

Antifouling Paint Composition

This invention relates to an antifouling paint composition comprising a (meth)acrylic copolymer comprising silyl ester groups, cuprous oxide and hollow spheres. The composition may additionally contain an acrylic copolymer and/or a monocarboxylic acid or metal salt thereof. The invention further relates to a method of protecting objects from fouling by applying the antifouling coating composition of the invention to the object, and to objects coated with the antifouling composition of the invention.

Background

Copper containing self-polishing paints are the most commonly used antifouling paints. Cuprous oxide is a broad-spectrum biocide active against animal fouling. After release into seawater, the cuprous oxide transforms into less toxic compounds relatively quickly and for this reason it can be used in antifouling paints at high concentration. However, reduction in the overall use of biocides would be beneficial from an environmental perspective as long as the overall performance of the antifouling paint could be maintained. Cuprous oxide is still a preferred biocide in antifouling paints but more efficient use of the added cuprous oxide will provide a more sustainable and more economical product.

The present inventors therefore sought an antifouling paint in which the levels of cuprous oxide could be reduced. However, reducing the cuprous oxide level is not trivial. If cuprous oxide content in the paint is reduced then there is a corresponding requirement to increase the content of something else to ensure that the other properties of the paint remain the same.

For example, cuprous oxide has a relatively low oil absorption compared to many of the typical fillers used in antifouling paints and therefore a 1:1 replacement by volume of cuprous oxide with a filler is not a viable solution as such a product will be much more viscous and will consequently require more solvent to keep the viscosity of the paint at an acceptable level for application. More solvent means more volatiles and many countries have strict limits on the volatile content in paints.

Simply substituting less of a higher oil absorbing filler is also problematic as the resulting paint composition will have a lower pigment volume concentration negatively affecting the properties of the coating film. Reformulating the antifouling paint to reduce the cuprous oxide content is therefore challenging.

5 The present inventors propose to use hollow spheres, in particular hollow microspheres, as a partial replacement for cuprous oxide. The inventors have surprisingly found that the use of hollow spheres as a partial replacement for cuprous oxide results not only in a functioning antifouling paint but is also associated with several further benefits.

10 The density of copper containing antifouling paints is close to 2 g/mL, meaning that a 20 L paint container supplied to customers weighs close to 40 kg. Replacing parts of the cuprous oxide (specific gravity 5.8 g/cm³) with light weight hollow spheres (specific gravity e.g. 0.2-0.5 g/cm³) can provide antifouling paint with much lower weight. If a 20 L can weigh 30 kg rather than 40 kg, handling
15 during transportation and in the shipyards will be easier, and fuel consumption under transportation will be lowered. In addition, if the same dry film thickness is applied to a substrate, such as a vessel, the reduction of weight of the antifouling coating on the vessel will be significant leading to less fuel consumption when such a vessel is sailing. Lower fuel consumption due to lighter weight will lead to reduced emission
20 of greenhouse gases.

 Organic solvents such as xylene are needed in solventborne paints to keep the viscosity at an acceptable level for application e.g. by spray application. Hollow spheres have a low oil absorption and high volume/weight ratio due to low specific gravity. The inventors have found that replacing cuprous oxide (or other
25 conventional fillers) with hollow spheres tends to reduce viscosity, meaning the amount of organic solvent can be reduced while still having a paint suitable for spray application. Reduction in volatile organic content (VOC) is advantageous from an environmental and health and safety point of view.

 The combination of reduced biocide level, lower VOC and lower density
30 products results in an antifouling product with an improved sustainability profile. In one embodiment, hollow spheres should preferably not be polymeric, due to the non-desirable environmental effect of plastic pollution being released during

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polishing of the paint on a vessel. The use of hollow glass or ceramic spheres is therefore preferred.

5 Removing some of the cuprous oxide and replacing with hollow spheres will also reduce cost as the price of cuprous oxide is high. If these aims can be achieved without any substantial loss in antifouling performance, such a product is clearly advantageous.

The literature does contain some paint compositions in which hollow spheres are used.

10 GB2099444 describes an anti-fouling composition containing a binder resin, biocide, solvent and hollow particles. The target in GB2099444 is to slow down biocide release in a coating that can be applied in high film thickness without cracking. The binders used in the examples are not based on silyl ester copolymers.

15 In WO2014/055418 an antifouling coating composition using an acrylic resin, fluorinated resin and/or fumed silica and copper flakes is described. Cuprous oxide is preferably to be avoided. The use of microspheres is exemplified in example 1 but not with a self-polishing silyl ester copolymer binder.

The present invention looks to provide a more sustainable, environmentally friendly, economic, low density antifouling coating composition with good antifouling performance in the context of a self-polishing antifouling coating.
20 Through the use of hollow spheres, in particular hollow microspheres, as a partial replacement for cuprous oxide, the inventors have surprisingly found that the resulting composition is not only a functioning antifouling paint, but is also associated with the benefits highlighted above.

25 **Summary of Invention**

Viewed from one aspect the invention provides an antifouling coating composition comprising:

- 30 (A) a binder comprising a (meth)acrylic copolymer comprising silyl ester groups (i);
(B) 2.0 to 30 % solids volume cuprous oxide; and
(C) 2.0 to 65 % solids volume hollow spheres.

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Viewed from another aspect the invention provides an antifouling coating composition comprising:

(A) a binder comprising a (meth)acrylic copolymer comprising at least one tri(C₁₋₆ alkyl)silyl (meth)acrylate monomer, preferably at least one triisopropylsilyl (meth)acrylate monomer;

(B) 2.0 to 30 % solids volume cuprous oxide; and

(C) 2.0 to 65 % solids volume hollow spheres.

Viewed from another aspect the invention provides an antifouling coating composition comprising:

(A) a binder comprising

(i) a (meth)acrylic copolymer comprising silyl ester groups, such as a copolymer comprising at least one tri(C₁₋₆ alkyl)silyl (meth)acrylate monomer, preferably at least one triisopropylsilyl (meth)acrylate monomer;

(ii) a monocarboxylic acid or metal salt thereof;

(B) 2.0 to 30 % solids volume cuprous oxide; and

(C) 2.0 to 65 % solids volume hollow spheres.

Viewed from another aspect the invention provides an antifouling coating composition comprising:

(A) a binder comprising a (meth)acrylic copolymer comprising silyl ester groups (i);

(B) 10 to 47 wt% cuprous oxide; and

(C) 0.25 to 15 wt % hollow spheres.

Viewed from one aspect the invention provides an antifouling coating composition comprising:

(A) a binder comprising

(i) a (meth)acrylic copolymer comprising silyl ester groups, preferably a copolymer comprising at least one tri(C₁₋₆ alkyl)silyl (meth)acrylate monomer, preferably at least one triisopropylsilyl (meth)acrylate monomer;

(ii) a monocarboxylic acid or metal salt thereof;

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(B) 10 to 47 wt% cuprous oxide; and

(C) 0.25 to 15 wt % hollow spheres

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
5 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.

Definitions

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The terms “marine antifouling coating composition”, “antifouling coating composition”, “antifouling paint 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. These terms are used interchangeably herein.

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The antifouling coating compositions of the invention should be considered to be “self-polishing” coatings. By “self-polishing” or “polishing” we mean that the coating is subject to a reduction in 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.

20

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.

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

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

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

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.

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The term (meth)acrylic copolymer comprising silyl ester groups defines the nature of a component of the binder essential in the invention. This component may

also be called the “silyl ester copolymer” and/or “(meth)acrylic silyl ester copolymer” herein.

The terms “(meth)acrylic polymer” and “(meth)acrylic copolymer comprising silyl ester groups” refers to polymers comprising repeating units derived from (meth)acrylate monomers. Generally, a “(meth)acrylic polymer” and “(meth)acrylic copolymer comprising silyl ester groups” will comprise at least 50 wt% 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 each monomer present in the polymer.

The term “(meth)acrylate” encompasses both methacrylate and acrylate.

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 the (meth)acrylic copolymer comprising silyl ester groups and any other components which together form a matrix giving strength and/or flexibility to the coating film. For example, the term “binder” used herein means the (meth)acrylic copolymer comprising silyl ester groups together with the monocarboxylic acid and optionally the acrylic copolymer, i.e. components (i), (ii) and (iii) as defined herein.

The term ‘T_g’ means glass transition temperature.

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.

The term cuprous oxide refers to the chemical compound copper(I) oxide, Cu₂O. 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.

The term “dry 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 ignoring the weight of any solvents.

Solids volume (SV) is a measure of the volume of solid film-forming ingredients that remain after the paint has dried. % Solids volume is expressed as:

$$\% \text{ SV} = (\text{Volume of solid components}) / (\text{Total wet paint volume}) \times 100$$

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Solids volume is a commonly used parameter in the coating industry.

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.

10 The term “antifouling agent” or “biocide” refers to a biologically active compound or a mixture of biologically active compounds that prevents or reduces the settlement and/or the growth of marine organisms on a surface.

Detailed description of invention

15 The invention relates to a new antifouling coating composition comprising a binder (A) comprising a (meth)acrylic copolymer comprising silyl ester groups (i). Preferably the (meth)acrylic copolymer comprising silyl ester groups (i) is a copolymer of at least one (meth)acrylate monomer and at least one silyl ester (meth)acrylate monomer. More preferably the (meth)acrylic copolymer comprising
20 silyl ester groups comprises a triisopropylsilyl (meth)acrylate monomer.

It is preferred if the binder (A) further comprises (ii) a monocarboxylic acid or metal salt thereof; and optionally (iii) a (meth)acrylic polymer; such as a (meth)acrylic polymer (iii-a) and/or a (meth)acrylic polymer (iv) as defined herein.

25 These binder components are used together with cuprous oxide and hollow spheres in particular weight/solids volume ratios to form the antifouling coating composition of the invention.

Through the use of hollow spheres in the coating composition, the amount of cuprous oxide can be reduced leading to more sustainable and environmentally friendly paints. Moreover, replacement of cuprous oxide with the hollow spheres
30 also enables a reduction in VOC content in the paint thus making stringent governmental restrictions on VOC content easier to achieve.

Furthermore, the paints of the invention are lighter than paints made with higher contents of cuprous oxide. Lower density leads to lower fuel costs both in terms of transportation of the product to a site of application and on a vessel which carries the coating. In a ship as large as a container vessel, the weight of the antifouling coating applied is significant. A reduction in the weight of that coating can reduce fuel costs for that vessel.

Finally, hollow spheres are less expensive than cuprous oxide. If an antifouling paint composition of similar efficacy can be prepared with reduced cuprous oxide then costs can be significantly reduced.

Despite the lower level of biocide, the antifouling performance of the compositions is maintained as we demonstrate in the examples. The new combination of the invention also occurs in the context of a self-polishing paint composition. The antifouling coatings of this invention are based on (meth)acrylic copolymers having pendant hydrolysable silyl groups. In seawater the copolymer will gradually degrade by hydrolysis of pendant silyl groups on the polymer backbone. The remaining (meth)acrylic copolymer, now containing pendant carboxylic acid groups, becomes sufficiently hydrophilic to be washed out or eroded away from the coating surface. This controlled dissolution or self-polishing effect provides a controlled release of the biocide in the coating, resulting in excellent antifouling efficiency and smooth surfaces and hence reduced frictional resistance. The use of hollow spheres in such a self-polishing paint composition is new.

Binder (A)

(Meth)acrylic copolymer comprising silyl ester groups (i)

The binder (A) comprises at least one (meth)acrylic copolymer comprising silyl ester groups (i).

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

The (meth)acrylic copolymers comprising silyl ester groups (i) comprise repeating units derived from (meth)acrylate monomers. Preferably the (meth)acrylic

copolymer comprising silyl ester groups (i) 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 copolymer comprising silyl ester groups (i) comprises at least 80 wt%, more preferably at least 85 wt% and still more preferably at least 90 wt% repeating units derived from (meth)acrylate monomers. Preferred (meth)acrylic copolymers comprising silyl ester groups 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.

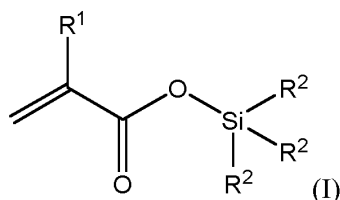
In one preferred embodiment the (meth)acrylic copolymers comprising silyl ester groups comprise 100 wt% of structural units derived from (meth)acrylate monomers, i.e. they do not comprise any monomers of another type.

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 described in GB2576431. Alternatively, only one (meth)acrylic silyl ester copolymer binder (i) is used.

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

(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):



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;

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

5 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.

10 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, *tert*-butyldimethylsilyl (meth)acrylate, hexyldimethylsilyl (meth)acrylate, tri-2-ethylhexylsilyl (meth)acrylate, *tert*-butyldiphenylsilyl (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 preferably isopropyl therefore.

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The 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.

25 The (meth)acrylic silyl ester copolymer (i) preferably comprises at least 30 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 35 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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The (meth)acrylic silyl ester copolymer (i) preferably comprises less than 80 wt% silyl ester monomers e.g. those of formula (I), 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 the monomers present in the copolymer, more preferably at 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).

10 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.

15 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, 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, 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, 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, 4-glycidyoxybutyl (meth)acrylate and 2-(trimethylsilyloxy)ethyl (meth)acrylate; an organosiloxane group-containing (meth)acrylate, such as 3-tris(trimethylsiloxy)silylpropyl (meth)acrylate, α -(meth)acryloyloxypropyl- ω -butyl polydimethylsiloxane, α -(meth)acryloyloxypropyl- ω -trimethylsilyl polydimethylsiloxane, α -

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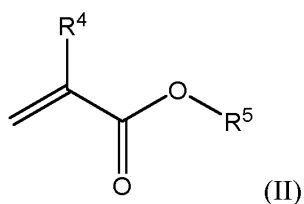
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(meth)acryloyloxyethyl- ω -trimethylsilyl polydimethylsiloxane and α,α' -(methyl methacryloyloxypropyl)-bis(ω -butyl) polydimethylsiloxanes.

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)



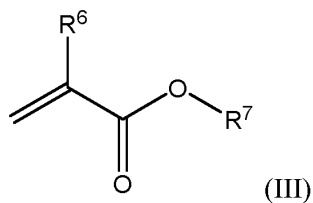
wherein R^4 is H or CH_3 , and R^5 is a C1-C20 hydrocarbyl substituent, preferably a C1-10 alkyl substituent, such as a C1-8 alkyl. The R^5 group can be linear or branched. Most preferably R^5 is a methyl, ethyl, propyl, butyl, hexyl, octyl or decyl group which (if possible) may be linear or branched. Ideally options for R^5 are methyl, ethyl, n-propyl, n-butyl or isobutyl.

Examples of suitable monomers of Formula (II) as monomer (a2) in (meth)acrylic silyl ester polymer (i) 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, and isobornyl (meth)acrylate.

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

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 C3-20 substituent containing at least one oxygen.

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 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) in this embodiment 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 isopropylidenglycerol methacrylate.

5 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.

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

If monomer (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.

15 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
20 methacrylate and 2-(2-ethoxyethoxy)ethyl acrylate.

Preferably, the content of the silyl ester monomer(s) (a1) in the (meth)acrylic silyl ester copolymer (i) (such as monomers of formula (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 the (meth)acrylic silyl ester copolymer as a whole.

25 Preferably, the (meth)acrylic silyl ester copolymer (i) comprises 20 to 70 wt% of the monomer (a2) (such as those of formula (II) or (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%.

30 Preferably, the (meth)acrylic silyl ester copolymer (i) comprises at least 15 wt% of the monomer 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 of Formula (III), more preferred 2.0 to 35 wt%.

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.

5 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.

 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
10 are preferred, such as less than 70 °C, e.g. less than 60 °C or less than 55 °C.

 The (meth)acrylic silyl ester copolymers (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.

15 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 3.0 to 25 wt%, in particular 5.0 to 20 wt% based on the total coating composition.

 In one preferred embodiment the antifouling coating composition of the
20 invention preferably comprises 5 to 40 wt% of the (meth)acrylic silyl ester copolymer (i), such as 7 to 30 wt%, in particular 10 to 25 wt% based on the total dry weight of the coating composition.

 In one preferred embodiment the antifouling coating composition of the
25 invention preferably comprises 5.0 to 60 solids vol% of the (meth)acrylic silyl ester copolymer (i), such as 10 to 50 solids vol%, in particular 15 to 40 vol% based on the total weight of the coating composition

 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.

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Monocarboxylic acid or a metal salt thereof (ii)

The antifouling coating composition of the present invention preferably comprises a monocarboxylic acid or metal salt thereof. This component forms part of the binder (A).

5 The monocarboxylic acid or metal salt thereof 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.

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

Metal salts of monocarboxylic acid include alkali metal carboxylate, alkaline earth metal carboxylate (e.g. calcium carboxylate, magnesium carboxylate) and transition metal carboxylate (e.g. zinc carboxylate, copper carboxylate).
15 Preferably the metal carboxylate is a transition metal carboxylate, particularly preferably the metal carboxylate is a zinc carboxylate or a copper carboxylate. The metal carboxylate may be generated in situ in the antifouling coating composition.

The term resin acids refers to mixtures of monocarboxylic acids present in rosin. Resin acids are also referred to as rosin acids.

20 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 rosin is derived from natural sources and as such typically exist as a mixture of acids.

25 Representative examples of sources of rosin 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.

Commercial grades of gum rosin typically have an acid value from 155 to
30 180 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
5 acids, dihydropimaric acids and tetrahydroabietic acids and modified mixtures of resin acids from natural sources such as partly hydrogenated rosin, fully hydrogenated rosin and disproportionated rosin.

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

10 Representative examples of C5-C24 acyclic aliphatic monocarboxylic acids include Versatic™ 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
15 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
20 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 rosin, modified rosin, acyclic C10 – C24 monocarboxylic acid, C6 – C20 cyclic monocarboxylic acid or metal salts thereof. Preferably the metal salts of the monocarboxylic acids are copper or zinc
25 salts of rosin or copper or zinc salts of modified rosin such as rosin, modified rosin or metal salts thereof.

More preferably the monocarboxylic acid is rosin or a metal salt of rosin.

Further preferred the monocarboxylic acid or metal salts thereof are gum
rosin, hydrogenated gum rosin, copper salt of gum rosin, zinc salt of gum rosin,
30 copper salt of hydrogenated gum rosin, zinc salt of hydrogenated gum rosin and mixtures thereof.

Gum rosin is most preferred.

In one embodiment, the antifouling coating composition contains less than 1.0 wt% of any liquid, acyclic, saturated C12-24 monocarboxylic acids or salts thereof or liquid, acyclic, branched C12-24 monocarboxylic acids or salts thereof, such as less than 0.5 wt%, especially less than 0.1 wt% of any liquid, acyclic, saturated C12-24 monocarboxylic acids or salts thereof or liquid, acyclic, branched C12-24 monocarboxylic acids or salts thereof. The coating composition may be free of any liquid, acyclic, saturated C12-24 monocarboxylic acids or salts thereof or liquid, acyclic, branched C12-24 monocarboxylic acids or salts thereof. The term liquid means at 23°C and 1 atm pressure.

The amount of monocarboxylic acid or the metal salt thereof present in the binder (A) is preferably 5.0 to 55 wt% (dry solids), more preferably 10 to 50 wt% (dry solids), further preferred 15-45 wt% (dry solids), based on the total weight of the binder (A).

The final antifouling coating composition of the invention preferably comprises 1.0 to 30 wt% of the monocarboxylic acid or metal salt thereof, such as 2 to 20 wt% (dry solids), in particular 3.0 to 15 wt% (dry solids) based on the total coating composition.

The final antifouling coating composition of the invention preferably comprises 2.0 to 25 solids volume % of the monocarboxylic acid or metal salt thereof, preferably 3.0 to 20% solids volume, such as 3.0 to 15% solids volume.

If a blend of monocarboxylic acids or metal salts thereof is used then these percentages refer to the total amounts of monocarboxylic acids or metal salts thereof present.

Viewed from another aspect the invention provides an antifouling coating composition comprising:

(A) a binder comprising

- (i) a (meth)acrylic copolymer comprising silyl ester groups;
- (ii) a monocarboxylic acid or metal salt thereof;

wherein the antifouling coating composition comprising 4.0 to 20 % solids volume of component (ii) and 10 to 60 % solids volume component (i);

(B) 2.0 to 30 % solids volume cuprous oxide; and

5 (C) 2.0 to 65 % solids volume hollow spheres.

(Meth)acrylic polymer (iii)

10 In some embodiments, the binder used in the antifouling coating composition of the invention comprises a (meth)acrylic polymer (iii). This too forms part of the binder component (A) of the composition.

In the context of the present invention, the term “(meth)acrylic polymer” refers to polymers comprising at least one monomer based on acrylic acid, methacrylic acid, esters of acrylic acid and or esters of methacrylic acid. In one
15 preferred embodiment the Binder A of the coating composition of the invention comprises (iii) a (meth)acrylic copolymer comprising 0.5 to 10 wt% (meth)acrylic acid monomers relative to the total weight of monomers in the copolymer.

It is a requirement that the copolymer (iii) is different to the copolymer (i) in the binder (A) of the invention.

20 The (meth)acrylic polymer (iii) of the invention comprises 10 wt% or less silyl ester monomers, e.g. those of formula (a1) above, preferably less than 5 wt%, such as less than 2 wt% or less than 1 wt% relative to the total weight of monomers present in the (meth)acrylic polymer (iii). Most preferred the (meth)acrylic polymer (iii) is free of any silyl ester groups.

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

30 It is further preferred if the (meth)acrylic polymer (iii) 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 (iii) comprise 100 wt% of structural units derived from (meth)acrylate monomers, i.e. they do not comprise any monomers of another type.

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

In one embodiment, the binder A in coating composition of the invention comprises at least one (meth)acrylic polymer (iii) in addition to the (meth)acrylic silyl ester copolymer (i) and the monocarboxylic acid (ii).

10 The (meth)acrylic polymer (iii) has a Tg below 10 °C, more preferred below 0 °C, even more preferred below -5 °C, further 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.

15 In one embodiment the (meth)acrylic polymer (iii) 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 (iii-a) is preferably in the range of 0.5 to 10 wt% such as 0.5 to 5.0 wt%, preferably 1.0 to 4.0 wt%.

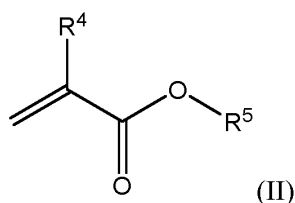
20 Preferably the (meth)acrylic polymer (iii) has acid number below 60 mg KOH/g polymer, more preferred below 40 mg KOH/g polymer, even more preferred below 25 mg KOH/g polymer. Preferably the acid number is above 2 mg KOH/g polymer, such as above 5 mg KOH/g polymer. The acid number is determined according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

25 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.

The (meth)acrylate monomers (a4) preferably form at least 50 wt% of the (meth)acrylic polymer (iii), such as at least 75 wt% or at least 80 wt%, especially 90 to 99.5 wt% such as 95.0 to 99.5 wt%.

30 The (meth)acrylic polymer (iii) 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:



5 wherein R^4 is H or CH_3 , and R^5 is a C1-C20 hydrocarbyl substituent, 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. Ideal options for R^5 are methyl, ethyl, n-propyl, n-butyl, isobutyl or
10 isooctyl.

 Preferences for formula (II) above described in connection with the silyl ester copolymer (i) also apply to (meth)acrylic polymer (iii).

 Examples of suitable monomers of Formula (II) as monomer (a4) in (meth)acrylic polymer (iii) include methyl (meth)acrylate, ethyl (meth)acrylate, n-butyl (meth)acrylate, isobutyl (meth)acrylate, tert-butyl (meth)acrylate, 2-ethylhexyl
15 (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) as monomer (a4) in
20 (meth)acrylic polymer (iii) include methyl methacrylate, ethyl acrylate, n-butyl acrylate, n-butyl methacrylate, 2-ethylhexyl acrylate, 2-octyl acrylate or isooctyl acrylate.

 Mixtures of different monomers of formula (II) may also be used in (meth)acrylic polymer (iii). The use of two different monomers of formula (II) is especially preferred. The use of two different monomers of formula (II) is
25 especially preferred along with (meth)acrylic acid.

 Preferably the (meth)acrylic polymer (iii) comprises structural units derived from (meth)acrylic acid monomers (a3) and (meth)acrylate monomers (a4).

In one preferred embodiment the (meth)acrylic polymer (iii) 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 and/or isooctyl acrylate.

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

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

 The (meth)acrylic polymer (iii) 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
15 composition as a whole.

 The (meth)acrylic polymer (iii) 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.

 The (meth)acrylic polymer (iii) is typically present in an amount of 2.0 to
20 15% solids volume, preferably 3.0 to 10% solids volume in the coating composition.

(Meth)acrylic copolymer (iv)

 In one embodiment binder A of the coating composition of the present invention may comprises a (meth)acrylic polymer (iv). This is different to the
25 (meth)acrylic silyl ester copolymer (i) or the (meth)acrylic polymer (iii).

 In one preferred embodiment the binder A of the coating composition of the present invention comprises the combination of a (meth)acrylic silyl ester copolymer (i), a monocarboxylic acid or metal salt thereof (ii) and a (meth)acrylic polymer (iii-a) and a (meth)acrylic copolymer (iv) as herein defined.

30 The (meth)acrylic polymer (iv) 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 Tg 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 (meth)acrylic polymer (iv) of the invention comprises 10 wt% or less silyl ester monomers, e.g. those of formula (a1) above, preferably less than 5 wt%,
5 such as less than 2 wt% or less than 1 wt% relative to the total weight of monomers present in the (meth)acrylic polymer (iv). Most preferred the (meth)acrylic polymer (iv) is free of any silyl ester groups.

The (meth)acrylic polymer (iv) preferably does not contain an acid monomer (a3).

10 The (meth)acrylic polymers (iv) of the present invention comprise repeating units derived from (meth)acrylate monomers. Preferably the (meth)acrylic polymer (iv) 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 (iv) comprises at least 60
15 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 (iv) comprise 100 wt% of structural units derived from (meth)acrylate monomers, i.e. they do not comprise any monomers of another type.

20 The (meth)acrylic polymer (iv) preferably 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, 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 (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-

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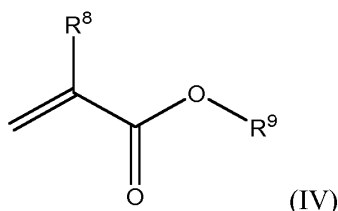
methoxy-2-oxoethoxy)-2-oxoethyl (meth)acrylate, 2-(2-ethoxy-2-oxoethoxy)-2-oxoethyl (meth)acrylate, oligo(oxycarbonylmethyl) methyl (meth)acrylate, oligo(oxycarbonylmethyl) ethyl (meth)acrylate, tetrahydrofurfuryl (meth)acrylate, glycerolformal (meth)acrylate, isopropylideneglycerol (meth)acrylate, glycerolcarbonate (meth)acrylate, cyclic trimethylolpropane formal (meth)acrylate, glycidyl (meth)acrylate and 4-glycidyloxybutyl (meth)acrylate;

More preferred examples of (meth)acrylate monomers (a5) are of formula (II) as hereinbefore defined for (meth)acrylic silyl ester copolymer (i).

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. It is especially preferred if (meth)acrylate polymer (iv) comprises two monomers of formula (II).

The (meth)acrylate monomer (a5) may also comprise hydrophilic groups. Examples of suitable monomers are shown in formula (IV) below:



wherein R^8 is H or CH_3 , and R^9 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^9 represents a poly(alkylene glycol) group.

The (meth)acrylic copolymer (iv) may comprise at least one monomer of Formula (IV) above in which the R^9 group is of formula $(CH_2CH_2O)_n-R^{10}$ where R^{10} 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^9 is of formula $(CH_2CH_2O)_n-R^{10}$ where R^{10} 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 (iv) comprises one or more of 2-methoxyethyl acrylate, or 2-(2-ethoxyethoxy)ethyl acrylate.

The (meth)acrylic polymer (iv) may comprise at least one monomer of Formula (IV) above in which the R^9 group is a poly(alkylene glycol) group such as a poly(ethylene glycol) group. Such a group might have a formula $(CH_2CH_2O)_m-R^{10}$ or $(CH_2CH(CH_3)O)_m-R^{11}$ where R^{11} 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 (M_n) of 300-1000, more preferably 300-550.

The (meth)acrylic polymer (iv) may also comprise at least one monomer of Formula (IV) above in which the R^9 group is of formula $(CH_2C(O)O)_p-R^{12}$ or $(CH(CH_3)C(O)O)_p-R^{12}$ where R^{12} 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 (iv) may comprise at least one monomer of Formula (IV) above in which the R^9 group is a cyclic group containing at least one oxygen or nitrogen atom, preferably at least one oxygen atom. More preferably, R^9 is a group $W-R^{13}$ having up to 40 carbon atoms wherein R^{13} 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.

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

Monomers of Formula (IV) preferably form at least 15 wt% of the (meth)acrylic polymer (iv). Particularly preferred amounts of the monomer of Formula (IV) in the copolymer (iv) are 10 to 65 wt%, preferably 15 to 60 wt%, such
10 as 18 to 50 wt%. Where a mixture of monomers of Formula (IV) are present, these amounts relate to the combined weight fraction of the monomers of Formula (IV) in the copolymer.

Monomers of Formula (II) preferably form at least 15 wt% of the (meth)acrylic polymer (iv). Particularly preferred amounts of the monomer of
15 Formula (II) in the copolymer (iv) are 20 to 90 wt%, preferably 50 to 90 wt%, such as 60 to 80 wt%. Where a mixture of monomers of Formula (II) are present, these amounts relate to the combined weight fraction of the monomers of Formula (II) in the copolymer.

In one preferred embodiment the (meth)acrylic polymer (iv) comprises at
20 least one monomer of formula (II) and at least one monomer of formula (IV).

In a preferred embodiment, the (meth)acrylic polymer component (iv) consists of monomers of Formula (II) and (IV) only.

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

The (meth)acrylic polymer (iv) 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
30 section.

The (meth)acrylic polymer (iv) preferably has a polydispersity index (PDI) of from 1.5 to 5.0.

The (meth)acrylic polymer (iv) 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. The (meth)acrylic polymer (iv) may be present in an amount of 5.0 to 30% solids volume, preferably 7.0 to 25 % solids volume. The
5 (meth)acrylic polymer (iv) 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 coating composition as a whole.

Preparation of (meth)acrylic silyl ester copolymer (i), and (meth)acrylic polymers(iii) and (iv)

10

The (meth)acrylic silyl ester copolymer (i), (meth)acrylic polymer (iii) and (meth)acrylic polymer (iv) 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
15 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. In preparing a coating composition
20 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.

Examples of suitable initiators for free-radical polymerization in solvent include azo compounds such as dimethyl 2,2'-azobis(2-methylpropionate), 2,2'-
25 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-
30 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
5 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,
10 isobutanol, methyl isobutyl carbinol, benzyl alcohol; ether alcohols such as 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.

Other Binder components

15

In addition to components (i), (ii), (iii) and (iv) described above, an additional 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
20 poly(ethylene glycol) copolymers;

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

metal (meth)acrylate copolymers, such as zinc (meth)acrylate copolymers
25 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;

30 alkyd resins and modified alkyd resins;

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

5 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;

10 plasticizers, such as polymeric plasticizers, non-reactive silicone oils, mineral oils, chlorinated paraffins, phthalates, phosphate esters, sulphonamides, adipates, epoxidized vegetable oils and sucrose acetate isobutyrate.

If, in addition to components (i), (ii) (iii) and (iv), further binder components are present, the weight of these components is preferably less than 20 wt% of the binder (A), such as less than 10 wt%.

15 It is preferred if no other binder components are present than the binder (A) consists of component (i), optionally component (ii) and optionally component (iii) and optionally component (iv).

Hollow Spheres

20 The antifouling paint composition of the invention must also comprise hollow spheres, in particular hollow microspheres. The term hollow implies a cavity

in the centre of the generally spherical particles. The hollow spheres are typically less than 1.0 mm in diameter and can be called microspheres herein.

It is preferred if the hollow spheres are inorganic in nature, i.e. ceramic or glass hollow spheres.

5 Preferably the hollow spheres are glass or ceramic spheres.

The hollow glass spheres may be made from glass materials such as fused silica glass, vitreous glass, soda lime borosilicate, sodium borosilicate glass, lead oxide glass, aluminosilicate glass, calcium sodium silicate glass and oxide glass.

10 Preferably the hollow glass spheres are made from sodium borosilicate or soda lime borosilicate.

Examples of suitable ceramic hollow spheres are spheres based on aluminosilicate.

15 The hollow spheres may be coated or uncoated. The hollow spheres may be treated or untreated. Treated hollow spheres are often treated with silanes, such as vinyl silane.

Preferably the hollow glass spheres are neutral or alkaline. The pH of the hollow spheres may be in the range of 7 to 12, preferably 7 to 10. The pH of the glass spheres can be determined by mixing the glass spheres in water at a 5 volume% loading and measure the pH of the slurry.

20 The antifouling paint composition comprises at least 2.0 solids vol% hollow spheres, preferably at least 5.0 solids vol%, more preferably at least 10 solids vol% hollow spheres. In some embodiments, e.g. where light weight hollow glass spheres are used, it is even preferred if there is at least 15 solids vol%, or even at least 20 solids vol% hollow spheres. The antifouling paint composition comprises less than

65 solids vol% hollow spheres, preferably less than 55 solids vol%, preferably not more than 50 solids vol%, such as below 40 solids vol%.

A minimum of 2.5 solids vol% of hollow spheres is preferred to achieve a significant reduction in the cuprous oxide content.

5 In wt%, the amount of hollow spheres preferred are in the range 0.1 wt% to 12.0 wt%, more preferred 0.4 wt% to 10.0 wt%, even more preferred 0.7 wt% to 7.0 wt%.

 The ratio (solids vol%/solids vol%) between hollow spheres and cuprous oxide is preferably in the range of 0.1 to 15, preferably 0.1 to 10, especially 0.5 to
10 5.0.

 The sum of the % solids volumes (vol%) of hollow spheres and cuprous oxide is preferably 15 to 70 solids vol%, especially 15 to 60 solids vol%, more preferably 20 to 50 solids vol%. The volume of hollow spheres is then sufficient to reduce the amount of cuprous oxide, reduce VOC and give a lighter product, while
15 maintaining good antifouling properties and mechanical properties. In one embodiment, the solids volume % of the hollow spheres is higher, such as at least 1% higher, than the solids volume of the cuprous oxide.

 In the examples below, we exemplify a ratio of the solids volume of hollow
20 spheres to solids volume of cuprous oxide in the inventive examples are from 0.1:1 to 10:1, the preferred ratio of spheres to cuprous oxide is around 1, e.g., 0.5:1 to 3:1.

 The hollow spheres of the invention are generally microspheres. The size of the spheres should not be too large as it will increase the surface roughness of the

coating and it may affect application by airless spray. The sizes of the hollow microspheres are given by the supplier, generally as d50 or as a range of sizes.

The (d50) may be in the range of 10 to 100 μm , more preferred 10 to 90 μm , even more preferred 15 to 70 μm , most preferred 15 to 55 μm .

5 The topcut (d90) may be 200 μm or less, more preferred 150 μm or less, even more preferred 120 μm or less.

There is really no absolute lower limit on particle size, but if very small particles are used the benefit of reduced density will be less significant. D50 sizes of 1 μm or more are preferred.

10 The particle sizes of the hollow spheres can be determined using e.g. sieves and laser diffraction analysis. The density of the hollow spheres varies with the nature of the hollow sphere in question. For hollow ceramic spheres or hollow glass spheres with somewhat higher density the limits in vol% are somewhat lower. The density of the hollow spheres of the invention may range from 0.1 to 1.0 g/cm^3 .

15 The crush strength of the hollow spheres should preferably be at least 1500 psi, such as at least 3000 psi to withstand spray application and the shear forces during paint preparation (grinding). If low crush strength hollow spheres are used, they should not be included in the grinding phase and they might not withstand spray application of the paint which should thus be applied with brush or roller.

20 Suitable hollow glass spheres are commercially available e.g., glass bubbles K, S, iM and XLD Series from 3M or Q-cel and Sphericel® from Potters, hollow glass microspheres from Sinosteel Maanshan and SMC Minerals and Chemicals, poraSpheres from Poraver, Eccospheres from Trelleborg, hollow glass from Cenostar. Cenospheres are available e.g., from Cenostar, Fillite from Omya.

25

Biocide

The terms antifouling agent, anti-foulant, biocide, toxicant are used in the industry to describe known compounds that act to prevent marine fouling on a surface. The antifouling agents of the invention are marine antifouling agents.

30 The coating composition include cuprous oxide. The cuprous oxide material has a typical particle diameter distribution of 0.1-70 μm and an average particle size (d50) of 1-25 μm . The cuprous oxide material may comprise a stabilizing agent to

prevent surface oxidation and agglomeration. Examples of commercial available cuprous oxide include Nordox Cuprous Oxide Red Paint Grade, Nordox XLT from Nordox AS, Cuprous oxide from Furukawa Chemicals Co., Ltd.; Red Copp 97N, Purple Copp, Lolo Tint 97N, Chemet CDC, Chemet LD from American Chemet Corporation; Cuprous Oxide Red from Spiess-Urania; Cuprous oxide Roast, Cuprous oxide Electrolytic from Taixing Smelting Plant Co., Ltd.

The antifouling coating composition of the invention may have 2.0 to 30 solids vol% of cuprous oxide, preferably 5.0 to 25 % solids volume, more preferably 5.0 to 20 % solids volume.

The antifouling coating composition of the invention may have 10 to 47 wt% of cuprous oxide, such as 12 to 40 wt% by the total weight of the coating composition. The coating composition may contain 10 to 30.0 wt% cuprous oxide, such as 10 to 27 wt% cuprous oxide.

The coating compositions of the invention may contain additional antifouling agents.

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

Examples of inorganic antifouling agents are copper thiocyanate, copper sulfide and metallic copper such as copper powder or copper flakes.

Examples of organometallic marine antifouling agents include zinc pyrithione, copper pyrithione, zinc bis(dimethyldithiocarbamate) [ziram], zinc ethylenebis(dithiocarbamate) [zineb], copper di(ethyl 4,4,4-trifluoroacetoacetate) and copper and zinc compounds as described in WO2021113564A1.

Examples of organic 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 [dichlofluanid], *N*-dichlorofluoromethylthio-*N'*,*N'*-dimethyl-*N*-*p*-tolylsulfamide [tolylfluanid], *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, 4-

[1-(2,3-dimethylphenyl)ethyl]-1H-imidazole [medetomidine] and 4-bromo-2-(4-chlorophenyl)-5-(trifluoromethyl)-1H-pyrrole-3-carbonitrile [tralopyril].

Other examples of marine antifouling agents may be tetraalkylphosphonium halogenides, guanidine derivatives such as dodecylguanidine monohydrochloride; macrocyclic lactones including avermectins and derivatives thereof such as ivermectine; spinosyns and derivatives such as spinosad; capsaicin and derivatives such as phenylcapsaicin; and enzymes such as oxidase, proteolytically, hemicellulolytically, cellulolytically, lipolytically and amylolytically active enzymes.

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 [dichlofluanid], N-dichlorofluoromethylthio-N',N'-dimethyl-N-p-tolylsulfamide [tolylfluanid], triphenylborane pyridine [TPBP], 4-[1-(2,3-dimethylphenyl)ethyl]-1H-imidazole [medetomidine], 4-bromo-2-(4-chlorophenyl)-5-(trifluoromethyl)-1H-pyrrole-3-carbonitrile [tralopyril], copper di(ethyl 4,4,4-trifluoroacetoacetate) and phenylcapsaicin. More preferred biocides are zinc pyrithione, copper pyrithione, zinc ethylenebis(dithiocarbamate) [zineb], 4,5-dichloro-2-n-octyl-4-isothiazolin-3-one [DCOIT], 4-[1-(2,3-dimethylphenyl)ethyl]-1H-imidazole [medetomidine] and 4-bromo-2-(4-chlorophenyl)-5-(trifluoromethyl)-1H-pyrrole-3-carbonitrile [tralopyril].

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

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.

The use of cuprous oxide and copper pyrithione is especially preferred.

The combined amounts of biocides may form up to 55 wt% of the coating composition, such as 10 to 55 wt%, e.g. 15 to 50 wt%. The combined amounts of biocides in the dry coating composition, may form up to 40 vol% of the dry coating composition, e.g. up to 35 vol%, or up to 30 vol%, preferably the combined amounts

of biocides make up at least 5 vol% of the coating composition, such as at least 10 vol%.

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.

Viewed from another aspect the invention provides an antifouling coating composition comprising:

(A) a binder comprising a (meth)acrylic copolymer comprising silyl ester groups (i);

(B) 2.0 to 30 % solids volume cuprous oxide; and

(C) 2.0 to 65 % solids volume hollow spheres.

wherein the total amount of cuprous oxide and hollow spheres combined is in the range of 15 to 70 % solids volume.

In particular, the invention provides an antifouling coating composition comprising:

(A) a binder comprising a (meth)acrylic copolymer comprising silyl ester groups (i);

(B) 4.0 to 25 % solids volume cuprous oxide; and

(C) 4.0 to 60 % solids volume hollow spheres.

wherein the total amount of cuprous oxide and hollow spheres combined is in the range of 15 to 65 % solids volume.

Pigments and extenders

The coating compositions of the invention may further comprise pigments and/or extenders.

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 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.

A variety of inorganic or organic surface treatments may be used, e.g. to improve 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.

The extenders may be natural minerals or synthetic materials. Examples of inorganic extenders include dolomite, plastorite, 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.

The use of zinc oxide is especially preferred. It is however preferred that there is no more than 15 % solids volume in the antifouling composition of the invention.

Preferably the total amount of extender and/or pigment present in the compositions of the invention is 1 to 40 wt%, more preferably 2 to 30 wt% and still more preferably 4 to 20 wt%, based on the total weight of the composition. Hollow spheres and biocides are here not included as a pigment and/or filler. Preferably the total amount of extender and/or pigment present in the compositions of the invention is 1 to 30% solids volume, more preferably 2 to 20% solids volume, such as 4 to 15% solids volume. 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.

Other components

The antifouling coating composition according to the present invention may optionally further comprise one or more components selected among additives, solvents and thinners.

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

- 5 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 0-5.0 wt%, more preferably 0.2-3.0 wt% and still more preferably 0.5-2.0 wt%, based on the total weight of the coating composition.
- 10 Dehydrating agents 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 or desiccant. The dehydrating agents may be hygroscopic materials that absorb water or bind water as crystal water or compounds that
- 15 chemically react with water. Examples of such dehydrating agents include anhydrous calcium sulphate, calcium sulphate hemihydrate, anhydrous magnesium sulphate, anhydrous sodium sulphate, anhydrous zinc sulphate, molecular sieves, zeolites, orthoesters such as trimethyl orthoformate, triethyl orthoformate, tripropyl orthoformate, triisopropyl orthoformate, tributyl orthoformate, trimethyl
- 20 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; alkoxysilanes such as trimethoxymethylsilane, triethoxymethylsilane, tetraethoxysilane, phenyltrimethoxysilane, vinyltrimethoxysilane,
- 25 vinyltriethoxysilane and ethyl polysilicate; and isocyanates, such as p-toluenesulfonyl isocyanate.
- 30

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 tetraethoxysilane is especially preferred.

5 Preferably the dehydrating agent is added to the compositions of the invention in an amount of 0-5 wt%, more preferably 0.5-2.5 wt%, such as 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
10 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
15 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;
20 and optionally a mixture of two or more solvents and thinners.

Preferred solvents are aromatic hydrocarbon solvents ketone solvents and ether alcohols, 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 40 wt% of the
25 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 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.

30 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 antifouling coating composition of the invention should preferably have a solids volume above 45%, preferably above 50%, preferably above 55%, such as e.g., 60%.

5 More preferably the antifouling coating composition should have a content of volatile organic compounds (VOC) below 500 g/L, preferably below 420 g/L, more preferably below 400 g/L, e.g. below 380 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.

10 Pigment volume concentration (PVC) of formulations containing hollow spheres is preferably 35% to 80%, such as 40% to 65%.

Density of the paint is preferably from 1 g/cm³ to 1.8 g/cm³, e.g., 1.4-1.6, and density of the coating is preferably from 1 g/cm³ to 2.6, preferably 1.2 g/cm³ to 2.0 g/cm³.

15 The antifouling paint composition of the invention may have a viscosity of 150 to 2000 cP measured by Cone and Plate at 23 °C (ISO 2884-1:2006), such as 200 to 800 cP.

 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
20 as recommended by the suppliers of the ingredients and the mixing equipment.

Application

 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
25 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,
30 the surface will need to be separated from the seawater to allow coating. The application of the coating can be achieved as conventionally known in the art.

When applying the antifouling coating to an object (e.g. a ship hull) the surface of the object is 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. 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.

When two or more coats of antifouling coating composition is applied, the different coats can be antifouling coatings of different compositions.

The antifouling coating layers may differ in type, amount of biocide, 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.

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 underwater cleaning is for example described in WO2019170888, WO2020207791 and WO2020207792. Cleaning settings that can be used when using brushes is for example described in WO2021180588.

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

Examples

Materials and methods

5 Determination of polymer solution viscosity

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.

10

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 3251:2019. 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 expressed as weight fraction in percent. The value given is the average of three parallel measurements.

15

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. The columns were calibrated by conventional calibration using narrow polystyrene standards. The analysis conditions were as set out below.

25

Table 1

Detector	RI
Wavelength	640 nm
Flow cell volume	12 μL
Column Set	Agilent PLgel $5\text{ }\mu\text{m}$ 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 μ L
Autosampler Temperature	25 $^{\circ}$ C
Column Oven Temperature	35 $^{\circ}$ C
Detector Oven Temperature	35 $^{\circ}$ C
Data Processing	Omnisec 5.1
Calibration standards	Agilent Polystyrene Medium EasiVials (4 mL) Red, Yellow and Green

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.

- 5 Before analysis the samples were filtered through 0.45 μ m Nylon filters. The weight-average molecular weight (M_w) and the polydispersity index (PDI), given as M_w/M_n , are reported.

Determination of the glass transition temperature

- 10 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 $^{\circ}$ C to 150 $^{\circ}$ C, with a heating rate of 10 $^{\circ}$ C/min and cooling rate of 10 $^{\circ}$ C/min and using an empty pan as reference. The data were
- 15 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.

- 20 Samples were prepared by making drawdown of the polymer solutions on individual glass panels using an applicator with 100 μ m gap size. The glass panels were dried over night at room temperature and subsequently 24 hours at 50 $^{\circ}$ 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.

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.

Testing of antifouling performance on raft in Singapore

Poly(vinyl chloride) (PVC) panels (20 x 30 cm) that had been degreased with solvent and sanded for improved adhesion of the coating were used for the test. The panels were coated with a first coat of commercial tiecoat (Safeguard Plus, two-component polyamide cured vinyl epoxy based coating, manufactured by Chokwang Jotun Ltd, Korea) using airless spray. After a minimum drying time of 24 hours at room temperature a second coat of commercial antifouling paint (SeaQuantum Ultra S, one-component silyl acrylate antifouling coating, manufactured by Jotun Paints (Europe) Ltd, England). The curing/drying time and film thicknesses of the first and the second coat were within the recommended intervals in the technical data sheets for the products.

After a minimum drying time of 24 hours at room temperature the antifouling coating compositions of the invention were applied directly to the pre-coated PVC panels as a last coat using a film applicator with a 300 µm gap size. The test areas of the coating films were approx. 6cm x 20cm. The edges of the panels were sealed with a commercial antifouling product.

The panels were exposed on a raft in Singapore where the panels were submerged 0.5-1.5m below the sea surface. Microfouling organisms, such as biofilm or slime, which can easily be removed by hand, is not included in the rating. The panels were evaluated by visual inspection and rated according to the scale below. The score is given for the total fouling of animals; such as barnacles, tubeworms, mussels, sponges and hydroids.

Score/rating of animal fouling:

0 – Excellent – <5% of area fouled

- 1 – Good – 5-20% of area fouled
- 2 – Fair – 21-35% of area fouled
- 3 – Poor – 36-50% of area fouled
- 4 – Very poor – >50% of area fouled

5

Antifouling performance given for 4 months exposure in Singapore unless otherwise specified.

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 is calculated in accordance with ASTM D5201-01.

Gravimetric water uptake in freshwater/deionized water

15

The water uptake in the coating films were determined by gravimetric method. The paints were applied on pre-weighed and numbered sandblasted glass panels (5.0 x 7.5 cm) using a film applicator with 300µm gap size. The films were dried under ambient conditions for at least 1 day, at 50 °C overnight and then in a desiccator under vacuum for 24 h. After drying, the coated glass panels were weighed and placed in containers filled with distilled water. At the time of the reading, the panels and paint surfaces were quickly dried using compressed air. The panels were weighed (m_{directly}) and thereafter allowed to dry under ambient conditions for 2 days and then placed in a desiccator under vacuum for 24 hours before they were weighed again (m_{dry}). The difference in weight before and after drying relative to the dry weight of the paint film after exposure is expressed as the water uptake in percentage.

20

25

$$\text{Amount of water uptake (wt\%)} = (m_{\text{directly}} - m_{\text{dry}}) / (m_{\text{dry}} - m_{\text{empty panel}}) \times 100$$

30

The readings were done after 5 weeks and 15 weeks, where the last reading is shown in the Tables. A water uptake below 50 wt% in 15 weeks is considered acceptable.

Accelerated cracking testing of coating films

Poly(vinyl chloride) (PVC) panels are coated with an appropriate anticorrosive primer. The antifouling coatings were applied on the panels using a film applicator with gap size of 800 μm . The panels were dried for 72 hours at 52 °C before immersion in seawater (SW) at 40 °C. At regular intervals, the panels are taken out and evaluated. The panels are evaluated for cracking visually and under 10 x magnifications upon drying at room temperature and again after drying at 52 °C for 24 hours. The panels were then re-immersed. The rating after drying at 52 °C are reported in the tables with the paint examples.

The panels were rated as follows:

0 – No cracks

1 – Very few cracks

2 – Moderate number of cracks

3 – Considerable number of cracks

4 – Dense cracking

Accelerated blistering testing of coating films

Poly(vinyl chloride) (PVC) panels are coated with an appropriate anticorrosive primer. The antifouling coatings were applied on the panels using a film applicator with gap size of 800 μm . The panels were dried for 72 hours at 52 °C before immersion in freshwater (FW) at 30 °C. At regular intervals, the panels are taken out and evaluated. The panels are evaluated for blistering visually at room temperature. The panels were then re-immersed. The ratings are reported in the tables with the paint examples.

The panels were rated as follows:

0 – No blisters

1 – Very few blisters

2 – Moderate number of blisters

3 – Considerable number of blisters

4 – Dense blistering

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

The polishing rate is determined by measuring the reduction in film thickness of a coating film over time. For this test poly(vinyl chloride) (PVC) discs are used. The coating compositions are applied as radial stripes on the disc using a film applicator with a gap size of 600 μm . The thickness of the dry coating films is measured by a surface profiler. Typical initial dry film will depend on the solids content of the applied antifouling coating composition and the speed of application. Typical initial film thickness for the tested coatings in the example part is 220 ± 20 μm . The PVC discs are mounted on a shaft and rotated in a container in which seawater is flowing through. The speed of the rotated shaft gives an average simulated speed of 16 knots on the disc. Natural seawater (SW) which has been filtered and temperature-adjusted to $30\text{ }^{\circ}\text{C} \pm 2\text{ }^{\circ}\text{C}$ is used. The PVC discs are taken out at regular intervals for measuring the film thickness. The discs are rinsed and allowed to dry overnight at room temperature before measuring the film thickness. The results are given as film reduction, i.e. the difference between the initial film thickness and the measured thickness at the given time. The coating film is considered to be polished through when a thin, non-polishing leached layer is remaining on the surface, typically 10-20 μm in thickness, or when the film is totally polished away from the surface. This is denoted as PT (if applicable) in the result tables.

Determination of degree of swelling in freshwater

The degree of swelling in freshwater (FW) is determined by measuring the change in film thickness of a coating film over time. For this test poly(vinyl chloride) (PVC) discs are used. The coating compositions are applied as radial stripes on the disc using a film applicator with a gap size of 300 μm . The thickness of the dry coating films is measured by a surface profiler. Typical initial dry film 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 in the example part is 100 ± 10 μm . The PVC discs are immersed in freshwater,

temperature-adjusted to $30\text{ }^{\circ}\text{C} \pm 2\text{ }^{\circ}\text{C}$. The PVC discs are taken out at 4 weeks and 8 weeks measuring the film thickness. The discs are rinsed and allowed to dry overnight at room temperature before measuring the film thickness. The results are given as the difference between the initial film thickness and the measured thickness

5 at the given time. An increase in film thickness is observed when the coating is swelling. Swelling as percentage of dry film thickness (DFT) is used for rating the degree of swelling as the coatings have different volume solids and hence will have different DFT.

10 Swelling was rated by the following scheme:

1 – $<30\%$ – good

2 – $30\text{-}50\%$ – acceptable

3 – $>50\%$ – poor, high degree of swelling

15

Binder Production Examples

Procedure for preparation of copolymer solution A1

40.0 parts xylene and 10.0 parts 1-methoxy-2-propanol were charged to a
5 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 90.0 parts n-butyl acrylate), 7.0 parts
n-butyl methacrylate, 3.0 parts methacrylic acid and 1.40 parts t-amyl peroxy-2-
ethylhexanoate was prepared. The pre-mix was charged to the reaction vessel at a
10 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 t-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
15 given above are all parts by weight.

The copolymer solution A1 had the following properties:

NVM 66.0 wt%; Viscosity 369 cP; Mw 22.1k; PDI 2.93; Tg -41 °C

Procedure for preparation of copolymer solution A2

20 48.5 parts xylene and 11.5 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 95 °C. A pre-mix of 40.0 parts 2-methoxyethyl acrylate,
60.0 parts methyl methacrylate and 1.60 parts 2,2'-azobis(2-methylbutyronitril) was
25 prepared. The pre-mix was charged to the reaction vessel at a constant rate over 2.5
hours under a nitrogen atmosphere using a metering pump. After further 1 hour
reaction a boost initiator solution of 0.40 parts 2,2'-azobis(2-methylbutyronitril) and
7.5 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 hour
30 and then cooled to room temperature. The parts given above are all parts by weight.

The copolymer solution A2 had the following properties:

NVM 55.9 wt%; Viscosity 1515 cP; Mw 24.5k; PDI 2.37; Tg 29 °C

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 85 °C. A pre-mix of 50.0 parts triisopropylsilyl methacrylate, 30.0 parts 2-methoxyethyl methacrylate, 10.0 parts n-butyl acrylate, 10.0 parts methyl methacrylate and 1.00 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 0.20 parts 2,2'-azobis(2-methylbutyronitril) and 7.4 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 110 °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 60.0 wt%; Viscosity 1790 cP; Mw 42.3k; PDI 3.11; Tg 37 °C

Copolymer solution S2 and S3 were prepared using the process described for copolymer solution S1 above.

Procedure for preparation of copolymer solution S4

41.6 parts methyl amyl ketone (2-heptanone) 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 100 °C. A pre-mix of 55.0 parts triisopropylsilyl methacrylate (TIPSMA), 20.0 parts n-butyl acrylate (n-BA), 25.0 parts methyl methacrylate (MMA) and 1.85 parts 2,2'-azobis(2-methylbutyronitril) (AMBN) was prepared. The pre-mix was charged to the reaction vessel at a constant rate over 3.0 hours under a nitrogen atmosphere using a metering pump. Next, a boost initiator solution of 0.25 parts 2,2'-azobis(2-methylbutyronitril) and 2.2 parts methyl amyl ketone was fed to the reaction vessel at a constant rate over 10 minutes. The reaction vessel was maintained at the

reaction temperature for a further 2.0 hours. Finally, the reactor was cooled to room temperature. The parts given above are all parts by weight.

The copolymer solution S4 had the following properties:

NVM 69.4 wt%; Viscosity 4099 cP; Mw 16.3k; PDI 2.20; Tg 36 °C.

5

The various ratios of the components in examples A1, A2 and S1-S4 and their properties are illustrated in table 2 below.

Preparation of zinc rosinate solution

10 150 parts Portuguese gum rosin solution (60 % rosin in xylene; acid number of solution 110 mg KOH/g), 12 parts zinc oxide and 8 g xylene were charged to a temperature-controlled reaction vessel equipped with a stirrer and a reflux condenser. The reaction mixture was heated slowly to 70 °C and maintained at that temperature for 2 hours. The reaction content was cooled to room temperature under
15 stirring to get a homogenous solution.

 The zinc rosinate solution had a non-volatile matter of 62.1 wt%, density of 1.04 g/cm³.

 Table 3 illustrates the further components used in the examples. Table 4
20 illustrates the hollow spheres used in the examples.

Table 2 – (Meth)acrylic silyl ester copolymer (i), (meth)acrylic polymer (iii) and (meth)acrylic copolymer (iv) monomer ratios

Component		A1	A2	S1	S2	S3	S4
Monomers (parts by weight)	Triisopropylsilyl methacrylate			50	55		55
	Triisopropylsilyl acrylate					60	
	2-(2-Ethoxyethoxy)ethyl acrylate				10		
	2-Methoxyethyl methacrylate			30			
	2-Methoxyethyl acrylate		40				
	Tetrahydrofurfuryl acrylate					5	
	Methacrylic acid	3					
	Methyl methacrylate		60	10	30	35	25
	n-Butyl acrylate	90		10	5		20
	n-Butyl methacrylate	7					
Properties	Non-volatile matter (wt%)	66.0	55.9	60.0	60.3	50.9	69.4
	Viscosity (cP)	369	1515	1790	1570	225	4099
	Density (g/cm ³)	0.98	1.02	0.98	0.98	0.96	0.97
	Mw (x 10 ³)	22.1	24.5	42.3	28.2	32.3	16.3
	PDI	2.93	2.37	3.11	2.71	4.12	2.20
	Tg (°C)	-41	29	37	48	39	36

Table 3: Ingredients used in the examples.

Ingredients	Trade name and manufacturer/supplier	Remarks
Binders		
Gum Rosin	Portuguese gum rosin WW from A. V. Pound	Used as 60% in xylene (Gum rosin solution I) and 60% in methyl amyl ketone (MAK) (Gum rosin solution II)
Biocides		
Cuprous oxide I	Nordox	Cuprous oxide PG red
Cuprous oxide II	Nordox	Cuprous oxide PG orange
Cuprous oxide III	LoLo Tint LM from American Chemet	
Copper pyrrithione	CleanBio-Cu from Kolon	
Copper pyrrithione and Copper chelate complex ² mixture	Arxada	Biocide from Arxada
Medetomidine	Selektope from I-tech	Used as a 20 wt% solution in 1-methoxy-2-propanol (PM)
Zineb	Perozin Marine from Agria	Zinc ethylenebis (dithiocarbamate) (polymERIC)
Pigments and extenders		
Iron oxide red	Bayferrox Red 130 M from Lanxess	Pigment
TiO ₂	Tiona 121 from Tronox	Pigment
Talc	Fimntalc M12 from Elementis	Platy extender
Zinc oxide	Zinc oxide red seal from Everzinc	Extender
Microdol	Microdol 1 from Onya	Nodular extender
Additives		
Polyamide wax	Disparlon A603-20X from Kusomoto	Rheology additive. Solid content: 20 wt% in xylene
Polyolefin wax	Disparlon 4401-25X from Kusomoto	Rheology additive. Solid content: 25 wt% in xylene

Ingredients	Trade name and manufacturer/supplier	Remarks
Tetraethoxy silane		Dehydrating agent
Solvents		
Xylene		Bp 136-145 °C
Aromatic hydrocarbons		Bp 150-185 °C, aromatic content ≥ 96 vol%
MAK	Methyl amyl ketone	Bp 152 °C

¹ Preparation method described in experimental section. ² As described in WO2020115323A1

The following hollow spheres are used in the invention. Properties of the hollow spheres are provided in e.g. technical datasheets from the suppliers.

Table 4: Hollow spheres used in the examples.

Hollow spheres	Material	Manufacturer/ Supplier	True density (g/cc)	d50 [μm]	Particle size range (d10 – d90) [μm]	Effective topcut [μm]	pH	Crush strength [psi]	Coated/ treated
Fillite 106	Ceramic hollow microspheres: cenospheres (fuel ash), aluminosilicate	Onya	0.85- 0.95	50	5-106	106	7.6	1500- 3000	No
Fillite 160	Ceramic hollow microspheres: cenospheres (fuel ash), aluminosilicate	Onya	0.66/0.78	80-90	5-160	180	~7	1500- 3000	No
K37	Hollow glass microspheres - soda-lime borosilicate	3M	0.37	45	20-80	85	9.1-9.9	3000	No
K46	Hollow glass microspheres - soda-lime borosilicate	3M	0.46	40	15-70	80	9.1-9.9	6000	No
S28HS	Hollow glass microspheres - soda lime borosilicate	3M	0.28	30			9.5	3000	No
H38HS	Hollow glass microspheres - soda lime borosilicate	Sinosteel Maanshan Ltd and SMC Minerals and Chemicals	0.36- 0.40	40	22-70	70	7-9	5500	Vinyl silane
S38	Hollow glass microspheres – soda lime borosilicate	3M	0.38	40	15-75	85	9.1-9.9	4000	No

Hollow spheres	Material	Manufacturer/ Supplier	True density (g/cc)	d50 [μm]	Particle size range (d10 – d90) [μm]	Effective topcut [μm]	pH	Crush strength [psi]	Coated/ treated
iM30K	Hollow glass microspheres – soda lime borosilicate	3M	0.6	15.3	8.6-23.6	26.7	9.1-9.9	27000	No
C60	Hollow glass -borosilicate	Cenostar	0.6	50	2-60	80	8-9.5	10000	Silane
Microbubbles H60	Hollow glass -borosilicate	Sinosteel Maanshan Ltd and SMC Minerals and Chemicals	0.6	50	25-85	85	8-10	10000	Yes
Eccospheres SID230Z	Hollow glass	Trelleborg AB	0.23	52			8.4	2100	Yes
Poraspheres	Hollow glass-soda lime	Poraver	0.88	61	13-87	90	8-12	6800	
Spherical 34P30	Hollow glass - high strength	Potters	0.34	26-30	15-46	46		3000	

General Paint preparation protocol

The components were mixed in the proportions given in Tables 5 to 12. The order of mixing the ingredients and preparation of pre-mix of selected ingredients
5 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.

The hollow spheres can be added before or after the grinding step, however, better mixing and better fineness of grind is seen when the spheres are included in
10 the grinding process. Paint samples with hollow spheres added before or after grinding were compared, and no sign of destroying the spheres were observed. Storage stability was not affected if the hollow spheres were added after grinding compared to before (one would expect an increase of viscosity over time if the spheres where destroyed). Both wet paint and dry films were examined in the
15 microscope (magnification x70) and spheres appeared intact.

In these examples hollow spheres were added before grinding.

Table 5: Inventive and comparative paint examples

		CoEx-1		Ex-1		Ex-2		Ex-3		Ex-4		Ex-5		Ex-6	
		wt%	%SV	wt%	%SV	wt%	%SV	wt%	%SV	wt%	%SV	wt%	%SV	wt%	%SV
Binder (i)	S2	20.2	39.9	21.9	39.9	23.9	39.9	26.4	39.9	29.4	39.9	33.2	39.9	22.9	39.9
Binder (ii)	Gum rosin solution I	6.7	13.3	7.3	13.3	8.0	13.3	8.8	13.3	9.8	13.3	11.1	13.3	7.7	13.3
Hollow Spheres	S28HS			0.4	5.1	0.9	10.0	1.6	15.0	2.3	20.0	3.3	25.1		
	Fillite 106													2.4	10.0
Cu ₂ O	Cuprous oxide I	49.6	30.2	44.8	25.1	39.3	20.1	32.5	15.1	24.2	10.1	13.8	5.1	45.4	20.1
Biocides, pigments and extenders	Copper pyrrhione	2.2	4.2	2.3	4.2	2.6	4.2	2.8	4.2	3.1	4.2	3.5	4.2	2.4	4.2
	Iron oxide red	2.1	1.5	2.3	1.5	2.5	1.5	2.7	1.5	3.0	1.5	3.4	1.5	2.4	1.5
	TiO ₂	1.0	0.9	1.1	0.9	1.3	0.9	1.4	0.9	1.5	0.9	1.7	0.9	1.2	0.9
	Talc	4.0	5.1	4.4	5.1	4.8	5.1	5.3	5.1	5.9	5.1	6.6	5.1	4.6	5.1
	Zinc oxide	4.0	2.5	4.4	2.5	4.8	2.5	5.3	2.5	5.9	2.5	6.6	2.5	4.6	2.5
	Polyamide wax	1.0	0.7	1.1	0.7	1.2	0.7	1.3	0.7	1.5	0.7	1.7	0.7	1.1	0.7
Additives	Polyethylene wax	1.0	0.9	1.1	0.9	1.2	0.9	1.3	0.9	1.5	0.9	1.7	0.9	1.1	0.9
	Tetraethoxysilane	1.0	0.8	1.1	0.8	1.2	0.8	1.3	0.8	1.5	0.8	1.7	0.8	1.2	0.8
Solvents	Xylene	7.2		7.8		8.5		9.3		10.4		11.8		10.9	

Table 5 cont.

		CoEx-1			Ex-1			Ex-2			Ex-3			Ex-4			Ex-5			Ex-6		
		wt%	%SV		wt%	%SV		wt%	%SV		wt%	%SV		wt%	%SV		wt%	%SV		wt%	%SV	
		100	100		100	100		100	100		100	100		100	100		100	100		100	100	
	sum																					
Coating composition properties calculated	%SV spheres	0			5			10			15			20			25			10		
	%SV Cu ₂ O	30			25			20			15			10			5			20		
	Sum %SV spheres + Cu ₂ O	30			30			30			30			30			30			30		
	Ratio %SV spheres / Cu ₂ O	0.0			0.2			0.5			1.0			2.0			4.9			0.5		
	Volume solids (%)	55			55			55			55			55			55			55		
	VOC (g/L)	391			391			391			391			391			391			416		
	Density coating (g/cm ³)	2.8			2.5			2.3			2.0			1.7			1.4			2.3		
	PVC (%)	44			44			44			44			44			44			44		
	Viscosity (cP)	553			472			398			362			326			279			385		
	Swelling FW 8 weeks	1			1			1			1			1			1			1		
Test results	Blistering FW 8 weeks	0			0			0			0			0			0			0		
	Cracking SW 12 weeks	0			0			0			0			0			0			0		
	Antifouling performance 4 months	0			1			0			0			0			1			0		

Table 6: Inventive and comparative examples

		Ex-7		Ex-8		Ex-9		Ex-10		Ex-11	
		wt%	%SV	wt%	%SV	wt%	%SV	wt%	%SV	wt%	%SV
	Binder (i)	36.5	39.9	20.4	31.9	22.6	31.9	22.4	31.9	22.7	30.4
	Binder (ii)	12.2	13.3	6.8	10.6	7.6	10.6	7.5	10.6	7.6	10.1
	Hollow Spheres	4.3	30.2	2.0	20.0	2.8	25.0	2.8	25.0	3.5	30.0
	Cu ₂ O	15.1	5.1	41.7	20.0	34.7	15.0	38.2	16.7	36.4	15.0
Biocides, pigments and extenders	Copper pyrithione	3.9	4.2	3.4	5.2	3.7	5.2	3.7	5.2	3.2	4.3
	Iron oxide red			3.3	1.8	3.6	1.8	2.5	1.3	1.2	0.6
	TiO ₂			1.7	1.2	1.8	1.2				
	Talc	4.7	3.3	3.6	3.6	4.0	3.6	4.0	3.6	4.6	3.9
	Zinc oxide	4.7	1.6	6.3	3.1	7.0	3.1	6.9	3.1	7.6	3.2
	Polyamide wax	1.8	0.7	1.3	0.7	1.4	0.7	1.4	0.7	1.5	0.7
Additives	Polyethylene wax	1.8	0.9	1.3	0.9	1.4	0.9	1.4	0.9	1.5	0.9
	Tetraethoxysilane	1.8	0.8	1.3	0.8	1.4	0.8	1.4	0.8	1.5	0.8
Solvents	Xylene	13.0		7.0		7.8		7.7		8.8	
	sum	100	100	100	100	100	100	100	100	100	100
Coating composition properties calculated	%SV spheres	30		20		25		25		30	
	%SV Cu ₂ O	5		20		15		17		15	
	Sum %SV spheres + Cu ₂ O	35		40		40		42		45	
	Ratio %SV spheres / Cu ₂ O	6.0		1.0		1.7		1.5		2.0	
	Volume solids (%)	55		60		60		60		60	
	VOC (g/L)	391		347		347		347		347	

		Ex-7	Ex-8	Ex-9	Ex-10	Ex-11
Test results	Density coating (g/cm ³)	1.2	2.2	1.9	2.0	1.8
	PVC (%)	44	55	55	55	57
	Viscosity (cP)	246	657	611	658	471
	Swelling FW 8 weeks	1	0	0	0	0
	Blistering FW 8 weeks	1	1	1	1	1
	Cracking SW 12 weeks	1	1	0	0	0
	Antifouling performance 4 months	0	0	0	0	0

Table 7: Inventive and comparative examples

		Ex-12		Ex-13		Ex-14		CoEx-2	
		wt%	%SV	wt%	%SV	wt%	%SV	wt%	%SV
Binder (i)	S2	22.7	26.7	27.3	24.4	17.5	16.2	12.3	8.8
Binder (ii)	Gum rosin solution I	7.6	8.9	9.1	8.1	5.8	5.4	5.3	3.8
Hollow Spheres	S28HS	5.4	40.0	8.8	50.1	10.2	60.0	16.5	74.9
Biocides, pigments and extenders	Cu ₂ O	27.7	10.0	18.2	5.0	35.2	10.0	22.9	5.0
	Copper pyrrithione	3.5	4.0	4.8	4.2	4.5	4.1	3.6	2.6
	Iron oxide red	1.9	0.8	2.7	0.8				
	TiO ₂								
	Talc	4.9	3.7	4.5	2.5			3.7	1.7
Additives	Zinc oxide	9.5	3.5	8.2	2.3	6.2	1.8	3.7	0.9
	Polyamide wax	1.7	0.7	2.2	0.7	2.1	0.7	2.8	0.7
	Polyethylene wax	1.7	0.9	2.2	0.9	2.2	0.9	2.8	0.9
	Tetraethoxysilane	1.7	0.8	2.3	0.8	2.2	0.8	2.8	0.8
	Xylene	11.7		9.7		14.1		23.4	
Solvents	sum	100	100	100	100	100	100	100	100
Coating composition properties calculated	%SV spheres	40		50		60		75	
	%SV Cu ₂ O	10		5		10		5	
	Sum %SV spheres + Cu ₂ O	50		55		70		80	
	Ratio %SV spheres / Cu ₂ O	4.0		10.0		6.0		14.9	
	Volume solids (%)	60		65		65		65	
	VOC (g/L)	347		304		304		304	

		Ex-12	Ex-13	Ex-14	CoEx-2
Test results	Density coating (g/cm ³)	1.5	1.1	1.2	0.8
	PVC (%)	62	65	76	85
	Viscosity (cP)	316	444	199	136
	Swelling FW 8 weeks	1	1	1	1
	Blistering FW 8 weeks	1	1	0	0
	Cracking SW 12 weeks	0	0	0	0
	Antifouling performance 4 months	1	1	1	2

Table 8: Inventive examples

		Ex-15		Ex-16		Ex-17		Ex-18		Ex-19		Ex-20	
		wt%	%SV	wt%	%SV	wt%	%SV	wt%	%SV	wt%	%SV	wt%	%SV
Binder (i)	S2	23.4	31.9	25.8	31.9	28.9	31.9	22.2	31.9	19.2	31.9	22.3	35.7
Binder (ii)	Rosin solution	7.8	10.6	8.6	10.6	9.7	10.6	7.4	10.6	6.4	10.6	7.5	11.9
Hollow spheres	S28HS	2.9	25.0	3.8	30.0	5.0	35.0	2.7	25.0			1.5	15.0
	Fillite 106									5.1	20.0		
	Cuprous oxide I	29.8	12.5										
	Cuprous oxide II			25.4	10.0			32.8	15.0			39.4	20.0
Biocides, pigments and extenders	Cuprous oxide III					15.3	5.0			34.1	16.8		
	Medetomidine (20% solution)	2.0	0.9	0.5	0.2	2.0	0.7	2.0	0.9				
	Copper pyrithione	3.2	4.3	4.1	5.0	4.1	4.5			3.2	5.2		
	Copper pyrithione and Copper chelate complex ¹ mixture											4.2	6.9
	Red iron oxide	3.6	1.8	3.2	1.4	4.6	1.8	3.5	1.8	3.1	1.8	2.0	1.2
	TiO ₂	1.9	1.2	2.1	1.2	2.4	1.2	1.8	1.2	1.6	1.2	1.1	0.8
	Talc	7.2	6.3	5.2	4.1	5.2	3.6	6.8	6.3	5.9	6.3	4.0	4.1
	Zinc oxide	7.2	3.1	8.0	3.1	8.9	3.1	10.4	4.8	7.0	3.7	4.0	2.1
Additives	Polyamide wax	1.5	0.7	1.6	0.7	1.8	0.7	1.4	0.7	1.2	0.7	1.2	0.7
	Polyethylene wax	1.5	0.9	1.6	0.9	1.8	0.9	1.4	0.9	1.2	0.9	1.3	0.9
	Tetraethoxysilane	1.5	0.8	1.6	0.8	1.8	0.8	1.4	0.8	1.2	0.8	1.3	0.8
Solvents	Xylene	6.5		8.5		8.4		6.1		10.9		10.3	
	sum	100	100	100	100	100	100	100	100	100	100	100	100
	%SV spheres	25		30		35		25		20		15	

		Ex-15	Ex-16	Ex-17	Ex-18	Ex-19	Ex-20
Coating composition properties calculated	%SV Cu ₂ O	12	10	5	15	17	20
	Sum %SV spheres + Cu ₂ O	37	40	40	40	37	35
	Ratio %SV spheres / Cu ₂ O	2.0	3.0	7.0	1.7	1.2	0.8
	Volume solids (%)	60	60	60	60	62	55
	VOC (g/L)	347	347	347	348	389	391
	Density coating (g/cm ³)	1.9	1.6	1.4	2.0	1.5	2.1
	PVC (%)	55	55	55	55	55	50
	Viscosity (cP)	673	517	445	785	188	228
	Swelling FW 8 weeks	1	1	1	1	1	1
	Blistering FW 8 weeks	0	0	0	0	1	0
Test results	Cracking SW 8 weeks	0	0	0	0	0	0
	Antifouling performance 4 months	0	0	0	1	1	1

Table 9: Inventive examples

		Ex-21		Ex-22		Ex-23		Ex-24		Ex-25	
		wt%	%SV	wt%	%SV	wt%	%SV	wt%	%SV	wt%	%SV
Binders (i)	S2	33.8	49.0	24.5	43.2	27.6	35.7	25.9	33.3		
	S4									17.2	28.3
Binders (ii)	Gum rosin solution I	6.0	8.6	8.2	14.4						
	Gum rosin solution II									13.3	18.5
	Zn-rosinate solution					9.8	11.9	11.9	14.3		
Hollow spheres	S28HS			0.5	5.0	3.0	25.0	3.1	25.0	2.4	21.7
	Fillite 106	3.8	13.0								
Cu ₂ O	Cuprous oxide I	29.2	13.0					31.8	12.5	37.9	16.3
	Cuprous oxide II			18.0	10.1	36.5	15.0				
Biocides, pigments and extenders	Medetomidine (20% solution)										
	Copper pyrithione	0.6	0.3	2.0	1.1						
	Iron oxide red	4.0	5.8			3.2	4.1	3.2	4.1	2.7	3.8
	TiO ₂	2.6	1.3	2.1	1.3	1.4	0.7	2.7	1.3	2.3	1.1
	Talc	2.5	1.6	1.1	0.8	1.8	1.1	1.8	1.1	1.2	0.7
	Zinc oxide	5.0	4.6	4.1	4.6	5.1	4.2	7.0	5.7	5.5	4.7
Additives	Polyamide wax	0.9	0.4	30.5	17.1			0.9	0.4	8.6	3.8
	Polyethylene wax	1.4	0.7	1.1	0.7	1.5	0.7	1.5	0.7	1.0	0.5
	Tetraethoxysilane	1.4	0.9	1.1	0.9	1.5	0.9	1.6	0.9	1.0	0.7
	Xylene	1.4	0.8	1.1	0.8	1.6	0.8	1.6	0.8	0.6	
Solvents	Methyl amyl ketone	7.5		5.5		7.0		7.0		6.2	

	Ex-21			Ex-22			Ex-23			Ex-24			Ex-25		
	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
	sum			13			5			25			21.7		
	%SV spheres			13			10			15			16.3		
	%SV Cu ₂ O			26			15			40			37.9		
Coating composition properties calculated	Sum %SV spheres + Cu ₂ O			1.0			0.5			1.7			1.3		
	Ratio %SV spheres / Cu ₂ O			60			55			60			64		
	Volume solids (%)			385			392			347			300		
	VOC (g/L)			1.9			2.4			1.7			2.0		
	Density coating (g/cm ³)			40			40			50			53		
	PVC (%)			565			847			534			552		
Test results	Viscosity (cP)			1			1			1			-		
	Swelling FW 8 weeks			0			0			0			0		
	Blistering FW 8 weeks			0			0			0			0		
	Cracking SW 12 weeks			0			0			0			0		
	Antifouling performance 4 months			0			0			0			1		

		CoEx-3	Ex-26	Ex-27	Ex-28	CoEx-4
Coating composition properties calculated	%SV Spheres	0	15	7.5	30	20
	%SV Cu ₂ O	20	15	15	5	0
	Sum %SV spheres + Cu ₂ O	20	30	22	35	20
	Ratio %SV spheres / Cu ₂ O	-	1.0	0.5	6.0	-
	Volume solids (%)	54	60	60	65	54
	VOC (g/L)	418	384	384	340	433
	Density coating (g/cm ³)	2.5	1.9	2.2	1.3	1.3
Test results	PVC (%)	39	45	45	50	39
	Viscosity (cP)	399	433	481	751	200
	Swelling FW 8 weeks	2	2	1	1	3
	Blistering FW 8weeks	1	1	1	1	1
	Cracking SW 12weeks	0	0	0	0	0
	Antifouling performance 4 months	1	1	0	1	4*

* Fully fouled after 1M exposure.

Table 11: Inventive examples

[illegible]

		Ex-29	Ex-30	Ex-31	Ex-32	Ex-33	Ex-34
Coating composition properties calculated	%SV spheres	20.2	21.7	19.7	16.0	19.0	20.7
	%SV Cu ₂ O	17.2	16.3	16.8	17.3	17.1	17.1
	Sum %SV spheres + Cu ₂ O	37.4	38.0	36.5	33.3	36.1	37.8
	Ratio %SV spheres / Cu ₂ O	1.2	1.3	1.2	0.9	1.1	1.2
	Volume solids (%)	54	54	53	52	53	54
	VOC (g/L)	401	402	407	418	409	403
	Density coating (g/cm ³)	2.1	2.0	2.0	2.1	2.1	2.4
	PVC (%)	50	50	49	46	48	50
	Viscosity (cP)	504	513	480	435	534	462
	Blistering FW 8 weeks	0	0	0	0	0	0
Test results	Cracking SW 12 weeks	0	0	0	0	0	0
	Antifouling performance 1 month*	1	1	0	0	0	0
	Polishing (µm@86 weeks)	30	32	34	30	29	30
	Water uptake FW 15 weeks (wt%)	3.8	5.4	5.3	5.0	6.9	3.9

Table 12: Inventive examples

		Ex-35		Ex-36		Ex-37		Ex-38		Ex-39		Ex-40	
		wt%	%SV	wt%	%SV	wt%	%SV	wt%	%SV	wt%	%SV	wt%	%SV
Binder (i)	S1	21.5	26.6	22.9	34.0	22.6	30.9	23.2	28.5	23.1	28.1	23.0	28.9
	S3	9.2	11.1	9.8	14.1	9.6	12.9	9.9	11.8	9.8	11.7	9.8	12.0
Binder (ii)	Gum rosin solution I	5.2	6.6	5.5	8.5	5.4	7.7	5.6	7.1	5.6	7.0	5.6	7.2
	Microbubbles H60	6.6	28.6										
Hollow spheres	Poraspheres 0-90 um test			2.9	10.1								
	C60 Cenostar glass bubble					3.7	17.8						
	Sphericell 34P30							2.1	24.8				
	Eccospheres SID270Z									2.3	25.8		
	S28HS											2.5	23.6
	Cuprous oxide I	35.0	15.6	35.0	18.7	35.0	17.3	35.1	15.5	35.1	15.4	35.0	15.8
Biocides, pigments and extenders	Copper pyrrhione	1.7	2.4	1.8	3.0	1.7	2.8	1.8	2.6	1.8	2.5	1.8	2.6
	Iron oxide red	1.8	1.0	2.0	1.2	1.9	1.1	2.0	1.0	2.0	1.0	2.0	1.0
	TiO ₂	0.9	0.6	1.0	0.7	1.0	0.7	1.0	0.6	1.0	0.6	1.0	0.6
	Talc	4.4	4.0	4.7	5.1	4.7	4.6	4.9	4.2	4.8	4.2	4.8	4.3
	Zinc oxide	4.6	2.1	4.9	2.7	4.8	2.5	5.0	2.3	4.9	2.2	4.9	2.3
	Polyamide wax	2.2	1.2	2.4	1.5	2.3	1.3	2.4	1.2	2.4	1.2	2.4	1.3
Additives	Polyethylene wax	0.6	0.4	0.6	0.5	0.6	0.4	0.6	0.4	0.6	0.4	0.6	0.4
	Tetraethoxysilane	0.5		0.5		0.5		0.5		0.5		0.5	
	Xylene	2.8		2.9		2.9		3.0		3.0		3.0	
Solvents	Aromatic hydrocarbons	3.1		3.3		3.2		3.3		3.3		3.3	

		Ex-35			Ex-36			Ex-37			Ex-38			Ex-39			Ex-40		
	Sum	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
Coating composition properties calculated	%SV spheres	28.6			10.1			17.8			24.8			25.8			23.6		
	%SV Cu ₂ O	15.6			18.7			17.3			15.5			15.4			15.8		
	Sum %SV spheres + Cu ₂ O	44.2			28.8			35.1			40.3			41.2			39.4		
	Ratio %SV spheres / Cu ₂ O	1.8			0.5			1.0			1.6			1.7			1.5		
	Volume solids (%)	56			50			53			55			55			54		
	VOC (g/L)	380			433			412			394			391			397		
	Density coating (g/cm ³)	1.9			2.2			2.1			1.9			1.8			1.9		
	PVC (%)	55			42			48			52			53			51		
Test results	Viscosity (cP)	593			437			422			416			572			533		
	Blistering FW 8 weeks	0			0			0			0			0			0		
	Cracking SW 12 weeks	0			0			0			0			0			0		
	Antifouling performance 1 month*	1			1			1			1			1			0		
	Polishing (µm@86 weeks)	34			27			34			31			35			35		
	Water uptake FW 15 weeks (wt%)	9.6			5.2			6.0			5.6			3.9			6.5		

*Antifouling performance after 1 month in Singapore.

Results

Table 5: Comparative example CoEx-1 shows a high-copper formulation with nearly 50 wt% cuprous oxide similar to several antifouling paints on the market. This equals to 30 vol% (%SV) cuprous oxide with a silyl copolymer and rosin acid as the binder system.

In examples Ex-1 to Ex-6, the sum of %SV of cuprous oxide and hollow spheres is kept at the same level as for the comparative example (30 vol%), while the ratio between spheres and cuprous oxide varies from 0.2 to 5. The viscosity of the paint is reduced when the content of the hollow spheres is increased as is expected. A benefit is here that volume solids could be increased (leading to decreased VOC) with introduction of hollow spheres. The reduction in copper content still gives good to excellent antifouling performance as can be seen from the 4 months raft exposure in Singapore. None of the examples in Table 5 show any undesirable effect when immersed in freshwater or seawater, no extensive swelling, blistering or cracking is observed. Example Ex-6 shows that hollow ceramic spheres can be utilized as well as those made from glass.

Table 6: The sum of the %SV spheres and %SV cuprous oxide can be increased while antifouling performance is still excellent and freshwater and seawater properties are still good. The examples show that the volume solids in the paint formulations can be increased as the viscosity is reduced when adding hollow spheres, which leads to reduced VOC. The examples show up to 50%, or even 60%, of the solids volume can be hollow glass spheres. Comparative example CoEx-2 show that a higher degree of fouling is observed when the content of hollow spheres is too high.

Table 7 and Table 8: Several grades of cuprous oxide can be used; cuprous oxide with larger particle sizes or smaller size while still having the desired antifouling performance. Combinations with the biocide medetomidine against barnacle fouling are also shown. As can be seen from example Ex-22, zinc oxide will give an increase in viscosity when used in larger amounts and hence cannot be used alone as a substitute for cuprous oxide. The experiments show that both rosin acid and metal rosin salts can be used in the invention, with or without additional zinc oxide in the formulation (Ex-23 and Ex-24). The level of zinc oxide can be

varied, even below 1wt% in the formulation. Different hollow spheres can be used, glass or ceramic (Ex-19). In Ex-25, silyl copolymer S4 is used, and the solvent is changed to MAK and VOC of 300 g/L.

5 Table 9: The results show a silyl acrylate copolymer combined with a (meth)acrylate copolymer in addition to rosin. A good antifouling performance can be maintained with reduced cuprous oxide content. The comparative example CoEx-3 shows a formulation with %SV cuprous oxide of 20%, without any hollow spheres. The inventive examples perform as well as this example. Comparative
10 example CoEx-4 contains no cuprous oxide, and already after 1 month raft exposure in Singapore the coating was fully fouled. The use of cuprous oxide is therefore essential.

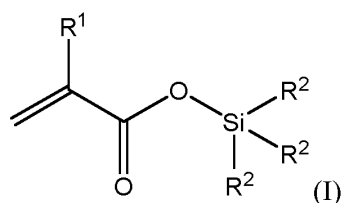
Table 10 to Table 12: The results show that the antifouling performance is maintained with a variety of different hollow spheres, both treated/untreated hollow glass spheres and hollow ceramic spheres. The level of cuprous oxide is kept at 35
15 wt% of the formulation in these examples. The choice of spheres does not greatly influence the polishing rate as can be seen from the polishing on rotating discs after 21 months.

The ratio of the solids volume of hollow spheres to solids volume of cuprous oxide in the inventive examples are from 0.1:1 to 10:1 demonstrating a broad range
20 of performance.

Claims

1. An antifouling coating composition comprising:
(A) a binder comprising a (meth)acrylic copolymer comprising silyl ester
5 groups (i);
(B) 2.0 to 30 % solids volume cuprous oxide, such as 5.0 to 20 % solids
volume; and
(C) 2.0 to 65 % solids volume hollow spheres, such as 10 to 55 solids vol%.
- 10 2. An antifouling coating composition as claimed in any preceding claim
wherein the hollow spheres comprise ceramic or glass.
3. An antifouling coating composition as claimed in any preceding claim
wherein the total amount of cuprous oxide and hollow spheres combined is in the
15 range 15 to 70 % solids volume based on the antifouling coating composition as a
whole, such as 15 to 60 % solids volume.
4. An antifouling coating composition as claimed in any preceding claim
wherein the hollow spheres are hollow microspheres and preferably have a d₅₀
20 between 10 and 100 μm.
5. An antifouling coating composition as claimed in any preceding claim
wherein the (meth)acrylic copolymer comprising silyl ester groups (i) comprises a
triisopropylsilyl (meth)acrylate monomer.
25
6. An antifouling coating composition as claimed in any preceding claims
wherein the (meth)acrylic silyl ester copolymer (i) comprises structural units derived
from the following monomers:
(a) a silyl ester monomer of formula (I),

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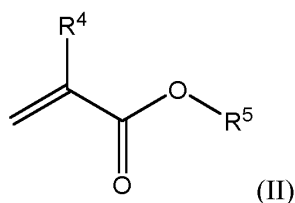


wherein R^1 is H or CH_3 ;

R^2 is each independently selected from C1-C8 hydrocarbyl groups;
preferably triisopropylsilyl acrylate or triisopropylsilyl methacrylate;

5

(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.

10

7. An antifouling coating composition as claimed in any preceding claim
wherein the (meth)acrylic copolymer comprising silyl ester groups (i) comprises one
or more of 2-methoxyethyl acrylate, 2-methoxyethyl methacrylate, 2-ethoxyethyl
methacrylate, 2-(2-ethoxyethoxy)ethyl acrylate, 2-(2-ethoxyethoxy)ethyl
15 methacrylate and tetrahydrofurfuryl acrylate.

8. An antifouling coating composition as claimed in any preceding claim
wherein the (meth)acrylic copolymer comprising silyl ester groups (i) comprises one
or more of methyl methacrylate and n-butyl (meth)acrylate.

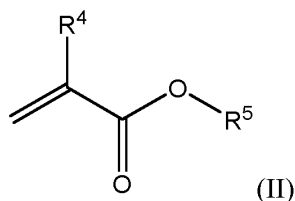
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9. An antifouling coating composition as claimed in any preceding claim
wherein the binder (A) further comprises a monocarboxylic acid or metal salt
thereof (ii), preferably rosin or a metal salt thereof.

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10. An antifouling coating composition as claimed in any preceding claim wherein binder (A) further comprises a meth(acrylic) polymer (iii) having a T_g below 10 °C and comprising 0.5 to 10 wt% of a (meth)acrylic acid monomer and a (meth)acrylate monomer of formula (II):

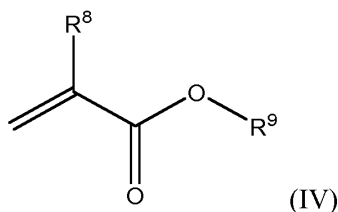
5



wherein R⁴ is H or CH₃, and R⁵ is a C1-C20 hydrocarbyl substituent, preferably a C1-10 alkyl substituent, such as a C1-8 alkyl.

10 11. An antifouling coating composition as claimed in any preceding claim wherein binder (A) further comprises a meth(acrylic) polymer (iv) having a glass transition temperature (T_g) of at least 10 °C and comprising at least one monomer of formula (II) as defined in claim 10; and optionally one or more monomers of formula (IV):

15



wherein R⁸ is H or CH₃, and R⁹ 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 R⁹ represents a poly(alkylene glycol) group.

20

12. An antifouling coating composition as claimed in any preceding claim further comprising at least one additional biocide such as copper pyrithione, zinc pyrithione, zineb and 4,5-dichloro-2-octyl-4-isothiazolin-3-one, preferably copper pyrithione

25

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13. An antifouling coating composition as claimed in any preceding claim comprising a silane, such as tetraethoxysilane.
14. An antifouling coating composition as claimed in any preceding claim
5 comprising:
 (A) a binder comprising a (meth)acrylic copolymer comprising silyl ester groups (i);
 (B) 5.0 to 25 % solids volume cuprous oxide; and
 (C) 5.0 to 60 % solids volume hollow spheres.
10 wherein the total amount of cuprous oxide and hollow spheres combined is in the range of 15 to 65 % solids volume.
15. An antifouling coating composition as claimed in any preceding claim which contains less than 1.0 wt% of a liquid, acyclic, saturated C12-24 monocarboxylic
15 acid or salt thereof or liquid, acyclic branched C12-24 monocarboxylic acid or salt thereof, such as contains no such material.
16. An antifouling coating composition as claimed in any preceding claim comprising only one (meth)acrylic copolymer comprising silyl ester groups.
20
17. A process for protecting an object from fouling, said process comprising coating at least a part of said object which is subject to fouling with an antifouling coating composition as claimed in any of claims 1 to 16.
- 25 18. A substrate coated with an antifouling coating composition as claimed in any of claims 1 to 16.