silyl ester copolymers (i) comprise repeating units derived from (meth)acrylate monomers. Preferably the (meth)acrylic silyl ester copolymer (i) comprises at least 80 wt% of the repeating units derived from (meth)acrylate monomers, i.e. acrylate and/or methacrylate monomers. It is further preferred if the (meth)acrylic silyl ester copolymer (i) comprises at least 85 wt%, more preferably at least 90 wt% and still more preferably at least 95 wt% repeating units derived from

(meth)acrylate monomers. Preferred (meth)acrylic silyl ester copolymers present in the composition of the present invention comprise 80 to 100 wt%, more preferably 85 to 100 wt% and still more preferably 90 to 100 wt% repeating units derived from (meth)acrylate monomers.

5 In one preferred embodiment the (meth)acrylic silyl ester copolymers comprise 100 wt% of structural units derived from (meth)acrylate monomers, i.e. they do not comprise any monomers of another type.

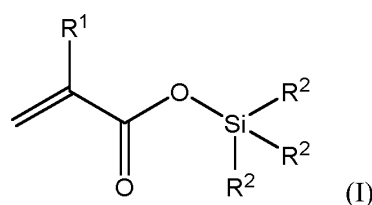
The coating composition of the present invention may comprise a mixture of two or more different (meth)acrylic silyl ester copolymers (i) for example as
10 described in GB2576431.

The (meth)acrylic silyl ester copolymer of the present invention preferably comprises structural units derived from (meth)acrylic silyl ester monomers (a1) and structural units derived from polymerizable ethylenically unsaturated monomers (a2).

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(Meth)acrylic silyl ester monomer (a1)

Preferably the (meth)acrylic silyl ester copolymer (i) comprises the residue of at least one silyl ester monomer (a1) of formula (I):



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wherein

R^1 is H or CH_3 ;

R^2 is each independently selected from C1-C10 hydrocarbyl groups and $\text{OSi}(\text{R}^3)_3$ groups;

25 wherein R^3 is each independently selected from the group consisting of linear or branched C1-C10 alkyl groups.

The term "hydrocarbyl" is intended to cover linear or branched alkyl groups such as methyl, isopropyl, propyl, butyl, iso-butyl, tert-butyl, 1,1,2-trimethylpropyl

and 2-ethylhexyl, cycloalkyl groups such as cyclohexyl and substituted cyclohexyl and aryl groups such as phenyl and substituted phenyl. It is preferred if each R^2 is independently a C1-8 alkyl group. It is preferred if all R^2 groups are the same.

5 It is preferred if each R^3 is independently a C1-4 alkyl group. It is preferred if all R^3 groups are the same.

Monomers (a1) as defined by the general formula (I) include silyl ester monomers such as tri-n-propylsilyl (meth)acrylate, triisopropylsilyl (meth)acrylate, tri-n-butylsilyl (meth)acrylate, triisobutylsilyl (meth)acrylate, tri-2-ethylhexylsilyl (meth)acrylate, tert-butyl dimethylsilyl (meth)acrylate, hexyl dimethylsilyl (meth)acrylate, tert-butyl diphenylsilyl (meth)acrylate, bis(trimethylsiloxy)methylsilyl (meth)acrylate and tris(trimethylsiloxy)silyl (meth)acrylate.

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The use of triisopropylsilyl acrylate and/or triisopropylsilyl methacrylate is preferred. R^2 is therefore preferably isopropyl.

15 The (meth)acrylic silyl ester monomer of formula (I) can be used alone, or two or more silyl ester monomers of formula (I) can be used in combination. The (meth)acrylic silyl ester copolymer (i) preferably comprises 1 or 2 different monomers of formula (I), especially one.

The (meth)acrylic silyl ester copolymer (i) preferably comprises at least 15 wt% silyl ester monomers, relative to the total weight of monomers present in the copolymer, e.g. those of formula (I) herein. Preferably, the (meth)acrylic silyl ester copolymer comprises at least 30 wt% silyl ester monomers, relative to the total weight of monomers present in the copolymer, more preferably at least 40 wt%, such as at least 45 wt%.

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25 The (meth)acrylic silyl ester copolymer (i) preferably comprises less than 80 wt% silyl ester monomers, relative to the total weight of monomers present in the copolymer. Preferably, the (meth)acrylic silyl ester copolymer comprises less than 75 wt% silyl ester monomers, relative to the total weight of monomers present in the copolymer, more preferably less than 70 wt%, such as less than 65 wt%.

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Ethylenically unsaturated monomer (a2)

The (meth)acrylic silyl ester copolymer (i) of the present invention preferably comprises the residue of at least one ethylenically unsaturated monomer (a2) that will polymerize with the (meth)acrylic silyl ester monomer (a1).

5 Monomers (a1) and (a2) are different. Monomer (a2) is preferably free of silyl ester groups. Monomer (a2) is preferably free of metal ester groups.

The ethylenically unsaturated monomer (a2) is preferably selected from (meth)acrylate monomers and vinyl monomers. Preferably the ethylenically unsaturated monomer (a2) is a (meth)acrylate monomer.

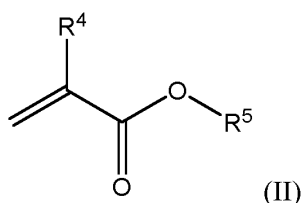
10 Examples of suitable (meth)acrylate monomers (a2) include methyl (meth)acrylate, ethyl (meth)acrylate, n-butyl (meth)acrylate, isobutyl (meth)acrylate, tert-butyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, 2-octyl (meth)acrylate, isooctyl (meth)acrylate, 2-propylheptyl (meth)acrylate, isodecyl (meth)acrylate, cyclohexyl (meth)acrylate, 3,5,5-trimethylcyclohexyl (meth)acrylate, isobornyl
15 (meth)acrylate, benzyl (meth)acrylate, 2-hydroxyethyl (meth)acrylate, 2-methoxyethyl (meth)acrylate, 2-ethoxyethyl (meth)acrylate, 2-butoxyethyl (meth)acrylate, 2-(2-ethoxyethoxy)ethyl (meth)acrylate, methoxycarbonylmethyl (meth)acrylate, ethoxycarbonylmethyl (meth)acrylate, 2-(2-methoxy-2-oxoethoxy)-2-oxoethyl (meth)acrylate, 2-(2-ethoxy-2-oxoethoxy)-2-oxoethyl (meth)acrylate,
20 oligo(oxycarbonylmethyl) methyl (meth)acrylate, oligo(oxycarbonylmethyl) ethyl (meth)acrylate, tetrahydrofurfuryl (meth)acrylate, glycerolformal (meth)acrylate, isopropylideneglycerol (meth)acrylate, glycerolcarbonate (meth)acrylate, cyclic trimethylolpropane formal (meth)acrylate, glycidyl (meth)acrylate and 4-glycidyoxybutyl (meth)acrylate;

25 Examples of suitable vinyl monomers (a2) are styrene, vinyl 2-ethylhexanoate and vinyl neodecanoate.

Mixtures of different monomers (a2) may be used.

Preferably the ethylenically unsaturated monomer (a2) is of formula (II)

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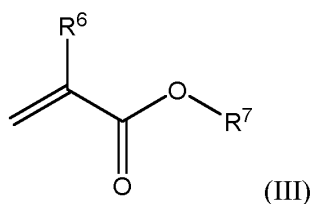
wherein R^4 is H or CH_3 , and R^5 is a C1-C20 hydrocarbyl substituent, preferably a C1-C10 alkyl substituent, such as a C1-C8 alkyl. The R^5 group can be linear or branched. Most preferably R^5 is a methyl, ethyl, propyl, butyl, hexyl, octyl
 5 or decyl group which (if possible) may be linear or branched. Ideally options for R^5 are methyl, ethyl, n-butyl, isobutyl or isooctyl.

Examples of suitable monomers of formula (II) as monomer (a2) in (meth)acrylic polymer (ii-a) include methyl (meth)acrylate, ethyl (meth)acrylate, n-butyl (meth)acrylate, isobutyl (meth)acrylate, tert-butyl (meth)acrylate, 2-ethylhexyl
 10 (meth)acrylate, 2-octyl (meth)acrylate, isooctyl (meth)acrylate, 2-propylheptyl (meth)acrylate, isodecyl (meth)acrylate, cyclohexyl (meth)acrylate, 3,5,5-trimethylcyclohexyl (meth)acrylate, and isobornyl (meth)acrylate.

Preferred options for monomers of formula (II) include methyl methacrylate, ethyl acrylate, n-butyl acrylate, n-butyl methacrylate or isobutyl methacrylate.

15 Mixtures of different monomers of formula (II) may be used.

The ethylenically unsaturated monomer (a2) may also be of formula (III)



wherein R^6 is H or CH_3 , and R^7 is a C3-C40 substituent containing at least one oxygen or nitrogen atom, preferably at least one oxygen, preferably a C3-C20
 20 substituent containing at least one oxygen atom.

Preferably the R^7 group is of formula $(CH_2CH_2O)_n-R^8$ where R^8 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^7 is of formula $(CH_2CH_2O)_n-R^8$ where R^8 is a C1-C10 alkyl substituent, preferably CH_3 or
 25 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 (meth)acrylate, 2-ethoxyethyl (meth)acrylate, 2-butoxyethyl (meth)acrylate, 2-(2-methoxyethoxy)ethyl (meth)acrylate, 2-(2-ethoxyethoxy)ethyl (meth)acrylate, 2-(2-butoxyethoxy)ethyl (meth)acrylate, 2-[2-(2-methoxyethoxy)ethoxy]ethyl (meth)acrylate or 2-[2-(2-ethoxyethoxy)ethoxy]ethyl (meth)acrylate.

Preferred monomers (a2) of formula (III) are 2-methoxyethyl acrylate, 2-methoxyethyl methacrylate, 2-ethoxyethyl methacrylate, 2-(2-ethoxyethoxy)ethyl acrylate or 2-(2-ethoxyethoxy)ethyl methacrylate.

The R^7 group may also be of formula $(CH_2C(O)O)_p-R^9$ or $(CH(CH_3)C(O)O)_p-R^9$ where R^9 is a C1-C10 hydrocarbyl substituent, preferably a C1-C10 alkyl or C6-C10 aryl substituent, and p is an integer in the range of 1 to 10, preferably 1 to 4.

Such a monomer of formula (III) might be methoxycarbonylmethyl (meth)acrylate, ethoxycarbonylmethyl (meth)acrylate, 2-(2-methoxy-2-oxoethoxy)-2-oxoethyl (meth)acrylate, 2-(2-ethoxy-2-oxoethoxy)-2-oxoethyl (meth)acrylate, oligo(oxycarbonylmethyl) methyl (meth)acrylate and oligo(oxycarbonylmethyl) ethyl (meth)acrylate.

The R^7 group may also be a cyclic group containing at least one oxygen or nitrogen atom, preferably at least one oxygen atom. In this embodiment, R^7 may be a group $W-R^{10}$ wherein R^{10} is a cyclic ether, such as oxirane, furan, oxolane, oxane, dioxolane, dioxane optionally alkyl substituted, and W is a C1-C4 alkylene.

Such a monomer of formula (III) might be furfuryl (meth)acrylate, tetrahydrofurfuryl (meth)acrylate, glycerol formal (meth)acrylate, isopropylideneglycerol (meth)acrylate, glycerol carbonate (meth)acrylate, cyclic trimethylolpropane formal (meth)acrylate, glycidyl (meth)acrylate and 4-glycidyoxybutyl (meth)acrylate. Preferred cyclic ethers should contain at least 4 atoms in the ring such as tetrahydrofurfuryl acrylate and isopropylideneglycerol methacrylate.

The monomer of formula (III) is preferably 2-methoxyethyl acrylate, 2-methoxyethyl methacrylate, 2-ethoxyethyl methacrylate, 2-(2-ethoxyethoxy)ethyl acrylate, 2-(2-ethoxyethoxy)ethyl methacrylate or tetrahydrofurfuryl acrylate.

Mixtures of different monomers of formula (III) may be used.

Mixtures of different monomers of formula (II) and formula (III) may also be used together.

If monomer of formula (III) is present in the (meth)acrylic silyl ester copolymer (i) of the present invention it is preferred if at least one monomer of formula (II) is also present.

Preferred (meth)acrylic silyl ester copolymers (i) of the present invention comprise structural units derived from one or more monomers of formula (I), such as triisopropylsilyl acrylate and/or triisopropylsilyl methacrylate and structural units derived from one or more monomers of formula (II) such as methyl methacrylate and/or butyl acrylate and optionally structural units derived from one or more monomers of formula (III) such as 2-methoxyethyl acrylate, 2-methoxyethyl methacrylate and 2-(2-ethoxyethoxy)ethyl acrylate.

Preferably, the content of the (meth)acrylic silyl ester monomer(s) (a1) (such as monomers of formula (I)) in the (meth)acrylic silyl ester copolymer (i) is in the range 30 to 80 wt%, preferably 35 to 75 wt%, such as 40 to 70 wt% and 45 to 65 wt%, relative to the total weight of monomers present in the (meth)acrylic silyl ester copolymer as a whole.

Preferably, the (meth)acrylic silyl ester copolymer (i) comprises 20 to 70 wt% of the monomer (a2) (such as those of formula (II) or formula (III)), such as 30 to 60 wt% and 35 to 55 wt%, relative to the total weight of monomers present in the (meth)acrylic silyl ester copolymer as a whole, more preferably 35 to 55 wt%.

Preferably, the (meth)acrylic silyl ester copolymer (i) comprises at least 15 wt% of the monomer(s) of formula (II) component, especially 15 to 65 wt%.

Preferably, the (meth)acrylic silyl ester copolymer (i) comprises less than 40 wt% of the monomer(s) of formula (III), more preferred 2.0 to 35 wt%.

When the R^7 group in formula (III) is a group of formula $-(CH_2CH_2O)_n-R^8$ the (meth)acrylic silyl ester copolymer (i) may comprise 2.0 to 40 wt% of the monomer(s) of formula (III).

When the R^7 group in formula (III) is a cyclic group the (meth)acrylic silyl ester copolymer (i) may comprise 5.0 to 40 wt% of the monomer(s) of formula (III).

The (meth)acrylic silyl ester copolymer (i) preferably has a weight-average molecular weight (Mw) from 5,000 to 70,000, preferably from 8,000 to 55,000,

more preferably from 20,000 to 45,000. Mw is determined as described in the examples section. The (meth)acrylic silyl ester copolymer (i) preferably has a polydispersity index (PDI) of from 1.5 to 8.0, more preferred from 2.0 to 5.0.

5 The copolymer preferably has a glass transition temperature (T_g) of at least 15 °C, preferably at least 20 °C, such as at least 25 °C, all values being measured according to the T_g test described in the examples section. Values less than 80 °C are preferred, such as less than 70 °C, e.g. less than 60 °C or less than 55 °C.

The (meth)acrylic silyl ester copolymer (i) may be provided as a polymer solution, such as a xylene solution. The polymer solution is desirably regulated to have a solid content from 30 to 90 % by weight, preferably from 40 to 85 % by weight, more preferably from 45 to 75 % by weight.

In one preferred embodiment the antifouling coating composition of the invention preferably comprises 2.0 to 30 wt% of the (meth)acrylic silyl ester copolymer (i), such as 5.0 to 25 wt%, in particular 7.0 to 20 wt% or 7.0 to 15 wt% based on the total coating composition.

In one preferred embodiment the antifouling coating composition of the invention preferably comprises 5.0 to 40 wt% of the (meth)acrylic silyl ester copolymer (i), such as 7.0 to 30 wt%, in particular 10 to 25 wt% based on the total dry weight of the coating composition.

20 In one preferred embodiment the amount of the (meth)acrylic silyl ester copolymer (i) is present in the antifouling coating compositions of the invention in 20 to 70 wt%, preferably 30 to 65 wt%, more preferably 40 to 60 wt%, based on the total dry weight of binders in the coating composition.

25 If the antifouling coating composition comprises a mixture of two or more different (meth)acrylic silyl ester copolymers (i) then these percentages apply to the content of all (meth)acrylic silyl ester copolymers (i) present. It is preferred if only one (meth)acrylic silyl ester copolymer (i) is present.

(Meth)acrylic polymer (ii)

30 The (meth)acrylic polymer (ii) of the present invention comprises structural units derived from carboxylic acid containing (meth)acrylic monomers and/or (meth)acrylate monomers. The (meth)acrylic polymer (ii) comprises 10 wt% or less

of silyl ester monomers and 5.0 wt% or less of metal ester monomers relative to the total weight of monomers present in the polymer.

The (meth)acrylic polymers (ii) of the present invention preferably comprise repeating units derived from (meth)acrylate monomers. Preferably the (meth)acrylic polymer (ii) comprises at least 50 wt% of the repeating units derived from (meth)acrylate monomers, i.e. acrylate and/or methacrylate monomers.

It is further preferred if the (meth)acrylic polymer (ii) comprises at least 60 wt%, more preferably at least 75 wt% and still more preferably at least 90 wt% repeating units derived from (meth)acrylate monomers.

In one embodiment the (meth)acrylic polymers (ii) comprise 100 wt% of structural units derived from (meth)acrylate monomers, i.e. they do not comprise any monomers of another type.

The (meth)acrylic polymer (ii) of the invention comprises 10 wt% or less silyl ester monomers, e.g. those of formula (I) above, preferably less than 5.0 wt%, such as less than 2.0 wt% or less than 1.0 wt%, and 5.0 wt% or less of metal ester monomers, preferably less than 3.0 wt% such as such as less than 2.0 wt% or less than 1.0 wt%, relative to the total weight of monomers present in the (meth)acrylic polymer (ii). Most preferred the (meth)acrylic polymer (ii) is free of any silyl ester groups.

It is also preferred if the (meth)acrylic polymer (ii) of the invention is free of any metal ester groups.

The (meth)acrylic polymer (ii) can be a homopolymer or a copolymer, preferably a copolymer.

The (meth)acrylic polymer (ii) may be provided as a polymer solution, such as a solution in solvents. The polymer solution is desirably regulated to have a solid content from 30 to 90 % by weight, preferably from 40 to 85 % by weight, more preferably from 45 to 75 % by weight.

In one embodiment the coating composition of the invention contains at least one (meth)acrylic polymer (ii), e.g. a (meth)acrylic polymer (ii-a). It is possible however to use two (meth)acrylic polymers (ii), such as a (meth)acrylic polymer (ii-a) and a (meth)acrylic polymer (ii-b).

In one embodiment, the coating composition of the invention does not contain a (meth)acrylic silyl ester copolymer component (i) but includes two (meth)acrylic polymers (ii), such as a (meth)acrylic polymer (ii-a) and a (meth)acrylic polymer (ii-b).

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(Meth)acrylic polymer (ii-a)

In one embodiment the (meth)acrylic polymer (ii) is a (meth)acrylic polymer (ii-a).

The (meth)acrylic polymer (ii-a) has a Tg below 10.0 °C, preferably below 0 °C, more preferred below -5 °C, even more preferred below -10°C, all values being measured according to the Tg test described in the examples section. Values more than -65 °C are preferred, e.g. more than -55 °C, or more than -45 °C.

10

In one embodiment the (meth)acrylic polymer (ii-a) comprises a (meth)acrylic acid monomer (a3). Suitable (meth)acrylic acid monomers (a3) are methacrylic acid or acrylic acid. The (meth)acrylic acid (a3) content within the (meth)acrylic polymer (ii-a) is preferably in the range of 0.5 to 10.0 wt%, such as 1.0 to 5.0 wt%.

15

Preferably the (meth)acrylic polymer (ii-a) has acid number below 60 mg KOH/g polymer, more preferred below 40 mg KOH/g polymer, even more preferred below 25 mg KOH/g polymer. Preferably the acid number is above 2 mg KOH/g polymer, such as above 5 mg KOH/g polymer. The acid number is determined according to the procedure described in ISO 2114:2000 Method A.

20

When a (meth)acrylic acid monomer (a3) is present, it is preferred if a second (meth)acrylate monomer (a4) as described below is present to thus form a copolymer.

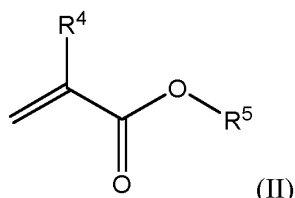
25

In another embodiment, the (meth)acrylic polymer (ii-a) contains at least one (meth)acrylate monomer (a4). The (meth)acrylate monomers (a4) preferably form at least 50 wt% of the (meth)acrylic polymer (ii-a), such as at least 75 wt% or at least 80 wt%, especially 95.0 to 99.5 wt%.

30

The (meth)acrylic polymer (ii-a) may be a homopolymer comprising only structural units derived from (meth)acrylate monomers (a4).

Examples of suitable (meth)acrylate monomers (a4) are of formula (II) as hereinbefore defined:



- wherein R^4 is H or CH_3 , and R^5 is a C1-C20 hydrocarbyl substituent,
- 5 preferably a C1-10 alkyl substituent, such as a C1-8 alkyl. The R^5 group can be linear or branched. Most preferably R^5 is a methyl, ethyl, propyl, butyl, hexyl, octyl or decyl group which (if possible) may be linear or branched. Preferences for formula (II) above described in connection with the (meth)acrylic silyl ester copolymer (i) also apply to (meth)acrylic polymer (ii-a).
- 10 Examples of suitable monomers of formula (II) as monomer (a4) in (meth)acrylic polymer (ii-a) include methyl (meth)acrylate, ethyl (meth)acrylate, n-butyl (meth)acrylate, isobutyl (meth)acrylate, tert-butyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, 2-octyl (meth)acrylate, isooctyl (meth)acrylate, 2-propylheptyl (meth)acrylate, isodecyl (meth)acrylate, cyclohexyl (meth)acrylate, 3,5,5-
- 15 trimethylcyclohexyl (meth)acrylate, and isobornyl (meth)acrylate.
- Preferred options for monomers of formula (II) as monomer (a4) in (meth)acrylic polymer (ii-a) include methyl methacrylate, ethyl acrylate, n-butyl acrylate, n-butyl methacrylate, 2-ethylhexyl acrylate, 2-octyl acrylate, isooctyl acrylate or isodecyl acrylate.
- 20 Mixtures of different monomers of formula (II) may also be used in (meth)acrylic polymer (ii-a).
- Preferably the (meth)acrylic polymer (ii-a) comprises structural units derived from (meth)acrylic acid monomers (a3) and (meth)acrylate monomers (a4).
- 25 In one preferred embodiment the (meth)acrylic polymer (ii-a) comprises structural units derived from acrylic acid and/or methacrylic acid and methyl methacrylate, ethyl acrylate, n-butyl acrylate, n-butyl methacrylate, 2-ethylhexyl acrylate, 2-octyl acrylate, isooctyl acrylate and/or isodecyl acrylate.

The (meth)acrylic polymer (ii-a) may also comprise structural units derived from other ethylenically unsaturated monomers such as vinyl monomers, e.g. styrene, vinyl 2-ethylhexanoate and vinyl neodecanoate.

5 The (meth)acrylic polymer (ii-a) preferably has a weight-average molecular weight of from 5,000 to 100,000, preferably of from 10,000 to 80,000, especially 15,000 to 50,000. Mw is determined as described in the examples section. The (meth)acrylic polymer (ii-a) preferably has a polydispersity index (PDI) of from 1.5 to 5.0.

10 The (meth)acrylic polymer (ii-a) is typically present in an amount of 0.5 to 10 wt%, preferably 1.0 to 5.0 wt%, relative to the total weight of the coating composition as a whole when a (meth)acrylic silyl ester copolymer (i) is used.

The (meth)acrylic polymer (ii-a) is typically present in an amount of 1.0 to 12 wt%, preferably 2.0 to 7.0 wt%, relative to the total dry weight of the coating composition as a whole when a (meth)acrylic silyl ester copolymer (i) is used.

15 The (meth)acrylic copolymer (ii-a) is typically present in an amount 2.0 to 25 wt%, preferably 5.0 to 20 wt%, based on the total dry weight of binders in the coating composition of the invention when the (meth)acrylic silyl ester copolymer (i) is used.

20 When the (meth)acrylic polymer (ii-a) is used in the absence of the (meth)acrylic silyl ester copolymer (i) it may be present in an amount of 1.0 to 12 wt%, preferably 2.0 to 7.0 wt%, relative to the total weight of the coating composition as a whole.

25 When the (meth)acrylic polymer (ii-a) is used in the absence of the (meth)acrylic silyl ester copolymer (i) it may be present in an amount of 1.5 to 15 wt%, preferably 2.5 to 10 wt%, relative to the total dry weight of the coating composition .

30 When the (meth)acrylic copolymer (ii-a) is used in the absence of the (meth)acrylic silyl ester copolymer (i) it may be present in the in an amount 5 to 30 wt%, preferably 10 to 25 wt%, based on the total dry weight of binders in the coating composition.

(Meth)acrylic polymer (ii-b)

In one embodiment the coating composition of the present invention may further comprise a (meth)acrylic polymer (ii-b).

If both (meth)acrylic polymer (ii-a) and (meth)acrylic polymer (ii-b) are present it is preferred if there is no (meth)acrylic silyl ester copolymer (i) present.

5 The (meth)acrylic polymer (ii-b) has a glass transition temperature (T_g) of at least 10 °C, preferably at least 15 °C, such as at least 17 °C or at least 20 °C, all values being measured according to the T_g test described in the examples section. Values less than 80 °C are preferred, such as less than 70 °C, e.g. less than 55 °C. The T_g of (meth)acrylic polymer (ii-b) is therefore at least 10°C whereas that of
10 (meth)acrylic polymer (ii-a) is less than 10°C. Preferably, the T_g of (meth)acrylic polymer (ii-b) is at least 10°C whereas that of (meth)acrylic polymer (ii-a) is 0°C or less.

In one embodiment the (meth)acrylic polymer (ii-b) does not contain a (meth)acrylic acid monomer (a3).

15 The (meth)acrylic polymer (ii-b) comprises at least one (meth)acrylate monomer (a5).

Examples of suitable (meth)acrylate monomers (a5) include methyl (meth)acrylate, ethyl (meth)acrylate, n-butyl (meth)acrylate, isobutyl (meth)acrylate, tert-butyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, 2-octyl (meth)acrylate,
20 isooctyl (meth)acrylate, 2-propylheptyl (meth)acrylate, isodecyl (meth)acrylate, cyclohexyl (meth)acrylate, 3,5,5-trimethylcyclohexyl (meth)acrylate, isobornyl (meth)acrylate, benzyl (meth)acrylate, 2-hydroxyethyl (meth)acrylate, oligo(ethylene glycol) (meth)acrylate, poly(ethylene glycol) (meth)acrylate, 2-methoxyethyl (meth)acrylate, 2-ethoxyethyl (meth)acrylate, 2-butoxyethyl
25 (meth)acrylate, 2-(2-ethoxyethoxy)ethyl (meth)acrylate, oligo(ethylene glycol) methyl ether (meth)acrylate, poly(ethylene glycol) methyl ether (meth)acrylate, methoxycarbonylmethyl (meth)acrylate, ethoxycarbonylmethyl (meth)acrylate, 2-(2-methoxy-2-oxoethoxy)-2-oxoethyl (meth)acrylate, 2-(2-ethoxy-2-oxoethoxy)-2-oxoethyl (meth)acrylate, oligo(oxycarbonylmethyl) methyl (meth)acrylate,
30 oligo(oxycarbonylmethyl) ethyl (meth)acrylate, tetrahydrofurfuryl (meth)acrylate, glycerolfomal (meth)acrylate, isopropylideneglycerol (meth)acrylate,

glycerolcarbonate (meth)acrylate, cyclic trimethylolpropane formal (meth)acrylate, glycidyl (meth)acrylate and 4-glycidyoxybutyl (meth)acrylate;

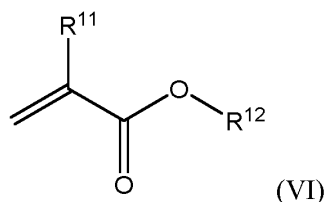
More preferred examples of (meth)acrylate monomers (a5) are of formula (II) as hereinbefore defined for (meth)acrylic ester polymer (ii-a).

5 Preferred options for monomers of formula (II) as monomer (a5) include methyl methacrylate, n-butyl acrylate, n-butyl methacrylate and isobutyl methacrylate.

Mixtures of different monomers of (a5) may also be used.

The (meth)acrylate monomers (a5) may also comprise hydrophilic groups.

10 Examples of suitable monomers are shown in formula (VI) below:



Wherein R^{11} is H or CH_3 , and R^{12} is a C3-C40 substituent, such as C3-C20 substituent, containing at least one oxygen or nitrogen atom, preferably at least one oxygen atom or R^{12} represents a poly(alkylene glycol) group.

The (meth)acrylic copolymer (ii-b) may comprise at least one monomer of formula (VI) above in which the R^{12} group is of formula $(CH_2CH_2O)_n-R^{13}$ where R^{13} 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

20 R^{12} is of formula $(CH_2CH_2O)_n-R^{13}$ where R^{13} 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 (meth)acrylate, 2-ethoxyethyl (meth)acrylate, 2-butoxyethyl (meth)acrylate, 2-(2-methoxyethoxy)ethyl (meth)acrylate, 2-(2-ethoxyethoxy)ethyl (meth)acrylate, 2-(2-butoxyethoxy)ethyl (meth)acrylate, 2-[2-(2-methoxyethoxy)ethoxy]ethyl (meth)acrylate or 2-[2-(2-ethoxyethoxy)ethoxy]ethyl (meth)acrylate.

Preferably the (meth)acrylic polymer (ii-b) comprises one or more of 2-methoxyethyl acrylate, or 2-(2-ethoxyethoxy)ethyl acrylate.

The (meth)acrylic polymer (ii-b) may comprise at least one monomer of formula (VI) above in which the R^{12} 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 $(CH_2CH(CH_3)O)_m-R^{14}$ where R^{14} 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 25, preferably 5 to 15.

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 300-1000, more preferably 300-550.

The (meth)acrylic polymer (ii-b) may also comprise at least one monomer of formula (VI) above in which the R^{12} group is of formula $(CH_2C(O)O)_p-R^{15}$ or $(CH(CH_3)C(O)O)_p-R^{15}$ where R^{15} is a C1-C10 hydrocarbyl substituent, preferably a C1-C10 alkyl or C6-C10 aryl substituent, and p is an integer in the range of 1 to 10, preferably 1 to 4.

Such a monomer might be methoxycarbonylmethyl (meth)acrylate, ethoxycarbonylmethyl (meth)acrylate, 2-(2-methoxy-2-oxoethoxy)-2-oxoethyl (meth)acrylate, 2-(2-ethoxy-2-oxoethoxy)-2-oxoethyl (meth)acrylate, oligo(oxycarbonylmethyl) methyl (meth)acrylate and oligo(oxycarbonylmethyl) ethyl (meth)acrylate.

The (meth)acrylic polymer (ii-b) may comprise at least one monomer of formula (VI) above in which the R^{12} group is a cyclic group containing at least one oxygen or nitrogen atom, preferably at least one oxygen atom. More preferably, R^{12} is a group $W-R^{16}$ having up to 20 carbon atoms wherein R^{16} is a cyclic ether, such as oxirane, furan, oxolane, oxane, dioxolane, dioxane optionally alkyl substituted, and W is a C1-C4 alkylene.

Such a monomer might be furfuryl (meth)acrylate, tetrahydrofurfuryl (meth)acrylate, glycerol formal (meth)acrylate, isopropylideneglycerol (meth)acrylate, glycerol carbonate (meth)acrylate, cyclic trimethylolpropane formal

(meth)acrylate, glycidyl (meth)acrylate and 4-glycidyoxybutyl (meth)acrylate. Preferred cyclic ethers should contain at least 4 atoms in the ring. More preferably tetrahydrofurfuryl acrylate and isopropylideneglycerol methacrylate.

5 The monomer of formula (VI) is preferably 2-methoxyethyl acrylate, 2-(2-ethoxyethoxy)ethyl acrylate or poly(ethylene glycol) methyl ether methacrylate.

Monomers of formula (VI) preferably form at least 10 wt% of the (meth)acrylic polymer (ii-b). Particularly preferred amounts of the monomer of formula (VI) in the copolymer (ii-b) are 10 to 65 wt%, preferably 15 to 55 wt%, such as 18 to 50 wt%. Where a mixture of monomers of formula (VI) are present,
10 these amounts relate to the combined weight fraction of the monomers of formula (VI) in the copolymer.

In one preferred embodiment the (meth)acrylic polymer (ii-b) comprises at least one monomer of formula (II) and at least one monomer of formula (VI).

In a preferred embodiment, the (meth)acrylic polymer component (ii-b)
15 consists of monomers of formula (II) and formula (VI) only. The (meth)acrylic polymer (ii-b) preferably does not contain a (meth)acrylic acid monomer (a3).

The (meth)acrylic polymer (ii-b) may also comprise structural units derived from other ethylenically unsaturated monomers such as vinyl monomers, e.g. styrene, vinyl 2-ethylhexanoate, vinyl neodecanoate and *N*-vinylpyrrolidone.

20 The (meth)acrylic polymer (ii-b) preferably has a weight-average molecular weight (Mw) of from 10,000 to 100,000, preferably of from 15,000 to 70,000, especially 20,000 to 50,000. Mw is determined as described in the examples section. The (meth)acrylic polymer (ii-b) preferably has a polydispersity index (PDI) of from 1.5 to 5.0.

25 When the (meth)acrylic polymer (ii-b) is used it may be present in an amount of 1.0 to 15 wt%, preferably 2.0 to 12 wt%, relative to the total weight of the coating composition as a whole.

When the (meth)acrylic polymer (ii-b) is used it may be present in an amount of 1.5 to 20 wt%, preferably 2.5 to 15 wt%, relative to the total dry weight of the
30 coating composition. .

When the (meth)acrylic copolymer (ii-b) is used in the antifouling coating compositions of the invention it may be present in the in an amount 5.0 to 40 wt%,

preferably 10 to 35 wt%, based on the total dry weight of binders in the coating composition.

Preparation of (meth)acrylic silyl ester copolymer (i) and (meth)acrylic polymer (ii)

5 The (meth)acrylic silyl ester copolymer (i) and (meth)acrylic polymer (ii) can be prepared using polymerization reactions known in the art. The polymers can be obtained by polymerizing a monomer mixture in the presence of a polymerization initiator by any of various methods such as solution polymerization, bulk polymerization, emulsion polymerization, dispersion polymerization and suspension polymerization in a conventional way, such as free-radical polymerization, or by controlled polymerization techniques. In the case of copolymers, the final polymer may be a random copolymer, an alternate copolymer, a gradient copolymer or a block copolymer.

15 In preparing a coating composition using any of the polymers, 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.

20 Examples of suitable initiators for free-radical polymerization in solvents 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*-amyl peroxy-pivalate, *tert*-butyl peroxy-pivalate *tert*-amyl peroxy-2-ethylhexanoate, *tert*-butyl peroxy-2-ethylhexanoate, 1,1,3,3-tetramethylbutyl peroxy-2-ethylhexanoate, *tert*-butyl peroxydiethylacetate, *tert*-butyl peroxyisobutyrate, *tert*-butyl peroxybenzoate, 1,1-di(*tert*-amyl peroxy)cyclohexane, *tert*-amylperoxy 2-ethylhexyl carbonate, *tert*-butylperoxy isopropyl carbonate, *tert*-butylperoxy 2-ethylhexyl carbonate, polyether poly-*tert*-butylperoxy carbonate, di-*tert*-butyl peroxide and dibenzoyl peroxide. These compounds are used alone or as a mixture of two or more thereof.

30 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, diisobutyl ketone, cyclopentanone, cyclohexanone; esters such as butyl acetate, *tert*-butyl acetate, amyl

acetate, propyl propionate, n-butyl propionate, isobutyl isobutyrate, ethylene glycol methyl ether acetate; ethers such as ethylene glycol dimethyl ether, diethylene glycol dimethyl ether, dibutyl ether, dioxane, tetrahydrofuran, alcohols such as n-butanol, isobutanol, methyl isobutyl carbinol, benzyl alcohol; ether alcohols such as
5 butoxyethanol, 1-methoxy-2-propanol; aliphatic hydrocarbons such as white spirit, limonene. These solvents are used alone or as a mixture of two or more thereof.

Monocarboxylic acid (iii)

The antifouling coating compositions of the present invention comprise a
10 monocarboxylic acid or a metal salt thereof.

The monocarboxylic acid present in the antifouling coating composition of the present invention is preferably selected from rosin, modified rosin, C₆-C₂₀ cyclic monocarboxylic acid, C₅-C₂₄ acyclic aliphatic monocarboxylic acid, C₇-C₂₀ aromatic monocarboxylic acid and metal salts thereof. Metal salts of
15 monocarboxylic acids include alkali metal carboxylate, alkaline earth metal carboxylate (e.g. calcium carboxylate, magnesium carboxylate) and transition metal carboxylate (e.g. zinc carboxylate, copper carboxylate). Preferably the metal carboxylate is a transition metal carboxylate, particularly preferably the metal carboxylate is a zinc carboxylate or copper carboxylate. The metal carboxylate may
20 be generated in situ in the antifouling coating composition.

It is preferred if the monocarboxylic acid is a cyclic monocarboxylic acid. Rosin is a mixture of monocarboxylic acids called resin acids. Resin acids are also referred to as rosin acids. Representative examples of resin acids include abietic acid, neoabietic acid, dehydroabietic acid, palustric acid, levopimaric acid, pimaric
25 acid, isopimaric acid, sandaracopimaric acid, communic acid and mercusic acid, secodehydroabietic acid. It will be appreciated that rosins are derived from natural sources and as such they typically comprise a mixture of acids.

Representative examples of rosins include gum rosin, wood rosin and tall oil rosin. Gum rosin, also referred to as colophony and colophonium, is particularly
30 preferred. Preferred rosins are those comprising more than 85 % resin acids and still more preferably more than 90 % resin acids.

Commercial grades of gum rosin typically have an acid value from 155 to 180 mg KOH/g as specified in ASTM D465. Preferred rosin for the compositions of the invention has an acid value from 155 to 180 mg KOH/g, more preferred 160 to 175 mg KOH/g, even more preferred 160 to 170 mg KOH/g. Commercial grades of rosin typically have a softening point (Ring & Ball) of 70 °C to 80 °C as specified in ASTM E28. Preferred rosin for the compositions of the invention has a softening point of 70 °C to 80 °C, more preferred 75 °C to 80 °C.

Representative examples of modified resin acids include dihydroabietic acids, dihydropimaric acids and tetrahydroabietic acids; and modified rosins such as partly hydrogenated rosin, fully hydrogenated rosin, disproportionated rosin.

Representative examples of C6-C20 cyclic monocarboxylic acids include naphthenic acid and trimethyl isobutylene cyclohexene carboxylic acids.

Representative examples of C5-C24 acyclic aliphatic monocarboxylic acids include VersaticTM acids, neodecanoic acid, 2,2,3,5-tetramethylhexanoic acid, 2,4-dimethyl-2-isopropylpentanoic acid, 2,5-dimethyl-2-ethylhexanoic acid, 2,2-dimethyloctanoic acid, 2,2-diethylhexanoic acid, pivalic acid, 2,2-dimethylpropionic acid, trimethylacetic acid, neopentanoic acid, 2-ethylhexanoic acid, isononanoic acid, 3,5,5-trimethylhexanoic acid, isopalmitic acid, isostearic acid, 16-methylheptadecanoic acid and 12,15-dimethylhexadecanoic acid. The acyclic aliphatic monocarboxylic acid is preferably selected from liquid, acyclic C10-C24 monocarboxylic acids or liquid, branched C10-C24 monocarboxylic acids. It will be appreciated that many of the acyclic C10-C24 monocarboxylic 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 degree of branching.

Preferably the monocarboxylic acids are selected from rosin, modified rosin, acyclic C10-C24 monocarboxylic acids, C6-C20 cyclic monocarboxylic acids or metal salts thereof.

Preferably the metal salts of the monocarboxylic acids are copper or zinc salts of rosin or copper or zinc salts of modified rosin.

More preferably, the monocarboxylic acid is rosin or a modified rosin or a metal salt thereof.

Further preferred the monocarboxylic acid or metal salt thereof is gum rosin, hydrogenated gum rosin, copper salt of gum rosin, zinc salt of gum rosin copper salt of hydrogenated gum rosin, zinc salt of hydrogenated gum rosin and mixtures thereof. Gum rosin is most preferred.

5 The final antifouling coating composition of the invention preferably comprises 5.0 to 30 wt% of the monocarboxylic acid and/or the metal salt thereof, such as 5.0 to 25 wt% or 10 to 25 wt% based on the total coating composition.

 The final coating composition of the invention preferably comprises 7.0 to 40 wt% of the monocarboxylic acid or metal salt thereof based on the total dry
10 weight of the coating composition, preferably 12 to 32 wt%.

 The antifouling coating composition of the invention preferably comprises rosin and/or modified rosin and metal salts thereof (iii) present in the antifouling coating compositions of the invention in 25 to 65 wt%, preferably 35 to 60 wt%, more preferably 40 to 60 wt% based on the total dry weight of binders in the coating
15 composition.

 Components (i) to (iii) make up the binder in the final coating composition of the invention. The wt% of binder, in particular the weight percent of components (i) to (iii) combined, in the final coating composition is 15 to 50 wt% of the total coating composition.

20 The wt% of binder, in particular the weight percent of components (i) to (iii) combined, in the final coating composition is 20 to 65 wt%, preferably 25 to 45 wt% of the total dry weight of the coating composition.

Other binder components

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

 hydrophilic copolymers, such as poly(*N*-vinyl pyrrolidone) copolymers and poly(ethylene glycol) copolymers; vinyl ether polymers and copolymers, such as
30 poly(methyl vinyl ether), poly(ethyl vinyl ether), poly(isobutyl vinyl ether), poly(vinyl chloride-*co*-isobutyl vinyl ether);

metal containing (meth)acrylate copolymers, such as zinc (meth)acrylate copolymers and copper (meth)acrylate copolymers;

saturated 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;

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;

plasticizers, such as polymeric plasticizers, non-reactive silicone oils, mineral oils, chlorinated paraffins, phthalates, phosphate esters, sulphonamides, adipates, epoxidized vegetable oils, methyl ester of rosin, methyl ester of branched fatty acids and sucrose acetate isobutyrate.

In one particularly preferred embodiment of the invention, the coating composition does not comprise a plasticizer which is a paraffin, especially not a paraffin comprising aromatic groups.

Preferably further binders are present in the compositions of the invention in an amount of 0 to 10 wt%, more preferably 0.5 to 7.0 wt% and still more preferably 1.0 to 5.0 wt%, based on the total weight of the coating composition.

Biocides (iv)

The antifouling coating composition additionally comprises biocides, i.e. compounds capable of reducing or preventing settlement and/or growth of marine fouling on a surface. The terms antifouling agent, antifoulant, biocide and 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. These compounds are present in a total amount of 10.0 wt% or less, relative to the total weight of the coating composition as a whole. Preferably, the coating composition comprises 8.0 wt% or less of biocides, even more preferably 5.0 wt% or less. Example ranges for the amount of biocides include 0.2 to 10.0 wt%, 0.5 to

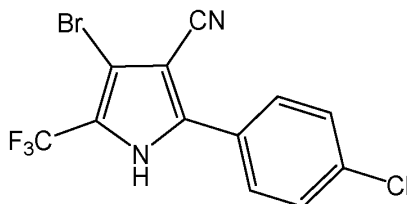
8.0 wt% and 1.0 to 5.0 wt%, relative to the total weight of the coating composition as a whole.

Alternatively viewed, these compounds are present in a total amount of 13.5 wt% or less, relative to the total weight of the dry coating composition. Preferably, the coating composition comprises 10.0 wt% or less of biocides, even more preferably 7.0 wt% or less. Example ranges for the amount of biocides include 0.2 to 13.5 wt%, 0.5 to 10.0 wt% and 1.0 to 7.0 wt%, relative to the total dry weight of the coating composition.

The biocides must comprise tralopyril (iv-a) and one or more copper compounds (iv-b) as defined below.

Tralopyril (iv-a)

As discussed above, 4-bromo-2-(4-chlorophenyl)-5-(trifluoromethyl)-1H-pyrrole-3-carbonitrile [tralopyril], having the structure below, must be present in the compositions of the invention:



Example of commercially available tralopyril include Econe[®] from Janssen PMP.

In all embodiments, it is preferred if tralopyril is present in an amount of 0.1 to 5.0 wt%, relative to the total weight of the composition, preferably 0.2 to 3.0 wt%, more preferably 0.3 to 2.0 wt%, even more preferably 0.4 to 1.5 wt%, such as 0.4 to 1.0 wt%.

In all embodiments, it is preferred if tralopyril is present in an amount of 0.2 to 6.5 wt%, relative to the total dry weight of the coating composition, preferably 0.3 to 4.0 wt%, more preferably 0.4 to 2.5 wt%, even more preferably 0.5 to 1.5 wt%.

Typically, tralopyril is present in an amount of 5.0 to 60.0 wt%, relative to the total weight of biocides (iv), preferably 7.0 to 60.0 wt%, more preferably 8.0 to 60.0 wt%, even more preferably 9.0 to 60.0 wt%, further preferred 10.0 to 60.0 wt%.

5 **Copper compound (iv-b)**

The copper compound may be any suitable copper antifouling compound having a copper content of at least 40 wt%, relative to the total weight of the copper compound. Preferably, the copper compound has a copper content of at least 45 wt%, at least 50 wt%, at least 55 wt%, or at least 60 wt%, such as at least 70 wt% or
10 at least 75 wt%, relative to the total weight of the copper compound. It will be understood that the copper content is calculated as the mass of copper atoms present in the chemical formula of the copper compound, excluding carrier materials.

In the table below is a list of commonly used copper compounds and the calculated copper content in the compounds:

15

Chemical name	Formula	FW	Copper (Cu) content, wt%
Copper(I) oxide	Cu ₂ O	143.09	89
Copper(II) oxide	CuO	79.55	80
Copper(II) sulfide	CuS	95.61	66
Copper(I) thiocyanate	CuSCN	121.63	52
Copper(II) carbonate	CuCO ₃	123.55	51
Copper(II) acetate	Cu(C ₂ H ₃ O ₂) ₂	181.63	35
Copper(II) acetylacetonate	Cu(C ₅ H ₈ O ₂) ₂	261.76	24
Copper(II) pyrithione	Cu(C ₅ H ₄ NOS) ₂	315.86	20
Copper(II) 2-ethylhexanoate	Cu(C ₈ H ₁₅ O ₂) ₂	349.95	18

A single copper compound may be used, or alternatively a mixture of two or more copper compounds may be employed.

The copper compound may be present with carrier materials such as
20 encapsulated copper compounds, copper glass, particles coated with copper compounds and porous particles with copper compounds. The wt% copper

requirement refers to the amount of copper in the chemical copper compound and hence ignores the weight of any carrier.

Particularly preferred copper compounds are metallic copper, such as copper powder and copper flakes, copper(I) oxide, copper (II) sulfide and copper(I) thiocyanate. Copper(I) oxide is also referred to as cuprous oxide.

Preferably the copper compound is an inorganic copper compound such as metallic copper, copper(I) oxide and copper (II) sulfide, more preferred metallic copper powder and copper(I) oxide.

In one particularly preferred embodiment the copper compound is copper(I) oxide.

The copper(I) oxide material preferably has a typical particle diameter distribution of 0.1-70 μm and an average particle size (d_{50}) of 1-25 μm . The copper(I) oxide material may contain a stabilizing agent to prevent surface oxidation and caking. Examples of commercially available copper(I) oxide include Nordox Cuprous Oxide Red Paint Grade, Nordox Cuprotech, 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 from Taixing Smelting Plant Co., Ltd.

In all embodiments, it is preferred if the copper compound(s) is present in an amount of 0.1 to 8.0 wt%, relative to the total weight of the composition, preferably 0.2 to 5.0 wt%, more preferably 0.3 to 3.0 wt%, even more preferably 0.3 to 2.0 wt%, further preferred 0.3 to 1.0 wt%.

If a blend of copper compounds is present then each may be present in an amount of 0.1 to 6.0 wt%, relative to the total weight of the composition, preferably 0.2 to 5.0 wt%, more preferably 0.3 to 3.0 wt%, even more preferably 0.3 to 2.0 wt%, further preferred 0.3 to 1.0 wt%.

It is to be understood that the total amount of biocides in the coating composition of the invention cannot exceed 10.0 wt%. Suitable amounts and number of copper compounds can be selected accordingly.

More preferably the coating composition of the invention comprises 8.0 wt% or less of biocides, relative to the total weight of the coating composition as a whole, preferably 5.0 wt% or less.

5 In all embodiments, it is preferred if the copper compound is present in an amount of 0.1 to 9.9 wt%, relative to the total dry weight of the coating composition, preferably 0.2 to 7.0 wt%, more preferably 0.3 to 4.0 wt%, even more preferably 0.3 to 2.5 wt%, further preferred 0.3 to 1.5 wt%. It is also preferred if the total amount of biocides in the total dry weight of the coating composition of the invention does not exceed 13.0 wt%.

10 Typically, the one or more copper compounds is present in an amount of 5.0 to 90.0 wt%, relative to the total weight of biocides (iv), preferably 6.0 to 87.0 wt%, more preferably 7.0 to 85.0 wt%, even more preferably 8.0 to 82.0 wt%, further preferred 9.0 to 80.0 wt%. In some embodiments, the one or more copper compounds is present in an amount of 5.0 to 85.0 wt%, relative to the total weight of
15 biocides (iv), further preferred 6.0 to 82.0 wt%.

In those embodiments wherein more than one copper compound of the invention is present, it will be understood that these wt% ranges apply to the total amount of all copper compounds present. Note that if a copper compound is present that does not have 40 wt% copper then it is not a copper compound of the invention.

20

Other biocides

In addition to these biocides, other antifouling compounds can be present. The antifouling agent may be inorganic, organometallic or organic. Suitable antifouling agents are commercially available.

25 Examples of organometallic marine antifouling agents include zinc pyrithione, copper pyrithione, copper di(ethyl 4,4,4-trifluoroacetoacetate), zinc bis(dimethyldithiocarbamate) [ziram] and zinc ethylenebis(dithiocarbamate) [zineb]. and copper and zinc compounds as described in WO2021113564A1. It should be noted that copper pyrithione and copper di(ethyl 4,4,4-trifluoroacetoacetate) have a
30 copper content of less than 40 wt% based on formula weight and are therefore not included under the definition of a copper compound in the present invention.

Examples of organic marine antifouling agents include 2-(*tert*-butylamino)-4-(cyclopropylamino)-6-(methylthio)-1,3,5-triazine [cybutryne], 4,5-dichloro-2-*n*-octyl-4-isothiazolin-3-one [DCOIT], 3-(3,4-dichlorophenyl)-1,1-dimethylurea [diuron] *N*-dichlorofluoromethylthio-*N'*,*N'*-dimethyl-*N*-phenylsulfamide [dichlofluamid], *N*-dichlorofluoromethylthio-*N'*,*N'*-dimethyl-*N*-*p*-tolylsulfamide [tolylfluamid], *N*-(2,4,6-trichlorophenyl)maleimide, triphenylborane pyridine [TPBP], 3-iodo-2-propynyl *N*-butylcarbamate [IPBC], 2,4,5,6-tetrachloroisophthalonitrile [chlorothalonil], *p*-((diiodomethyl)sulphonyl)toluene and 4-[1-(2,3dimethylphenyl)ethyl]-1H-imidazole [medetomidine].

Other examples of marine antifouling agents may be tetraalkylphosphonium halogenides, macrocyclic lactones including avermectins and derivatives thereof such as ivermectine; furanone and lactam compounds such as 4-(4-chlorophenyl)-5-hydroxy-5-methyl-2(5H)-furanone and 4-(4-chlorophenyl)-5-methylene-1H-pyrrol-2(5H)-one; 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.

Preferred biocides are zinc pyrithione, copper pyrithione, zinc ethylenebis(dithiocarbamate) [zineb], 4,5-dichloro-2-*n*-octyl-4-isothiazolin-3-one [DCOIT], *N*-dichlorofluoromethylthio-*N'*,*N'*-dimethyl-*N*-phenylsulfamide [dichlofluamid], 4-[1-(2,3-dimethylphenyl)ethyl]-1H-imidazole [medetomidine], copper di(ethyl 4,4,4-trifluoroacetoacetate) and phenylcapsaicin.

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

If biocides other than (iv-a) and (iv-b) are used, these will still be counted towards the total biocide content and hence the 10.0 wt% maximum.

Some biocides may be encapsulated, adsorbed on an inert carrier or bonded to other materials for controlled release. The weight of any such carrier is not to be considered when determining the 10.0 wt% maximum.

Pigments and extenders (v)

The coating compositions of the invention further comprises pigments and/or extenders. The total amount of extenders and/or pigments and biocides present in the compositions of the invention is preferably at least 35 wt%, relative to the total weight of the coating composition as a whole. Having a total amount of extender
5 and/or pigments and biocides of 35 wt% or more is important in order to achieve the appropriate self-polishing properties, coating film properties and sufficient antifouling performance.

Preferable total amounts of extenders and/or pigments and biocides are 35 to 65 wt%, more preferably 40 to 60 wt% and still more preferably 45 to 60 wt%,
10 based on the total weight of the composition.

Preferable total amounts of extenders and/or pigments and biocides are 40 to 80 wt%, more preferably 45 to 75 wt% and still more preferably 50 to 75 wt%, based on the total dry weight of the coating composition.

The skilled person will appreciate that the extender and pigment content will
15 vary depending on the particle size distribution, the particle shape, the surface morphology, the particle surface-resin affinity, the other components present and the end use of the coating composition.

Pigments are materials that provide colour to the coating composition. They are generally in the form of fine particles which are insoluble in the paint. The
20 pigments may be inorganic pigments, organic pigments or a mixture thereof. Inorganic pigments are preferred. Examples of inorganic pigments include titanium dioxide, red iron oxide, yellow iron oxide, black iron oxide, zinc sulfide, lithopone and graphite. Examples of organic pigments include carbon black, phthalocyanine blue, phthalocyanine green, naphthol red and diketopyrrolopyrrole red. Pigments may
25 be surface treated. A variety of inorganic or organic surface treatments are used, e.g. to improved storage stability and to enhance pigment performance, such as rheological properties and dispersibility in the coating composition. As an example, titanium dioxide may be surface treated with a silicon compound, a zirconium compound, an aluminum compound and/or a zinc compound.

30 Extenders are materials added to paint to adjust or improve their properties. These materials have typically low colour strength and hence are distinguished from pigments. Extenders are typically in granular or powder form and are insoluble in

the paint. The extenders may be inorganic or organic materials. Inorganic extenders are preferred. Inorganic extenders may be natural minerals or synthetic materials.

Examples of inorganic extenders include dolomite, platorite, calcite, quartz, baryte, magnesite, silica, nepheline syenite, wollastonite, talc, chlorite, mica, kaolin, pyrophyllite, feldspar, calcium carbonate, magnesium carbonate, barium sulphate, zinc oxide, zinc phosphate, calcium silicate, and silica. Apart from the before mentioned extenders, the coating composition may also comprise reinforcing agents such as flakes and fibres, e.g. as described in WO 00/77102.

Preferably the antifouling coating compositions of the invention comprises zinc oxide as an extender.

Other components

In addition to the components and optional components described above, the antifouling coating composition according to the present invention may optionally further comprise one or more components selected among other additives, solvents and thinners.

Examples of additives that can be added to an antifouling coating composition are rheology modifiers, wetting and dispersing agents and dehydrating agents.

Examples of rheology modifiers include thixotropic agents, thickening agents and anti-settling agents. Representative examples of rheology modifiers 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. Rheology modifiers that need activation may be added to the coating composition as is and activated during the paint production process or they can be added to the coating composition in a pre-activated form, e.g. solvent paste. Preferably rheology modifiers are each present in the composition of the invention in an amount of 0 to 5.0 wt%, more preferably 0.2 to 3.0 wt% and still more preferably 0.5 to 2.0 wt%, based on the total weight of the coating composition.

Dehydrating agents improve the storage stability of the antifouling coating compositions comprising (meth)acrylic silyl ester copolymer (i). The dehydrating

agent is preferably a compound which removes moisture and water from the coating composition. It is also referred to as water scavenger, drying agent or dessicant. The dehydrating agents may be hygroscopic materials that absorb water or bind water as crystal water or compounds that chemically react with water. Examples of

5 dehydrating agents include materials such as anhydrous calcium sulphate, calcium sulphate hemihydrate, anhydrous magnesium sulphate, anhydrous sodium sulphate, anhydrous zinc sulphate, molecular sieves and zeolites; orthoesters such as trimethyl orthoformate, triethyl orthoformate, tripropyl orthoformate, triisopropyl orthoformate, tributyl orthoformate, trimethyl orthoacetate, triethyl orthoacetate

10 tributyl orthoacetate and triethyl orthopropionate; ketals; acetals; enolethers; orthoborates such as trimethyl borate, triethyl borate, tripropyl borate, triisopropyl borate, tributyl borate and tri-*tert*-butyl borate; alkoxysilanes such as trimethoxymethylsilane, triethoxymethylsilane, tetraethoxysilane, phenyltrimethoxysilane, vinyltrimethoxysilane, vinyltriethoxysilane and ethyl

15 polysilicate; and isocyanates, such as p-toluenesulfonyl isocyanate.

The preferred dehydrating agents are alkoxysilanes, such as tetraethoxysilane, and inorganic desiccants, such as anhydrous calcium sulphate, calcium sulphate hemihydrate and zeolite powders. The use of an alkoxysilane is especially preferred.

20 Preferably the dehydrating agents are added to the compositions of the invention in an amount of 0 to 5.0 wt%, more preferably 0.5 to 2.5 wt% and still more preferably 1.0 to 2.0 wt%, based on the total weight of the composition.

Preferably the dehydrating agents are added to the compositions of the invention in an amount of 0 to 7.0 wt%, more preferably 0.5 to 4.0 wt% and still

25 more preferably 1.0 to 3.0 wt%, based on the total dry weight of the coating composition.

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

30 such as methyl ethyl ketone, methyl propyl ketone, methyl isobutyl ketone, methyl isoamyl ketone, methyl amyl ketone, diisobutyl ketone, cyclopentanone, cyclohexanone; esters such as butyl acetate, *tert*-butyl acetate, amyl acetate, isoamyl

acetate, propyl propionate, n-butyl propionate, isobutyl isobutyrate; ether esters such as ethylene glycol methyl ether acetate, ethyl 3-ethoxypropionate; ethers such as ethylene glycol dimethyl ether, diethylene glycol dimethyl ether, dibutyl ether, dioxane, tetrahydrofuran; alcohols such as *n*-butanol, isobutanol, methyl isobutyl carbinol, benzyl alcohol; ether alcohols such as butoxyethanol, 1-methoxy-2-propanol; terpenes such as limonene; aliphatic hydrocarbons such as white spirit; and optionally a mixture of two or more solvents and thinners.

Preferred solvents are aromatic hydrocarbon solvents, ketones and alcohols and mixtures thereof, especially xylene and mixtures of aromatic hydrocarbons.

The amount of solvent is preferably as low as possible. The solvent content may be up to 45 wt% of the composition, preferably up to 35 wt% of the composition, such as up to 30 wt% but may be as low as 20 wt% or less, e.g. 15 wt% or less. Again, the skilled person will appreciate that some raw materials comprise solvent and contribute to the total solvent content as specified above and that the solvent content will vary depending on the other components present and the end use of the coating composition.

The skilled person will appreciate that the solvent used will depend on the recommended application method of the final product.

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.

Coating composition

The composition as described herein may be prepared in a suitable concentration for use, e.g. in spray application. In this case, the composition is itself a paint. Alternatively, the composition may be a concentrate for preparation of paint. In this case, further solvent and optionally other components are added to the composition described herein to form a paint. Preferred solvents are as hereinbefore described in relation to the composition.

The coating composition may be supplied as one-pack or as a two-pack or as a three-pack. If a curing agent is present it will obviously be kept separate from the curable component until application on a substrate. Whilst the biocides can be kept

in a separate component from the binder, it is preferred if these are present together in the supplied formulation.

When supplied as a one-pack, the composition is preferably supplied in a ready-mixed or ready to use form. Optionally the one-pack product may be thinned
5 with solvents prior to application.

The antifouling coating composition of the invention should preferably have solids content above 60 wt%, e.g. above 65 wt%, preferably above 70 wt%.

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

10 More preferably the antifouling coating composition should have a volatile organic compound content (VOC content) below 500 g/L, preferably below 420 g/L, more preferably below 400 g/L, e.g. below 380 g/L, below 350 g/L and below 300 g/L. VOC content can be calculated, e.g. as described in ASTM D5201-01 or IED 2010/75/EU, or measured, e.g. as described in US EPA Method 24 or ISO 11890-2.

15 The viscosity of the coating composition may be in the range of less than 2000 cP, such as less than 1000 cP, e.g. less than 800 cP and less than 500 cP when measured using a Cone and Plate viscometer in accordance with ISO 2884-1:2006. Viscosities of 200 cP or more can be used.

In one embodiment, the antifouling coating composition comprises
20 component (i) in an amount of 2.0 to 40 wt%, relative to the total weight of the coating compositions as a whole, preferably 5.0 to 30 wt%;
component (ii) in an amount of 0.5 to 10 wt%, relative to the total weight of the coating compositions as a whole, preferably 1.0 to 5 wt%;
and component (iii) in an amount of 5.0 to 25 wt% based on the total weight
25 of the coating composition as a whole.

In one embodiment, the antifouling coating composition comprises
component (i) in an amount of 2.0 to 40 wt%, relative to the total weight of the coating compositions as a whole, preferably 5.0 to 30 wt%;
component (ii) in an amount of 0.5 to 10 wt%, relative to the total weight of
30 the coating compositions as a whole, preferably 1.0 to 5.0 wt%;
component (iii) in an amount of 5.0 to 25 wt% based on the total weight of the coating composition as a whole;

tralopyril in an amount of 0.1 to 5.0 wt%, relative to the total weight of the composition, preferably 0.2 to 3.0 wt%, more preferably 0.3 to 2.0 wt%, even more preferably 0.4 to 1.0 wt%; and

5 one or more copper compounds is present in an amount of 0.1 to 8.0 wt%, relative to the total weight of the composition, preferably 0.2 to 5.0 wt%, more preferably 0.3 to 3.0 wt%, even more preferably 0.3 to 2.0 wt%, further preferred 0.3 to 1.0 wt%.

In one embodiment, the antifouling coating composition comprises component (ii-a) in an amount of 0.5 to 10 wt%, relative to the total weight
10 of the coating compositions as a whole, preferably 1.0 to 6.0 wt%;

component (ii-b) in an amount of 0.5 to 10 wt%, relative to the total weight of the coating compositions as a whole, preferably 1.0 to 6.0 wt%;

component (iii) in an amount of 5.0 to 25 wt% based on the total weight of the coating composition as a whole;

15 tralopyril in an amount of 0.1 to 5.0 wt%, relative to the total weight of the composition, preferably 0.2 to 3.0 wt%, more preferably 0.3 to 2.0 wt%, even more preferably 0.4 to 1.0 wt%; and

one or more copper compounds is present in an amount of 0.1 to 8.0 wt%, relative to the total weight of the composition. preferably 0.2 to 5.0 wt%, more
20 preferably 0.3 to 3.0 wt%, even more preferably 0.3 to 2.0 wt%, further preferred 0.3 to 1.0 wt%.

In all embodiments, the coating composition as a whole comprises 10.0 wt% or less of biocides.

25 **Method for producing antifouling coating composition**

The antifouling coating composition can be prepared using any process known in the art. The order of adding and mixing the ingredients is preferably done as recommended by the suppliers of the ingredients and the mixing equipment.

Biocides can be pre-mixed in a solution or a paste containing a binder
30 component and/or a solvent and/or pigment, such as zinc oxide, for safer and easier handling during the paint production process, for improved storage stability of the

coating composition and/or improved antifouling performance of the applied coating.

Application

5 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
10 coating composition can be accomplished by any convenient means, e.g. via painting (e.g. with brush or roller) or spraying (e.g. airless spray) 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.

15 When applying the antifouling coating to an object (e.g. a ship hull) the surface of the object is 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
20 mixtures thereof). Starting with an uncoated surface (e.g. steel, aluminium, composite) the full coating system will typically comprise one or two layers of a primer or an anticorrosive coating (e.g. curable epoxy coating or curable modified epoxy coating), one layer of tie-coat (e.g. curable modified epoxy coating or physical drying vinyl coating) and one or two layers of antifouling paint. In
25 exceptional cases further layers of antifouling paint may be applied. 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. When two or more coats of antifouling coating composition is applied, the different coats can be antifouling coatings of different compositions
30 creating a coating system with different antifouling coating layers.

 The antifouling coating layers may differ in type and/or amount of biocide and binder, binder composition and/or polishing rate.

In certain cases, for example for outfitting applications, it is preferred if antifouling coating compositions having different polishing rates are used in different coating layers. It is then preferred if the outermost layer has a higher polishing rate than the subsequent layers.

5 The coating formed from the coating composition of the invention can also be cleaned by for example robots, remotely operated vehicles (ROVs) or manually operated equipment. The cleaning can be reactive or proactive. The underwater cleaning can for example be made using mechanical means (such as brushes, squeegee), high pressure water, UV light, laser or ultrasound. Robots used for
10 underwater cleaning is for example described in WO2019/170888, WO2020/207791 and WO2020/207792. Cleaning settings that can be used when using brushes are for example described in WO2021180588.

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

15

Examples

Materials and methods

Determination of polymer solution viscosity

20 The viscosity of the polymers was determined in accordance with ASTM D2196 Test Method A using Brookfield DV-I Prime digital viscometer with a LV-2 (62) spindle at a rotational speed of 12 rpm. The polymer solutions were conditioned to a temperature of $23.0\text{ }^{\circ}\text{C} \pm 0.5\text{ }^{\circ}\text{C}$ before the measurements.

Determination of non-volatile matter content of the polymer solutions

25 The non-volatile matter content in the polymer solutions was determined as described in ISO 3251:2019. A test sample of $0.5\text{ g} \pm 0.1\text{ g}$ was taken out and dried in a ventilated oven at $105\text{ }^{\circ}\text{C}$ for 3 hours. The weight of the residual material was considered to be the non-volatile matter (NVM). The non-volatile matter content is
30 expressed as weight fraction in percent. The value given is the average of three parallel measurements.

Determination of polymer molecular weights distribution

5 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. The analysis conditions were as set out below.

Detector	RI
Wavelength	640 nm
Flow cell volume	12 µl
Column Set	Agilent PLgel 5 µm Mixed-D, 2 columns in series
Mobile Phase	• THF (standard) • THF with 1% acetic acid for polymers having carboxylic acid functionality
Flow rate	1 ml/min
Injection volume	100 µl
Autosampler Temperature	25 °C
Column Oven Temperature	35 °C
Detector Oven Temperature	35 °C
Data Processing	Omnisec 5.1
Calibration standards	Agilent Polystyrene Medium EasiVials (4 ml) Red, Yellow and Green

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

Determination of the glass transition temperature

The glass transition temperature (T_g) was obtained by Differential Scanning Calorimetry (DSC) measurements. The DSC measurements were performed on a TA Instruments DSC Q200 by running a heat-cool-heat procedure, within a temperature range from -80 °C to 150 °C, with a heating rate of 10 °C/min and cooling rate of 10 °C/min and using an empty pan as reference. The data were processed using Universal Analysis software from TA Instruments. The inflection point of the glass transition range, as defined in ISO 11357-2:2020, of the second heating is reported as the T_g of the polymers.

Samples were prepared by making drawdown of the polymer solutions on individual glass panels using an applicator with 100 µm gap size. The glass panels were dried over night at room temperature and subsequently 24 hours at 50 °C in a ventilated heating cabinet. The dry polymer material was scraped off the glass panels and approx. 10 mg of the dry polymer material was transferred to an aluminium pan. The pan was sealed with a non-hermetic lid for the measurement.

Procedure for preparation of copolymer solution S1

60.0 parts xylene was charged to a temperature-controlled reaction vessel equipped with a stirrer, a condenser, a nitrogen inlet, and a feed inlet. The reaction vessel was heated and maintained at the reaction temperature of 95 °C. A pre-mix of 55.0 parts triisopropylsilyl methacrylate, 5.0 parts 2-(2-ethoxyethoxy)ethyl acrylate, 10.0 parts n-butyl acrylate, 30.0 parts methyl methacrylate and 1.10 parts 2,2'-azobis(2-methylbutyronitril) was prepared. The pre-mix was charged to the reaction vessel at a constant rate over 2 hours under a nitrogen atmosphere using a metering pump. After further 30 minutes reaction, a boost initiator solution of 0.25 parts 2,2'-azobis(2-methylbutyronitril) and 7.6 parts xylene was fed to the reaction vessel at a constant rate over 20 minutes. The reaction vessel was maintained at the reaction temperature for a further 1.5 hours. The reactor was then heated to 105 °C and kept at that temperature for 1 hour. Finally, the reactor was cooled to room temperature. The parts given above are all parts by weight.

The copolymer solution S1 had the following properties:

NVM: 60.1 wt%; Viscosity 1089 cP; Mw 23 936; PDI 2.43; T_g 47 °C

Copolymer solution S2 to S11 were made in a similar manner as described above. The monomer compositions and procedure details are given in Table 1.

5 Procedure for preparation of copolymer solution A1

40.0 parts xylene and 10.0 parts 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 the reaction temperature of 100°C. A pre-mix of 75.0 parts n-butyl acrylate, 22.0 parts methyl methacrylate, 3.0 parts methacrylic acid and 1.60 parts *tert*-amyl peroxy-2-ethylhexanoate was prepared. The pre-mix was charged to the reaction vessel at a constant rate over 3 hours under a nitrogen atmosphere using a metering pump. After further 30 minutes reaction a boost initiator solution of 0.40 parts *tert*-amyl peroxy-2-ethylhexanoate and 5.0 parts xylene was fed to the reaction vessel at a constant rate over 20 minutes. The reaction vessel was maintained at the reaction temperature for a further 1.5 hour and then cooled to room temperature. The parts given above are all parts by weight.

The copolymer solution A1 had the following properties:

NVM: 65.4 wt%; Viscosity 1095 cP; Mw 26,530; PDI 2.93; Tg -20 °C

20

Copolymer solution A2 to A4 were made in a similar manner as described above. In the preparation of A3 and A4 *tert*-butyl peroxy-2-ethylhexanoate was used as initiator. The monomer compositions and procedure details are given in Table 2.

25 Procedure for preparation of zinc rosinate solution Z1

88 parts rosin solution (60 wt% gum rosin in xylene, 7 parts zinc oxide and 5 parts xylene were charged to a temperature-controlled reaction vessel equipped with a stirrer and a reflux condenser. The mixture was slowly heated to 70 °C and kept at that temperature for 2 hours. The temperature was turned off and the solution was stirred during the cooling to room temperature.

30

The zinc rosinate solution Z1 had NVM of 62.1 wt%.

Table 2: Summary of (meth)acrylic polymer (ii-a) and (ii-b) examples.

		A1	A2	A3	A4
Monomers (parts by weight)	n-Butyl acrylate	75	85	93	20
	Methyl methacrylate	22	12	4	60
	2-(2-Ethoxyethoxy)ethyl acrylate				20
	Methacrylic acid	3	3	3	
	Sum	100	100	100	100
Procedure details	Polymerization temperature (°C)	100	100	100	105
	Initiator in monomer feed (wt% of monomers)	1.60	1.50	1.20	1.70
Properties	Non-volatile matter (wt%)	65.4	65.3	65.4	51.9
	Viscosity (cP)	1095	579	477	597
	M _w (x 10 ³)	26.5	23.8	27.4	26.9
	M _n (x 10 ³)	9.1	8.2	8.3	8.8
	T _g (°C)	-20	-32	-38	23

Table 3: Ingredients used in the examples.

Ingredients	Trade name	Manufacturer / supplier	Purpose	Remarks
Copper(I) oxide #1	Cuprous oxide PG red	Nordox	Cu compound	
Copper(I) oxide #2	Cuprous oxide PG orange	Nordox	Cu compound	
Copper(I) oxide #3	Cuprotech	Nordox	Cu compound	
Copper(I) oxide #4	Lolo tint LM	American Chemet	Cu compound	
Copper(I) oxide #5	Red Copp 97N	American Chemet	Cu compound	
Copper powder #1	Chem Copp 1700 FPM	American Chemet	Cu compound	
Copper flakes #1	Standart ActiMar Cu 1700	Eckart	Cu compound	
Copper(II) sulfide	Q+	Kolon Life Science	Cu compound	
Copper(II) hydroxide		Sigma-Aldrich	Cu compound	
Copper(I) thiocyanate	Cuprous thiocyanate	Bardylke Chemicals	Cu compound	
Copper glass	Corning Guardiant	Corning	Cu compound	Contains 33 wt% copper oxide
Copper(II) acetate		Sigma-Aldrich	Cu compound	Comparative. Water solubility approx. 72 g/L at 25 °C
Copper(II) acetylacetonate		Sigma-Aldrich	Cu compound	Comparative
Copper(II) 2-ethylhexanoate		Sigma-Aldrich	Cu compound	Comparative. Soluble in most organic solvents.
Tralopyril	Econea	Janssen	Biocide	

Ingredients	Trade name	Manufacturer / supplier	Purpose	Remarks
Copper pyrrithione	CleanBio-Cu	Kolon	Biocide	
Copper pyrrithione and copper chelate complex ¹ mixture		Arxada	Biocide	
Zinc pyrrithione	Zinc Omadine	Arxada	Biocide	
Zineb	Perozin Marine	Agria	Biocide	
Medetomidine	Selektope	I-Tech	Biocide	
DCOIT #1	Sea-Nine 211	Lanxess	Biocide	Supplied as 30 wt% in xylene
Gum rosin	Portuguese gum rosin WW	A. V. Pound	Monocarboxylic acid compound	Used as a 60 wt% solution in xylene
Isostearic acid (liquid)	Radiacid 0907	Oleon	Monocarboxylic acid compound	Contains 87% branched C16-C18 fatty acids; Acid value 185-195 mg KOH/g
Polyamide wax	Disparlon A603-20X	Kusomoto	Rheology modifier	Supplied as 20 wt% in xylene
Organoclay	Bentone 52	Elementis Specialities	Rheology modifier	
Iron oxide black	Bayferrox 318 M	Lanxess	Pigment	
Iron oxide red	Bayferrox 130 M	Lanxess	Pigment	
Titanium dioxide	Tiona 121	Tronox	Pigment	
Dolomite	Microdol 1	Omya	Extender	
Talc	Finntalc M12	Elementis	Extender	

Ingredients	Trade name	Manufacturer / supplier	Purpose	Remarks
Zinc phosphate	Delaphos 2M	Delaphos	Extender	
Zinc oxide	Zinc oxide red seal	Everzinc	Extender	
Tetraethoxysilane			Water scavenger	
Xylene			Solvent	Mixture of isomers; contains less than 15 wt% ethylbenzene
Aromatic hydrocarbons			Solvent	Contains more than 96% aromatic hydrocarbons. Boiling point range 150-185 °C.
Baryte	Portaryte B 4	Sibelco	Extender	
Hydrophobic fumed silica	Aerosil R 972	Evonik	Rheology modifier/extender	
Phenylcapsaicin	Phenylcapsaicin	aXichem	Biocide	

¹ As described in WO2020115323A1

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

The volatile organic compound (VOC) content of the antifouling coating composition was calculated in accordance with ASTM D5201-01.

5

Determination of paint viscosity using Cone and Plate viscometer

The viscosity of the antifouling paint composition was determined in accordance with ISO 2884-1:2006 using a digital Cone and Plate viscometer set at a temperature of 23 °C, working at a shear rate of 10 000 s⁻¹ and providing viscosity measurement range of 0-10 P. The result is given as the average of three measurements.

10

Testing of antifouling performance

Polyvinyl chloride (PVC) panels (20 cm x 30 cm) were used for the test. The panels were coated with a first coat of a commercial tie-coat (Safeguard Plus, manufactured by Chokwang Jotun Ltd., Korea) using airless spray and a second coat of a commercial antifouling paint (SeaQuantum Ultra III, manufactured by Jotun Paints (Europe) Ltd., England). The curing/drying time and film thicknesses of the first coat and the second coat were within the recommended intervals in the technical data sheets for the products.

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The antifouling coating compositions of the examples were applied directly to the pre-coated PVC panels as a last coat using a film applicator with a 400 µm gap size. The test areas of the applied coating films were approx. 6.5 cm x 25 cm. The edges of the panels were sealed with a commercial antifouling product. The antifouling coating compositions of the examples were applied within 3 to 10 days after paint preparation.

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The panels were exposed on raft in Singapore where the panels were submerged 0.5 to 1.5 m below the sea surface. The panels were evaluated by visual inspection and rated according to the scale below. Macroalgae, such as seaweed, and animal fouling, such as barnacles, tubeworms, mussels, sponges and hydroids, were included in the rating. Microfouling organisms, such as biofilm or slime, which can

30

easily be removed by hand, is not included in the rating. Edge effects were excluded from the evaluation.

Table 4: Rating scale for degree of fouling

Rating	Area covered by fouling
0	Only slime
1	1-10%
2	11-25 %
3	26-50 %
4	51-100%

5

General procedure for preparation of antifouling coating compositions

10 The components were mixed in the proportions given in Tables 5 to 15. The order of mixing the ingredients and preparation of pre-mix of selected ingredients were done in accordance with the raw material suppliers' guidelines. The ingredients were dispersed and grinded in the presence of glass beads (approx. 3-4 mm in diameter) in a 250 ml paint can using a vibrational shaker.

	1	2	3	4	5	6	7	8	9
Additives									
	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Solvents									
	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0
	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
	101.0	101.0	101.0	101.0	101.0	101.0	101.0	103.0	101.0
Calculated values for coating composition									
	0.99	0.99	0.99	0.99	0.99	0.99	0.99	0.97	0.99
	0.99	0.99	0.99	0.99	0.99	0.99	0.99	2.91*	0.99
	2.97	2.97	2.97	2.97	2.97	2.97	2.97	4.85*	2.97
	52.5	52.05	52.5	52.5	52.5	52.5	52.5	52.9*	52.5
	360	360	360	360	360	360	360	355	360
Test results									
	617	645	594	736	440	619	658	625	732
	0	0	0	0	0	0	0	0	0
	0	0	0	1	0	0	0	0	0
	0	1	1	1	0	0	0	1	0
	1	1	1	0	0	0	1	1	0

* value includes carrier material

Table 6: Examples

[illegible]

		10	11	12	13	14	14	16	17	18
Calculated values for coating composition	Tralopyril (iv-a) content (wt%)	1.00	1.00	0.50	0.50	0.93	1.96	0.48	1.47	0.95
	Cu compound (iv-b) content (wt%)	0.50	0.20	1.00	0.50	7.41	0.98	4.78	1.47	4.76
	Total biocides (iv) content (wt%)	2.49	2.20	2.49	2.00	9.26	3.92	6.22	3.92	6.67
	Total pigment, extender and biocide content (wt%)	51.7	51.6	51.7	51.5	53.2	52.5	53.6	52.5	53.8
	VOC (g/L)	361	361	362	362	373	356	357	357	355
Test results	Cone & plate viscosity (cP)	602	599	570	581	706	438	668	450	705
	Raft Singapore	0	0	0	0	0	0	0	0	0
		0	0	0	0	0	0	1	0	0
		1	1	0	1	0	0	1	0	0
		1	1	0	1	0	0	0	0	0

Table 7: Examples

	19	20	21	22	23	24	25	26	27	28
Binders (i)										
	S1	19.5	19.5	19.5	19.5	19.5	19.5	19.5	19.5	19.5
Binders (ii-a)										
	A1	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0
Binder (iii)										
	Rosin solution (60% in xylene)	17.5	17.5	17.5	17.5	17.5	17.5	17.5	17.5	17.5
Biocide (iv-a)										
	Tralopyril	1.0	1.0	1.5	2.5	1.0	2.0	3.0	1.0	1.0
Cu compounds (iv-b)	Copper powder #1	2.0	3.0	1.0	1.0					
	Copper(II) sulfide									
	Copper(I) thiocyanate									
Other biocide										
	Copper pyrithione	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Pigments and extenders (v)	Iron oxide red	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
	Talc	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0
	Zinc phosphate	28.5	28.5	28.5	28.5	26.5	28.5	28.5	28.5	26.5
	Zinc oxide	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0
Additives	Tetraethoxysilane	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
	Polyamide wax (20% in xylene)	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Solvents	Xylene	4.0	4.0	4.0	4.0	5.0	4.0	4.0	4.0	4.0
	Aromatic hydrocarbons	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
	Sum total	102.0	103.0	101.5	102.5	102.0	107.0	103.0	105.0	106.0

[illegible]

Table 8: Comparative examples

		C1	C2	C3	C4	C5	C6
Binder (i)	S1	19.5	19.5	19.5	19.5	19.5	19.5
Binder (ii-a)	A1	3.0	3.0	3.0	3.0	3.0	3.0
Binder (iii)	Rosin solution (60% in xylene)	17.5	17.5	17.5	17.5	17.5	17.5
Biocide (iv-a)	Tralopyril	1.0					
Cu compounds (iv-b)	Copper(I) oxide #1		1.0	5.0			
	Copper powder #1				1.0		
	Copper flakes #1					1.0	
	Copper(I) thiocyanate						1.0
Other biocide	Copper pyrithione	1.0	1.0	1.0	1.0	1.0	1.0
Pigments and extenders (v)	Iron oxide red	5.0	5.0	5.0	5.0	5.0	5.0
	Talc	10.0	10.0	10.0	10.0	10.0	10.0
	Zinc phosphate	28.5	28.5	28.5	28.5	28.5	28.5
Additives	Zinc oxide	6.0	6.0	6.0	6.0	6.0	6.0
	Tetraethoxysilane	1.0	1.0	1.0	1.0	1.0	1.0
	Polyamide wax (20% in xylene)	1.5	1.5	1.5	1.5	1.5	1.5
Solvent	Xylene	4.0	4.0	4.0	4.0	4.0	4.0
	Aromatic hydrocarbons	2.0	2.0	2.0	2.0	2.0	2.0

		C1	C2	C3	C4	C5	C6
	Sum total	100.0	100.0	104.0	100.0	100.0	100.0
Calculated values for coating composition	Talopyril (iv-a) content (wt%)	1.00	-	-	-	-	-
	Cu compound (iv-b) content (wt%)	-	1.00	4.81	1.00	1.00	1.00
	Total biocides (iv) content (wt%)	2.00	2.00	5.77	2.00	2.00	2.00
	Total pigment, extender and biocide content (wt%)	51.5	51.5	53.4	51.5	51.5	51.5
	VOC (g/L)	361	363	359	364	364	362
Test results	Cone & plate viscosity (cP)	617	613	610	590	598	606
	Raft Singapore	0	0	1	0	0	1
		1	1	1	0	0	2
		3	2	2	3	2	4
		4	2	2	2	2	4

Table 9: Comparative examples

		C7	C8	C9	C10	C11	C12
Binder (i)	S1	19.5	19.5	19.5	19.5	19.5	19.5
Binder (ii-a)	A1	3.0	3.0	3.0	3.0	3.0	3.0
Binder (iii)	Rosin solution (60% in xylene)	17.5	17.5	17.5	17.5	17.5	17.5
Biocide (iv-a)	Tralopyril	1.0	1.0	1.0	1.0	1.0	1.0
Cu compounds (iv-b)	Copper(II) acetate	1.0	2.5				
	Copper(II) acetylacetonate			1.0	4.0		
	Copper(II) ethylhexanoate					1.0	5.0
Other biocide	Copper pyrithione	1.0	1.0	1.0	1.0	1.0	1.0
Pigments and extenders (v)	Iron oxide red	5.0	5.0	5.0	5.0	5.0	5.0
	Talc	10.0	10.0	10.0	10.0	10.0	10.0
	Zinc phosphate	28.5	28.5	28.5	28.5	28.5	28.5
	Zinc oxide	6.0	6.0	6.0	6.0	6.0	6.0
Additives	Tetraethoxysilane	1.0	1.0	1.0	1.0	1.0	1.0
	Polyamide wax (20% in xylene)	1.5	1.5	1.5	1.5	1.5	1.5
Solvent	Xylene	6.0	6.0	4.0	4.0	5.0	5.0
	Aromatic hydrocarbons	2.0	2.0	2.0	2.0	2.0	2.0
	Sum total	103.0	104.5	101.0	104.0	102.0	106.0

Calculated values for coating composition	Tralopyril (iv-a) content (wt%)		0.97	0.96	0.99							
	Cu compound (iv-b) content (wt%)		0.97	2.39	0.99							
	Total biocides (iv) content (wt%)		2.91	4.31	2.97							
	Total pigment, extender and biocide content (wt%)		51.0	51.7	52.0							
	VOC (g/L)		374	370	352							
Test results	Cone & plate viscosity (cP)		652	758	481							
	Raft Singapore	1 month	0	0	0							
		2 months	2	1	3							
		4 months	4	4	4							
		6 months	4	4	4							

Comments to tables 5 to 9:

Examples 1-28 show that it is possible to make antifouling coating compositions comprising less than 10.0 wt% of biocides that have excellent antifouling properties. This is achieved by using the combination of a copper compound comprising more than 40 wt% copper and tralopyril together with a (meth)acrylic silyl ester copolymer (i) and a (meth)acrylic polymer (ii-a), a monocarboxylic acid (iii) and by having a total amount of pigment, extender and biocide of more than 35 wt%.

In examples 1-9 in Table 5 different copper compounds and tralopyril are tested. All the formulations in examples 1-9 gave good antifouling performance.

In examples 10-28 in Table 6 and Table 7 different types of copper compounds and different amounts of copper compounds and tralopyril and combinations of these are tested. All the formulations in examples 10-28 gave good antifouling performance.

Comparative example C1 in Table 8 is directly comparable to example 1 in Table 5. In comparative example C1 the copper compound is missing. The antifouling performance after 6 months is then poor. Comparative example C1 show that it is not enough to use tralopyril alone to achieve good long term antifouling performance.

Comparative example C2 can also be directly compared with example 1. In comparative example 2, tralopyril is missing. The antifouling performance after 6 months is then poorer showing that the combination of the copper compound and tralopyril is essential for achieving good long-term antifouling performance in coating compositions comprising less than 10.0 wt% in total amount of biocides.

Comparative example C3 show that increasing the amount of copper(I) oxide from 1 wt% in comparative example C2 to 5 wt% in comparative example C3 does not improve the antifouling performance when tralopyril is missing.

Comparative examples C4, C5 and C6 show that the antifouling performance is reduced if tralopyril is not present also when other copper compounds are used.

Comparative examples in Table 9 show copper compounds outside the invention. Comparative examples C7 to C12 contain copper compounds having a

copper content below 40 wt%. All formulations in comparative examples C7 to C12 show poor long term antifouling performance.

Table 10: Examples

[illegible]

		29	30	31	32	33	34	35	36	37	38
Solvents	Xylene	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0
	Aromatic hydrocarbons	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
	Sum total	101.0	101.0	101.0	101.0	101.0	101.0	101.0	101.0	101.0	101.0
Calculated values for coating composition	Tralopyril content (iv-a) (wt%)	0.99	0.99	0.99	0.99	0.99	0.99	0.99	0.99	0.99	0.99
	Cu compound (iv-b) content (wt%)	0.99	0.99	0.99	0.99	0.99	0.99	0.99	0.99	0.99	0.99
	Total biocides content (wt%)	2.97	2.97	2.97	2.97	2.97	2.97	2.97	2.97	2.97	2.97
	Pigment, extender and biocide content (wt%)	52.0	52.0	52.0	52.0	52.0	52.0	52.0	52.0	52.0	52.0
	VOC (g/L)	358	359	359	361	360	359	359	359	358	358
Test results	Cone & plate viscosity (cP)	678	646	582	774	589	634	705	526	631	696
	Raft Singapore	0	0	0	0	0	0	0	0	0	0
		1	0	0	0	0	0	0	0	0	1
		1	0	1	1	1	1	0	0	0	0
		1	0	1	1	0	1	1	0	0	0

		39	40	41	42	43	44	45	46	47	48
	Zinc oxide	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0
Additives	Tetraethoxysilane	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
	Polyamide wax (20% in xylene)	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Solvents	Xylene	4.0	4.0	4.0	4.0	4.0	4.5	5.0	4.0	5.0	5.0
	Aromatic hydrocarbons	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
	Sum total	101.0	101.0	101.0	101.0	101.0	101.5	102.0	101.0	102.0	104.0
Calculated values for coating composition	Tralopyril content (iv-a) (wt%)	0.99	0.99	0.99	0.99	0.99	0.98	0.97	0.99	0.97	0.96
	Cu compound (iv-b) content (wt%)	0.99	0.99	0.99	0.99	0.99	0.98	0.97	0.99	0.97	2.88*
	Total biocides content (wt%)	2.97	2.97	2.97	2.97	2.97	2.94	2.91	2.97	2.91	4.81*
	Pigment, extender and biocide content (wt%)	52.0	52.0	52.0	52.0	52.0	51.5	51.0	52.0	51.0	52.4*
	VOC (g/L)	359	359	361	357	359	368	378	359	377	363
Test results	Cone & plate viscosity (cP)	659	724	548	605	628	741	717	405	646	700
	Raft Singapore	0	0	0	0	0	0	0	0	0	0
		0	1	0	0	1	0	0	0	0	0
		0	0	0	0	1	0	0	1	0	0
		0	1	0	0	1	0	0	1	0	0

* value includes carrier material

Table 12: Comparative examples

		C13	C14	C15	C16
Binder (i)	S1	30.0	34.0	37.0	40.0
Binder (ii-a)	A1	5.0	6.0	3.0	
Binder (iii)	Rosin solution (60 % in xylene)	27.0			
Biocide (iv-a)	Tralopyril	1.0	1.0	1.0	1.0
Cu compounds (iv-b)	Copper(I) oxide #1	1.0	1.0	1.0	1.0
Other biocides	Copper pyrithione	1.0	1.0	1.0	1.0
Pigments and extenders (v)	Iron oxide red	5.0	5.0	5.0	5.0
	Talc	5.0	10.0	10.0	10.0
	Zinc phosphate	14.0	28.5	28.5	28.5
Additives	Zinc oxide	3.0	6.0	6.0	6.0
	Tetraethoxysilane	1.0	1.0	1.0	1.0
	Polyamide wax (20% in xylene)	1.5	1.5	1.5	1.5
Solvents	Xylene	4.0	9.0	9.0	4.0
	Aromatic hydrocarbons	2.0	2.0	2.0	2.0

		C13	C14	C15	C16
	Sum total	99.5	106.0	106.0	101.0
Calculated values for coating composition	Tralopyril (iv-a) content (wt%)	1.01	0.94	0.94	0.99
	Cu compound (iv-b) content (wt%)	1.01	0.94	0.94	0.99
	Total biocides content (wt%)	3.02	2.83	2.83	2.97
	Pigment, extender and biocide content (wt%)	30.2	49.5	49.5	52.0
	Paint VOC (g/L)	391	399	401	362
Test results	Cone & plate viscosity (cP)	457	565	498	866
	Raft Singapore	4	0	1	1
		4	1	3	3
		4	4	4	4
		4	4	4	4

Comments to tables 10 to 12:

5 In examples 29-38 in Table 10 different (meth)acrylic silyl ester copolymers (i) and (meth)acrylic polymers (ii-a) are tested. Different combinations of these polymers are also tested. All the formulations in examples 29-47 gave good antifouling performance.

Examples 39-48 in Table 11 show examples of different (meth)acrylic silyl ester copolymers (i) and copper compounds. All the examples show good antifouling performance.

10 Comparative example C13 in Table 12 show that if the total amount of pigment, extender and biocides are less than 35 wt% based on the total weight of the coating composition the antifouling performance is poor already after 1 month.

15 Comparative examples C14, C15 and C16 show that if there is no monocarboxylic acid present in the coating compositions the antifouling performance is poor.

Table 13: Examples

[illegible]

		49	50	51	52	53	54	55	56	57	58
		0	0	0	0	0	0	0	0	0	0
		0	0	0	1	1	1	0	1	1	1
		0	0	0	1	1	1	0	1	1	1

Table 14: Examples

		59	60	61	62	63	64	65	66
Binders (i)	S1		19.5	19.5	19.5			19.5	
	S2					19.5	19.5		19.5
	S3	17.0							
Binder (ii-a)	A1	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0
Binder (iii)	Rosin solution (60% in xylene)	18.5	17.5	17.5	17.5	17.5	17.5	17.5	17.5
Biocide (iv-a)	Tralopyril	1.0	1.0	2.0	1.0	1.0	1.0	1.0	1.0
Cu compounds (iv-b)	Copper(I) oxide #1	1.0	1.0	4.0					
	Copper(I) oxide #4				1.0				
	Copper powder #1	1.0				1.0	1.0		
	Copper(II) sulfide							1.0	5.0
	Copper(I) thiocyanate	1.0		1.0					

		59	60	61	62	63	64	65	66
Other biocides	Copper pyrithione	1.0	1.0		1.0	1.0	1.0	1.0	1.0
	Zinc pyrithione			2.0					
	DCOIT #1			1.0					
	Medetomidine		0.2						
	Zineb			1.0					
Pigments and extenders (v)	Iron oxide red	5.0	5.0	5.0					
	Iron oxide black				1.0	1.0	5.0	5.0	5.0
	Titanium dioxide				4.0	4.0			
	Talc	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0
	Zinc phosphate	28.5	28.5	28.5	28.5	28.5	28.5	28.5	28.5
Additives	Zinc oxide	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0
	Tetraethoxysilane	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
	Polyamide wax (20% in xylene)	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Solvents	Xylene	3.5	4.0	4.0	4.0	4.0	4.0	4.0	5.0
	Aromatic hydrocarbons	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
	Sum total	101.0	101.2	109.1	101.0	101.0	101.0	101.0	106.0
	Tralopyril content (iv-a) (wt%)	0.99	0.99	1.83	0.99	0.99	0.99	0.99	0.94

		59	60	61	62	63	64	65	66
Calculated values for coating composition	Cu compound (iv-b) content (wt%)	2.97	0.99	4.58	0.99	0.99	0.99	0.99	4.72
	Total biocides content (wt%)	4.95	3.16	9.53	2.97	2.97	2.97	2.97	6.60
	Pigment, extender and biocide content (wt%)	54.0	52.1	54.9	52.0	52.0	52.0	52.0	53.3
	VOC (g/L)	352	358	350	359	359	359	359	363
Test results	Cone & plate viscosity (cP)	651	765	867	704	756	786	772	760
	Raft Singapore	0	0	0	0	0	0	0	0
		0	1	0	0	0	1	0	0
		0	1	0	0	0	0	0	0
		0	1	0	0	0	1	0	1

Table 15: Examples

		67	68	69	70	71	72	73	74	75
Binder (ii-a)	A2	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5
Binder (ii-b)	A4	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0
Binder (iii)	Rosin solution (60% in xylene)	20.5	20.0	20.0	20.0	20.0	20.0	20.0	20.0	20.0
	Isostearic acid	0.7	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Biocide (iv-a)	Tralopyril	1.0	1.0	1.0	1.0	1.0	1.5	3.0	0.5	1.0
Cu compounds (iv-b)	Copper(I) oxide #1	1.0	2.0	5.0			1.0	1.0	2.0	1.0
	Copper powder #1	1.0			1.0	2.0				
Other biocides	Copper pyrrithione	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
	Medetomidine									0.2
Pigments and extenders (v)	Iron oxide red	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
	Dolomite	40.0	40.0	40.0	40.0	40.0	40.0	40.0	40.0	40.0
	Zinc oxide	7.0	7.0	7.0	7.0	7.0	7.0	7.0	7.0	7.0
Additives	Organoclay	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
	Wetting and dispersing agent	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Solvents	Xylene	8.5	7.0	7.0	7.0	7.0	7.0	7.0	7.0	7.0
	Aromatic hydrocarbons		2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
	Sum total	101.2	101.5	104.5	100.5	101.5	101.0	102.5	101.0	100.7

		67	68	69	70	71	72	73	74	75
Calculated values for coating composition	Tralopyril content (iv-a) (wt%)	0.99	0.99	0.96	1.00	0.99	1.49	2.93	0.50	0.99
	Cu compound (iv-b) content (wt%)	1.98	1.97	4.78	1.00	1.97	0.99	0.98	1.98	0.99
	Total biocides content (wt%)	3.95	3.94	6.70	2.99	3.94	3.47	4.88	3.47	3.18
	Pigment, extender and biocide content (wt%)	56.3	56.2	57.4	55.7	56.2	55.9	56.6	55.9	55.8
	VOC (g/L)	351	354	351	355	354	353	348	355	354
Test results	Cone & plate viscosity (cP)									
	Raft Singapore	1 month	0	0	0	0	0	0	0	0
		2 months	0	0	0	0	0	0	0	0
		4 months	1	1	1	0	0	0	0	0
		6 months	1	1	1	0	0	0	0	0

Comments to Table 13 to Table 15:

- 5 In examples 49 - 75 in Table 12 to Table 15 different binder, biocide and pigment combinations are tested. Examples 50 and 51 in Table 13 show that a zinc salt of rosin (Zn rosinate Z1) can also be used. Examples 67-75 in Table 15 show the use of the combination of a (meth)acrylic polymer (ii-a) and a second (meth)acrylic polymer (ii-b) with no (meth)acrylic silyl ester copolymer (i) present. All examples gave good antifouling performance.

[illegible]

		76	77	78	79	80	81	82	83	84
	4 months	0	0	1	0	0	0	0	0	1
	6 months	1	1	1	1	0	1	1	0	1

Table 17: Examples

		85	86	87	88	89	90	91	92
Binders (i)	S2	13.5	17.0	13.0	4.0	1.5	4.0	5.5	3.0
	S3				9.5	11.5	11.5	16.0	18.5
Binders (ii-a)	A1	7.5	7.5		7.5			2.0	0.5
	A3			5.0		5.0	3.0	1.0	3.0
Binders (iii)	Rosin solution (60% in xylene)	18.5	11.0	17.0	18.5	17.0	20.5	13.5	11.5
	Isostearic acid						0.5		
Biocide (iv-a)	Tralopyril	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Cu compound (iv-b)	Copper(I) oxide #1	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Other biocide	Copper pyrithione	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Pigments and extenders (v)	Iron oxide red	5.5	6.0	6.0	5.5	6.0	5.5	5.5	5.5
	Talc	11.0	12.0	12.0	11.0	12.0	11.0	11.5	12.0
	Zinc phosphate	26.0	26.0	26.0	23.0	29.0	23.0	25.0	25.0

		85	86	87	88	89	90	91	92
	Zinc oxide	5.5	10.0	10.5	11.0	5.0	11.0	8.5	10.0
Additives	Tetraethoxysilane	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
	Polyamide wax (20% in xylene)	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Solvent	Xylene	7.0	8.0	7.5	7.0	7.5	7.0	6.5	7.5
	Sum total	100.0	103.0	102.5	102.5	100.0	102.5	101.0	102.0
Calculated values for coating composition	Tralopyril (iv-a) content (wt%)	1.00	0.97	0.98	0.98	1.00	0.98	0.99	0.98
	Cu compound (iv-b) content (wt%)	1.00	0.97	0.98	0.98	1.00	0.98	0.99	0.98
	Total biocides content (wt%)	3.00	2.91	2.93	2.93	3.00	2.93	2.97	2.94
	Total pigment, extender and biocide content (wt%)	51.0	55.3	56.1	52.2	55.0	52.2	53.0	54.4
	VOC (g/L)	367	367	363	366	364	366	366	367
Test results	Cone & plate viscosity (cP)	659	669	522	471	444	542	446	601
	Raft Singapore	1 month	0	0	0	0	0	0	0
		2 months	0	0	0	0	0	0	0
		4 months	0	0	0	0	0	1	0
		6 months	0	0	0	1	0	1	1

		93	94	95	96	97	98	99	100	101
Solvent	Xylene	10.0	9.5	11.0	7.5	7.5	7.5	8.5	7.5	6.0
	Sum total	101.5	101.0	100.5	100.5	100.0	101.0	100.5	101.5	100.5
Calculated values for coating composition	Tralopyril content (iv-a) (wt%)	0.99	0.99	1.00	1.00	1.00	0.99	1.00	0.99	0.80
	Cu compound (iv-b) content (wt%)	0.99	0.99	1.00	1.00	1.00	0.99	1.00	0.99	1.19
	Total biocides content (wt%)	2.96	2.97	2.99	2.99	3.00	2.97	2.99	2.96	2.99
	Pigment, extender and biocide content (wt%)	56.7	58.4	57.7	56.7	55.2	57.4	57.7	56.7	52.2
	VOC (g/L)	375	375	373	374	372	375	372	374	376
Test results	Cone & plate viscosity (cP)	564	362	336	424	360	555	560	721	750
	Raft Singapore	0	0	0	0	0	0	0	0	0
		1	0	0	1	0	0	1	0	0
		0	0	0	1	0	0	1	0	0
		0	1	0	1	1	0	1	0	0

Table 19: Examples

		102	103	104	105	106
Binder (ii-a)	A2	8.0		4.5	1.5	1.5
Binder (ii-b)	A4	13.5	15.0	13.0	14.5	5.5
Binder (iii)	Rosin solution (60% in xylene)	20.5	20.5	20.0	20.5	20.0
	Isostearic acid		2.5			3.5
Biocide (iv-a)	Tralopyril	1.0	1.0	1.0	1.0	1.0
Cu compounds (iv-b)	Copper(I) oxide #1				1.0	1.0
	Copper powder #1	1.0	1.0	1.0	1.0	1.0
Other biocides	Copper pyrithione	1.0	1.0	1.0	1.0	1.0
	Medetomidine			0.05	0.20	0.20
Pigments and extenders (v)	Iron oxide red	3.5	3.5	3.5	3.5	3.5
	Titanium dioxide	1.0	1.0	1.0	1.0	1.0
	Dolomite	3.5		9.5		22.0
	Zinc phosphate	10.5	22.0	15.0	37.0	
	Talc	1.5	12.0	11.0		
	Zinc oxide	28.0	10.0	9.5	9.0	26.5
Additives	Organoclay	1.0	1.0	1.0	1.0	1.0

			102	103	104	105	106
	Wetting and dispersing agent		1.0	1.0	1.0	1.0	1.0
Solvent	Xylene		6.0	8.5	8.0	7.0	11.0
	Sum total		101.0	100.0	100.05	100.2	100.7
Calculated values for coating composition	Tralopyril content (iv-a) (wt%)		0.99	1.00	1.00	1.00	0.99
	Cu compound (iv-b) content (wt%)		0.99	1.00	1.00	2.00	1.99
	Total biocides content (wt%)		2.97	3.00	3.05	4.19	4.17
	Pigment, extender and biocide content (wt%)		51.5	52.5	53.5	55.6	57.8
	VOC (g/L)		378	374	376	373	373
Test results	Cone & plate viscosity (cP)		925	424	580	412	225
	Raft Singapore	1 month	0	0	0	0	0
		2 months	0	1	0	0	0
		4 months	0	1	0	0	0
		6 months	1	1	0	1	0

Table 20: Comparative examples

		C17	C18	C19	C20	C21	C22
Binder (ii-a)	A2	7.5	7.5	7.5	7.5	1.5	7.0
Binder (ii-b)	A4	6.0	6.0	6.0	6.0	6.5	11.0
Binder (iii)	Rosin solution (60% in xylene)	20.0	20.0	20.0	20.0	20.0	20.0
	Isostearic acid	1.0	1.0	1.0	1.0	4.0	
Biocide (iv-a)	Tralopyril	0.5	2.0			1.0	1.0
Cu compounds (iv-b)	Copper(I) oxide #1			3.0	1.0		
	Copper powder #1				1.0		
	Copper(II) sulfide				5.0		
Other biocides	Copper pyrithione	1.0	1.0	1.0	1.0	1.0	1.0
Pigments and extenders (v)	Iron oxide red	5.0	5.0	5.0	5.0	3.5	3.5
	Titanium dioxide					1.0	1.0
	Dolomite	40.0	40.0	40.0	40.0	35.5	8.5
	Talc						14.0
Additives	Zinc oxide	7.0	7.0	7.0	7.0	10.0	23.5
	Organoclay	1.0	1.0	1.0	1.0	1.0	1.0
	Wetting and dispersing agent	1.0	1.0	1.0	1.0	1.0	1.0

		C17	C18	C19	C20	C21	C22
Solvents	Xylene	7.0	7.0	7.0	7.0	12.0	7.5
	Aromatic hydrocarbons	2.0	2.0	2.0	2.0		
	Sum total	99.0	100.5	101.5	105.5	100.0	100.0
Calculated values for coating composition	Tralopyril content (iv-a) (wt%)	0.52	1.99	-	-	1.00	1.00
	Cu compound (iv-b) content (wt%)	-	-	2.96	6.64	-	-
	Total biocides content (wt%)	1.52	2.99	3.94	7.58	2.00	2.00
	Pigment, extender and biocide content (wt%)	55.1	55.7	56.2	57.8	53.0	53.5
	VOC (g/L)	357	352	356	352	373	375
Test results	Cone & plate viscosity (cP)	436	487	341	347	123	347
	Raft Singapore	0	1	1	0	0	1
		1	0	1	1	0	2
		3	1	2	2	1	3
		4	3	2	2	3	4

Comments to Table 16

These examples use different biocide contents and biocide combinations along with the (meth)acrylic silyl polymer (i), (meth)acrylic polymer (ii), and a rosin. All the examples show good antifouling performance.

5

Comments to Table 17

These examples use a variety of binder combinations including a large range of (meth)acrylic silyl polymer (i), a (meth)acrylic polymer (ii) and monocarboxylic acid (iii). All the examples show good antifouling performance.

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Comments to Tables 18-19

These examples show the use of a wide range of extenders, and different rosins along with the combination of a (meth)acrylic polymer (ii-a) and a second (meth)acrylic polymer (ii-b) with no (meth)acrylic silyl ester copolymer (i) present.

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All the examples show good antifouling performance.

Comments to Table 20

The comparative examples show that the antifouling performance is poor when either tralopyril(iv-a) or Cu compound (iv-b) (containing at least 40wt% Cu) is missing in compositions with a combination of a (meth)acrylic polymer (ii-a), a second (meth)acrylic polymer (ii-b) and carboxylic acid (iii).

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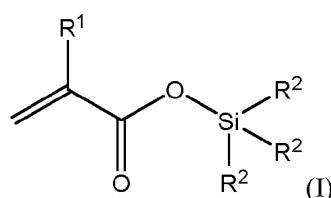
Claims

1. An antifouling coating composition comprising:
 - (i) a (meth)acrylic silyl ester copolymer comprising at least 15 wt% silyl ester monomers, relative to the total weight of monomers in the (meth)acrylic silyl ester copolymer and/or
 - (ii) a (meth)acrylic polymer comprising 10 wt% or less of silyl ester monomers and 5.0 wt% or less of metal ester monomers, relative to the total weight of monomers in the (meth)acrylic polymer;
 - (iii) a monocarboxylic acid or a metal salt thereof;
 - (iv) biocides comprising:
 - a. tralopyril; and
 - b. one or more copper compounds having a copper content of at least 40 wt%, relative to the formula weight of the copper compound wherein the coating composition as a whole comprises 10.0 wt% or less of biocides; and
 - (v) at least 35 wt% of pigments, extenders and biocides combined, relative to the total weight of the coating composition as a whole.
2. The antifouling coating composition as claimed in claim 1, wherein said composition comprises a (meth)acrylic silyl ester copolymer (i) or both a (meth)acrylic silyl ester copolymer (i) and a (meth)acrylic polymer (ii).
3. The antifouling coating composition as claimed in any preceding claim, wherein the composition comprises 8.0 wt% or less of biocides, relative to the total weight of the coating composition as a whole, preferably 5.0 wt% or less.
4. The antifouling coating composition as claimed in any preceding claim, wherein the copper compound has a copper content of at least 45 wt%, preferably at least 50 wt%, especially metallic copper or copper(I) oxide.
5. The antifouling coating composition as claimed in any preceding claim, wherein tralopyril is present in an amount of 0.1 to 5.0 wt%, relative to the total weight of the composition, preferably 0.2 to 3.0 wt%, more preferably 0.3 to 2.0 wt%, even more preferably 0.4 to 1.0 wt% and/or

wherein the one or more copper compounds is present in an amount of 0.1 to 8.0 wt%, relative to the total weight of the composition, preferably 0.2 to 5.0 wt%, more preferably 0.3 to 3.0 wt%, even more preferably 0.3 to 2.0 wt%, further preferred 0.3 to 1.0 wt%.

6. The antifouling coating composition as claimed in any preceding claim, wherein the (meth)acrylic silyl ester copolymer (i) comprises structural units derived from the following monomers:

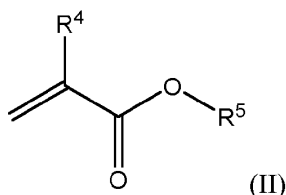
(a) a silyl ester monomer of formula (I),



wherein R^1 is H or CH_3 ;

R^2 is each independently selected from C1-C10 hydrocarbyl groups preferably isopropyl;

(b) one or more monomer(s) of formula (II)



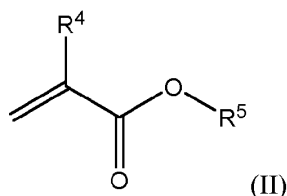
wherein R^4 is H or CH_3 , and R^5 is a C1-C20 hydrocarbyl substituent, preferably a C1-10 alkyl substituent.

7. The antifouling coating composition as claimed in any preceding claim wherein the coating composition comprises a (meth)acrylic polymer (ii).

8. The antifouling coating composition as claimed in any preceding claim wherein the (meth)acrylic polymer (ii) is a (meth)acrylic polymer (ii-a) that has a T_g of less than 10 °C, further preferred less than 0 °C, such as less than -10 °C.

9. The antifouling coating composition as claimed in claim 8, wherein the (meth)acrylic copolymer (ii-a) comprises

- (a) (meth)acrylic acid and
- (b) one or more monomer(s) of formula (II)

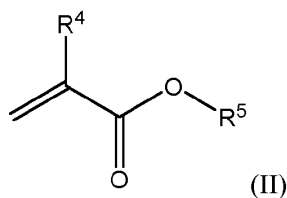


wherein R^4 is H or CH_3 , and R^5 is a C1-C20 hydrocarbyl substituent preferably a C1-10 alkyl substituent, most preferably methyl, ethyl, n-propyl, n-butyl or 2-ethylhexyl.

10. The antifouling coating composition as claimed in any preceding claim, wherein the (meth)acrylic polymer (ii) is a (meth)acrylic polymer (ii-b) and has a glass transition temperature (T_g) of at least 10 °C.

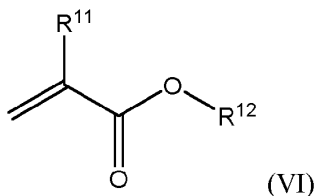
11. The antifouling coating composition as claimed in claim 10 wherein the (meth)acrylic ester polymer (ii-b) comprises:

- (a) one or more monomer(s) of formula (II)



wherein R^4 is H or CH_3 , and R^5 is a C1-C20 hydrocarbyl substituent preferably a C1-10 alkyl substituent, most preferably methyl, ethyl, n-propyl, n-butyl or 2-ethylhexyl; and

- (b) one or more monomers of formula (VI)



wherein R^{11} is H or CH_3 , and R^{12} is a C3-40 substituent, such as C3-C20 substituent, containing at least one oxygen or nitrogen atom, preferably at least one oxygen atom or R^{12} represents a poly(alkylene glycol) group.

12. The antifouling coating composition as claimed in any preceding claim, wherein component (i) is present in an amount of 2.0 to 30 wt%, relative to the total weight of the coating compositions as a whole, preferably 5.0 to 25 wt%; and/or wherein component (ii-a) is present in an amount of 0.5 to 12 wt%, relative to the total weight of the coating compositions as a whole, preferably 1.0 to 7.0 wt%; and/or component (ii-b) is present in an amount of 1.0 to 15 wt.% relative to the total coating composition as a whole, preferably 2.0 to 12 wt%; and wherein the monocarboxylic acid or metal salt thereof (iii) is present in an amount of 5.0 to 30 wt% based on the total weight of the coating composition as a whole, preferably 5.0 to 25 wt%.

13. The antifouling coating composition as claimed in any preceding claim, wherein the monocarboxylic acid or metal salt thereof (iii) is rosin, modified rosin or metal salts thereof, especially gum rosin, hydrogenated gum rosin, copper salt of gum rosin, zinc salt of gum rosin, copper salt of hydrogenated gum rosin, zinc salt of hydrogenated gum rosin and mixtures thereof.

14. The antifouling coating composition as claimed in any preceding claim, further comprising one or more biocides selected from zinc pyrithione, copper pyrithione, zineb and 4,5-dichloro-2-octyl-4-isothiazolin-3-one.

15. The antifouling coating composition as claimed in any preceding claim, wherein tralopyril is present in an amount of 5.0 to 60.0 wt%, relative to the total weight of biocides (iv), preferably 7.0 to 60.0 wt%, more preferably 8.0 to 60.0 wt%, even more preferably 9.0 to 60.0 wt%, further preferred 10.0 to 60.0 wt% and/or

wherein the one or more copper compounds is present in an amount of 5.0 to 90.0 wt%, relative to the total weight of biocides (iv), preferably 6.0 to 87.0 wt%, more preferably 7.0 to 85.0 wt%, even more preferably 8.0 to 82.0 wt%, further preferred 9.0 to 80.0 wt%.

16. 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 1 to 15.

17. An object coated with the antifouling coating composition as claimed in any of claims 1 to 15.