

Antifouling Paint Composition

This invention relates to an antifouling paint composition comprising a (meth)acrylic copolymer comprising (meth)acrylic acid monomers and/or a metal
5 containing (meth)acrylic copolymer, cuprous oxide and hollow spheres. The composition may additionally contain a silyl ester 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
10 of the invention.

Background

Copper containing self-polishing paints are the most commonly used
15 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
20 in antifouling paints but more efficient use of the added cuprous oxide will provide a more sustainable and 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
25 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
30 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.

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.

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 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 of greenhouse gases.

Organic solvents such as xylene are needed in solvent borne 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 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 products results in an antifouling product with an improved sustainability profile. In one embodiment, hollow spheres should preferably not be polymeric, due to the

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non-desirable environmental effect of plastic pollution being released during 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 produce is clearly advantageous.

The literature does contain paint compositions in which hollow spheres are used to reduce the amount of cuprous oxide.

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.

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.

20 The present invention looks to provide a more environmentally friendly, sustainable, economic, low density antifouling coat composition with good antifouling performance in the context of a self-polishing antifouling coating. 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.

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Summary of Invention

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

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(A) a binder comprising

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(i) a (meth)acrylic copolymer comprising 0.5 to 10 wt%, such as 0.5 to 5.0 wt% (meth)acrylic acid monomers relative to the total weight of monomers in the (meth)acrylic copolymer; and/or

5 (ii) a metal containing (meth)acrylic copolymer wherein the metal is selected from Zn or Cu;

(B) 1.0 to 25 % solids volume cuprous oxide; and

(C) 1.0 to 65 % solids volume hollow spheres.

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

10 (A) a binder comprising

(i) a (meth)acrylic copolymer comprising 0.5 to 10 wt%, such as 0.5 to 5.0 wt% (meth)acrylic acid monomers relative to the total weight of monomers in the (meth)acrylic copolymer;

(B) 1.0 to 25 % solids volume cuprous oxide; and

15 (C) 1.0 to 65 % solids volume hollow spheres.

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

(A) a binder comprising

20 (i) a (meth)acrylic copolymer comprising 0.5 to 10 wt%, such as 0.5 to 5.0 wt% (meth)acrylic acid monomers relative to the total weight of monomers in the (meth)acrylic copolymer; and/or

(ii) a metal containing (meth)acrylic copolymer wherein the metal is selected from Zn or Cu;

(iii) a monocarboxylic acid or metal salt thereof;

25 (B) 1.0 to 25 % solids volume cuprous oxide; and

(C) 1.0 to 65 % solids volume hollow spheres.

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

(A) a binder comprising

30 (i) a (meth)acrylic copolymer comprising 0.5 to 10 wt%, such as 0.5 to 5.0 wt% (meth)acrylic acid monomers relative to the total weight of monomers in the (meth)acrylic copolymer; and/or

- 5 -

(ii) a metal containing (meth)acrylic copolymer wherein the metal is selected from Zn or Cu;

(B) 7.0 to 40 wt% cuprous oxide; and

(C) 0.2 to 12 wt % hollow spheres.

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

(A) a binder comprising

(i) a (meth)acrylic copolymer comprising 0.5 to 10 wt%, such as 0.5 to 5.0 wt% (meth)acrylic acid monomers relative to the total weight of monomers in the (meth)acrylic copolymer; and/or

10 (ii) a metal containing (meth)acrylic copolymer wherein the metal is selected from Zn or Cu;

(iii) a monocarboxylic acid or metal salt thereof;

(B) 7.0 to 40 wt% cuprous oxide; and

15 (C) 0.2 to 12 wt % hollow spheres

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

(A) a binder comprising

(i) a (meth)acrylic copolymer comprising 0.5 to 10 wt%, such as 0.5 to 5.0 wt% (meth)acrylic acid monomers relative to the total weight of monomers in the (meth)acrylic copolymer; and

20 (iv) a (meth)acrylic polymer

(B) 1.0 to 25 % solids volume cuprous oxide; and

(C) 1.0 to 65 % solids volume hollow spheres.

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

(A) a binder comprising

(i) a (meth)acrylic copolymer comprising 0.5 to 10 wt%, such as 0.5 to 5.0 wt% (meth)acrylic acid monomers relative to the total weight of monomers in the (meth)acrylic copolymer;

30 (iii) a monocarboxylic acid or metal salt thereof; and

(iv) a (meth)acrylic polymer

(B) 1.0 to 25 % solids volume cuprous oxide; and

(C) 1.0 to 65 % solids volume 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.

15

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 the film thickness due to removal of coating material at the surface of the coating film over time as the result of degradation and/or erosion by the surrounding water medium.

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.

25

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 terms “(meth)acrylic polymer” refers to polymers comprising repeating units derived from (meth)acrylate monomers. Generally, a “(meth)acrylic polymer”

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.

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

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

10 The term “binder” defines part of the composition (A) which includes the (meth)acrylic copolymer comprising (meth)acrylic acid monomers and/or the metal containing (meth)acrylic copolymer 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 binder comprising a (meth)acrylic copolymer comprising (meth)acrylic acid monomers (i) and/or metal containing (meth)acrylic
15 copolymer groups (ii) together with any monocarboxylic acid (iii) and optionally the (meth)acrylic polymer (iv) as defined herein.

The term ‘T_g’ means glass transition temperature.

20 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.

25 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.

30 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:

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

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.

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

Detailed description of invention

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The invention relates to a new antifouling coating composition comprising a binder (A). Binder (A) comprises (i) a (meth)acrylic copolymer comprising 0.5 to 10 wt%, preferably 0.5 to 5.0 wt% (meth)acrylic acid monomers and/or (ii) a (meth)acrylic copolymer comprising Zn or Cu containing groups.

- 15 It is preferred if the binder (A) further comprises (iii) a monocarboxylic acid or metal salt thereof; and optionally (iv) a (meth)acrylic polymer

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

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

- 25 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
- 30 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.

Binder (A)

Binder (A) of the coating composition of the present invention comprises (i) a (meth)acrylic copolymer comprising 0.5 to 10 wt%, such as 0.5 to 5.0 wt% (meth)acrylic acid monomers and/or (ii) a metal containing (meth)acrylic copolymer wherein the metal is selected from Zn or Cu.

It is preferred if the binder (A) further comprises (iii) a monocarboxylic acid or metal salt thereof; and optionally (iv) a (meth)acrylic polymer.

In one preferred embodiment the binder A comprises (i) a (meth)acrylic copolymer comprising 0.5 to 10 wt% (meth)acrylic acid monomers.

In second preferred embodiment the binder A comprises (ii) a metal containing (meth)acrylic copolymer wherein the metal is selected from Zn or Cu.

In a third preferred embodiment the binder A comprises (i) a (meth)acrylic copolymer comprising 0.5 to 10 wt% (meth)acrylic acid monomers and (iii) a monocarboxylic acid or metal salt thereof.

In a fourth preferred embodiment the binder A comprises (i) a (meth)acrylic copolymer comprising 0.5 to 10 wt% (meth)acrylic acid monomers, (iii) a monocarboxylic acid or metal salt thereof and (iv) a (meth)acrylic polymer.

The (meth)acrylic polymers (i), (ii) and (iv) of the present invention comprise repeating units derived from (meth)acrylic monomers. Preferably the (meth)acrylic polymers (i), (ii) and (iv) comprise at least 50 wt% of the repeating units derived from (meth)acrylic monomers, i.e. acrylic and methacrylic monomers.

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

In one embodiment the (meth)acrylic polymers (i), (ii) and (iv) comprise 100 wt% of structural units derived from (meth)acrylic monomers, i.e. they do not comprise any monomers of another type. The term (meth)acrylic monomers covers therefore (meth)acrylic acids and (meth)acrylic esters.

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(Meth)acrylic copolymer (i)

The (meth)acrylic copolymer (i) comprises a (meth)acrylic acid monomer (a1). Suitable (meth)acrylic acid monomers (a1) are methacrylic acid or acrylic acid. The (meth)acrylic copolymer (i) preferably comprises the (meth)acrylic acid monomer (a1) in the range of 0.5 to 5.0 wt%, preferably 1.0 to 4.0 wt%.

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High viscosity of the (meth)acrylic copolymer (i) means that higher amounts of solvent are needed for preparation and application of the paint. This is unwanted due to strict VOC regulations.

Preferably the (meth)acrylic copolymer (i) 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.

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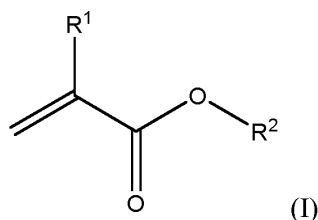
Preferably a (meth)acrylate monomer (a2) as described below is present in the (meth)acrylic copolymer (i) to thus form a copolymer with the (meth)acrylic acid monomer (a1).

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The (meth)acrylate monomers (a2) preferably form at least 50 wt% of the (meth)acrylic copolymer (i), 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%.

25

Examples of suitable (meth)acrylate monomers (a2) are of formula I:



wherein R^1 is H or CH_3 , and R^2 is a C1-C20 hydrocarbyl substituent, preferably a C1-10 alkyl substituent, such as a C1-8 alkyl.

The R^2 group can be linear or branched. Most preferably R^2 is a methyl, ethyl, propyl, butyl, hexyl, octyl or decyl group which (if possible) may be linear or branched. Ideal options for R^2 are methyl, ethyl, n-propyl, n-butyl, isobutyl or isooctyl.

5 Examples of suitable monomers of Formula I as monomer (a2) in (meth)acrylic 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.

10 Preferred options for monomers of Formula (I) as monomer (a2) in (meth)acrylic copolymer (i) include methyl methacrylate, ethyl acrylate, n-butyl acrylate, n-butyl methacrylate, 2-ethylhexyl acrylate, 2-octyl acrylate or isooctyl acrylate.

15 Mixtures of different monomers of formula (I) may also be used in (meth)acrylic copolymer (i). The use of two different monomers of formula (I) is especially preferred. The use of two different monomers of formula (I) is especially preferred along with (meth)acrylic acid.

20 Preferably the (meth)acrylic copolymer (i) comprises structural units derived from (meth)acrylic acid monomers (a1) and (meth)acrylate monomers (a2).

In one preferred embodiment the (meth)acrylic copolymer (i) 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.

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

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

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

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

10 The (meth)acrylic copolymer (i) may be present in an amount of 1.0 to 12 wt%, preferably 2.0 to 7.0 wt%, relative to the total weight of the coating composition as a whole.

The (meth)acrylic copolymer (i) may be present in an amount of 1.5 to 15 wt%, preferably 2.5 to 10 wt%, relative to the total dry weight of the coating composition as a whole.

15 The (meth)acrylic copolymer (i) may be present in an amount of 1.0 to 20 % solids volume, such as 2.0 to 15% solids volume, preferably 3.0 to 12% solids volume in the coating as a whole.

Metal containing (meth)acrylic copolymer comprising Zn or Cu (ii)

20 In one preferred embodiment, the binder A of the coating composition of the invention comprises a metal containing (meth)acrylic copolymer comprising Zn or Cu (ii).

The (meth)acrylic copolymer (ii) typically has side chain groups represented by the general formula (II):

25



wherein M represents zinc or copper and R³ represents an organic group. Such a side chain may be present in a (meth)acrylate monomer.

30 The group R³ is preferably a saturated or unsaturated aliphatic group having 2 to 50 carbon atoms, preferably 2 to 30 carbon atoms, especially 2 to 20 carbon

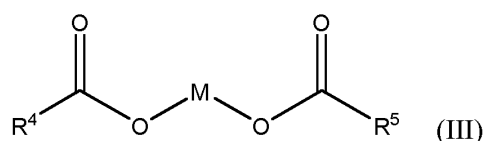
atoms such as a saturated alicyclic group having 3 to 20 carbon atoms; or R^3 is an aromatic group having 6 to 18 carbon atoms.

In a preferred embodiment, the $O-CO-R^3$ group as a whole is derived from a monocarboxylic acid such as versatic acid, palmitic acid, isostearic acid, stearic acid, oleic acid, linoleic acid, linolenic acid, abietic acid, neoabietic acid, pimaric acid, dehydroabietic acid, 12-hydroxystearic acid, naphthenic acid and the like.

In another preferred embodiment the R^3 group contains an ethylenically unsaturated terminal group. The R^3 group may comprise an ester bond, an amide bond, and an ether bond in the carbon chain. Suitable $-OCO-R^3$ groups may be derived from acrylic acid, methacrylic acid, 3-butenic acid, 4-pentenoic acid, 10-undecenoic acid and 3-(meth)acryloxypropionic acid.

The metal containing (meth)acrylic copolymer comprising Zn or Cu (ii) may comprise structural units derived from a Zn or Cu containing monomer a3.

Examples of suitable metal containing (meth)acrylate monomers (a3) are represented by the general formula (III):



wherein M in formula (III) is represented by copper or zinc.

R^4 is a monovalent group comprising a terminal ethylenically unsaturated group. Preferably R^4 comprises 2 to 50 carbon atoms, more preferably 2 to 30 carbon atoms, further preferred 2 to 10 carbon atoms. R^4 may comprise an ester group, an amide group or an ether group in the carbon chain.

Examples of suitable $O-CO-R^4$ groups are groups derived from acrylic acid, methacrylic acid, 3-butenic acid, 4-pentenoic acid, 10-undecenoic acid and 3-(meth)acryloxypropionic acid. Preferred $O-CO-R^4$ groups are derived from acrylic acid and methacrylic acid.

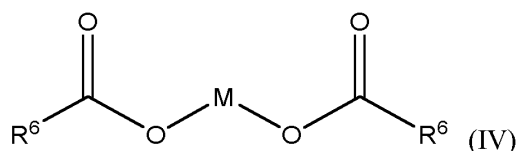
R^5 is monovalent organic group comprising 1 to 30 carbon atoms. R^5 does not comprise a terminal ethylenically unsaturated group. Examples of R^5 include an aliphatic hydrocarbon group comprising 1 to 30 carbon atoms, an alicyclic hydrocarbon group having 3 to 30 carbon atoms and an aromatic hydrocarbon group

comprising 6 to 30 carbon atoms. The R^5 hydrocarbon groups may be straight chained or branched. The R^5 group may comprise a substituent such as a hydroxyl group. The R^5 hydrocarbon chains may be unsaturated as long as the unsaturated group is not terminal.

5 Examples of suitable O-CO- R^5 groups are groups derived from monocarboxylic acids such as versatic acid, palmitic acid, isostearic acid, stearic acid, oleic acid, linoleic acid, linolenic acid, abietic acid, neoabietic acid, pimelic acid, dehydroabietic acid, 12-hydroxystearic acid, naphthenic acid and the like. OCO- R^5 groups derived from abietic acid, versatic acid, or naphthenic acid are
10 preferred, abietic acid or versatic acid is most preferred.

 Examples of suitable monomers of a3 of formula (III) are zinc 3-(meth)acryloyloxypropionate abietate, zinc 3-(meth)acryloyloxypropionate versate, zinc (meth)acrylate abietate, zinc (meth)acrylate versate, zinc
15 (meth)acrylate naphthenate, copper 3-(meth)acryloyloxypropionate abietate, copper 3-(meth)acryloyloxypropionate versate, copper (meth)acrylate abietate, copper (meth)acrylate versate, and copper (meth)acrylate naphthenate.

 Suitable metal containing (meth)acrylate monomers (a3) may also be represented by the general formula (IV):



20 wherein M represents copper or zinc and each R^6 is independently selected from a monovalent group comprising a terminal ethylenically unsaturated group. Preferably R^6 comprises 2 to 50 carbon atoms, more preferably 2 to 30 carbon atoms, further preferred 2 to 10 carbon atoms. Each R^6 may comprise an ester group, an amide group or an ether group in the carbon chain.

25 Examples of suitable O-CO- R^6 groups are groups derived from acrylic acid, methacrylic acid, 3-butenic acid, 4-pentenoic acid, 10-undecenoic acid and 3-(meth)acryloxypropionic acid. Preferred O-CO- R^6 groups are derived from acrylic acid and methacrylic acid.

Examples of suitable monomers a3 of formula (IV) are zinc diacrylate, zinc dimethacrylate, zinc acrylate methacrylate, zinc di(3-acryloyloxypropionate), zinc di(3-methacryloyloxypropionate), zinc di(3-acryloyloxy-2-methylpropionate), zinc di(3-methacryloyloxy-2-methylpropionate), copper diacrylate, copper

5 dimethacrylate, copper acrylate methacrylate, copper di(3-acryloyloxypropionate), copper di(3-methacryloyloxypropionate), copper di(3-acryloyloxy-2-methylpropionate) and copper di(3-methacryloyloxy-2-methylpropionate).

Zinc diacrylate, zinc dimethacrylate, zinc acrylate methacrylate, copper diacrylate, copper dimethacrylate and copper acrylate methacrylate are most

10 preferred.

Mixtures of monomers of formula (III) and (IV) may be used.

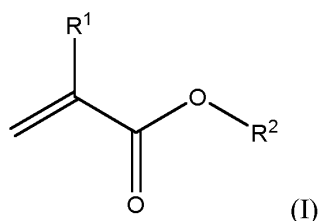
The metal containing (meth)acrylic copolymer (ii) preferably comprises 1.0 to 60 wt% of monomers (a3), such as 5.0 to 40 wt%, further preferred 10 to 30 wt% based on the total weight of monomers in the (meth)acrylic copolymer (ii).

15 Preferably a (meth)acrylate monomer (a5) as described below is present in the (meth)acrylic copolymer (ii) to thus form a copolymer with the metal containing monomer (a3).

The (meth)acrylate monomers (a5) preferably form at least 40 wt% of the metal containing (meth)acrylic polymer (ii), such as at least 60 wt% or at least 70

20 wt%.

Examples of suitable (meth)acrylate monomers (a5) are of formula (I) as herein before defined:



wherein R¹ is H or CH₃, and R² is a C1-C20 hydrocarbyl substituent,

25 preferably a C1-C10 alkyl substituent, such as a C1-C8 alkyl.

The R² group can be linear or branched. Most preferably R² is a methyl, ethyl, propyl, butyl, hexyl, octyl or decyl group which (if possible) may be linear or

branched. Ideally options for R^2 are methyl, ethyl, n-propyl, n-butyl, isobutyl or isooctyl.

Examples of suitable monomers of Formula (I) as monomer (a5) in metal containing (meth)acrylic copolymer (ii) include methyl (meth)acrylate, ethyl
5 (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, and isobornyl (meth)acrylate.

Preferred options for monomers of Formula (I) as monomer (a5) in
10 (meth)acrylic copolymer (ii) include methyl methacrylate, ethyl acrylate, n-butyl acrylate, n-butyl methacrylate, 2-ethylhexyl acrylate or isooctyl acrylate.

Mixtures of different monomers of formula (I) may also be used in (meth)acrylic copolymer (ii).

Preferably the (meth)acrylic copolymer (ii) comprises structural units
15 derived from metal containing monomers (a3) and (meth)acrylate monomers (a5).

The (meth)acrylic copolymer (ii) may also comprise additional monomers such as:

an alkoxyalkyl (meth)acrylate, such as 2-methoxyethyl (meth)acrylate, 2-ethoxyethyl (meth)acrylate, 3-methoxybutyl (meth)acrylate, 4-methoxybutyl
20 (meth)acrylate, 3-methoxy-n-propyl (meth)acrylate, 2-propoxyethyl (meth)acrylate, 2-butoxyethyl (meth)acrylate, isobutoxybutyldiglycol (meth)acrylate, 2-phenoxyethyl (meth)acrylate, methoxypolyethylene glycol (meth)acrylate, ethoxypolyethylene glycol (me)acrylate, butoxypolyethylene glycol (meth)acrylate, and phenoxypolyethylene glycol (meth)acrylate;

25 a hydroxyalkyl (meth)acrylate, such as hydroxymethyl (meth)acrylate, 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, 4-hydroxybutyl (meth)acrylate, and 2-hydroxy-3-phenoxypropyl (meth)acrylate; glycidyl (meth)acrylate;

an organosiloxane group-containing (meth)acrylate; and

30 a vinyl compound, such as styrene, α -methylstyrene, vinyl acetate, vinyl benzoate, vinyltoluene, acrylonitrile, vinylpyridine, vinylpyrrolidone, and vinyl

chloride. These monomers may be used alone or as a combination of two or more kinds thereof.

5 The metal containing (meth)acrylic copolymer (ii) preferably has a content of copper and/or zinc of from 0.5 to 25 wt%, more preferably from 1 to 20 wt%, based on the weight of the (meth)acrylic copolymer (ii).

The metal containing (meth)acrylic copolymer (ii) preferably has an acid value of from 30 to 300 mgKOH/g, more preferably from 60 to 250 mgKOH/g.

10 The number average molecular weight (Mn) of the (meth)acrylic copolymer (ii) is preferably from 500 to 100,000, and more preferably from 700 to 50,000. The weight average molecular weight (Mw) of the (meth)acrylic copolymer (ii) is preferably from 1,000 to 200,000, more preferably from 1,200 to 100,000, and further preferably from 3,000 to 100,000. Mw and Mn can be determined as described in the examples section.

15 The (meth)acrylic copolymer (ii) may be used alone or combination of two or more (meth)acrylic copolymer (ii) may be used.

The antifouling coating composition preferably comprises (meth)acrylic copolymer (ii) in 3 to 50 wt%, more preferably 5 to 20 wt%, and further preferably from 7 to 15 wt% based on the total weight of the coating composition.

20 **Monocarboxylic acid (iii)**

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

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

30 The monocarboxylic acid present in the antifouling coating composition of the present invention is preferably selected from a rosin, modified rosin, C6-C20 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). Preferably the metal carboxylate is a transition metal carboxylate, particularly preferably the metal carboxylate is a zinc carboxylate or copper carboxylate. The metal carboxylate may 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.

Representative examples of resin acids include abietic acid, neoabietic acid, dehydroabietic acid, palustric acid, levopimaric acid, pimaric acid, isopimaric acid, sandaracopimaric acid, communic acid and mercusic acid, secodehydroabietic acid. It will be appreciated that the rosins are derived from natural sources and as such they typically exist as a mixture of acids. 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 rosin typically have an acid value from 155 to 180 mg KOH/g as specified in ASTM D465. Preferred rosin for the compositions of the invention has an acid value from 155 to 180 mg KOH/g, more preferred 160 to 175 mg KOH/g, even more preferred 160 to 170 mg KOH/g. Commercial grades of rosin typically have a softening point (Ring & Ball) of 70 °C to 80 °C as specified in ASTM E28. Preferred rosin for the compositions of the invention has a softening point of 70 °C to 80 °C, more preferred 75 °C to 80 °C.

Representative examples of modified resin acids include dihydroabietic acid, dihydropimaric acid and tetrahydroabietic acid and modified rosin 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.

Representative examples of C5-C24 acyclic aliphatic monocarboxylic acids include VersaticTM acids, neodecanoic acid, 2,2,3,5-tetramethylhexanoic acid, 2,4-dimethyl-2-isopropylpentanoic acid, 2,5-dimethyl-2-ethylhexanoic acid, 2,2-

dimethyloctanoic acid, 2,2-diethylhexanoic acid, pivalic acid, 2,2-dimethylpropionic acid, trimethylacetic acid, neopentanoic acid, 2-ethylhexanoic acid, isononanoic acid, 3,5,5-trimethylhexanoic acid, isopalmitic acid, isostearic acid, 16-methylheptadecanoic acid and 12,15-dimethylhexadecanoic acid. The acyclic aliphatic monocarboxylic acid is preferably selected from liquid, acyclic C10-C24 monocarboxylic acids or liquid, branched C10-C24 monocarboxylic acids. It will be appreciated that many of the acyclic C10-C24 monocarboxylic acids may be derived from natural sources, in which case in isolated form they typically exist as a mixture of acids of differing chain lengths with varying degree of branching.

10 Preferably the monocarboxylic acid is rosin, modified rosin, acyclic C10-C24 monocarboxylic acid, C6-C20 cyclic monocarboxylic acid or metal salts thereof, such as rosin, modified rosin or metal salts thereof.

More preferably the monocarboxylic acid is rosin or modified rosin.

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

Gum rosin is most preferred.

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 metal salt thereof present in the binder (A) is 15 to 75 wt% preferably 25 to 60 wt%, based on the total weight of the binder (A).

30 The final antifouling coating composition of the invention preferably comprises 5.0 to 30 wt% of the monocarboxylic acid or metal salt thereof, such as 8 to 25 wt% based on the total coating composition.

The final antifouling coating composition of the invention preferably comprises 5.0 to 30 wt% of rosin, modified rosin or metal salt thereof, such as 8 to 25 wt% rosin, modified rosin or metal salt thereof based on the total coating composition.

5

The final antifouling coating composition of the invention preferably comprises 8.0 to 40 % solids volume of the monocarboxylic acid or metal salt thereof, such as 10 to 35 % solids volume, based on the total coating composition.

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

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

(A) a binder comprising

(i) a (meth)acrylic copolymer comprising 0.5 to 10 wt% (meth)acrylic acid monomers relative to the total weight of the monomers present in the copolymer;

15

(iii) a monocarboxylic acid or metal salt thereof;

wherein the antifouling coating composition comprising 8.0 to 40 % solids volume of component (iii) and 1.0 to 20 % solids volume component (i);

20

(B) 2.0 to 25 % solids volume cuprous oxide; and

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

25 **(Meth)acrylic polymer (iv)**

In one embodiment binder A of the coating composition of the present invention may further comprise a (meth)acrylic polymer (iv). This is different to (meth)acrylic copolymer (i) or (ii).

In one particularly preferred embodiment the binder A of the coating composition of the present invention comprises the combination of a (meth)acrylic copolymer (i) and a (meth)acrylic polymer (iv) as herein defined.

30

The (meth)acrylic polymer (iv) does not contain a metal containing monomer unit such as metal (meth)acrylate monomer (a3). The (meth)acrylic polymer (iv) does not contain an acid monomer (a1).

5 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, 2-octyl (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-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;

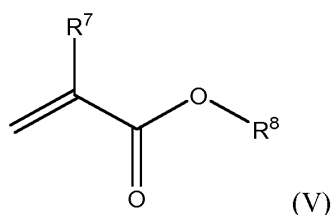
More preferred examples of (meth)acrylate monomers (a5) are of formula (I) as hereinbefore defined for (meth)acrylic copolymer (i).

25 Preferred options for monomers of Formula (I) 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 (I).

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

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wherein R^7 is H or CH_3 , and R^8 is a C3-C40 substituent, such as C3-C20 substituent, containing at least one oxygen or nitrogen atom, preferably at least one oxygen atom or R^8 represents a poly(alkylene glycol) group.

5 The (meth)acrylic copolymer (iv) may comprise at least one monomer of Formula (V) above in which the R^8 group is of formula $(CH_2CH_2O)_n-R^9$ where R^9 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^8 is of formula $(CH_2CH_2O)_n-R^9$ where R^9 is a C1-C10 alkyl substituent, preferably
 10 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.
 15

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 (V) above in which the R^8 group is a poly(alkylene glycol) group such as a
 20 poly(ethylene glycol) group. Such a group might have a formula $(CH_2CH_2O)_m-R^{10}$ or $(CH_2CH(CH_3)O)_m-R^{10}$ where R^{10} 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)
 25 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 (V) above in which the R^8 group is of formula $(CH_2C(O)O)_p-R^{11}$ or $(CH(CH_3)C(O)O)_p-R^{11}$ where R^{11} 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,
 5 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(oxy carbonylmethyl) methyl (meth)acrylate and oligo(oxy carbonylmethyl)
 10 ethyl (meth)acrylate.

The (meth)acrylic polymer (iv) may comprise at least one monomer of Formula (V) above in which the R^8 group is a cyclic group containing at least one oxygen or nitrogen atom, preferably at least one oxygen atom. More preferably, R^8 is a group $W-R^{12}$ having up to 40 carbon atoms wherein R^{12} is a cyclic ether, such as
 15 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-
 20 glycidyloxybutyl (meth)acrylate. Preferred cyclic ethers should contain at least 4 atoms in the ring. More preferably tetrahydrofurfuryl acrylate and isopropylideneglycerol methacrylate.

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

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

Monomers of Formula (I) preferably form at least 15 wt% of the (meth)acrylic polymer (iv). Particularly preferred amounts of the monomer of

Formula (I) 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 (I) are present, these amounts relate to the combined weight fraction of the monomers of Formula (I) in the copolymer.

5 In one preferred embodiment the (meth)acrylic polymer (iv) comprises at least one monomer of formula (I) and at least one monomer of formula (V).

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

 The (meth)acrylic polymer (iv) may also comprise structural units derived
10 from other ethylenically unsaturated monomers such as vinyl monomers vinyl 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,
15 especially 20,000 to 50,000. Mw is determined as described in the examples section. The (meth)acrylic polymer (iv) preferably has a polydispersity index (PDI) of from 1.5 to 5.0.

 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
20 values being measured according to the T_g test described in the examples section. Values less than 80 °C are preferred, such as less than 70 °C, e.g. less than 55 °C.

 The (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
25 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.

 The (meth)acrylic polymer (iv) may be present in an amount of 3.0 to 30% solids volume, preferably 5.0 to 25 % solids volume in the antifouling coating composition.

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

 (B) a binder comprising

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- (i) a (meth)acrylic copolymer comprising 0.5 to 10 wt% (meth)acrylic acid monomers relative to the total weight of the monomers present in the copolymer;
- (iii) a monocarboxylic acid or metal salt thereof;
- 5 (iv) a (meth)acrylic polymer preferably comprising at least one monomer of formula (I) as hereinbefore defined;
- wherein the antifouling coating composition comprising 8.0 to 40 % solids volume of component (iii), 3.0 to 30 % solids volume of component (iv), and 1.0 to 20 % solids volume component (i);
- 10 (B) 2.0 to 25 % solids volume cuprous oxide; and
- (C) 2.0 to 65 % solids volume hollow spheres.

Preparation of (meth)acrylic copolymers (i), (ii) and (iv)

The (meth)acrylic copolymer (i) 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 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. Optionally, chain transfer agent can be used to control the chain lengths in free-radical polymerization. In preparing a coating composition using any of the polymers, the polymer is preferably diluted with an organic solvent to give a polymer solution having an appropriate viscosity. From this standpoint, it is desirable to employ solution polymerization. In the case of copolymers, the polymer may be a random copolymer, an alternate copolymer, a gradient copolymer or a block copolymer.

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

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

Examples of the organic solvent include aromatic hydrocarbons such as xylene, toluene, mesitylene; ketones such as methyl ethyl ketone, methyl isobutyl ketone, methyl amyl ketone, methyl isoamyl ketone, diisobutyl ketone, cyclopentanone, cyclohexanone; esters such as butyl acetate, *tert*-butyl acetate, amyl acetate, propyl propionate, n-butyl propionate, isobutyl isobutyrate, ethylene glycol methyl ether acetate; ethers such as ethylene glycol dimethyl ether, diethylene glycol dimethyl ether, dibutyl ether, dioxane, tetrahydrofuran, alcohols such as n-butanol, isobutanol, methyl isobutyl carbinol, benzyl alcohol; ether alcohols such as 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.

Examples of chain transfer agent include aromatic compounds such as α -methylstyrene dimer; thioglycolic acid and thioglycolates such as methyl thioglycolate, ethyl thioglycolate, 2-ethylhexyl thioglycolate, octyl thioglycolate and isooctyl thioglycolate; mercaptopropionic acid and mercaptopropionates such as ethyl 2-mercaptopropionate, methyl 3-mercaptopropionate, ethyl 3-mercaptopropionate, butyl 3-mercaptopropionate, isooctyl 3-mercaptopropionate, octadecyl 3-mercaptopropionate and poly(propylene glycol) 3-mercaptopropionate; and thiols such as 1-propanethiol, 2-propanethiol, 2-methyl-1-propanethiol, 2-methyl-2-propanethiol, 1-butanethiol, 2-butanethiol, 3-methyl-1-butanethiol, 1-pentanethiol, 1-hexanethiol, 1-heptanethiol, 1-octanethiol, *sec*-octanethiol, *tert*-octanethiol, 1-nonanethiol, *tert*-nonanethiol, 1-decanethiol, 1-dodecanethiol, *tert*-dodecanethiol, 1-tetradecanethiol, 1-hexadecanethiol, and 1-octadecanethiol. The chain transfer agents may be used alone or as a combination of two or more thereof.

The metal-containing (meth)acrylic copolymer (ii) can be produced, for example, by using copolymerizing a metal-containing monomer (a3) by any free-

radical polymerization processes described above, preferably in the presence of a chain transfer agent. Alternatively, the metal-containing (meth)acrylic copolymer (ii) may be produced by a method of reacting a polymer having carboxylic acid groups, a monocarboxylic acid compound, and a metal compound, such as an inorganic metal compound, specific examples of which include an oxide, a hydroxide of copper or zinc, and/or an organic acid salt of copper or zinc (e.g., zinc acetate)), to introduce a metal containing group to the carboxylic acid group of the polymer.

The metal containing monomer (a3) can be synthesized, for example, by a known method, in which a metal compound, such as an inorganic metal compound, specific examples of which include an oxide, a hydroxide, a chloride and/or an organic acid salt of copper or zinc (e.g., zinc acetate), methacrylic acid and/or acrylic acid and optionally a monocarboxylic acid are heated to a suitable and stirred in the presence of an organic solvent and water.

Other Binder components

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:

(meth)acrylic polymers comprising silyl ester monomers such as triisopropyl methacrylate and triisopropyl acrylate;

hydrophilic copolymers, such as poly(*N*-vinyl pyrrolidone) copolymers and poly(ethylene glycol) copolymers;

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

saturated aliphatic polyesters, such as poly(lactic acid), poly(glycolic acid), poly(2-hydroxybutyric acid), poly(3-hydroxybutyric acid), poly(4-hydroxyvaleric acid), polycaprolactone and aliphatic polyester copolymer containing two or more of

the units selected from the above mentioned units;

alkyd resins and modified alkyd resins;

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 (these are not therefore monocarboxylic acids or salts thereof);

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;

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

The presence of a (meth)acrylic polymer comprising silyl ester monomers such as triisopropyl methacrylate and triisopropyl acrylate is especially preferred.

If, in addition to components (i), (ii), (iii) and (iv), a further binder
15 components are present, the weight of these components is preferably less than 20 wt% of the binder (A), such as less than 10 wt% or less than 5 wt%. It is preferred if no other binder components are present then the binder (A) consists of component (i) and/or component (ii) and optionally component (iii) and/or component (iv).

20 **Hollow spheres**

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.

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

Preferably the hollow microspheres 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
30 oxide glass, aluminosilicate glass, calcium sodium silicate glass and oxide glass.

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

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

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.

The antifouling paint composition comprises at least 2.5 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.

A minimum of 1.0 solids vol% of hollow spheres is preferred to achieve a significant reduction in the cuprous oxide content.

In wt%, the amount of hollow spheres preferred are likely in the range 0.1 to 15 wt%.

The ratio (solids vol%/solids vol%) between hollow spheres and cuprous oxide is preferably in the range of 0.1 to 20, preferably 0.1 to 10, especially 0.5 to 5.0.

The sum of the % solids volumes (vol%) of hollow spheres and cuprous oxide is preferably 8.0 to 70 SV% or 10 to 60 SV%. The sum of the % solids volumes (vol%) of hollow spheres and cuprous oxide is also preferably 15 to 70 solids vol%, especially 20 to 60 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 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 spheres to solids volume of cuprous oxide in the inventive examples are from 0.1:1 to 12:1, 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.

5 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 .

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

10 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.

The particle sizes of the hollow spheres can be determined using e.g. sieves and laser diffraction analysis.

15 The density of the hollow spheres varies with the nature of the hollow sphere in question.. The density of the hollow spheres of the invention may range from 0.1 to 1.0 g/cm^3 .

20 The crush strength of the hollow spheres should preferably be at least 1500 psi, or even more preferred 3000 psi or more, 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 might not withstand spray application and should thus be applied with brush or roller.

25 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.

Biocide

30 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.

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.

10 The antifouling coating composition of the invention may have 1.0 to 25 solids vol% of cuprous oxide, preferably 1.5 to 20 % solids volume, more preferably 5.0 to 15% solids volume.

The antifouling coating composition of the invention may have 8.0 to 47 wt% (dry) of cuprous oxide, such as 10 to 40 dry wt%. Where the coating composition is based on binder (i), the coating composition may contain 10 to 30.0 wt% cuprous oxide, such as 10 to 28 wt% cuprous oxide. Where the coating composition is based on binder (ii), the coating composition may contain 10 to 40 wt%, such as 10 to 35 wt%, preferably 10 to 30 wt% cuprous oxide.

20 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.

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

30 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-
 5 [1(2,3dimethylphenyl)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
 10 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
 15 ethylenebis(dithiocarbamate) [zineb], 4,5-dichloro-2-n-octyl-4-isothiazolin-3-one [DCOIT], *N*-dichlorofluoromethylthio-*N'*,*N'*-dimethyl-*N*-phenylsulfamide [dichlofluanid], 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.

20 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
 25 composition, such as 10 to 55 wt%, e.g. 15 to 50 wt%.

The combined amounts of biocides may form up to 50% solids volume of the coating composition, such as 2.0 to 40% solids volume, e.g. 5.0 to 30% solids volume.

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

- 33 -

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

- 5 (A) a binder comprising a (meth)acrylic copolymer (i) wherein the (meth)acrylic copolymer (i) is present in an amount of 1.0 to 12 wt%, preferably 2.0 to 7.0 wt%, relative to the total weight of the coating composition as a whole;
- (B) 1.0 to 30 % solids volume cuprous oxide; and
- (C) 1.0 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.

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

- (A) a binder comprising a (meth)acrylic copolymer (i) wherein the (meth)acrylic copolymer (i) is present in an amount of 1.0 to 12 wt%, preferably 2.0 to 7.0 wt%, relative to the total weight of the coating composition as a whole; and a
- 15 (meth)acrylic polymer (iv) wherein the (meth)acrylic polymer (iv) is 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;
- (B) 1.5 to 15 % solids volume cuprous oxide; and
- (C) 5.0 to 60 % solids volume hollow spheres
- 20 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 composition of the present invention may also comprise

25 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,

30 phthalocyanine blue, phthalocyanine green, naphthol red and diketopyrrolopyrrole red. Pigments may optionally be surface treated to be more easily dispersed in the paint composition.

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 minerals. Examples of extenders include dolomite, plastorite, calcite, quartz, barite, 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 10 % 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 3 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 rheology modifiers, wetting and dispersing agents and defoamers.

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.

Dehydrating agents improve the storage stability of the antifouling coating compositions comprising hydrolysable binder component such as (meth)acrylic silyl ester copolymer. 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. Example of dehydrating agents include 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. 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% and still more preferably 1.0-2.0 wt%, based on the total weight of the composition.

It is highly preferred if the antifouling composition contains a solvent. This solvent is preferably volatile and is preferably organic. Examples of organic solvents and thinners are aromatic hydrocarbons such as xylene, toluene, mesitylene; ketones such as methyl ethyl ketone, methyl propyl ketone, methyl isobutyl ketone, methyl isoamyl ketone, methyl amyl ketone, diisobutyl ketone, cyclopentanone, cyclohexanone; esters such as butyl acetate, *tert*-butyl acetate, amyl acetate, isoamyl acetate, propyl propionate, *n*-butyl propionate, isobutyl isobutyrate; ether esters such as ethylene glycol methyl ether acetate, ethyl 3-ethoxypropionate; ethers such as ethylene glycol dimethyl ether, diethylene glycol dimethyl ether, dibutyl ether, dioxane, tetrahydrofuran; alcohols such as *n*-butanol, isobutanol, methyl isobutyl

carbinol, benzyl alcohol; ether alcohols such as butoxyethanol, 1-methoxy-2-propanol; terpenes such as limonene; aliphatic hydrocarbons such as white spirit; and optionally a mixture of two or more solvents and thinners.

5 Preferred solvents are aromatic solvents, hydrocarbon solvents and ketone solvents, 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 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
10 comprise solvent and contribute to the total solvent content as specified above and that the solvent content will vary depending on the other components present and the end use of the coating composition.

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

15

Coating composition

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

20 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.

25 Pigment volume concentration (PVC) of formulations containing hollow spheres is preferably 30 to 80%, such as 40 to 65%. The density of antifouling paint may be e.g., 0.9 to 2.2 g/cm³, and density of the coating e.g., 1.0 to 2.5 g/cm³, such as 1.2 to 1.8 g/cm³.

The antifouling paint composition of the invention may have a viscosity of
30 150 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 as recommended by the suppliers of the ingredients and the mixing equipment.

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

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

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

15

Examples

Materials and methods

Determination of polymer solution viscosity

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

Determination of non-volatile matter content of the polymer solutions

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

Determination of polymer molecular weights distribution

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 μ 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.

Detector	RI
Wavelength	640 nm
Flow cell volume	12 μ l
Column Set	Agilent PLgel 5 μ 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 °C
Column Oven Temperature	35 °C
Detector Oven Temperature	35 °C
Data Processing	Omnisec 5.1
Calibration standards	Agilent Polystyrene Medium EasiVials (4 ml) Red, Yellow and Green

10

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

15

Determination of the glass transition temperature

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

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

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 tie-coat (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 III, 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.

5 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 300µm 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.

10 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.

15

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

20 3 – Poor – 36-50% of area fouled

4 – Very poor – >50% of area fouled

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

25

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.

30

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 h at 52 °C before immersion in seawater 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 h. The panels were then re-immersed. The rating after drying at 52 °C are reported in the tables with the paint examples.

- 10 The panels were rated as follows:
- 0 – No cracks
 - 1 – Very few cracks
 - 2 – Moderate number of cracks
 - 3 – Considerable number of cracks
 - 15 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 h at 52 °C before immersion in freshwater at 30 °C. At regular intervals, the panels are taken out and evaluated. The panels are evaluated for blistering visually. The panels were then re-immersed. The ratings are reported in the tables with the paint examples.

- 25 The panels were rated as follows:
- 0 – No blisters
 - 1 – Very few blisters
 - 2 – Moderate number of blisters
 - 3 – Considerable number of blisters
 - 30 4 – Dense blistering

Determination of degree of swelling in fresh water

The degree of swelling in fresh water 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 (DFT) for the tested coatings in the example part is $100 \pm 10 \mu\text{m}$. The PVC discs are immersed in freshwater, temperature-adjusted to $30 \text{ }^{\circ}\text{C} \pm 2 \text{ }^{\circ}\text{C}$ is used. The PVC discs are taken out at 4 weeks and 10 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 at the given time. An increase in film thickness is observed when the coating is swelling. Swelling as percentage of DFT is used for rating the degree of swelling as the coatings have different volume solids and hence will have different DFT.

Swelling was rated by the following scheme:

- 1 – $<30\%$ – good
- 20 2 – $30\text{-}50\%$ – acceptable
- 3 – $>50\%$ – poor, high degree of swelling

Binder production examples

25 Procedure for preparation of copolymer solution A1

40.0 parts xylene and 10.0 parts 1-methoxy-2-propanol were charged to a temperature-controlled reaction vessel equipped with a stirrer, a reflux condenser, a nitrogen inlet and a feed inlet. The reaction vessel was heated and maintained at the reaction temperature of $100 \text{ }^{\circ}\text{C}$. 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 tert-amyl peroxy-2-ethylhexanoate was prepared. The pre-mix was charged to the reaction vessel at a constant rate over 3 hours under a nitrogen atmosphere using a metering pump.

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After further 30 minutes reaction a boost initiator solution of 0.40 parts tert-amyl peroxy-2-ethylhexanoate and 5.0 parts xylene was fed to the reaction vessel at a constant rate over 20 minutes. The reaction vessel was maintained at the reaction temperature for a further 1.5 hour and then cooled to room temperature. The parts
5 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

10 54 parts xylene and 13 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 20 parts n-butyl acrylate, 60 parts methyl methacrylate, 20 parts 2-(2-ethoxyethoxy)ethyl acrylate, 11 parts xylene, 6
15 parts 1-methoxy-2-propanol and 1.5 parts 2,2'-azobis(2-methylbutyronitril) was prepared. The pre-mix was charged to the reaction vessel at a constant rate over 2.5 hours under a nitrogen atmosphere using a metering pump. After further 1 hour reaction a boost initiator solution of 0.4 parts 2,2'-azobis(2-methylbutyronitril) and 9 parts xylene was fed to the reaction vessel at a constant rate over 20 minutes. The
20 reaction vessel was maintained at the reaction temperature for a further 1.5 hour and then cooled to room temperature. The parts given above are all parts by weight.

The copolymer solution A2 had the following properties:

NVM 52.4 wt%; Viscosity 654 cP; Mw 24.4k; PDI 2.63; Tg 20 °C

25 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,
30 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

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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

10 Preparation of zinc rosinate solution Z1

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 stirring to get a homogenous solution.

The zinc rosinate solution Z1 had a non-volatile matter of 62.1 wt%, density of 1.04 g/cm³.

20 Synthesis zinc acrylate monomers ZnM1 to ZnM3

Procedure for preparation of copolymer solution ZnM1

16.0 parts xylene, 80.0 parts 1-methoxy-2-propanol and 34.0 parts zinc oxide 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 65 °C. A pre-mix of 30.1 parts acrylic acid, 35.9 parts methacrylic acid and 4.0 parts deionized water was prepared. The pre-mix was charged to the reaction vessel at a constant rate over 3 hours under a nitrogen atmosphere using a metering pump. The reaction vessel was maintained at the reaction temperature for a further 2 hours and then cooled to room temperature.

The parts given above are all parts by weight. NVM: 43.6 wt%

Procedure for preparation of copolymer solution ZnM2

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86.8 parts 1-methoxy-2-propanol and 27.6 parts zinc oxide 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 75 °C. A pre-mix of 17.1 parts acrylic acid, 20.4 parts methacrylic acid, 35.0 parts Versatic acid 10 was prepared. The pre-mix was charged to the reaction vessel at a constant rate over 3 hours under a nitrogen atmosphere using a metering pump. The reaction vessel was maintained at the reaction temperature for a further 2 hours and then cooled to room temperature. 13.2 parts 1-methoxy-2-propanol was added. The parts given above are all parts by weight. NVM: 55.8 wt%

Procedure for preparation of copolymer solution ZnM3

96.0 parts 1-methoxy-2-propanol and 33.9 parts zinc oxide 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 65 °C. A pre-mix of 30.1 parts acrylic acid, 36.0 parts methacrylic acid, 4.0 parts deionized water was prepared. The pre-mix was charged to the reaction vessel at a constant rate over 3 hours under a nitrogen atmosphere using a metering pump. The reaction vessel was maintained at the reaction temperature for a further 2 hours and then cooled to room temperature. The parts given above are all parts by weight. NVM: 44.9 wt%

Synthesis zinc acrylate copolymers M1 to M3

Procedure for preparation of zinc acrylate copolymer solution M1

61.3 parts xylene and 16.13 parts 1-methoxy-2-propanol were charged to a temperature-controlled reaction vessel equipped with a stirrer, a reflux condenser, a nitrogen inlet and a feed inlet. The reaction vessel was heated and maintained at the reaction temperature of 100 °C. A pre-mix of 68.7 parts ethyl acrylate, 5.4 parts 2-methoxyethyl acrylate, 25.9 parts ZnM1, 10.8 parts xylene, 0.98 parts 2,4-diphenyl-4-methyl-1-pentene, 2.5 parts 2,2'-azobis(2-methylpropionitrile) and 6.9 parts 2,2'-azodi(2-methylbutyronitrile). The pre-mix was charged to the reaction vessel at a

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constant rate over 4 hours under a nitrogen atmosphere using a metering pump. A boost initiator solution of 0.49 parts tert-butyl 2-ethylperoxyhexanoate and 7.5 parts xylene was fed to the reaction vessel at a constant rate over 30 minutes. The reaction vessel was maintained at the reaction temperature for a further 1.5 hour and then
5 cooled to room temperature. The copolymer solution was thinned with 3.9 parts xylene. The parts given above are all parts by weight.

The copolymer solution M1 had the following properties:

NVM: 47.0 wt%; Viscosity 8748 cP; Mw 5.4k; PDI 2.49; Tg 2 °C

10 Procedure for preparation of zinc acrylate copolymer solution M2

63.0 parts xylene and 10.0 parts 1-methoxy-2-propanol were charged to a temperature-controlled reaction vessel equipped with a stirrer, a reflux condenser, a nitrogen inlet and a feed inlet. The reaction vessel was heated and maintained at the reaction temperature of 100 °C. A pre-mix of 8.8 parts methyl methacrylate, 59.7
15 parts ethyl acrylate, 31.5 parts ZnM2, 10.0 parts 1-methoxy-2-propanol and 4.9 parts 2,2'-azodi(2-methylbutyronitrile). The pre-mix was charged to the reaction vessel at a constant rate over 4 hours under a nitrogen atmosphere using a metering pump. A boost initiator solution of 0.49 parts tert-butyl 2-ethylperoxyhexanoate and 7.0 parts xylene was fed to the reaction vessel at a constant rate over 30 minutes. The reaction
20 vessel was maintained at the reaction temperature for a further 1.5 hour and then cooled to room temperature. The copolymer solution was thinned with 9.8 parts xylene. The parts given above are all parts by weight.

The copolymer solution M2 had the following properties:

NVM: 45.8 wt%; Viscosity 1532 cP; Mw 5.0k; PDI 2.23; Tg 8 °C

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Procedure for preparation of zinc acrylate copolymer solution M3

60.0 parts xylene, 15.0 parts 1-methoxy-2-propanol and 3.9 parts ethyl acrylate 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
30 heated and maintained at the reaction temperature of 100 °C. A pre-mix of 14.8 parts methyl methacrylate, 47.3 parts ethyl acrylate, 14.8 parts n-butyl acrylate, 19.3 parts ZnM3, 10.0 parts xylene, 1.2 parts 2,4-diphenyl-4-methyl-1-pentene, 2.5 parts 2,2'-

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azobis(2-methylpropionitrile) and 6.4 parts 2,2'-azodi(2-methylbutyronitrile). The pre-mix was charged to the reaction vessel at a constant rate over 6 hours under a nitrogen atmosphere using a metering pump. A boost initiator solution of 0.49 parts tert-butyl 2-ethylperoxyhexanoate and 7.0 parts xylene was fed to the reaction vessel

5 at a constant rate over 30 minutes. The reaction vessel was maintained at the reaction temperature for a further 1.5 hour and then cooled to room temperature. The copolymer solution was thinned with 8.0 parts xylene. The parts given above are all parts by weight.

The copolymer solution M3 had the following properties: NVM: 47.5 wt%;

10 Viscosity 10348 cP; Mw 7.2k; PDI 2.97; Tg 4 °C

Table 2a gives comonomer ratios for the acrylic polymers and table 2b gives ratios for the preparation of zinc acrylate monomers ZnM1-3. Table 2c gives the monomer ratios for the preparation of copolymers M1-M3. Table 3 illustrates the

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

Table 2a – Copolymer monomer ratios

Component		A1	A2	S1
Monomers (parts by weight)	Methacrylic acid	3		
	n-Butyl acrylate	90	10	10
	n-Butyl methacrylate	7		
	Methyl methacrylate		60	10
	Triisopropylsilyl methacrylate			50
	2-(2-Ethoxyethoxy)ethyl acrylate		30	
	2-Methoxyethyl methacrylate			30
	Non-volatile matter (wt%)	66.0	52.4	60.0
Properties	Viscosity (cP)	369	654	1790
	Density (g/cm ³)	0.98	1.00	0.98
	M _w (x10 ³)	11.9	24.4	42.3
	PDI	4.7	2.6	3.1
	Tg (°C)	-41	20	30

Table 2b - Zinc acrylate monomers

Component		ZnM1	ZnM2	ZnM3
	ZnO	34.0	27.6	34.0

Component		ZnM1	ZnM2	ZnM3
Monomers (parts by weight)	Acrylic acid	30.1	17.1	36.0
	Methacrylic acid	36.0	20.4	30.0
	Versatic acid 10		35.0	
Properties	Non-volatile matter (wt%)	43.6	55.8	44.9
	Reaction temperature (°C)	65	75	65

Table 2c - Zinc acrylate copolymers

Component		M1	M2	M3
Monomers (parts by weight)	Methyl methacrylate		8.8	14.8
	Ethyl acrylate	68.7	59.7	51.2
	n-Butyl acrylate			14.8
	2-Methoxyethyl acrylate	5.4		
	ZnM1	25.9		
	ZnM2		31.5	
	ZnM3			19.3
Properties	Non-volatile matter (wt%)	47.0	45.8	47.5

Component	M1	M2	M3
	8748	1532	10348
	1.025	1.010	1.011
	5479	5003	7191
	2.49	2.23	2.97
	2	8	4

Table 3: Ingredients used in the examples

Ingredients	Trade name and/or manufacturer/supplier	Remarks
Binders*		
Gum Rosin	Portuguese gum rosin WW from A. V. Pound	Used as 60% in xylene (Gum rosin solution I)
Zn-rosinate ¹ Z1	Zinc rosinate/zinc salt of rosin	Solid content: 60 wt% in xylene
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 Pyrithione	CleanBio-Cu from Kolon	
Copper pyrrithione and Copper chelate complex ²	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		
Red iron oxide	Bayferrox Red 130 M from Lanxess	Pigment
TiO ₂	Tiona 121 from Tronox	Pigment
Talc	Finmtalc M12 from Elementis	Play extender
Zinc oxide	Zinc oxide red seal from Everzinc	Extender
Microdol	Microdol 11 from Onya	Nodular extender
Additives		
Bentonite clay	Bentone 52 – Bentonite clay LMP	Rheology additive
Wetting and dispersing agent 1		Polyamide PE salt

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

¹Preparation method described in experimental section. ² As described in WO2021113564A1

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 (10 μm – 90 μm) [μm]	Effective topcut [μm]	pH	Crush strength [psi]	Coated/ treated
Fillite 106	Ceramic hollow microspheres: cenospheres (fuel ash), aluminosilicate	Omaya	0.85-0.95	50	5-106	106	7.6	1500-3000	No

Hollow spheres	Material	Manufacturer/ Supplier	True density (g/cc)	d50 [μm]	Particle size range (10 μm – 90 μm) [μm]	Effective topcut [μm]	pH	Crush strength [psi]	Coated/ treated
Fillite 160	Ceramic hollow microspheres: cenospheres (fuel ash), aluminosilicate	Omya	0.66/0.78	80-90	5-160	180	~7	1500-3000	No
S28HS	Hollow glass microsphere, soda lime borosilicate	3M	0.28	30			9.5	3000	No
H38HS	Hollow glass microsphere, soda lime borosilicate	Sinosteel Maanshan Ltd and SMC Minerals and Chemicals AB	0.36-0.40	40	22 - 70	70	7-9	5500	Vinyl silane
iM30K	Hollow glass microspheres – soda lime borosilicate	3M	0.6	15.3	8.6-23.6	26.7	9.5	27000	No

General Paint preparation protocol

The components were mixed in the proportions given in Tables 5 to 9. The order of mixing the ingredients and preparation of pre-mix of selected ingredients were done in accordance with the raw material suppliers' guidelines. The ingredients were dispersed and grinded in the presence of glass beads (approx. 3-4 mm in diameter) in a 250 ml paint can using a vibrational shaker. 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 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 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)	A1	6.1	11.6		6.3	11.6		6.4	11.3		7.1	11.3		6.7	10.4		8.1	10.8		7.5	9.9	
Binder (iii)	Gum rosin solution	17.0	28.9		17.6	28.9		18.0	28.2		20.0	28.2		18.9	26.0		22.8	27.0		21.2	24.6	
Binder (iv)	A2	15.0	20.5		15.6	20.5		15.9	20.0		17.6	20.0		16.7	18.4		20.1	19.1		18.7	17.4	
Hollow spheres	Glass sphere S28HS				0.2	2.0		0.5	5.0		1.1	10.0		1.7	15.0		2.6	20.0		3.4	25.0	
Cu ₂ O	Cuprous oxide I	32.0	16.7		29.8	15.0		31.1	15.0		23.0	10.0		23.6	10.0					14.0	5.0	
	Cuprous oxide III																14.2	5.0				
Biocides, pigments and extenders	Copper pyrithione	1.4	2.3		1.4	2.3		1.4	2.3		1.6	2.3		1.5	2.0		1.6	1.8		1.7	1.9	
	Zincb	6.0	9.3		6.1	9.1		6.0	8.7		6.7	8.7		7.2	9.1		6.8	7.4		7.3	7.8	
	Iron oxide red	2.8	1.7		2.8	1.6		2.8	1.6		3.1	1.6		2.6	1.3		2.8	1.2		2.8	1.2	
	TiO ₂	2.8	2.1		2.8	2.0		2.8	2.0		3.2	2.0		2.7	1.6		2.8	1.5		2.8	1.4	
	Zinc oxide	7.2	3.9		7.4	3.9		6.0	3.0		6.7	3.0		6.7	2.9		8.0	3.0		7.0	2.6	
Additives	Bentonite clay	0.9	1.8		0.9	1.8		0.9	1.8		1.0	1.8		1.1	1.8		1.2	1.8		1.2	1.8	
	Wetting and dispersing agent I	0.9	1.3		0.9	1.3		0.9	1.3		1.0	1.3		1.1	1.3		1.2	1.3		1.2	1.3	
Solvents	Xylene	5.3			5.5			4.3			4.8			6.4			4.3			7.5		
	Aromatic hydrocarbons	2.2			2.2			2.2			2.5			2.6			2.9			3.0		
	Ethanol	0.5			0.5			0.5			0.6			0.6			0.7			0.7		

[illegible]

Table 6: Inventive paint examples

		Ex-7		Ex-8		Ex-9		Ex-10		Ex-11		Ex-12		Ex-13	
		wt%	%SV	wt%	%SV	wt%	%SV	wt%	%SV	wt%	%SV	wt%	%SV	wt%	%SV
Binder (i)	A1	7.1	8.9	7.3	10.2	8.4	10.2	5.3	9.3	7.1	11.4	6.2	8.3	6.9	7.8
Binder (iii)	Gum rosin solution	19.9	22.2	20.6	25.5	23.6	25.5	14.9	23.2	19.9	28.4	17.3	20.8	19.5	19.4
Binder (iv)	A2	17.6	15.8	18.2	18.1	20.9	18.1	13.2	16.4	17.5	20.1	15.3	14.8	17.2	13.7
Hollow spheres	Glass sphere S28HS	4.2	30.0	2.5	20.0	3.6	25.0					3.9	30.0	6.3	40.0
	Fillite 106							4.1	15.0	2.9	10.0				
Cu ₂ O	Cuprous oxide I	14.5	5.0	19.6	7.5	7.5	2.5			22.8	10.0	27.1	10.0	16.4	5.0
	Cuprous oxide II							30.2	15.0						
Biocides, pigments and extenders	Medetomidine (20% solution)			1.1	0.4	1.1	0.4			1.0	0.5			1.1	0.3
	Copper pyrrithione	1.8	2.0	1.9	2.3	2.2	2.4	1.4	2.2	1.6	2.3	1.6	1.9	1.9	1.9
	Zincb	8.0	8.2	6.3	7.2	7.6	7.5	6.2	8.8	6.1	8.0	6.2	6.8	6.1	5.6
	Red iron oxide	2.8	1.1	2.8	1.2	2.8	1.1	2.8	1.5	2.8	1.4	1.5	0.6	0.8	0.3
	TiO ₂	2.8	1.4	2.8	1.5	2.8	1.3	2.8	1.9	2.8	1.8	2.7	1.4	1.6	0.7
	Zinc oxide	6.6	2.4	6.8	2.7	7.9	2.7	7.2	3.6	6.7	3.0	5.7	2.2	6.5	2.1
Additives	Bentonite clay	1.3	1.8	1.1	1.8	1.3	1.8	0.9	1.8	1.0	1.8	1.1	1.8	1.4	1.8
	Wetting and dispersing agent I	1.3	1.3	1.1	1.3	1.3	1.3	0.9	1.3	1.0	1.3	1.1	1.3	1.4	1.3
	Xylene	8.5		4.4		5.1		7.4		3.8		6.9		8.9	

		Ex-7		Ex-8		Ex-9		Ex-10		Ex-11		Ex-12		Ex-13	
	Aromatic hydrocarbons	3.0		2.7		3.1		2.3		2.5		2.7		3.3	
	Ethanol	0.7		0.7		0.8		0.5		0.6		0.7		0.8	
	Sum	100	100	100	100	100	100	100	100	100	100	100	100	100	100
Calculated paint properties	%SV Spheres	30		20		25		15		10		30		40	
	%SV Cu ₂ O	5		8		2		15		10		10		5	
	Sum %SV spheres + Cu ₂ O	35		27		28		30		20		40		45	
	Ratio %SV spheres / Cu ₂ O	6.0		2.7		10.0		1.0		1.0		3.0		7.9	
	Volume solids (%)	58		58		58		56		56		60		60	
	VOC (g/L)	367		367		367		383		384		350		350	
	Density dry coating (g/cm ³)	1.4		1.6		1.3		2.1		1.9		1.6		1.2	
Test results	PVC (%)	50		43		43		48		37		53		56	
	Viscosity (cP)	380		582		513		374		573		494		370	
	Antifouling performance 4 months	0		0		0		0		0		0		0	
	Swelling FW 4 weeks	1		1		1		1		1		1		1	
	Blistering FW 8 weeks	0		0		0		0		0		0		0	
	Cracking SW 12 weeks	0		0		0		1		0		0		0	

Table 7: Inventive and comparative paint examples

		Ex-14		Ex-15		Ex-16		Ex-17		CoEx-2	
		wt%	%SV	wt%	%SV	wt%	%SV	wt%	%SV	wt%	%SV
Binder (i)	A1	6.6	6.6	5.3	4.7	6.4	6.1	6.9	6.3	9.8	11.6
Binder (iii)	Gum rosin solution	18.7	16.5	14.9	11.8	17.9	15.1	19.4	15.6	27.6	28.9
Binder (iv)	A2	16.5	11.7	131	8.4	15.8	10.7	17.1	11.1	24.3	20.5
Hollow spheres	Glass sphere S28HS	8.8	50.0	11.9	60.0	9.3	50.0	9.8	50.0	3.0	20.0
Cu ₂ O	Cuprous oxide I	18.4	5.0	20.4	5.0	19.2	5.0	10.1	2.5		
Pigments and biocides	Medetomidine (20% solution)					2.0	0.6	2.1	0.5		
	Copper Pyrithione	1.6	1.4	1.6	1.3	2.2	1.9	2.3	1.9	1.9	2.0
	Zineb	4.7	3.8	6.1	4.4	6.6	5.1	7.7	5.7	9.0	8.6
	Red iron oxide					1.1	0.3	2.7	0.8	2.5	0.9
	TiO ₂					1.4	0.5	2.7	1.0	2.8	1.3
Additives	Zinc oxide	6.1	1.7	4.8	1.2	5.8	1.6	6.5	1.7	9.2	3.1
	Bentonite clay	1.5	1.8	1.6	1.8	1.4	1.8	1.5	1.8	1.3	1.8
	Wetting and dispersing agent I	1.5	1.3	1.6	1.3	1.4	1.3	1.5	1.3	1.3	1.3
Solvents	Xylene	11.2		13.9		5.3		5.1		3.1	
	Aromatic hydrocarbons	3.6		3.8		3.5		3.7		3.2	
	Ethanol	0.9		0.9		0.8		0.9		0.8	
	Sum	100	100	100	100	100	100	100	100	100	100
Calculated paint properties	Ratio %SV spheres: Cu ₂ O	10.0		12.1		10.0		20.0		-	

	Ex-14	Ex-15	Ex-16	Ex-17	CoEx-2
	Sum %SV spheres + Cu ₂ O	65	55	52	20
	%SV Spheres	50	50	50	20
	%SV Cu ₂ O	5	5	2	-
	Volume solids (%)	62	67	67	58
	VOC (g/L)	333	292	292	366
	Density dry coating (g/cm ³)	1.1	1.1	1.0	1.2
	PVC (%)	62	65	64	36
Test results	Viscosity (cP)	327	631	677	656
	Antifouling performance raft 4 months	0	0	0	4
	Swelling FW 4 weeks	1	1	1	1
	Blistering FW 8 weeks	0	0	0	2
	Cracking SW 12 weeks	0	0	0	0

Table 8: Inventive paint examples

		Ex-18		Ex-19		Ex-20		Ex-21	
		wt%	%SV	wt%	%SV	wt%	%SV	wt%	%SV
Binder (i)	A1	7.6	9.1	6.8	10.0	7.1	10.1	7.3	11.4
	Zn-rosinate Z1					21.1	25.1		
Binders (iii)	Gum rosin solution	21.3	22.7	21.4	27.9			20.6	28.4
	A2	18.7	16.1	18.5	19.4	17.6	17.8	18.2	20.1
Other binder	S1		1.2	1.5					
Hollow spheres	Glass sphere S28HS	3.7	25.0			2.5	20.0		
	Glass sphere H38HS							1.5	10.0
	Fillite 106			4.8	15.0				
Cu ₂ O	Cuprous oxide I	7.6	2.5	12.5	5.0	25.8	10.0	17.7	7.5
	Medetomidine (20% solution)			1.1	0.5	1.0	0.4		
Biocides, pigments and extenders	Copper pyrithione and copper chelate complex mixture	7.5	8.2						
	Copper pyrithione			1.7	2.2	1.7	2.1	1.7	2.4
	Zineb	8.6	8.4	7.7	9.2	7.5	8.7	7.6	9.5
	Red iron oxide	2.8	1.1	2.8	1.3	2.7	1.2	3.2	1.6
	TiO ₂	2.8	1.3	2.8	1.6	2.7	1.5	3.2	2.0
	Zinc	7.0	2.4	7.6	3.2			9.1	4.0
	Bentonite clay	1.3	1.8	1.1	1.8	1.1	1.8	1.1	1.8
Additives	Wetting and dispersing agent I	1.3	1.3	1.1	1.3	1.1	1.3	1.1	1.3
Solvents	Xylene	6.1		5.6		4.7		4.7	

Table 9: Inventive paint examples

		Ex-22			Ex-23			Ex-24			Ex-25		
		wt%	%SV		wt%	%SV		wt%	%SV		wt%	%SV	
Binder (i)		7.4	10.8		6.3	8.9		6.2	9.5		6.6	10.4	
Binder (iii)	A1												
	Gum rosin solution	20.9	27.0		17.8	22.2		17.4	23.7		18.6	26.0	
Binder (iv)	A2	18.4	19.1		15.7	15.8		15.3	16.8		16.4	18.4	
Hollow spheres	Glass sphere S28HS				3.1	25.0							
	Glass sphere H38HS	2.5	15.0										
	Glass sphere iM30K										3.6	15.0	
	Fillite 106												
	Fillite 160							5.3	20.0				
Cu ₂ O	Cuprous oxide III				26.8	10.0							
	Cuprous oxide I	18.9	7.5					23.9	10.0		23.2	10.0	
	Medetomidine (20% solution)												
Biocides, pigments and extenders	Copper pyrrithione and copper chelate complex				7.5	9.7							
	Copper pyrrithione	1.8	2.3					1.6	2.2		1.5	2.1	
	Zineb	7.7	9.1					7.1	8.8		6.9	8.9	
	Red iron oxide	2.9	1.3		2.8	1.3		2.8	1.4		2.8	1.4	
	TiO ₂	2.8	1.6		2.8	1.6		2.8	1.7		2.8	1.7	
	Zinc oxide	7.4	3.0		6.3	2.5		6.5	2.8		6.3	2.8	
Additives	Bentonite clay	1.1	1.8		1.1	1.8		1.0	1.8		1.0	1.8	

		Ex-22			Ex-23			Ex-24			Ex-25		
		wt%	%SV		wt%	%SV		wt%	%SV		wt%	%SV	
Solvents	Wetting and dispersing agent I	1.1	1.3		1.1	1.3		1.0	1.3		1.0	1.3	
	Xylene	3.9			5.6			6.0			6.2		
	Aromatic hydrocarbons	2.6			2.6			2.5			2.5		
	Ethanol	0.6			0.6			0.6			0.6		
	Sum	100	100		100	100		100	100		100	100	
Calculated paint properties	%SV Spheres	15			25			20			15		
	%SV Cu ₂ O	8			10			10			10		
	Sum %SV spheres + Cu ₂ O	23			35			30			25		
	Ratio %SV sphere / Cu ₂ O	2.0			2.5			2.0			1.5		
	Volume solids (%)	58			60			58			56		
	VOC (g/L)	366			350			367			383		
	Density dry coating (g/cm ³)	1.7			1.7			1.8			1.8		
	PVC (%)	40			50			47			42		
	Viscosity (cP)	598			461			434			445		
	Antifouling performance 4 months	0			0			0			0		
Test results	Swelling FW 4 weeks	1			1			1			1		
	Blistering FW 8 weeks	0			1			0			0		
	Cracking SW 12 weeks	1			0			1			0		

Table 10: Inventive examples

[illegible]

		Ex-26	Ex-27	Ex-28	Ex-29	Ex-30
Calculated paint properties	%SV Spheres	10	20	20	25	5.0
	%SV Cu ₂ O	15	10	7.0	5.0	5.0
	Sum %SV spheres + Cu ₂ O	25	30	27	30	10
	Ratio %SV spheres / Cu ₂ O	0.7	2.0	2.7	5.0	1.0
	Volume solids (%)	60.0	67.0	69.0	66.0	65.0
	VOC (g/L)	446	393	388	400	438
	Density dry coating (g/cm ³)	1.8	1.4	1.3	1.2	1.5
	PVC (%)	38	40	40	44	31
Test results	Viscosity (cP)	103	406	262	222	305
	Antifouling performance 4 months	0	0	1	0	0
	Swelling FW 4 weeks	1	1	1	1	1
	Blistering FW 8 weeks	0	0	0	0	0
	Cracking SW 12 weeks	0	0	0	0	0

Results

Table 5: CoEx-1 shows an antifouling paint with a binder system based on rosin and acrylic binders, containing 32 wt% cuprous oxide, corresponding to 17 vol% in the dry coating (%SV). The examples Ex-1 to Ex-6 show that parts of the cuprous oxide can be exchanged with hollow glass spheres (%SV Cu₂O by %SV hollow spheres) while still maintaining sufficient antifouling performance and mechanical properties.

Ex-1 and Ex-2 show 15 %SV of cuprous oxide, with 2 and 5 %SV hollow glass spheres. Ex-5 and Ex-6 show 5 %SV of cuprous oxide and 20 and 25 %SV of hollow glass spheres. As lightweight hollow spheres typically give a reduced viscosity, it is possible to increase the volume solids in the formulations with more spheres, such as volume solids of 58% in Ex-5. As can be seen from Table 5, the more hollow spheres used, the lighter the density of the coating meaning a lower weight of the coating if the same dry film thickness (DFT) is applied.

The Table 6 Examples show cuprous oxide content down to 2.5 %SV, Ex-9. Hollow cenospheres can be used, Ex-10 and Ex-11 show 15 and 10 %SV, respectively.

The Table 7 Examples show that the volume of spheres can be increased further, e.g. 50 %SV or 60 %SV shown by examples Ex-14 to Ex-17 without interfering with the antifouling performance or the mechanical properties. The volume solids of the formulations are increased to above 60%, meaning calculated VOC of 292-333 g/L. Comparative example CoEx-2 is without any cuprous oxide in the formulation and shows poor antifouling performance after 1 month exposure in Singapore. The formulation also shows somewhat lower resistance to blistering during freshwater immersion for 4 weeks.

The Table 8 Examples show some variations in the binder system; silyl acrylate can be included (Ex-19) and/or zinc rosinate (Ex-20 and Ex-21) while maintaining the antifouling performance. The experiments show that both rosin acid and metal salts of rosin can be used in the invention.

The Table 8 Examples also show use of the hollow glass spheres H38HS and iM30K, and the larger cenospheres Fillite 160. The results show that the antifouling

performance is maintained with a variety of different hollow spheres, both coated/uncoated hollow glass spheres and hollow ceramic spheres.

The sum of %SV cuprous oxide and %SV hollow spheres is shown from 17 %SV to 65.

- 5 Cuprous oxide of different particle sizes is used to show the effect is not limited to one grade/particle size of cuprous oxide. The color of cuprous oxide gives an indication of size; lighter/more orange for the finer particles and darker/more purple for the larger sizes. Cu orange is used in Ex-10 Table 6, LoLo Tint in Ex-5 Table 5 and Ex-23 Table 9.
- 10 The Table 10 Examples show that binder systems based on different metal-containing (meth)acrylic polymers and rosin can be used while maintaining the good mechanical properties and antifouling performance; either alone or together with e.g. a silyl acrylic copolymer (Ex-27). The level of cuprous oxide in Ex-26 to Ex-30 varies from 15 %SV to 5 %SV, while the level of glass spheres is 5 %SV to 25
- 15 %SV. Ex-29 and Ex-30 show good antifouling performance with 5 %SV cuprous oxide.

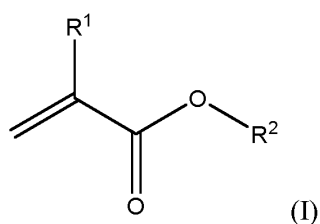
Claims

1. An antifouling coating composition comprising:
 - (A) a binder comprising
 - (i) a (meth)acrylic copolymer comprising 0.5 to 10 wt% (meth)acrylic acid monomers relative to the total weight of monomers in the (meth)acrylic copolymer; and/or
 - (ii) a metal containing (meth)acrylic copolymer wherein the metal is selected from Zn or Cu;
 - (B) 1.0 to 25 % solids volume cuprous oxide; and
 - (C) 1.0 to 65 % solids volume hollow spheres.
2. An antifouling coating composition as claimed in any preceding claim wherein the binder (A) further comprises a monocarboxylic acid or metal salt thereof (iii), preferably rosin, hydrogenated rosin or a metal salt thereof.
3. An antifouling coating composition as claimed in any preceding claim wherein the hollow spheres comprise ceramic or glass.
4. An antifouling coating composition as claimed in any preceding claim wherein the total amount of cuprous oxide and hollow spheres combined is in the range 8.0 to 70 SV%, such as 15 to 70 % solids volume based on the antifouling coating composition as a whole, such as 15 to 60 % solids volume.
5. An antifouling coating composition as claimed in any preceding claim wherein the hollow spheres are hollow microspheres and preferably have a d₅₀ between 10 and 100 µm.
6. An antifouling coating composition as claimed in any preceding claim comprising
 - (B) 1.5 to 15 % solids volume cuprous oxide; and
 - (C) 5.0 to 60 % solids volume hollow spheres.

7. An antifouling coating composition as claimed in any preceding claim wherein the binder (A) further comprises a (meth)acrylic polymer (iv).

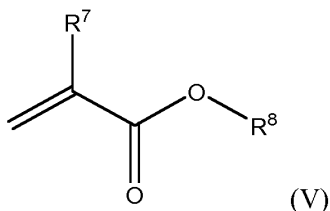
5 8. An antifouling coating composition as claimed in claim 7 wherein the (meth)acrylic polymer (iv) comprises as monomers:

i. at least one, such as at least two, (meth)acrylate of Formula (I):



10 wherein R¹ is H or CH₃, and R² is a C1-C20 hydrocarbyl substituent, preferably a C1-10 alkyl substituent, such as a C1-8 alkyl.

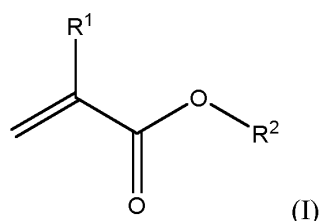
9. An antifouling coating composition as claimed in claim 8 wherein the (meth)acrylic polymer (iv) comprises at least one monomer of formula (V)



15 wherein R⁷ is H or CH₃, and R⁸ is a C3-40 substituent, such as C3-C20 substituent, containing at least one oxygen or nitrogen atom.

10. An antifouling coating composition as claimed in any preceding claim
20 wherein the (meth)acrylic copolymer (i) is present and comprises as monomers at least one, such as at least two, (meth)acrylate of Formula (I):

- 72 -



wherein R^1 is H or CH_3 , and R^2 is a C1-C20 hydrocarbyl substituent, preferably a C1-10 alkyl substituent, such as a C1-8 alkyl; and (meth)acrylic acid.

5

11. An antifouling coating composition as claimed in claim 1 to 10 comprising:
 (A) a binder comprising a (meth)acrylic copolymer (i) wherein the (meth)acrylic copolymer (i) is present in an amount of 1.0 to 12 wt%, preferably 2.0 to 7.0 wt%, relative to the total weight of the coating composition as a whole;

10

(B) 1.0 to 25% solids volume cuprous oxide; and
 (C) 1.0 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.

15

12. An antifouling coating composition as claimed in any preceding claim wherein the metal containing (meth)acrylic copolymer comprising a monomer which is a (meth)acrylate monomer comprising side chains of formula (II)



20

wherein M represents zinc or copper and R^3 represents an organic group.

13. 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

14. 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 acid or salt thereof or liquid, acyclic branched C12-24 monocarboxylic acid or salt thereof, such as contains no such material.

5

15. An antifouling coating composition as claimed in any preceding claim where if the coating composition is based on binder component (i), the coating composition contains 10 to 30.0 wt% cuprous oxide, such as 10 to 28 wt% cuprous oxide; or

10 where the coating composition is based on binder component (ii), the coating composition contains 10 to 40 wt%, such as 10 to 35 wt%, preferably 10 to 30 wt% cuprous oxide.

16. A process for protecting an object from fouling, said process comprising coating at least a part of said object which is subject to fouling with an antifouling
15 coating composition as claimed in any of claims 1 to 15.

17. A substrate coated with an antifouling coating composition as claimed in any of claims 1 to 15.

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