

Antifouling Composition

Field of the Invention

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The present invention relates to marine antifouling coating compositions, more specifically to marine antifouling coating compositions comprising a silyl ester copolymer comprising triisopropylsilyl methacrylate as a monomer. The composition additionally contains an acrylic copolymer having a low Tg and preferably containing an acidic monomer, a monocarboxylic acid or derivative thereof and tralopyril as a biocide. 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. It can also result in reduced manoeuvrability.

To prevent settlement and growth of marine organisms antifouling paints are used. These paints generally comprise a film-forming binder, together with different components such as pigments, fillers, 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 Maintenance of submerged objects is costly, so the applied antifouling coatings should be effective for the specified service interval. Typical service intervals for commercial vessels range from 24 to 90 months. It requires a controlled release of biocides from the coating film through the entire service interval to

protect the object from fouling. That can best be obtained by using a self-polishing antifouling coating having a controlled polishing rate. Too fast polishing will lead to a rapid consumption of the coating film, resulting in an unprotected surface. Too slow polishing will lead to insufficient release of the biocide, which is vital for effective protection from fouling. A controlled degradation over the life time will give a constant release of biocides and thereby excellent fouling protection.

The most successful antifouling coating systems on the market today are based on silyl ester copolymers. The binder matrix consists of silyl ester copolymers often together with other binders such as acrylates and rosin or rosin derivatives to adjust the self-polishing properties and the mechanical properties of antifouling coating films.

Traditionally, an antifouling coating contains copper based biocides such as cuprous oxide, copper thiocyanate and like. In the last decade, new metal-free organic biocides have been put on the market. Their efficiency allows lower loading of biocides in the formulation. Tralopyril is an organic biocide which has been shown to be very effective against a broad spectrum of hard-shelled fouling organisms including barnacles, hydroids, mussels, oysters and tube worms. Antifouling coating compositions based on silyl ester copolymers which employ tralopyril as a biocide are disclosed in, for example, EP 3078715 and JP2016089167A.

However, it is difficult to develop antifouling coatings without inorganic copper biocides using silyl (meth)acrylic binders that will last the specified service interval for the vessel. Replacing the inorganic copper biocides with organic biocides in the antifouling coating compositions will alter the finetuned balance between the raw materials. This will influence the coating film properties and may often result in uncontrolled or unpredictable degradation of the coating films.

Controlled polishing and good mechanical properties of coatings, such as cracking resistance and coating film hardness, can often be achieved by adjusting the ratios of the binder components. However, it is difficult to formulate antifouling coatings without inorganic copper biocides having the same controlled polishing and good mechanical properties as the traditional antifouling coatings by just varying the triisopropylsilyl methacrylate copolymer and rosin ratio. Antifouling coating

compositions comprising tralopyril provide a solution that gives broader protection against marine fouling than other solutions without inorganic copper biocides in the market.

5 In order to offer long-term antifouling solutions that are economically viable to the customer it is vital that the antifouling coating polishes at a constant rate through the whole life time of the coating system to provide good fouling protection. Insufficient fouling protection will increase the operational cost, such as fuel consumption and/or cost of underwater hull cleaning. It is also vital that the coating system can be applied in acceptable film thicknesses. High film thickness is costly
10 for the customer with respect to the cost of the paint applied and extended time in dock resulting in increased docking fees and extended time out of business. Other disadvantages of applying high film thickness is risk of sagging during application and poor release of solvents during drying resulting in increased drying times, soft coatings and/or risk of coating failures such as blistering and flaking when immersed
15 in sea water.

An antifouling coating composition comprising a silyl methacrylate copolymer and tralopyril having a controlled polishing and degradation rate of the coating system is therefore needed.

The present inventors have found that controlled polishing and good
20 mechanical properties can be achieved by employing a triisopropylsilyl methacrylate copolymer and a monocarboxylic acid together with acrylic copolymers as the third component of the binder matrix, followed by optimization of the final binder mixture. They have established that using this binder in combination with tralopyril provides a self-polishing antifouling system with improved antifouling performance.
25 Moreover, the antifouling composition of the invention has very good resistance to cracking and very good self-polishing properties.

Summary of invention

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

(A) a binder comprising:

- (i) 30 to 80 wt% of a silyl ester copolymer comprising triisopropylsilyl methacrylate monomers;
- (ii) 20 to 55 wt% of a monocarboxylic acid or derivative thereof; and
- 5 (iii) 5 to 20 wt% of an acrylic copolymer having a glass transition temperature (T_g) of less than 25 °C;

wherein components (i) and (iii) are different; and

(B) tralopyril.

10 In another aspect, the invention provides 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 defined herein.

The invention also relates to objects coated with the antifouling coating composition as defined herein.

15 Viewed from another aspect the invention relates to the use of the binder (A) as defined herein in an antifouling coating composition comprising tralopyril, i.e. as a binder for such a composition.

Definitions

20 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.

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

The term “acrylic copolymer” refers to a copolymer comprising repeating units derived from (meth)acrylate monomers. Generally an acrylic copolymer will comprise at least 80 wt% of the repeating units derived from (meth)acrylate monomers, i.e. acrylate and/or methacrylate monomers.

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The term “(meth)acrylate” means a methacrylate or acrylate.

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

As used herein the term “resin acid” refers to a mixture of carboxylic acids present in resins.

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

 The term “binder” defines part of the composition which includes the silyl ester copolymer and any other components which together form a matrix giving substance and strength to the composition. Typically, the term “binder” used herein
10 means the silyl ester copolymer together with the monocarboxylic acid and acrylic copolymer, i.e. components (i), (ii) and (iii) as defined herein.

 The term ‘Tg’ means glass transition temperature.

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

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

Detailed description of invention

20 The invention relates to a new antifouling coating composition comprising a binder, which contains a mixture of (i) a silyl ester copolymer comprising triisopropylsilyl methacrylate monomers; (ii) a monocarboxylic acid or derivative thereof; and (iii) an acrylic copolymer in particular weight ratios, together with
25 tralopyril.

Silyl ester copolymer (i)

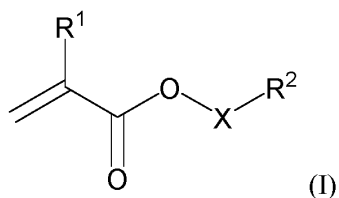
 The silyl ester copolymer contains monomers of triisopropylsilyl
30 methacrylate. In one embodiment, the silyl ester copolymer includes at least the monomers triisopropylsilyl methacrylate and a hydrophilic (meth)acrylate. Typically, the weight percentage of the triisopropylsilyl methacrylate monomer is in

the range 5 to 80 wt%, preferably 30 to 75 wt%, such as 40 to 70 wt%, relative to the total weight of the silyl ester copolymer as a whole. The hydrophilic (meth)acrylate monomer may be present in an amount of 2 to 50 wt%, such as 5 to 30 wt%, relative to the total weight of the silyl ester copolymer as a whole.

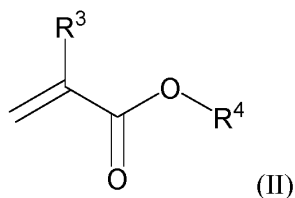
- 5 Additional silyl ester (meth)acrylate monomers, hydrophilic (meth)acrylate monomers, and/or non-hydrophilic (meth)acrylate monomers may additionally be present as described herein.

In a particularly preferable embodiment, the silyl ester copolymer comprises as monomers:

- 10 (a) triisopropylsilyl methacrylate;
(b) a compound of Formula (I)

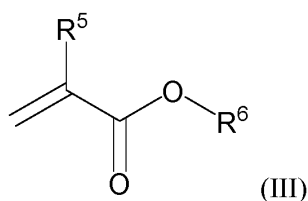


wherein R¹ is hydrogen or methyl, R² is a cyclic ether (such as oxolane, oxane, dioxolane, dioxane optionally alkyl substituted) and X is a C1-C4 alkylene;
15 and/or a compound of Formula (II)



wherein R³ is hydrogen or methyl, and R⁴ is a C3-C18 substituent with at least one oxygen or nitrogen atom, preferably at least one oxygen atom; and optionally

- 20 (c) one or more monomers of Formula (III)



wherein R⁵ is hydrogen or methyl, and R⁶ is a C1-C8 hydrocarbyl.

Monomers

5 In one embodiment, the silyl ester copolymer includes at least the monomers triisopropylsilyl methacrylate (a) and at least one hydrophilic monomer (b).

Where a wt% of a given monomer in the silyl ester copolymer is given, the wt% is relative to the sum total (weight) of each monomer present in the copolymer. Thus, if triisopropylsilyl methacrylate (a) and hydrophilic (meth)acrylate monomer (b) are the only monomers in the silyl ester copolymer, the wt% of triisopropylsilyl methacrylate is calculated as [triisopropylsilyl methacrylate (a) (weight) / (triisopropylsilyl methacrylate (a) (weight) + hydrophilic (meth)acrylate monomer (b) (weight))] x 100%. If only triisopropylsilyl methacrylate (a), hydrophilic (meth)acrylate monomer (b) and non-hydrophilic (meth)acrylate (c) are present, the wt% of triisopropylsilyl methacrylate is calculated as [triisopropylsilyl methacrylate (a) (weight) / (triisopropylsilyl methacrylate (a) (weight) + hydrophilic (meth)acrylate monomer (b) (weight) + non-hydrophilic (meth)acrylate (c) (weight))] x 100%.

20 The copolymer preferably comprises >80 wt%, preferably >90 wt%, more preferably >95 wt%, especially >98 wt% of the combination of triisopropylsilyl methacrylate (a), hydrophilic (meth)acrylate monomer(s) (b) and non-hydrophilic (meth)acrylate monomer(s) (c).

Component (a) is triisopropylsilyl methacrylate, which preferably forms 5 to 80 wt% of the copolymer, preferably 30 to 75 wt%, especially 40 to 70 wt%.

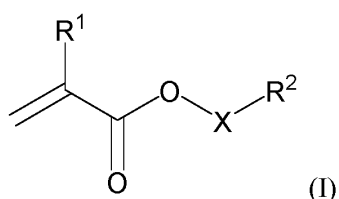
25 Component (b) (total) preferably forms 2 to 50 wt% of the copolymer, preferably 3 to 40 wt% of the copolymer, especially 4 to 35 wt% of the copolymer, more especially 5 to 30 wt%. These wt% values refer to the total of component (b) monomers present.

30 The ratio (a):(b) (weight/weight) is preferably in the range of 40:60 to 95:5, preferably in the range of 50:50 to 95:5, especially in the range of 55:45 to 93:7, most preferably in the range of 60:40 to 90:10. It is preferred that the weight fraction of (a) in the copolymer is greater than that of component (b).

The amount of (a)+(b) in the copolymer is preferably at most 95 wt%, such as at most 90 wt%, especially at most 85 wt%. The amount of (a)+(b) in the copolymer may be in the range of 30-95 wt% or 40-85 wt%.

5 Hydrophilic (meth)acrylate monomer(s) component (b)

In certain embodiments, the silyl ester copolymer contains at least one monomer of Formula (I)



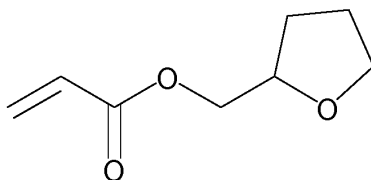
10 wherein R¹ is hydrogen or methyl, R² is a cyclic ether (such as oxolane, oxane, dioxolane, dioxane optionally alkyl substituted) and X is a C1-C4 alkylene, preferably a C1-C2 alkylene.

The cyclic ether may contain a single oxygen atom in the ring or 2 or 3 oxygen atoms in the ring. The cyclic ether may contain a ring comprising 2 to 8 carbon atoms, such as 3 to 5 carbon atoms. The whole ring might comprise 4 to 8 atoms, such as 5 or 6 atoms.

The cyclic ether ring may be substituted such as by one or more, such as one, C1-C6 alkyl group. That substituent group might be at any position on the ring including the position that binds to the X group.

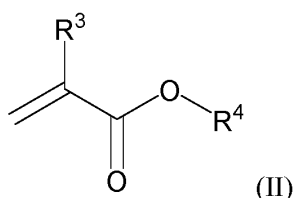
20 Suitable compounds of Formula (I) include tetrahydrofurfuryl acrylate, tetrahydrofurfuryl methacrylate, isopropylidenglycerol methacrylate, glycerolformal methacrylate and cyclic trimethylolpropane formal acrylate.

Formula (I) most preferably represents tetrahydrofurfuryl acrylate having the structure below:



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In a further embodiment, the copolymer may include one or more monomers of Formula (II):



5 wherein R³ is hydrogen or methyl, and R⁴ is a C3-C18 substituent containing at least one oxygen or nitrogen atom, preferably at least one oxygen atom.

As indicated in the above formula, the term “hydrophilic (meth)acrylate” requires the R⁴ group in Formula (II) to include at least one oxygen or nitrogen atom, preferably at least one oxygen atom. As explained in detail below, additional
 10 non-hydrophilic (meth)acrylate monomers of Formula (III) may also be present, in which the R⁶ unit consists of C and H atoms only.

In an embodiment, the silyl ester copolymer contains at least one monomer of Formula (II) above, in which the R⁴ group is of formula -(CH₂CH₂O)_m-R⁷, where R⁷ is a C1-C10 hydrocarbyl substituent, preferably a C1-C10 alkyl or a C6-C10 aryl
 15 substituent, and m is an integer in the range of 1 to 6, preferably 1 to 3. Preferably R⁴ is of formula -(CH₂CH₂O)_m-R⁷, where R⁷ is an alkyl substituent, preferably methyl or ethyl, and m is an integer in the range of 1 to 3, preferably 1 or 2.

In an embodiment, the silyl ester copolymer includes one or more of 2-methoxyethyl methacrylate, 2-methoxyethyl acrylate, 2-ethoxyethyl methacrylate, 2-(2-ethoxyethoxy)ethyl methacrylate and 2-(2-ethoxyethoxy)ethyl acrylate.
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Particularly preferred monomer(s) (b) include 2-methoxyethyl acrylate, 2-methoxyethyl methacrylate, 2-ethoxyethyl methacrylate, 2-(2-ethoxyethoxy)ethyl acrylate, 2-(2-ethoxyethoxy)ethyl methacrylate, tetrahydrofurfuryl acrylate, and tetrahydrofurfuryl methacrylate.

25 In one embodiment, the silyl ester copolymer does not contain 2-(2-ethoxyethoxy)ethyl acrylate as a monomer.

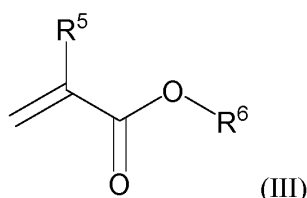
As used herein, Formula (I) and Formula (II) defines a “polar” (meth)acrylate monomer or “hydrophilic” (meth)acrylate monomer. The use of these

monomers with triisopropylsilyl methacrylate ensures the formation of a binder that has a controlled degradation.

It is preferred if the silyl ester copolymer comprises a monomer of Formula (I) or a monomer of Formula (II). It is generally not preferred to have a monomer
5 from both these formulae present.

Additional non-hydrophilic (meth)acrylate monomer(s) (c)

The silyl ester copolymer may include one or more additional non-
10 hydrophilic (meth)acrylate monomers of Formula (III)



wherein R⁵ is hydrogen or methyl, and R⁶ is a C1-C8 hydrocarbyl substituent, preferably a C1-C8 alkyl substituent, most preferably methyl, ethyl, n-butyl or 2-ethylhexyl. Monomers according to Formula (III) are referred to as “non-
15 hydrophilic” monomers herein.

In all embodiments of the invention the silyl ester copolymer preferably includes at least one additional non-hydrophilic methacrylate and/or non-hydrophilic acrylate monomer. Where one or more non-hydrophilic (meth)acrylate monomers are present, the sum of these non-hydrophilic (meth)acrylate monomers in the silyl
20 ester copolymer is preferably at most 60 wt%, preferably no more than 55 wt%, such as in the range of 5 to 55 wt%, especially in the range of 10 to 50 wt%.

In a preferred embodiment, the monomers triisopropylsilyl methacrylate (a), component (b) and any non-hydrophilic (meth)acrylate monomer(s) according to Formula (III) together form >80wt%, preferably >90 wt%, especially >95 wt% of
25 the monomers in the silyl ester copolymer.

In a preferred embodiment, the silyl ester copolymer includes one or more of the non-hydrophilic monomers methyl methacrylate and/or n-butyl acrylate.

In all embodiments of the invention it is preferred that methyl methacrylate is included. Where present, methyl methacrylate is preferably present in an amount of 2 to 60 wt%, preferably 5 to 50 wt% of the copolymer. In a preferred embodiment triisopropylsilyl methacrylate (a), component (b) and methyl methacrylate together
5 form >50 wt%, preferably >55 wt%, especially >60 wt% of the monomers in the silyl ester copolymer.

Where present, n-butyl acrylate is preferably present in an amount of 1 to 30 wt%, especially 2 to 20 wt%.

The silyl ester copolymer may include additional ethylenically unsaturated
10 monomers. Representative examples of suitable ethylenically unsaturated monomers include styrene, vinyl acetate, triisopropylsilyl acrylate, 2-(trimethylsiloxy)ethyl methacrylate, zinc (meth)acrylate, zinc acetate (meth)acrylate and zinc neodecanoate (meth)acrylate. Where present, any additional ethylenically unsaturated monomer preferably forms no more than 20 wt% of the copolymer,
15 preferably no more than 10 wt% of the copolymer.

Properties of the silyl ester copolymer

The silyl ester copolymer can be prepared using polymerization reactions
20 known in the art. The silyl ester copolymer 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 or by controlled polymerization techniques. In preparing a coating
25 composition using this silyl ester copolymer, the copolymer is preferably diluted with an organic solvent to give a polymer solution having an appropriate viscosity. From this standpoint, it is desirable to employ solution polymerization.

Examples of suitable initiators for free-radical polymerization include azo
compounds such as dimethyl 2,2'-azobis(2-methylpropionate), 2,2'-azobis(2-
30 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
5 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.

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,
10 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
15 butoxyethanol, 1-methoxy-2-propanol; aliphatic hydrocarbons such as white spirit, limonene; and optionally a mixture of two or more solvents.

These compounds are used alone or as a mixture of two or more thereof. The silyl ester copolymer may be a random copolymer, an alternate copolymer, a gradient copolymer or block copolymer. The copolymer is preferably a random
20 copolymer.

The thus-obtained polymer containing organosilyl ester groups preferably has a weight-average molecular weight (Mw) from 5,000 to 100,000, preferably from 15,000 to 80,000, more preferably from 20,000 to 60,000. Mw is measured as described in the examples section.

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

The silyl ester copolymer may be provided as a polymer solution, such as a
30 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.

The amount of silyl ester copolymer present in the compositions of the invention is 30 to 80 wt% (dry solids), preferably 30 to 75 wt%, more preferably 35 to 70 wt% (dry solids), even more preferably 40 to 60 wt% (dry solids), based on the total weight of the binder (A).

5 The final antifouling coating composition of the invention preferably comprises 2 to 40 wt% (dry solids) of the silyl ester copolymer, such as 3 to 30 wt% (dry solids), in particular 5 to 20 wt% (dry solids) based on the total coating composition.

10 **Monocarboxylic acid (ii)**

The antifouling coating compositions of the present invention comprise a monocarboxylic acid or derivative thereof.

15 The monocarboxylic acid present in the antifouling coating composition of the present invention preferably comprises 5 to 50 carbon atoms, more preferably 10 to 40 carbon atoms and still more preferably 12 to 25 carbon atoms.

20 The monocarboxylic acid present in the antifouling coating composition of the present invention is preferably selected from a resin acid, a derivative of a resin acid, C6-C20 cyclic monocarboxylic acid, C5-C24 acyclic aliphatic monocarboxylic acid, C7-C20 aromatic monocarboxylic acid and mixtures thereof.

25 Derivatives of monocarboxylic acid include metal salts of monocarboxylic acid, such as 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. The metal carboxylate may be generated in situ in the antifouling coating composition.

30 Representative examples of resin acids include abietic acid, neoabietic acid, dehydroabietic acid, palustric acid, levopimaric acid, pimaric acid, isopimaric acid, sandaracopimaric acid, communic acid and mercusic acid, secodehydroabietic acid. It will be appreciated that the resin acids are derived from natural sources and as such they typically exist as a mixture of acids. Resin acids are also referred to as

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

5 Commercial grades of rosin are often classified according to its colour by designation of letters on a colour scale XC (lightest), XB, XA, X, WW, WG, N, M, K, I, H, G, F, E, D (darkest) as specified in ASTM D509. Preferred colour grades for the compositions of the invention are X, WW, WG, N, M, K, I, and still more preferably WW. Commercial grades of rosin typically have an acid value from 155
10 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
15 point of 70 °C to 80 °C, more preferred 75 °C to 80 °C

Representative examples of resin acid derivatives include partly hydrogenated rosin, fully hydrogenated rosin, disproportionated rosin, dihydroabietic acids, dihydropimaric acids and tetrahydroabietic acids.

Representative examples of C6-C20 cyclic monocarboxylic acids include
20 naphthenic acid, 1,4-dimethyl-5-(3-methyl-2-butenyl)-3-cyclohexen-1-yl-carboxylic acid, 1,3-dimethyl-2-(3-methyl-2-butenyl)-3-cyclohexen-1-yl-carboxylic acid, 1,2,3-trimethyl-5-(1-methyl-2-propenyl)-3-cyclohexen-1-yl-carboxylic acid, 1,4,5-trimethyl-2-(2-methyl-2-propenyl)-3-cyclohexen-1-yl-carboxylic acid, 1,4,5-trimethyl-2-(2-methyl-1-propenyl)-3-cyclohexen-1-yl-carboxylic acid, 1,5,6-
25 trimethyl-3-(2-methyl-1-propenyl)-4-cyclohexen-1-yl-carboxylic acid, 1-methyl-4-(4-methyl-3-pentenyl)-4-cyclohexen-1-yl-carboxylic acid, 1-methyl-3-(4-methyl-3-pentenyl)-3-cyclohexen-1-yl-carboxylic acid, 2-methoxycarbonyl-3-(2-methyl-1-propenyl)-5,6-dimethyl-4-cyclohexen-1-yl-carboxylic acid, 1-isopropyl-4-methyl-bicyclo[2,2,2]2-octen-5-yl-carboxylic acid, 1-isopropyl-4-methyl-bicyclo[2,2,2]2-
30 octen-6-yl-carboxylic acid, 6-isopropyl-3-methyl-bicyclo[2,2,2]2-octen-8-yl-carboxylic acid and 6-isopropyl-3-methyl-bicyclo[2,2,2]2-octen-7-yl-carboxylic acid.

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 acid is gum rosin, derivatives of gum rosin, acyclic C10-C24 monocarboxylic acids, C6-C20 cyclic monocarboxylic acids or mixtures thereof. A mixture of acid preferably contains at least one resin acid, gum rosin or derivative of gum rosin. Gum rosin is most preferred.

In one embodiment, the derivative of the monocarboxylic acid is not a metal carboxylate.

The amount of monocarboxylic acid present in the compositions of the invention is 20 to 55 wt% (dry solids), preferably 25 to 51 wt% (dry solids), more preferably 30-50 wt% (dry solids), based on the total weight of the binder (A).

The final antifouling coating composition of the invention preferably comprises 2 to 30 wt% (dry solids) of the monocarboxylic acid, such as 4 to 25 wt% (dry solids), in particular 5 to 20 wt% (dry solids) based on the total coating composition.

Acrylic Copolymer (iii)

In the context of the present invention, the term “acrylic copolymer” refers to copolymers comprising at least one monomer based on acrylic acid, methacrylic acid, esters of acrylic acid and esters of methacrylic acid. It is a requirement that the copolymer (iii) is different to the copolymer (i) in the binder (A) of the invention.

The acrylic copolymer has a T_g below 25 °C, preferably below 10 °C, more preferred below 0 °C, even more preferred below -10°C, all values being measured according to the T_g test described in the examples section. It is envisaged that the use of an acrylic copolymer having a glass transition temperature (T_g) of less than
5 25 °C reduces the viscosity of the eventual antifouling coating composition and therefore reduces the solvent content that might be required.

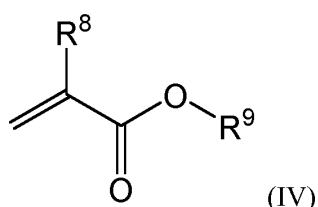
The acrylic copolymer preferably contains no hydrophilic monomers, except for monomers having an acid functionality.

Preferably the acrylic copolymer contains (meth)acrylic acid units, more preferred having acid number below 60 mg KOH/g polymer, more preferred below
10 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 measured as described in the examples section.

In one embodiment, the acrylic copolymer comprises 0.50-10 wt% of a
15 carboxylic acid-containing monomer, based on the total weight of the acrylic copolymer.

In a particular preferable embodiment, the acrylic copolymer comprises as monomers:

- i. at least one (meth)acrylate of Formula (IV):



20

wherein R⁸ is hydrogen or methyl, and R⁹ is a C1-C20 hydrocarbyl substituent; and

- ii. 0.5-10 wt% of at least one carboxylic acid-containing monomer, based on the total weight of the acrylic copolymer.

25 The combination of monomers defined under i. and ii. may make up at least 80 wt% of the acrylic copolymer such as at least 85 wt%, preferably at least 90 wt%, more preferably at least 95 wt%. In another particular embodiment, the combination

of monomers defined under i. and ii. represent up to 95 wt% of the acrylic copolymer, such as up to 99 wt% of the acrylic copolymer.

To be clear, the “combination of monomers defined under i. and ii.” includes the possibility of having two or more monomers of Formula (IV) or two or more carboxylic acid-containing monomers. The acrylic copolymer preferably contains less than 10 wt%, preferably less than 5 wt%, preferably less than 2 wt% of any monomer other than the monomers of Formula (IV) and carboxylic acid-containing monomer as described in i. and ii. above. In a particular embodiment, components i. and ii. make up the entirety of the monomer components of the acrylic copolymer.

In a particular embodiment, the acrylic copolymer does not comprise a hydrolysable monomer, such as a silyl ester monomer. Preferably, the acrylic copolymer is non-hydrolysable.

Preferably, the acrylic copolymer has a weight average molecular weight (Mw) of 10,000 to 50,000 g/mol, preferably 15,000 to 45,000.

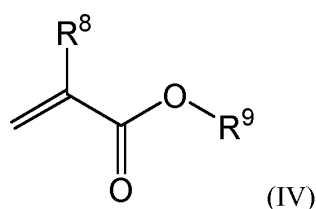
The acrylic copolymer may have an acid value of 2 to 60 mg KOH/g polymer as measured according to the acid value test described in the examples section, such as 5 to 40 mg KOH/g polymer.

The binder (A) comprises 5 to 20 wt% (dry solids) of the acrylic copolymer, preferably 7 to 15 wt% (dry solids), e.g. 10 wt%

In the present invention, the antifouling composition preferably comprises 1.0 to 15 wt% (dry solids) of the acrylic copolymer, preferably 1.2 to 10 wt% (dry solids), more preferably 1.5 to 8 wt% (dry solids) based on the total coating composition.

(Meth)acrylate monomer i.

The (meth)acrylate monomer to be used in the acrylic copolymer is preferably of Formula (IV):



wherein R⁸ is hydrogen or methyl, and R⁹ is a C1-C20 hydrocarbonyl, preferably a C1-8 alkyl substituent, most preferably methyl, ethyl, n-propyl, n-butyl or 2-ethylhexyl. Particularly preferred R⁹ groups are methyl, n-butyl, and 2-ethylhexyl.

5 Monomers according to Formula (IV) are referred to as “non-hydrophilic” monomers herein.

In a particular embodiment, the acrylic copolymer comprises at least one (meth)acrylate monomer of Formula (IV) selected from methyl methacrylate, ethyl acrylate, n-butyl acrylate, n-butyl methacrylate, 2-ethylhexyl acrylate and 2-ethylhexyl methacrylate. In a particular embodiment, the acrylic copolymer
10 comprises at least two different monomers of Formula (IV).

In a particular embodiment, the acrylic copolymer comprises methyl methacrylate as one monomer and at least one other monomer of Formula (IV). In a further particular embodiment, the acrylic copolymer comprises at least methyl
15 methacrylate and n-butyl (meth)acrylate. Where one or more (meth)acrylate monomers of Formula (IV) are present, the weight percentage of the sum of these (meth)acrylate monomers in the acrylic copolymer is preferably at most 99.5 wt%, such as at most 99.2 wt%, such as at most 99.0 wt%, such as at most 98.5 wt%, such as 98.0 wt% based on the total weight of the acrylic copolymer.

20 Furthermore, where one or more (meth)acrylate monomers of Formula (IV) are present, the weight percentage of the sum of these (meth)acrylate monomers in the acrylic copolymer is preferably at least 80 wt%, such as at least 85 wt%, such as at least 90 wt%, such as at least 92 wt% based on the total weight of the acrylic copolymer.

25 Where present, methyl methacrylate is preferably present in an amount of 1.0 to 50 wt% of the acrylic copolymer, preferably 1.5 to 30 wt%, more preferably 1.5 to 25 wt%.

Where present, n-butyl acrylate is preferably present in an amount of 50 to 99 wt% of the acrylic copolymer, preferably 55 to 98 wt%, more preferably 65 to
30 97 wt%, such as 70 to 95 wt%.

Carboxylic acid-containing monomer ii.

The carboxylic acid-containing monomer(s) to be used in the acrylic copolymer help to provide improved compatibility of the acrylic copolymer in the coating film. The carboxylic acid-containing monomer(s) are interchangeably referred to as acidic monomer(s) herein. It has been found that below the optimum range of acidic monomer content, the acrylic copolymer is prone to migrate in the coating film, whereas above the optimum range of acidic monomer content acrylic copolymers with high viscosities are obtained. High viscosity of the acrylic copolymer means that higher amounts of solvent are needed for preparation and application of the paint. This is unwanted due to strict VOC regulations.

Preferably, the acidic monomer is present in an amount of 0.5-10 wt% based on the weight of the acrylic copolymer. In further particular embodiments, the carboxylic acid-containing monomer is present in an amount of 0.5-8.0 wt%, such as 0.7- 8.6 wt%, such as 1.0-7.5 wt%, such as 1.2-7.0 wt%, such as 1.3-6.5 wt%, such as 1.4-6.0 wt%, based on the weight of the acrylic copolymer.

Examples of carboxylic acid containing monomers include acrylic acid, methacrylic acid, 2-carboxyethyl acrylate, 2-carboxymethyl methacrylate, mono-2-(methacryloyloxy)ethyl maleate and mono-2-(methacryloyloxy)ethyl succinate. Preferably, the carboxylic acid-containing monomer is acrylic acid or methacrylic acid, more preferably methacrylic acid. A combination of both acrylic acid and methacrylic acid may be used. The carboxylic acid-containing acrylic copolymer is preferably free of any N-vinyl lactam monomer. In particular, the absence of N-vinyl pyrrolidone is preferred.

Preparation of the acrylic copolymer

The acrylic copolymer may be prepared using polymerization reactions known in the art. Acrylic polymers are preferably prepared using addition polymerization or chain growth polymerization. The polymer may, for example, be obtained by polymerizing a monomer mixture in the presence of a polymerization initiator and optionally a chain transfer agent by any of various methods such as solution polymerization, bulk polymerization, emulsion polymerization, dispersion

polymerization and suspension polymerization in a conventional way or by controlled polymerization techniques. In preparing a coating composition using this polymer, the polymer is preferably diluted with an organic solvent to give a polymer solution having an appropriate viscosity. From this standpoint, it is desirable to employ solution polymerization.

Examples of suitable initiators for free-radical polymerization include azo compounds such as dimethyl 2,2'-azobis(2-methylpropionate), 2,2'-azobis(2-methylbutyronitrile), 2,2'-azobis(isobutyronitrile) and 1,1'-azobis(cyanocyclohexane); and peroxides such as *tert*-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.

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, ethylene glycol methyl ether acetate, propyl propionate, n-butyl propionate, isobutyl isobutyrate; ethers such as ethylene glycol dimethyl ether, diethylene glycol dimethyl ether, dibutyl ether, dioxane, tetrahydrofuran, alcohols such as n-butanol, isobutanol, 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. These compounds are used alone or as a mixture of two or more thereof. Preferred are mixtures of aromatic hydrocarbons and one or more solvent selected from ketones, esters, ethers, alcohols and ether alcohols.

The acrylic copolymer may be a random copolymer, an alternating copolymer, a gradient copolymer or a block copolymer. The acrylic copolymer is preferably a random copolymer.

Other Binder components

In addition to components (i), (ii) and (iii) described above, an additional
5 binder can be used to adjust the properties of the antifouling coating film. 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 poly(methyl vinyl ether),
10 poly(ethyl vinyl ether), poly(isobutyl vinyl ether), poly(vinyl chloride-*co*-isobutyl
vinyl ether);

(meth)acrylic homopolymers and copolymers, such as poly(*n*-butyl acrylate)
and poly(*n*-butyl acrylate-*co*-isobutyl vinyl ether);

polymeric plasticizers from any of the polymer groups specified above. The
15 term polymeric plasticizer refers to polymers having a glass transition temperature
(*T_g*) below 25°C.

Additional examples of other binders that may be present in the antifouling
coating composition of the invention include:

silyl ester (meth)acrylate copolymers, such as copolymers comprising
20 triisopropylsilyl acrylate;

metal (meth)acrylate copolymers, such as copolymers comprising zinc
(meth)acrylate, zinc hydroxide (meth)acrylate, zinc neodecanoate (meth)acrylate or
zinc oleate (meth)acrylate;

saturated aliphatic polyesters, such as poly(lactic acid), poly(glycolic acid),
25 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;

polyoxalates as described in WO2009100908;

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

dimerized and polymerized rosin;

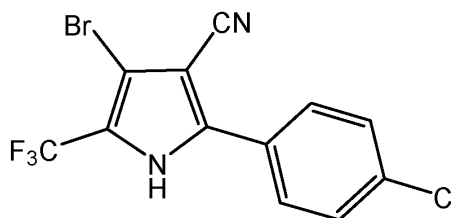
alkyd resins and modified alkyd resins;

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.

If, in addition to components (i), (ii) and (iii), a further binder is present, the weight ratio of binder (A):binder may range from 70:30 to 99:1, preferably from 75:25 to 95:5, especially 80:20 to 90:10.

10 Biocide

The antifouling coating composition additionally comprises a compound capable of preventing or removing marine fouling on or from a surface. In this regard, 4-bromo-2-(4-chlorophenyl)-5-(trifluoromethyl)-1H-pyrrole-3-carbonitrile [tralopyril], having the structure below, must be present.



Example of commercial available tralopyril include Econeal from Janssen PMP.

In addition to this biocide, other antifouling compounds can be present. 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.

Preferred additional biologically active agents are zinc pyrithione, copper pyrithione, zinc ethylenebis(dithiocarbamate) [zineb], 2-(tert-butylamino)-4-(cyclopropylamino)-6-(methylthio)-1,3,5-triazine [cubutryne], 4,5-dichloro-2-n-octyl-4-isothiazolin-3-one [DCOIT], N-dichlorofluoromethylthio-N',N'-dimethyl-N-

phenylsulfamide [dichlofluanid], N-dichlorofluoromethylthio-N',N'-dimethyl-N-p-tolylsulfamide [tolylfluanid], triphenylborane pyridine [TPBP] and 4-[1-(2,3-dimethylphenyl)ethyl]-1H-imidazole [medetomidine].

5 In one embodiment, the composition does not comprise 4-[1-(2,3-dimethylphenyl)ethyl]-1H-imidazole [medetomidine].

A mixture of biocides can be used as is known in the art as different biocides operate against different marine fouling organisms.

10 More preferred is a mixture of biocides active against marine invertebrates, such as barnacles, tubeworms, bryozoans and hydroids; plants, such as seaweed, algae and diatoms; and bacteria. In this regard, the most preferred option is a combination of tralopyril and one or more selected biocides selected from zinc pyrithione, copper pyrithione, zineb, dichlofluanid, and 4,5-dichloro-2-octyl-4-isothiazolin-3-one.

15 In one embodiment, the composition comprises less than 0.5 wt% of an inorganic copper biocide, preferably less than 0.2 wt% of an inorganic copper biocide, even more preferably less than 0.1 wt% of an inorganic copper biocide, relative to the total weight of the composition as a whole. Most preferably, the composition is free of an inorganic copper biocide.

20 In an alternative embodiment, the composition of the invention comprises copper pyrithione, an organometallic copper compound.

In an alternative embodiment, the composition is free of any copper based biocides.

25 The combined amounts of biocides (including tralopyril) may form up to 20 wt% of the coating composition, such as 0.5 to 15 wt%, e.g. 1.0 to 12 wt%. It will be appreciated that the amount of biocide will vary depending on the end use and the biocide used.

The amount of tralopyril used is low. Typical amounts in the composition are 0.5 to 10.0 wt%, such as 1.5 to 6.0 wt%, especially 2.0 to 4.5 wt%.

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

Other components

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

The 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 oxide, zinc sulfide, lithopone and graphite. Examples of organic pigments include carbon black, phthalocyanine blue, phthalocyanine green, naphthol red and diketopyrrolopyrrole red. Pigments may optionally be surface treated to be more easily dispersed in the paint composition.

Examples of extenders and fillers are minerals such as dolomite, platorite, calcite, quartz, barite, magnesite, silica, nepheline syenite, wollastonite, talc, chlorite, mica, kaolin, pyrophyllite and feldspar; synthetic inorganic compounds such as calcium carbonate, magnesium carbonate, barium sulphate, calcium silicate and silica; polymeric and inorganic microspheres such as uncoated or coated hollow and solid glass beads, uncoated or coated hollow and solid ceramic beads, porous and compact beads of polymeric materials such as poly(methyl methacrylate), poly(methyl methacrylate-co-ethylene glycol dimethacrylate), poly(styrene-co-ethylene glycol dimethacrylate), poly(styrene-co-divinylbenzene), polystyrene, poly(vinyl chloride).

Preferably the total amount of extender and/or pigment present in the compositions of the invention is 2-60 wt%, more preferably 5-50 wt% and still more preferably 7-45 wt%, based on the total weight of the composition. The skilled person will appreciate that the extender and pigment content will vary depending on the 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.

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

5 Examples of reinforcing agents are flakes and fibres. Fibres include natural and synthetic inorganic fibres and natural and synthetic organic fibres e.g. as described in WO 00/77102. Representative examples of fibres include mineral-glass fibres, wollastonite fibres, montmorillonite fibres, tobermorite fibres, atapulgitic fibres, calcined bauxite fibres, volcanic rock fibres, bauxite fibres, rockwool fibres, and processed mineral fibres from mineral wool. Preferably, the fibres have an
10 average length of 25 to 2,000 μm and an average thickness of 1 to 50 μm with a ratio between the average length and the average thickness of at least 5. Preferably reinforcing agents are present in the compositions of the invention in an amount of 0-20 wt%, more preferably 0.5-15 wt% and still more preferably 1-10 wt%, based on the total weight of the composition.

15 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
20 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 0-5.0 wt%, more preferably 0.2-3.0 wt% and still more preferably
25 0.5-2.0 wt%, based on the total weight of the coating composition.

 Examples of plasticizers are polymeric plasticizers, chlorinated paraffins, phthalates, phosphate esters, sulphonamides, adipates, epoxidised vegetable oils and sucrose acetate isobutyrate. Preferably plasticizers are present in the compositions of the invention in an amount of 0-10 wt%, more preferably 0.5-7 wt% and still more
30 preferably 1-5 wt%, based on the total weight of the coating composition.

 Dehydrating agents and stabilizers improve the storage stability of the antifouling coating compositions. The dehydrating agent is preferably a compound

which removes moisture and water from the coating composition. It is also referred to as water scavenger or drying agent. The dehydrating agents may be hygroscopic materials that absorb water or bind water as crystal water. These are often referred to as desiccants. Examples of such compounds include anhydrous calcium sulphate, calcium sulphate hemihydrate, anhydrous magnesium sulphate, anhydrous sodium sulphate, anhydrous zinc sulphate, molecular sieves and zeolites. The dehydrating agents may also be compounds that chemically react with water. Examples of dehydrating agents that react with water include orthoesters such as trimethyl orthoformate, triethyl orthoformate, tripropyl orthoformate, triisopropyl orthoformate, tributyl orthoformate, trimethyl orthoacetate, triethyl orthoacetate tributyl orthoacetate and triethyl orthopropionate; ketals; acetals; enolethers; orthoborates such as trimethyl borate, triethyl borate, tripropyl borate, triisopropyl borate, tributyl borate and tri-*tert*-butyl borate; organosilanes such as trimethoxymethylsilane, triethoxymethylsilane, tetraethoxysilane, phenyltrimethoxysilane, vinyltrimethoxysilane, vinyltriethoxysilane and ethyl polysilicate; and isocyanates, such as p-toluenesulfonyl isocyanate.

The preferred dehydrating agents are organosilanes, such as tetraethoxysilane, and inorganic desiccants. The use of a organosilane is especially preferred.

Stabilizers are preferably acid scavengers. Examples of stabilizers are carbodiimide compounds, such as bis(2,6-diisopropylphenyl)carbodiimide, bis(2-methylphenyl)carbodiimide, 1,3-di-*p*-tolylcarbodiimide and others as described in WO2014064049.

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

It is highly preferred if the antifouling composition contains a solvent. This solvent is preferably volatile and is preferably organic. Examples of organic solvents and thinners are aromatic hydrocarbons such as xylene, toluene, mesitylene; ketones such as methyl ethyl ketone, methyl 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,
5 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 solvents, especially xylene and mixtures of
10 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 40 wt% of the composition, such as up to 35 wt% but may be as low as 15 wt% or less, e.g. 10 wt% or less. Again, the skilled person will appreciate that some raw materials
15 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.

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.

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

More preferably the antifouling coating composition should have a content of volatile organic compounds (VOC) below 500 g/L, preferably below 420 g/L,
25 more preferably below 400 g/L, e.g. below 380 g/L. VOC content can be calculated (ASTM D5201-01) or measured, e.g. as described in US EPA Method 24 or ISO 11890-2, preferably measured.

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
30 permanently or intermittently underwater (e.g. through tide movement, different cargo loading or swell). The object surface will typically be the hull of a vessel or surface of a fixed marine object such as an oil platform or buoy. Application of the

coating composition can be accomplished by any convenient means, e.g. via painting (e.g. with brush or roller) or spraying the coating onto the object. Typically, the surface will need to be separated from the seawater to allow coating. The application of the coating can be achieved as conventionally known in the art.

- 5 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 mixtures thereof). Starting with an uncoated surface (e.g. steel, aluminium, plastic, composite, glass fiber or carbon fiber) the full coating system will typically comprise one or two layers of 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.
- 10
- 15 In 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.

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

Examples

Materials and methods

25 Testing

Determination of polymer solution viscosity

- The viscosity of the polymers was determined in accordance with ASTM D2196 Test Method A using a Brookfield DV-I viscometer with LV-2 or LV-4 spindle at 12 rpm. The polymer solutions were tempered to $23.0\text{ }^{\circ}\text{C} \pm 0.5\text{ }^{\circ}\text{C}$ before the
- 30 measurements.

Determination of non-volatile matter content of the polymer solutions

The non-volatile matter content in the polymer solutions was determined in accordance with ISO 3251. A test sample of $0.5 \text{ g} \pm 0.1 \text{ g}$ was taken out and dried in a ventilated oven at $150 \text{ }^{\circ}\text{C}$ for 30 minutes. The weight of the residual material was considered to be the non-volatile matter (NVM). The non-volatile matter content is expressed in weight percent. The value given is the average of three parallel measurements.

Determination of polymer molecular weights distribution

The polymers were characterised by Gel Permeation Chromatography (GPC) measurement. The molecular weight distribution (MWD) was determined using a Malvern Omnisec Resolve and Reveal system with two PLgel $5 \text{ }\mu\text{m}$ Mixed-D columns from Agilent in series, tetrahydrofuran (THF) as eluent at a constant flow rate of 1 ml/min and with a refractive index (RI) detector. The columns were calibrated using narrow polystyrene standards Polystyrene Medium EasiVials (4 ml) Red, Yellow and Green from Agilent. The column oven temperature and the detector oven temperature were $35 \text{ }^{\circ}\text{C}$. The sample injection volume was $100 \text{ }\mu\text{l}$. The data were processed using Omnisec 5.1 software from Malvern. Samples were prepared by dissolving an amount of polymer solution corresponding to 25 mg dry polymer in 5 ml THF. The samples were kept for minimum 3 hours at room temperature prior to sampling for the GPC measurements. Before analysis the samples were filtered through $0.45 \text{ }\mu\text{m}$ Nylon filters. The weight-average molecular weight (M_w) and the polydispersity index (PDI), given as M_w/M_n , are reported in the tables.

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. Samples were prepared by transfer of a small amount of polymer solution, corresponding to approx. 10 mg dry polymer material, to an aluminium pan and dry the samples for minimum 16-20 h at $50 \text{ }^{\circ}\text{C}$ with subsequent 3 h at $150 \text{ }^{\circ}\text{C}$ in a ventilated heating cabinet. The measurement was performed by

running a heat-cool-heat procedure, within a temperature range from -80 °C to 120 °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
5 ASTM E1356-08, of the second heating is reported as the Tg of the polymers.

Determination of acid value by colorimetric titration

The acid value of the polymers was determined according to the procedure described in ISO 2114:2000 Method A. A weighed quantity of the polymer solution was
10 dissolved in Jotun Thinner No. 17. Phenolphthalein was added as colour indicator and the solution was titrated with 0.1 M KOH solution in ethanol until a red colouration appeared and was stable for 10-15 s while the solution was stirred. The acid value for the dry polymers were calculated based on measured non-volatile matter of the tested polymer solution. The reported acid value is the average value of
15 three parallel measurements.

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
20 heated and maintained at the reaction temperature of 85 °C. A pre-mix of 50.0 parts triisopropylsilyl methacrylate, 30.0 parts 2-methoxy methacrylate, 10.0 parts n-butyl acrylate, 10.0 parts methyl methacrylate and 0.8 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. After further 1 hour
25 reaction, post-addition of a boost initiator solution of 0.2 parts 2,2'-azobis(2-methylbutyronitril) and 7.5 parts xylene was added. The reaction vessel was maintained at the reaction temperature for a further 1.5 hours. The reactor was then heated to 110 °C and kept at that temperature for 1 hour. Finally, 33.5 parts xylene was added and the reactor was cooled to room temperature. The parts given above
30 are all parts by weight.

Procedure for preparation of copolymer solution S8

Copolymer solution S8 was prepared using the process described for copolymer solution S1 above with a reaction temperature of 95°C and the amount of ingredients given in Table 1A.

5

General procedure for preparation of copolymer solution S2-S7 and CS1-CS2

A quantity of solvent 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 monomers, initiator and solvent was prepared. The pre-mix was charged to the reaction vessel at a constant rate over 2 hours under a nitrogen atmosphere. After further 1 hour reaction, post-addition of a boost initiator solution was added. 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 this temperature for 1 hour. Finally, the reactor was cooled to room temperature.

10
15Procedure for preparation of copolymer solution A1

49.5 parts xylene and 20.0 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 85°C. A pre-mix of 95.0 parts n-butyl acrylate, 4.2 parts methyl methacrylate, 2.8 parts methacrylic acid, 20.5 parts xylene and 1.60 parts 2,2'-azobis(2-methylbutyronitril) was prepared. The pre-mix was charged to the reaction vessel at a constant rate over 2.5 hours under a nitrogen atmosphere. After further 1 hour reaction a post-addition of a boost initiator solution of 0.32 parts 2,2'-azobis(2-methylbutyronitril) and 10.0 parts xylene was added. The reaction vessel was maintained at the reaction temperature for a further 1 hour and then cooled to room temperature. The amounts of ingredients are given in parts by weight.

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The copolymer solution had the following properties:

NVM: 49.4 wt%; Mw 28,700; Tg -35 °C; Acid number 19 mg KOH/g (dry polymer)

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Procedure for preparation of copolymer solution A2 to A4

The copolymer solutions were prepared using the procedure described for copolymer solution A1 with a reaction temperature of 95°C and with the amount of ingredients in the reactor charges, feed charges and boost charges as given in Table 1B.

- 5 Thinning of copolymer A3 was done prior to the cooling of the polymer solution to room temperature.

Preparation of zinc rosinate solution

- 10 1400 g solution of Portuguese gum rosin (60 % in xylene; acid number 109 mg KOH/g), 116.5 g zinc oxide and 57.5 g xylene were charged to a 2 L temperature controlled reaction vessel equipped with a stirrer, a Dean-Stark trap and a reflux condenser. The reaction mixture was heated to reflux. The reaction mixture was refluxed at 140-150°C until no more water condensed in the Dean-Stark trap. The produced solution of gum rosin zinc salt was filtered and diluted with xylene.
- 15 The zinc rosinate solution had a non-volatile matter of 64.1 wt%.

Table 1A. Silyl copolymer ingredients and properties (amounts given in parts by weight).

	Polymer	Copolymer solutions								Comparative	
		S1	S2	S3	S4	S5	S6	S7	S8	CS1	CS2
Reactor charge	Xylene	60.0	55.5	55.5	55.5	55.5	55.5	55.5	60.0	55.5	55.5
	Triisopropylsilyl methacrylate	50.0	51.1	53.6	56.5	56.9	57.0	65.9	55.0	56.2	-
	Triisopropylsilyl acrylate	-	-	-	-	-	-	-	-	-	57.7
	2-Methoxyethyl methacrylate	30.0	-	-	-	-	-	-	-	-	-
Feed charge	Tetrahydrofurfuryl acrylate	-	19.1	16.9	-	-	-	17.0	-	-	12.3
	2-(2-Ethoxyethoxy)ethyl acrylate	-	-	-	9.0	8.2	8.2	-	6.0	-	-
	n-Butyl acrylate	10.0	9.2	9.6	4.2	5.1	8.0	3.4	15.0	19.3	-
	Methyl methacrylate	10.0	20.7	19.9	30.3	29.8	26.8	13.7	24.0	24.5	30.0
Boost charge	2,2'-azobis(2-methylbutyronitril)	0.80	0.96	0.95	0.97	0.97	0.96	0.85	1.20	0.98	0.99
	Xylene	-	14.9	14.9	14.9	14.9	14.9	14.9	-	14.9	14.9
	2,2'-azobis(2-methylbutyronitril)	0.20	0.24	0.24	0.24	0.24	0.24	0.21	0.20	0.24	0.25
	Xylene	7.5	12.4	12.4	12.4	12.4	12.4	12.3	7.5	12.4	12.4
Thinning	Xylene	33.5	-	-	-	-	-	-	15.5	-	-
Copolymer solution properties	Non volatile matter (wt%)	49.4	54.7	54.6	54.3	54.2	54.3	54.5	54.4	53.6	54.3
	Viscosity (cP)	297	324	310	390	387	352	237	284	295	195
	Mw (kD)	45.6	24.3	24.9	26.6	26.4	26.3	22.1	23.4	22.8	19.0
	PDI	2.70	2.88	2.80	2.39	2.41	2.92	2.26	2.61	2.60	2.97
	Tg (°C)	42	37	38	42	43	40	34	32	37	32

Table 1B. Acrylic copolymer ingredients and properties (amounts given in parts by weight).

	Polymer	Acrylic copolymer solution			
		A1	A2	A3	A4
Reactor charge	Xylene	49.5	55.5	55.5	55.5
	1-Methoxy-2-propanol	20.0	7.5	7.5	7.5
Feed charge	n-Butyl acrylate	95.0	75.0	50.0	90.0
	Methyl methacrylate	4.2	22.0	49.0	5.0
	Methacrylic acid	2.8	3.0	1.0	5.0
	2,2'-azobis(2-methylbutyronitril)	1.60	1.60	1.70	1.30
	Xylene	20.5	-	-	-
Boost charge	2,2'-azobis(2-methylbutyronitril)	0.32	0.20	0.20	0.20
	Xylene	10.0	4.9	4.9	4.9
Thinning	Xylene	-	-	15.5	-
Copolymer properties	Non-volatile matter (wt%)	49.4	60.5	54.7	59.6
	Viscosity (cP)	98	627	712	407
	Mw (kD)	28.7	25.7	24.2	23.7
	PDI	3.12	2.90	2.63	2.96
	Tg (°C)	-35	-18	12	-30
	Acid number (mg KOH/g dry polymer)	19	19	6	32

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Table 2: Components for antifouling coating compositions

Chemical	Trade name and supplier	Purpose
Gum rosin	Portugese gum rosin, WW grade, AV Pound & Co.	Monocarboxylic acid
Tralopyril	Econea, Janssen PMP	Biocide
Zinc pyrithione	Zinc Omadine, Lonza	Biocide
Copper pyrithione	Copper Omadine, Lonza	Biocide
Encapsulated DCOIT	SeaNine TM Ultra, Dow Contains 80% DCOIT	Biocide

General procedure for preparation of antifouling coating compositions

10 The components were mixed in the proportions given in Table 3-4, Table 6-7 and Table 9. The mixture was dispersed in the presence of glass beads (approx. 2 mm in

diameter) in a paint can of 250 ml using a vibrational shaker for 15 minutes. The glass beads were filtered out before testing.

Determination of paint viscosity using Cone and Plate viscometer

- 5 The viscosity of the antifouling paint composition was determined in accordance with ISO 2884-1:1999 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 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.

- 15 Determination of König pendulum hardness of coating film

The hardness of the coating film was determined using a pendulum hardness tester. The tests were performed according to ISO 1522:2006.

- Each of the antifouling coating compositions was applied to a transparent glass plate (100×200×2 mm) using a film applicator with 300 µm gap size. The coating films were dried at 23°C and 50% relative humidity for 1 week and then dried at 50°C for 72 hours in a ventilated heating cabinet. The coating film hardness of the dry coating film was measured at a temperature of 23°C and 50% relative humidity using an Erichsen 299/300 pendulum hardness tester. The hardness is quantified as the number of pendulum swings to damp the amplitude from 6° to 3°. A higher number of swings indicates a higher hardness of the coating. The result is reported as the average of three parallel measurements on coating films after forced drying in the heating cabinet.
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Accelerated cracking testing of coating film

- 30 PVC panels were coated with Safeguard Plus (two-component polyamide cured vinyl epoxy based coating, manufactured by Chokwang Jotun Ltd., Korea) using airless spray. The panels were dried and cured according to the product application

guide. The antifouling coatings were applied on the cured, pre-coated panels using a film applicator with gap size of 800 μm . The applied coating films were dried for 72 h at 52 °C before immersion in seawater at 40 °C. At regular intervals, the panels are taken out and evaluated after drying under ambient conditions for 24 h and drying at 52 °C for 24 h. The panels were assessed for cracking visually and under 10 x magnifications and rated as described in ISO 4628-4:2005. The density and the size of the cracks were reported. The panels were then re-immersed. The result after 6 months of exposure is reported.

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

The polishing rate was determined by measuring the reduction in film thickness of a coating film over time. For this test PVC discs were used. The coating compositions were applied as radial stripes on the disc using a film applicator with a gap size of 600 μm . The thicknesses of the dry coating films were measured by a surface profiler. The initial dry film thickness will depend on the solids content of the applied antifouling coating composition and the speed of application. Typical initial dry film thickness for the tested coatings was $235 \pm 30 \mu\text{m}$.

The PVC discs were mounted on a shaft and rotated in a container in which seawater was flowing through. Natural seawater which has been filtered and temperature-adjusted to $25 \text{ }^{\circ}\text{C} \pm 2 \text{ }^{\circ}\text{C}$ was used. The speed of the rotated shaft provided an average simulated speed of 16 knots on the disc. The PVC discs were taken out at regular intervals for measuring the film thickness. The discs were rinsed and allowed to dry overnight at room temperature before measuring the film thicknesses.

The results were given as film consumption, i.e. the difference between the initial film thickness and the measured thickness at the given time. The coating film was considered to be polished through when a thin, non-polishing leached layer was remaining on the surface, typically 10-20 μm in thickness, or when the film was totally polished away from the surface. That is denoted as PT in the result tables.

The polishing index is obtained from the polishing rate between week 52 and week 78 divided by the polishing rate between week 26 and week 52. A coating film

having a polishing index value below 2.0 is considered to exhibit controlled polishing.

5 Table 3: Paint formulation compositions (amounts given in parts by weight).

		Paint examples				
		PA-1	PA-2	PA-3	PA-4	PA-5
Silyl copolymer solution (i)	S1	17.7	26.9	30.0	26.4	25.5
Monocarboxylic acid (ii)	Gum rosin solution (60 wt% in xylene)	18.7	11.7	12.5	12.5	12.9
Acrylic copolymer (iii)	A1	3.9	4.4	5.7	7.2	9.6
Biocides	Tralopyril	3.7	3.7	3.5	3.6	3.5
	Zinc pyrithione	3.2	3.2	3.0	3.1	3.0
Pigments and extenders	Iron oxide red	5.6	8.3	6.6	9.5	9.6
	Talc	-	8.8	9.1	9.7	10.4
	Dolomite	8.2	-	-	-	-
	Zinc phosphate	17.1	13.9	14.0	12.5	11.8
	Zinc oxide	11.8	11.1	8.9	8.2	6.7
Additives	Polyamide wax (20 wt% in xylene)	1.9	1.1	1.2	1.2	1.2
	Wetting agent	0.5	0.5	0.6	0.6	0.6
	Tetraethoxysilane	1.0	1.1	1.1	1.1	1.1
Solvent	Xylene	6.7	5.3	4.0	4.6	4.1

Table 4: Comparative paint formulation compositions (amounts given in parts by weight).

		Comparative examples								
		CPA-1	CPA-2	CPA-3	CPA-4	CPA-5	CPA-6	CPA-7	CPA-8	CPA-9
Silyl copolymer solution	S1	35.3	30.0	23.0	17.7	22.0	26.9	22.2	17.7	-
	CS2	-	-	-	-	-	-	-	-	17.7
Monocarboxylic acid (ii)	Gum rosin solution (60 wt% in xylene)	7.4	11.8	17.6	22.0	17.6	7.4	7.4	11.0	18.7
Acrylic copolymer (iii)	A1	-	-	-	-	1.0	13.4	13.1	13.1	3.9
	Tralopyril	3.7	3.7	3.7	3.7	3.7	3.4	3.7	3.7	3.7
Pigments and extenders	Zinc pyrrhione	3.2	3.2	3.2	3.2	3.2	2.9	3.2	3.2	3.2
	Iron oxide red	5.6	5.6	5.6	5.6	5.6	10.4	5.6	5.6	5.6
	Talc	-	-	-	-	-	5.6	-	-	-
	Dolomite	8.2	8.2	8.2	8.2	8.2	-	8.2	8.2	8.2
Additives	Zinc phosphate	17.1	17.1	17.1	17.1	17.1	13.2	17.1	17.1	17.1
	Zinc oxide	11.8	11.8	11.8	11.8	11.8	11.1	11.8	11.8	11.8
	Polyamide wax (20 wt% in xylene)	1.9	1.9	1.9	1.9	1.9	1.1	1.9	1.9	1.9
Solvent	Wetting agent	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
	Tetraethoxysilane	1.0	1.0	1.0	1.0	1.0	1.1	1.0	1.0	1.0
	Xylene	4.3	5.2	6.4	7.3	6.4	3.0	4.5	5.2	6.7

Table 5: Test results for paint examples with different binder compositions and comparative paint examples.

Paint	Binder (A) composition (wt%, dry solids)			Calc. VOC (g/L)	Viscosity (cP)	Pendulum hardness	Cracking 6 mth	Film consumption (μm)				Polishing index
	(i)	(ii)	(iii)					4 w	26 w	52 w	78 w	
PA-1	40	51	9	392	189	69	0	7	47	107	193	1.4
PA-2	59	31	10	392	465	61	0	5	41	127	209	1.0
PA-3	59	30	11	392	570	57	0	9	40	124	227	1.2
PA-4	54	31	15	392	486	51	0	6	49	133	198	0.8
PA-5	50	31	19	392	526	45	0	7	48	134	207	0.8
CPA-1	80	20	-	391	385	72	4(S4)	5	19	165	PT	-
CPA-2	68	32	-	391	330	76	0	5	14	182	PT	-
CPA-3	52	48	-	391	251	68	0	4	11	103	PT	-
CPA-4	40	60	-	391	137	72	0	7	16	37	170	6.3
CPA-5	50	48	2	391	210	68	0	6	16	137	PT	-
CPA-6	55	18	27	392	555	26	0	5	32	75	195	2.8
CPA-7	50	20	30	392	351	23	0	1	25	60	170	3.1
CPA-8	40	30	30	392	297	27	4(S3)	6	49	125	268	1.9
CPA-9	(40)	51	9	391	231	57	2(S2)	6	36	112	PT	-

The comparative examples CPA-1 to CPA-4 in Table 5 show that the polishing of the antifouling coating film is not controlled over a long period of time without the presence of component (iii) in the antifouling coating composition. The same applies when the amount of component (iii) is low, as shown in comparative example CPA-5.

The comparative examples CPA-6 to CPA-8 in Table 5 show that the antifouling coating films are soft and prone to mechanical damages when using high amount of component (iii) in the antifouling coating composition. The polishing of CPA-6 to CPA-7 is not controlled, as indicated by the high polishing index. The coating of CPA-8 has also poor cracking resistance.

The comparative examples CPA-9 in Table 5 shows that the use of a triisopropylsilyl acrylate copolymer gives an uncontrolled polishing of antifouling coating film.

Table 6: Paint formulation compositions (amounts given in parts by weight).

		Paint examples				
		PB-1	PB-2	PB-3	PB-4	PB-5
Silyl copolymer solution (i)	S2	19.8	-	-	-	-
	S3	-	19.8	-	-	-
	S4	-	-	19.7	-	-
	S5	-	-	-	19.7	-
	S6	-	-	-	-	26.0
Monocarboxylic acid (ii)	Gum rosin solution (60 wt% in xylene)	18.9	18.9	19.0	19.0	9.1
Acrylic copolymer (iii)	A1	4.0	4.0	4.0	4.0	3.4
Biocides	Tralopyril	2.5	2.5	2.5	2.5	2.5
	Zinc pyrithione	3.1	3.1	3.1	3.1	2.9
Pigments and extenders	Iron oxide red	6.9	6.9	6.9	6.9	8.8
	Talc	9.6	9.6	9.6	9.6	9.4
	Zinc phosphate	14.8	14.8	14.8	14.8	14.7
	Zinc oxide	9.4	9.4	9.4	9.4	11.8
Additives	Polyamide wax (20 wt% in xylene)	1.5	1.5	1.5	1.5	0.9
	Wetting agent	-	-	-	-	0.5
	Tetraethoxysilane	0.9	0.9	0.9	0.9	0.8
Solvent	Xylene	8.6	8.6	8.6	8.6	9.2

Table 7: Comparative paint formulation compositions (amounts given in parts by weight).

		Comparative examples								
		CPB-1	CPB-2	CPB-3	CPB-4	CPB-5	CPB-6	CPB-7	CPB-8	CPB-9
Silyl copolymer solution	S2	31.4	-	-	-	-	-	-	-	-
	S3	-	31.5	-	-	-	-	-	-	-
	S4	-	-	31.4	-	-	-	-	-	-
	S5	-	-	-	31.4	-	-	-	-	-
	S6	-	-	-	-	31.4	-	-	-	-
	CS1	-	-	-	-	-	19.9	26.2	-	-
Monocarboxylic acid (ii)	CS2	-	-	-	-	-	-	-	20.0	26.4
	Gum rosin solution (60 wt% in xylene)	7.0	7.0	7.0	7.0	7.0	19.0	9.2	18.9	9.1
Acrylic copolymer (iii)	A1	-	-	-	-	-	4.0	3.4	4.0	3.4
Biocides	Tralopyril	2.8	2.8	2.8	2.8	2.8	2.5	2.9	2.5	2.9
	Zinc pyrithione	2.5	2.5	2.5	2.5	2.5	3.1	2.5	3.1	2.5
	Iron oxide red	5.9	5.9	5.9	5.9	5.9	6.9	8.8	6.9	8.8
Pigments and extenders	Talc	6.9	6.9	6.9	6.9	6.9	9.6	9.4	9.6	9.4
	Zinc phosphate	18.2	18.2	18.3	18.3	18.3	14.8	14.7	14.8	14.7
	Zinc oxide	15.2	15.2	15.2	15.2	15.2	9.4	11.8	9.4	11.7
Additives	Polyamide wax (20 wt% xylene)	1.4	1.4	1.4	1.4	1.4	1.5	0.9	1.5	0.9
	Wetting agent	0.4	0.4	0.4	0.4	0.4	-	0.5	-	0.5
	Tetraethoxysilane	0.8	0.8	0.8	0.8	0.8	0.9	0.8	0.9	0.8
Solvent	Xylene	7.5	7.4	7.4	7.4	7.4	8.4	8.9	8.4	8.9

Table 8: Test results for paint examples with different silyl copolymers and comparative paint examples.

Paint	Binder (A) composition (wt%, dry solids)			Calc. VOC (g/L)	Viscosity (cP)	Pendulum hardness	Cracking 6 mth	Film consumption (μm)				Polishing index
	(i)	(ii)	(iii)					4 w	26 w	52 w	78 w	
PB-1	45	47	8	402	258	67	0	5	16	42	93	2.0
PB-2	45	47	8	402	249	64	0	4	15	41	71	1.2
PB-3	45	47	8	402	267	63	0	4	17	41	86	1.9
PB-4	45	47	8	402	257	62	0	4	15	37	66	1.3
PB-5	66	26	8	405	276	63	0	2	11	39	94	2.0
CPB-1	80	20	-	392	350	63	0	4	9	43	PT	-
CPB-2	80	20	-	392	356	64	0	3	9	30	244	10.0
CPB-3	80	20	-	392	363	66	0	3	8	38	PT	-
CPB-4	80	20	-	392	362	66	0	3	7	20	PT	-
CPB-5	80	20	-	392	336	65	0	3	7	19	53	2.8
CPB-6	44	48	8	392	183	70	0	3	7	12	19	1.4
CPB-7	66	26	8	405	220	61	0	2	4	8	12	1.0
CPB-8	(45)	47	8	402	159	58	Dissolved	13	PT	-	-	-
CPB-9	(67)	25	8	405	186	54	5(S3)	5	PT	-	-	-

The comparative examples CPB-1 to CPB-5 in Table 8 show that the polishing of the antifouling coating film is not controlled over a long period of time without the presence of component (iii) in the antifouling coating composition.

- 5 The comparative examples CPB-6 to CPB-7 in Table 8 show that the use of component (i) without hydrophilic monomer give too slow polishing to obtain sufficient release of antifouling agents over time.

- 10 The comparative examples CPB-8 to CPB-9 in Table 8 show that the use of a triisopropylsilyl acrylate copolymer gives an uncontrolled polishing of antifouling coating film.

Table 9: Paint formulation compositions (amounts given in parts by weight).

		Paint examples								
		PC-1	PC-2	PC-3	PC-4	PC-5	PC-6	PC-7	PC-8	PC-9
Silyl copolymer solution (i) Monocarboxylic acid and derivatives (ii)	S1	21.8	19.0	27.4	30.0	29.6	21.6	17.7	14.6	30.0
	Gum rosin solution (60 wt% in xylene)	19.0	17.6	12.9	12.5	12.3	-	18.8	20.1	12.5
	Zinc rosinate solution (64 wt% in xylene)	-	-	-	-	-	19.0	-	-	-
Acrylic copolymer (iii)	A1	4.0	3.2	7.4	5.7	5.6	3.9	-	-	-
	A2	-	-	-	-	-	-	3.3	-	-
	A3	-	-	-	-	-	-	-	8.8	-
	A4	-	-	-	-	-	-	-	-	4.9
Biocides	Tralopyril	3.1	3.7	3.6	3.5	3.4	3.1	3.7	4.9	3.5
	Zinc pyrithione	2.5	3.2	3.1	-	2.9	2.5	3.2	4.6	3.0
	Copper pyrithione	-	-	-	3.0	-	-	-	-	-
	Encapsulated DCOIT	-	-	-	-	1.1	-	-	-	-
Pigments and extenders	Iron oxide red	6.9	5.6	9.7	6.6	6.4	6.9	5.6	5.6	6.6
	Talc	9.6	-	10.0	9.1	8.9	9.5	-	-	9.1
	Dolomite	-	8.2	-	-	-	-	8.2	7.9	-
	Feldspar	-	-	10.1	-	-	-	-	-	-
Additives	Zinc phosphate	14.8	17.1	-	14.0	13.8	14.7	17.1	13.5	14.0
	Zinc oxide	9.4	11.8	8.4	8.9	8.7	9.3	11.8	10.7	8.9
	Polyamide wax (20 wt% in xylene)	1.5	1.9	1.2	1.2	1.1	1.4	1.9	1.9	1.2

		Paint examples								
		PC-1	PC-2	PC-3	PC-4	PC-5	PC-6	PC-7	PC-8	PC-9
	Wetting agent	-	0.5	0.6	0.6	0.5	-	0.5	0.6	0.6
	Tetraethoxysilane	0.9	1.0	1.1	1.1	1.1	0.9	1.0	1.0	1.1
Solvent	Xylene	6.5	6.3	4.5	3.8	4.4	7.2	7.2	5.8	4.6

Table 10: Test results for paint examples.

Paint	Binder (A) composition (wt%, dry solids)			Calc. VOC (g/L)	Viscosity (cP)	Pendulum hardness	Cracking 6 mth	Film consumption (μ m)		
	(i)	(ii)	(iii)					4 w	12 w	26 w
PC-1	45	47	8	402	330	58	0	7	15	38
PC-2	45	48	7	391	233	72	0	3	19	46
PC-3	54	31	15	392	442	57	0	5	24	66
PC-4	59	30	11	392	561	70	0	5	16	42
PC-5	59	30	11	392	544	59	0	5	16	44
PC-6	43	49	8	402	291	68	0	4	16	40
PC-7	40	51	9	391	227	74	0	3	12	30
PC-8	30	50	20	383	321	73	0	6	14	36
PC-9	59	30	11	391	550	62	0	4	11	29