WO95/10568 describes paint compositions comprising 1 to 20 wt% wood rosin, 20 to 70 wt% cuprous oxide, 1 to 25 wt% zinc pyrithione, and 0.3 to 15 wt% of oxalic acid or a carboxylic acid of formula (HOOC)nRCOOH where n is 0 or 1 and R is C1 to C20 alkyl, alkenyl, alkynyl, cycloalkyl, cycloalkenyl, cycloalkynyl, aryl, aralkyl and combinations thereof. Preferred carboxylic acids are those in which R is C3 to C10. Such compositions are said to have enhanced biocidal efficacy and enhanced resistance to gelation. With the exception of Formulation examples 2 and 12, the exemplified paint compositions also contain VAGH resin, which is a vinyl chloride-vinyl acetate-vinyl alcohol terpolymer. Formulation examples 2 and 12 include the acrylic acid/methyl methacrylate copolymer ACRYLOID B48M and a naphthenic acid. Formulation 12 does not contain wood rosin and is therefore a comparative example.

The inventors have now unexpectedly established that a coating composition having the features of claim 1, inter alia a (meth)acrylate binder, a rosin, a liquid, C12-C24 monocarboxylic acid component and a biocide, are effective antifouling coating compositions which exhibit reduced thickness of the leached layer. Furthermore, reduced thickness of the leached layer is achieved whilst maintaining or even reducing paint viscosity at a given VOC (volatile organic compounds) content. This makes it possible to make antifouling paints having higher volume solids and lower level of VOC. This results in improved paint manufacturing efficiency and an improved application process and reduced environmental impact.

Summary ~~of Invention~~

~~Viewed from a first aspect the invention~~The disclosure provides a marine antifouling coating composition comprising:

(i) an acrylic binder comprising at least one polymer comprising (meth)acrylate and/or silyl (meth)acrylate monomers;

(ii) one or more rosins or derivatives thereof;

(iii) one or more marine antifouling agents; and

(iv) one or more monocarboxylic acids selected from liquid, acyclic, saturated C12-C24 monocarboxylic acids or a salt thereof or liquid, acyclic, branched C12-C24 monocarboxylic acids or a salt thereof.

~~Viewed from another aspect the invention~~The disclosure provides a marine antifouling coating composition comprising:

(i) at least 5 wt% of an acrylic binder comprising at least one polymer comprising (meth)acrylate and/or silyl (meth)acrylate monomers;

(ii) one or more rosins or derivatives thereof;

(iii) one or more marine antifouling agents; and

(iv) one or more monocarboxylic acids selected from liquid, acyclic, saturated C12-C24 monocarboxylic acids or a salt thereof or liquid, acyclic, branched C12-C24 monocarboxylic acids or a salt thereof.

In one ~~embodiment~~example component (iv) is present in an amount of 0.5 to 10 wt% of the composition.

In one aspect, the present disclosure provides a marine antifouling coating composition comprising:

(i) 5.0 to 40 wt% of an acrylic binder comprising at least one polymer comprising (meth)acrylate and/or silyl (meth)acrylate monomers;

(ii) 0.5 to 30 wt% of one or more rosins or derivatives thereof;

(iii) 0.5 to 70 wt% of one or more marine antifouling agents; and

(iv) 0.5 to 10 wt% of one or more monocarboxylic acids or a salt thereof selected from liquid, acyclic, saturated C12-C24 monocarboxylic acids or a salt thereof or liquid, acyclic, branched C12-C24 monocarboxylic acids or a salt thereof.

In one ~~embodiment~~example component (iv) is a C14-C20 monocarboxylic acid or a salt thereof, such as C16-C20 monocarboxylic acid or a salt thereof.

In a further ~~embodiment~~example the degree of branching of the monocarboxylic acid component (iv) is greater than 70%.

In a further ~~embodiment~~example the monocarboxylic acid is at least one selected from isopalmitic acid or isostearic acid.

In a further ~~embodiment~~example the ratio of (ii):(iv) on a dry weight basis is in the range of 90:10 to 40:60.

In a further ~~embodiment~~example the rosin is gum rosin or a derivative thereof.

In a further ~~embodiment~~example the component (ii) is present in an amount of 2.5 to 20 wt% of the composition.

In a further ~~embodiment~~example the acrylic binder component (i) comprises at least one polymer comprising at least one of the following monomers: (meth)acrylic acid, methyl methacrylate, 2-methoxyethyl (meth)acrylate, n-butyl (meth)acrylate, 2-(2-ethoxyethoxy)ethyl (meth)acrylate, tetrahydrofurfuryl acrylate and triisopropylsilyl (meth)acrylate.

In a further ~~embodiment~~example the component (i) is present in an amount of 0.5 to 20 wt% of the composition.

In a further ~~embodiment~~example the marine antifouling agent (iii) comprises at least one of cuprous oxide, copper pyrithione or zineb.

In a further ~~embodiment~~example the antifouling coating composition has a VOC of less than 400 g/L.

~~Viewed from another aspect the invention~~The disclosure provides a process for protecting an object from fouling comprising coating at least a part of said object which is subject to fouling with an antifouling coating composition as hereinbefore described.

In another aspect, the present disclosure provides a process comprising the step of applying a marine antifouling coating composition as described herein on a substrate.

~~Viewed from another aspect the invention~~The disclosure provides an object coated with an antifouling coating composition as hereinbefore defined.

In another aspect, the present disclosure provides a substrate coated with an antifouling coating composition as described herein.

~~Viewed from another aspect the invention~~The disclosure provides the use of one or more monocarboxylic acids selected from liquid, acyclic, saturated C12-C24 monocarboxylic acids or a salt thereof or liquid, acyclic, branched C12-C24 monocarboxylic acids or a salt thereof as hereinbefore defined to reduce the leached layer formation in a marine coating composition comprising:

(i) an acrylic binder comprising at least one polymer comprising (meth)acrylate and/or silyl (meth)acrylate monomers;

(ii) rosin and/or derivatives thereof; and

(iii) a marine antifouling agent.

In another aspect, the present disclosure provides use of 0.5 to 10 wt% of one or more monocarboxylic acids selected from liquid, acyclic, saturated C12-C24 monocarboxylic acids or a salt thereof or liquid, acyclic, branched C12-C24 monocarboxylic acids or a salt thereof as described herein to reduce the leached layer thickness in a marine coating composition comprising:

(i) 5.0 to 40 wt% of an acrylic binder comprising at least one polymer comprising (meth)acrylate and/or silyl (meth)acrylate monomers;

(ii) 0.5 to 30 wt% of rosin and/or derivatives thereof; and

(iii) 0.5 to 70 wt% of a marine antifouling agent.

Definitions

The following terminology is used throughout unless context allows otherwise.

The term (meth)acrylic acid means acrylic acid or methacrylic acid.

The term (meth)acrylate covers methacrylate or acrylate.

The term liquid means that the monocarboxylic acid is in liquid form at 23°C and ambient pressure (1 atm).

The term “marine antifouling agent” refers to a compound or mixtures of compounds that prevents the settlement of marine organisms on a surface, and/or prevents the growth of marine organisms on a surface and/or encourages the dislodgement of marine organisms from a surface.

Claims

1. A marine antifouling coating composition comprising:

(i) 5.0 to 40 wt% of an acrylic binder comprising at least one polymer comprising (meth)acrylate and/or silyl (meth)acrylate monomers;

(ii) 0.5 to 30 wt% of one or more rosins or derivatives thereof;

(iii) 0.5 to 70 wt% of one or more marine antifouling agents; and

(iv) 0.5 to 10 wt% of one or more monocarboxylic acids or a salt thereof selected from liquid, acyclic, saturated C12-C24 monocarboxylic acids or a salt thereof or liquid, acyclic, branched C12-C24 monocarboxylic acids or a salt thereof.

~~2. A marine antifouling coating composition according to claim 1 wherein component (iv) is present in an amount of 0.5 to 10 wt% of the composition.~~

~~3~~2. A marine antifouling coating composition according to ~~any of claims 1 to 2~~claim 1 wherein said monocarboxylic acid comprises 14-20 carbon atoms, preferably 16 to 20 carbon atoms.

~~4~~3. A marine antifouling coating composition according to any preceding claim wherein the degree of branching of the monocarboxylic acid component (iv) is greater than 70%.

~~5~~4. A marine antifouling coating composition according to any preceding claim wherein the monocarboxylic acid comprises at least one selected from isopalmitic acid or isostearic acid, e.g. a mixture thereof.

~~6~~5. A marine antifouling coating composition according to any preceding claim wherein the ratio of (ii):(iv) on a dry weight basis is in the range of 90:10 to 40:60.

~~7~~6. A marine antifouling coating composition according to any preceding claim wherein the rosin is gum rosin or a derivative thereof.

~~8~~7. A marine antifouling coating composition according to any preceding claim wherein component (ii) is present in an amount of ~~0.25~~0.5 to 20 wt% of the composition.

~~9~~8. A marine antifouling coating composition according to any preceding claim wherein the acrylic binder component (i) comprises at least one polymer comprising the residue of at least one, preferably at least two of the following monomers: (meth)acrylic acid, methyl methacrylate, 2-methoxyethyl (meth)acrylate, n-butyl (meth)acrylate, 2-(2-ethoxyethoxy)ethyl (meth)acrylate, tetrahydrofurfuryl acrylate and triisopropylsilyl (meth)acrylate.

~~10~~9. A marine antifouling coating composition according to any preceding claim wherein component (i) is present in an amount of ~~0.5~~5.0 to 20 wt% of the composition.

~~11~~10. A marine antifouling coating composition according to any preceding claim wherein the marine antifouling agent (iii) comprises at least one of cuprous oxide, copper pyrithione or zinc ethylenebis(dithiocarbamate).

~~12~~11. A marine antifouling coating composition according to any preceding claim wherein the composition has a VOC of less than 400 g/L.

~~13~~12. A process comprising the step of applying a marine antifouling coating composition according to any of claims 1 to ~~12~~ 11 on a substrate.

~~14~~13. A substrate coated with an antifouling coating composition according to any of claims 1 to ~~12~~11.

~~15~~14. Use of 0.5 to 10 wt% of one or more monocarboxylic acids selected from liquid, acyclic, saturated C12-C24 monocarboxylic acids or a salt thereof or liquid, acyclic, branched C12-C24 monocarboxylic acids or a salt thereof as defined in any

of claims 1 to ~~12~~ 11 to reduce the leached layer thickness in a marine coating composition comprising:

(i) 5.0 to 40 wt% of an acrylic binder comprising at least one polymer comprising (meth)acrylate and/or silyl (meth)acrylate monomers;

(ii) 0.5 to 30 wt% of rosin and/or derivatives thereof; and

(iii) 0.5 to 70 wt% of a marine antifouling agent.