

DESCRIPTION

ANTIFOULING COATING COMPOSITION, PROCESS FOR PRODUCING THE
COMPOSITION, ANTIFOULING COATING FILM FORMED FROM THE COMPOSITION,
COATED OBJECT HAVING THE COATING FILM ON SURFACE, AND METHOD OF
5 ANTIFOULING TREATMENT BY FORMING THE COATING FILM

TECHNICAL FIELD

[0001]

The present invention relates to an antifouling coating
10 composition, a method for producing the composition, an
antifouling coating film formed using the composition, a coated
object having the coating film on its surface, and a method of
antifouling treatment by formation of the coating film.

15 BACKGROUND ART

[0002]

Aquatic fouling organisms such as barnacles, Tubeworms,
common mussels, *Bugula neritina*, sea squirts, green laver, sea
lettuce, and slimes attach to ships (especially the ship bottoms),
20 fishing tools such as fishing nets and fishing net accessories,
and structures submerged in seawater such as power plant
aqueducts, leading to dysfunction, impaired appearances, and
other problems of the ships and so on.

[0003]

25 The attachment of aquatic fouling organisms has been
heretofore prevented by coating surfaces of ships, fishing tools,
and submerged structures with antifouling coating materials that
include organic tin-containing copolymers. For example, a coating
film formed by application of an antifouling coating material
30 that contains a polymer with tributyltin groups gradually
dissolves the polymer component into seawater, causing constant
replacement of coating film surfaces, which enables the
prevention of the attachment of aquatic fouling organisms to the
coating film. After dissolution, the coating film can be re-
35 applied to exhibit continued antifouling performance. However,

the use of these antifouling coating materials has now been abandoned due to problems with marine pollution.

[0004]

5 Triorganosilyl ester-containing copolymers with triorganosilyl groups, which are less toxic and less environmentally harmful than organic tin groups, have recently been developed and used as hydrolyzable copolymers to replace organic tin-containing copolymers (Documents 1 to 12).

10 However, a coating film that includes a triorganosilyl ester-containing copolymer has the following drawbacks. When a copolymer obtained by copolymerizing a triorganosilyl ester-containing monomer having a tri-*n*-butylsilyl group or like straight alkyl chain group is used, the resulting coating film has a high hydrolysis rate. This causes the dissolving rate of
15 the coating film to gradually increase, and to become excessively high after a long period of time has elapsed. Furthermore, the resulting coating film has poor water resistance, and easily suffers from swelling or cracking, making it difficult to use the coating film for a long time.

20 [0005]

 In order to solve this problem, triorganosilyl ester-containing copolymers in which all organo groups have branched alkyl groups were considered (Patent Documents 6 to 12). However, while a triorganosilyl ester-containing copolymer containing only
25 branched alkyl groups has superior water resistance, the resulting coating film has an unduly slow hydrolysis rate. Therefore, it takes time before the coating film starts to dissolve, resulting in an undesirable antifouling effect at the initial stage. Aquatic fouling organisms thus adhere to the
30 coated surface during the initial period of time in regions where aquatic fouling organisms are active or seawater is relatively cold.

[0006]

 In order to solve these problems, an attempt has been
35 made to adjust the dissolving rate of the coating film by using

triorganosilyl ester-containing copolymers in combination with rosin (or rosin derivatives) (Patent Documents 2 to 10).

[0007]

However, when rosin (or a rosin derivative) is used, although a portion of the rosin reacts with a metal compound contained in the coating composition to form a metal salt during the manufacture of a coating material, the reactivity is insufficient, resulting in the rosin (or a rosin derivative) with free carboxylic acid remaining in the coating composition. In particular, when a large amount of rosin is used, there is a tendency for a high percentage of the rosin (or the rosin derivative) to remain in the coating composition. The rosin (or the rosin derivative) has a high hydrophilic property, and hence lowers the water resistance of the coating film. As a result, defects, such as blisters, cracks, and the like, tend to occur in the coating film.

[0008]

Therefore, a method wherein an excessive amount of metal compound and rosin are premixed has been proposed (Patent Documents 9 and 10). In this method, however, even though an excessive amount of metal compound is used, the metal compound and rosin do not react sufficiently, making it difficult to completely remove rosin (or a rosin derivative) containing free carboxylic acid.

[0009]

Furthermore, in view of environmental problems, solvent-type coating materials have become restricted worldwide in recent years, because solvent-type coating materials emit a large amount of organic solvent into the air. Accordingly, there have been attempts to reduce the content of organic solvent in coating materials (Patent Documents 11 and 12). It is difficult to provide antifouling coating materials having excellent coating properties and antifouling properties by using these methods.

[0010]

In order to effectively use a dock when building a new

ship, the ship body is sometimes built in the dock, then, after the bottom of the ship body is coated, the ship body is floated in seawater outside the dock and the interior of the ship body is prepared. After that, the ship is returned to the dock, and the finishing coats are applied. However, because it takes about three months to prepare the interior while floating the ship body on the seawater, organisms adhere to the surface of the coating film during this period. Alternatively, even if the adhesion of organisms can be prevented, slime may adhere to the coating film. These organisms and slime cannot satisfactorily be removed by washing with water. If the finishing coats are applied without satisfactorily removing the organisms or slime, the coating film may suffer from cracking, peeling, etc., while sailing.

[Patent Document 1] Japanese Unexamined Patent Publication No. 1998-30071

[Patent Document 2] Japanese Unexamined Patent Publication No. 1999-116857

[Patent Document 3] Japanese Unexamined Patent Publication No. 1999-116858

[Patent Document 4] Japanese Unexamined Patent Publication No. 2000-248228

[Patent Document 5] Japanese Unexamined Patent Publication No. 2000-265107

[Patent Document 6] Japanese Unexamined Patent Publication No. 2000-265107

[Patent Document 7] Japanese Unexamined Patent Publication No. 2002-53796

[Patent Document 8] Japanese Unexamined Patent Publication No. 2002-53797

[Patent Document 9] Japanese Unexamined Patent Publication No. 2002-97406

[Patent Document 10] Japanese Unexamined Patent Publication No. 2003-261816

[Patent Document 11] WO 2005/005516 A1

[Patent Document 12] Japanese Unexamined Patent Publication No.

2005-082725

DISCLOSURE OF THE INVENTION

Problem to be Solved by the Invention

5 [0011]

An object of the present invention is to provide an antifouling coating composition that makes it possible to form a coating film that exhibits, in seawater, stable solubility and an excellent antifouling effect from the initial stage as well as
10 sufficient water resistance, and that effectively exhibits an antifouling effect for a long period of time, while also being highly environmentally friendly by emitting only a small amount of volatile organic compounds (VOCs) into the air.

15 Means for Solving the Problem

[0012]

The present inventors conducted extensive research to solve the above problem, and found that the above object can be achieved by using a composition having a specific constitution.
20 The present invention has been accomplished based on this finding.
[0013]

Specifically, the present invention provides the antifouling coating composition, the method for producing the composition, the antifouling coating film formed by using the
25 composition, the coated object having the coating film on its surface, and the method of antifouling treatment by formation of the coating film as described below.

Item 1. An antifouling coating composition comprising:
30 Polymer (A), which is a polymer having a number average molecular weight of 1,000 to 20,000 that is obtained by polymerizing a polymerizable triorganosilyl unsaturated carboxylate; and

Zinc Salt (B), which is at least one zinc salt selected
35 from the group consisting of rosin zinc salts and zinc salts of

rosin derivatives;

the antifouling coating composition (1) having the weight ratio of the content of Polymer (A) to that of Zinc Salt (B) ((A)/(B)) of 45/55 to 10/90;

5 (2) having the nonvolatile matter content of not less than 75 weight%; and

(3) substantially being free from a rosin or rosin derivative containing a free carboxyl group.

10 Item 2. The antifouling coating composition according to Item 1, wherein Polymer (A) has a number average molecular weight of 2,000 to 15,000, and a degree of dispersion of molecular weight of less than 2.5.

Item 3. The antifouling coating composition according to Item 1 or 2, wherein Polymer (A) has a glass transition
15 temperature of 20 to 70°C.

Item 4. The antifouling coating composition according to Item 1, wherein Polymer (A) is triisopropylsilyl (meth)acrylate copolymer.

20 Item 5. The antifouling coating composition according to Item 3, wherein the triisopropylsilyl (meth)acrylate copolymer is obtained by copolymerizing (a) 30 to 60 weight% of triisopropylsilyl (meth)acrylate, (b) 10 to 50 weight% of methyl methacrylate, and (c) 0 to 60 weight% of (meth)acrylic ester other than those defined in (a) and (b).

25 Item 6. The antifouling coating composition according to Item 1, wherein the rosin zinc salt is at least one zinc salt selected from the group consisting of gum rosin zinc salts, wood rosin zinc salts and tall oil rosin zinc salts, and the zinc salt of the rosin derivative is at least one zinc salt selected from
30 the group consisting of hydrogenated rosin zinc salts and disproportionated rosin zinc salts.

Item 7. The antifouling coating composition according to Item 1, wherein the nonvolatile matter content is not less than 80 weight% and viscosity is 80 to 100 KU measured using a
35 Stormer viscometer at 25°C.

Item 8. The antifouling coating composition according to Item 1, wherein the content of the volatile organic compound is less than 400 g/L.

5 Item 9. The antifouling coating composition according to Item 1, which further comprises 10 to 100 parts by weight of zinc oxide per 100 parts by weight of total amount of Polymer (A) and Zinc Salt (B).

10 Item 10. The antifouling coating composition according to Item 1, which further comprises 100 to 400 parts by weight of cuprous oxide per 100 parts by weight of total amount of Polymer (A) and Zinc Salt (B).

Item 11. The antifouling coating composition according to Item 10, wherein the cuprous oxide has an average particle diameter of 8 to 20 μm .

15 Item 12. The antifouling coating composition according to Item 1, which further comprises 1 to 100 parts by weight of organic antifoulant per 100 parts by weight of total amount of Polymer (A) and Zinc Salt (B).

20 Item 13. The antifouling coating composition according to Item 1, which further comprises 1 to 50 parts by weight of plasticizer per 100 parts by weight of total amount of Polymer (A) and Zinc Salt (B).

Item 14. The antifouling coating composition according to Item 13, wherein the plasticizer is an epoxidized oil or fat.

25 Item 15. The antifouling coating composition according to Item 1, which comprises 1 to 50 parts by weight of dewatering agent per 100 parts by weight of total amount of Polymer (A) and Zinc Salt (B).

30 Item 16. The antifouling coating composition according to Item 15, wherein the dewatering agent is at least one dehumidifier selected from the group consisting of alkoxysilanes and alkyl orthoformates.

35 Item 17. The antifouling coating composition according to Item 1, which further comprises 1 to 50 parts by weight of fatty acid amide-based dispersant per 100 parts by weight of

total amount of Polymer (A) and Zinc Salt (B).

Item 18. An antifouling treatment method conducted using the antifouling coating composition of any one of Items 1 to 17 comprising a step of forming an antifouling coating film on
5 the surface of an object to be coated.

Item 19. An antifouling coating film formed by using the antifouling coating composition of any one of Items 1 to 17.

Item 20. A coated object having the antifouling coating film of Item 19 on its surface.

10 Item 21. A method for producing an antifouling coating composition comprising the steps of:

mixing Polymer (A), which is a polymer having a number average molecular weight of 1,000 to 20,000 that is obtained by polymerizing a polymerizable triorganosilyl unsaturated
15 carboxylate with Zinc Salt (B), which is at least one zinc salt selected from the group consisting of rosin zinc salts and zinc salts of rosin derivatives;

the antifouling coating composition (1) having the weight ratio of the content of Polymer (A) to the content of Zinc
20 Salt (B) ((A)/(B)) of 45/55 to 10/90;

(2) having the nonvolatile matter content of not less than 75 weight%; and

(3) substantially being free from a rosin or rosin derivative containing a free carboxyl group.

25 Item 22. The method for producing an antifouling coating composition according to Item 21, which comprises the steps of:

mixing Polymer (A) with Zinc Salt (B);

adding a cuprous oxide having an average particle
30 diameter of 3 to 10 μm to the mixture of Polymer (A) and Zinc Salt (B); and

mixing and dispersing the resulting mixture using a disperser.

Item 23. The method for producing an antifouling
35 coating composition according to Item 21, which comprises the

steps of:

mixing Polymer (A) with Zinc Salt (B);

dispersing the mixture using a disperser while mixing;

and

5 adding and mixing a cuprous oxide having an average
particle diameter of 10 to 20 μm .

[0014]

Antifouling Coating Composition

10 The antifouling coating composition of the present
invention comprises:

(A) a polymer (Polymer (A)) having a number average
molecular weight of 1,000 to 20,000 that is obtained by
polymerizing a polymerizable triorganosilyl unsaturated
carboxylate; and

15 (B) at least one zinc salt selected from the group
consisting of rosin zinc salts and zinc salts of rosin
derivatives (Zinc Salt (B)); wherein

(1) the weight ratio of the content of Polymer (A) to
the content of Zinc Salt (B) ((A)/(B)) is 45/55 to 10/90;

20 (2) the nonvolatile matter content is not less than 75
weight%; and

(3) the antifouling coating composition is
substantially free from a rosin or rosin derivative containing a
free carboxyl group.

25 [0015]

Polymer (A)

30 The antifouling coating composition of the present
invention comprises a polymer that is obtained by polymerizing a
polymerizable triorganosilyl unsaturated carboxylate (i.e., a
polymerizable triorganosilyl unsaturated carboxylate unit-
containing polymer) having a number average molecular weight (Mn)
of 1,000 to 20,000, and preferably of 2,000 to 15,000.

[0016]

35 The inclusion of Polymer (A) makes it possible to form
a coating film that can effectively exhibit antifouling effects

and desirably prevent the adhesion of aquatic fouling organisms.
[0017]

If Polymer (A) has an Mn of 1,000 to 20,000, the resulting coating film will have satisfactory physical properties
5 (hardness and strength). This prevents the occurrence of cracking and/or peeling, allowing the antifouling effect to be maintained for a long period of time. If the Mn is less than 1,000, although the dissolving amount of coating film increases, the coating film becomes too brittle and easily suffers from
10 cracking. If the Mn exceeds 20,000, the antifouling effect of the coating film cannot be maintained for a long period of time. Specifically, if the Mn exceeds 20,000, the resulting coating film becomes very strong, but has low resolvability; therefore, the antifouling effect may gradually deteriorate. If the Mn
15 exceeds 20,000, the viscosity of Polymer (A) becomes unduly high. The viscosity of the coating composition containing Polymer (A) also becomes very high. Therefore, a large amount of organic solvent (thinner) is necessary when such a coating composition is used as a coating material; this adversely affects both cost
20 effectiveness and the environment.
[0018]

One example of a method for measuring the Mn is gel permeation chromatography (GPC). When the Mn is measured by GPC, it is expressed as a value (using a polystyrene standard),
25 obtained by conducting the measurement after preparing a calibration curve using polystyrene as a reference material.
[0019]

It is preferable that Polymer (A) have a degree of dispersion of molecular weight of less than 3.0. If the degree of
30 dispersion of molecular weight is less than 3.0, the viscosity of the coating composition can be desirably reduced. This effectively reduces the amount of solvent used when such a coating composition is used as a coating material. This also makes it possible to obtain an antifouling coating material that
35 provides a coating film having excellent physical properties and

a desirable antifouling effect for a long period of time.

[0020]

In particular, a polymer having an Mn of 2,000 to 15,000, and a dispersion of molecular weight of less than 2.5 is preferable as Polymer (A). A polymer having an Mn of 5,000 to 10,000, and a dispersion of molecular weight of 2.0 to 1.0 is more preferable as Polymer (A).

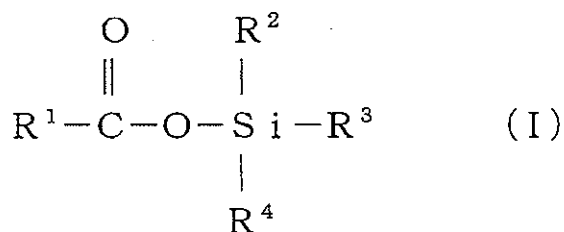
[0021]

It is preferable that Polymer (A) have a glass transition temperature (Tg) of 20 to 70°C, and more preferably 30 to 60°C. When the Tg is in the range of 20 to 70°C, the hardness and strength of the coating film is affected little by water temperature and atmospheric temperature, allowing a suitable hardness and strength to be maintained for a long period of time. If the Tg is lower than 20°C, the resulting coating film is unduly soft. When the water temperature and atmospheric temperature rise, the coating film becomes too soft, allowing cold flow and like defects to easily occur. If the Tg exceeds 60°C, the resulting coating film becomes too hard; this may result in the occurrence of cracking or peeling in the coating film.

[0022]

Polymer (A) can be obtained by polymerizing or copolymerizing at least a triorganosilyl group-containing monomer represented by General Formula (I) below.

[0023]



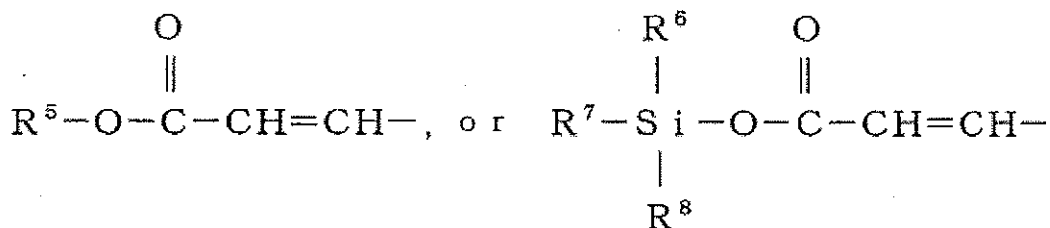
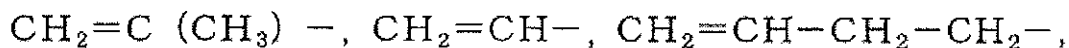
[0024]

R¹ in General Formula (I) is not particularly limited as

long as it is a hydrocarbon group that contains a polymerizable unsaturated double bond. However, a preferable example is as follows.

[0025]

5



[0026]

$\text{CH}_2=\text{C}(\text{CH}_3)-$, or $\text{CH}_2=\text{CH}-$ is more preferable.

[0027]

10 Examples of R^5 include a $\text{C}_1\text{-C}_8$ straight-chain or branched alkyl group, a cycloalkyl group, an unsaturated alkyl group, an aralkyl group, etc.

[0028]

15 Examples of $\text{C}_1\text{-C}_8$ straight-chain or branched alkyl groups include methyl group, ethyl group, *n*-propyl group, isopropyl group, isobutyl group, *s*-butyl group, *t*-butyl group, 2-methylbutyl group, 2-ethylbutyl group, pentyl group, 3-methylpentyl group, hexyl group, heptyl group, octyl group, etc.

[0029]

20 Examples of cycloalkyl groups include cyclopropyl group, cyclobutyl group, cyclopentyl group, cyclohexyl group, cycloheptyl group, cyclooctyl group, etc.

[0030]

25 Examples of unsaturated alkyl groups include 2-propenyl group, 2-butenyl group, 3-butenyl group, 2-pentenyl group, 3-pentenyl group, 4-pentenyl group, etc.

[0031]

 Examples of aralkyl groups include benzyl group, phenethyl group, phenylpropyl group, etc.

[0032]

The alkyl group, cycloalkyl group, unsaturated alkyl group, aralkyl group and the like may have a substituent.

Examples of substituents include alkoxy group, acyl group, etc.

5 The number of substituents and the site of substitution are not limited as long as the effects of the invention are not adversely affected.

[0033]

10 Examples of R^6 to R^8 may be the same or different and represent a C_3 - C_8 branched alkyl group or phenyl group. Examples of C_3 - C_8 branched alkyl groups include isopropyl group, isobutyl group, *s*-butyl group, *t*-butyl group, 2-methylbutyl group, isopentyl group, 2-ethylbutyl group, 3-methylpentyl group, etc. Preferable examples of R^6 to R^8 include isopropyl group, *s*-butyl
15 group, *t*-butyl group and phenyl group. Among these, isopropyl group is particularly preferable.

[0034]

In General Formula (I), R^2 to R^4 may be the same or different and it is preferable that each represents a C_3 - C_8
20 branched alkyl group or phenyl group. Examples of C_3 - C_8 branched alkyl groups are the same as the alkyl groups listed as examples of R^6 to R^8 . More specifically, isopropyl group, *s*-butyl group, *t*-butyl group and phenyl group are preferable as R^2 to R^4 , and isopropyl group is more preferable.

25 [0035]

Examples of triorganosilyl group-containing monomers represented by General Formula (I) include triisopropylsilyl group-containing monomers, triisobutylsilyl group-containing monomers, tri-*s*-butylsilyl group-containing monomers,
30 triisopentylsilyl group-containing monomers, triphenylsilyl group-containing monomers, diisopropylisobutylsilyl group-containing monomers, diisopropyl-*s*-butylsilyl group-containing monomers, diisopropylisopentylsilyl group-containing monomers, diisopropylphenylsilyl group-containing monomers,
35 isopropyl-diisobutylsilyl group-containing monomers, isopropyl-di-

s-butylsilyl group-containing monomers, t-butyldiisobutylsilyl group-containing monomers, t-butyldiisopentysilyl group-containing monomers, t-butyldiphenysilyl group-containing monomers, etc. These triorganosilyl group-containing monomers may
5 be used singly or in combination. Among these, triisopropylsilyl group-containing monomers, tri-s-butylsilyl group-containing monomers and t-butyldiphenysilyl group-containing monomers are preferable, and triisopropylsilyl group-containing monomers are more preferable. From the viewpoint of the production process,
10 production cost, availability of raw materials, and environmental safety, triisopropylsilyl group-containing monomers wherein R² to R⁴ are all isopropyl groups are preferable as a triorganosilyl group-containing monomer.

[0036]

15 Examples of triisopropylsilyl group-containing monomers include triisopropylsilyl (meth)acrylate, triisopropylsilyl 4-pentenoate, bis(triisopropylsilyl) maleate, methyl triisopropylsilyl maleate, ethyl triisopropylsilyl maleate, n-butyl triisopropylsilyl maleate, isobutyl triisopropylsilyl
20 maleate, t-butyl triisopropylsilyl maleate, n-pentyl triisopropylsilyl maleate, isopentyl triisopropylsilyl maleate, 2-ethylhexyl triisopropylsilyl maleate, cyclohexyl triisopropylsilyl maleate, bis(triisopropylsilyl) fumarate, methyl triisopropylsilyl fumarate, ethyl triisopropylsilyl
25 fumarate, n-butyl triisopropylsilyl fumarate, isobutyl triisopropylsilyl fumarate, n-pentyl triisopropylsilyl fumarate, isopentyl triisopropylsilyl fumarate, 2-ethylhexyl triisopropylsilyl fumarate, cyclohexyl triisopropylsilyl fumarate, etc. These monomers may be used singly or in combination. In
30 particular, triisopropylsilyl (meth)acrylate is preferable as a triisopropylsilyl group-containing monomer.

[0037]

Here, triisopropylsilyl (meth)acrylate means triisopropylsilyl acrylate and triisopropylsilyl methacrylate.

35 [0038]

A triisopropylsilyl (meth)acrylate copolymer (Copolymer (A)) is preferable as Polymer (A). In particular, a copolymer obtained by copolymerizing (a) generally 30 to 60 weight% and preferably 30 to 50 weight% of triisopropylsilyl (meth)acrylate,
5 (b) generally 10 to 50 weight% and preferably 10 to 40 weight% of methyl methacrylate, and (c) generally 0 to 60 weight% and preferably 0 to 50 weight% of (meth)acrylic esters other than (a) and (b) is preferable as Copolymer (A).

[0039]

10 The unit "weight%" indicates the percentage of each monomer when the total amount of the monomers to be copolymerized is defined as 100 weight%.

[0040]

If the content of Monomer (a) falls within the range of
15 30 to 60 weight%, the resulting coating film will effectively exhibit the desired antifouling effect. Furthermore, the hydrolysis rate of the coating film can be suitably controlled, maintaining the desirable antifouling effect for a long period of time. This also improves the water resistance and strength of the
20 resulting coating film.

[0041]

If the content of Monomer (a) is less than 30 weight%, the resulting coating film will have poor resolvability, making it difficult to exhibit the antifouling effect for a long period
25 of time. If the content of Monomer (a) exceeds 60 weight%, the resulting coating film will have unduly high resolvability, making it difficult to design the coating film. Furthermore, this will make it impossible to render satisfactory water resistance and strength to the coating film.

30 [0042]

When the content of Monomer (b) is in the range of 10 to 50 weight%, the resulting coating film will be able to maintain suitable hardness and strength for a long period of time. If the content of Monomer (b) is less than 10 weight%, the
35 resulting coating film will become too soft and tend to easily

suffer from cold flow and like defects. If the content of Monomer (b) exceeds 50 weight%, although the strength of the resulting coating film will be improved, the coating film will become too hard, leading to the risk of cracking or peeling.

5 [0043]

The term "other (meth)acrylic ester" (Monomer (c)) means acrylic esters or methacrylic esters other than methyl methacrylate. Specific examples thereof include methyl acrylate, ethyl (meth)acrylate, *n*-butyl (meth)acrylate, *i*-butyl (meth)acrylate, *t*-butyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, lauryl (meth)acrylate and like alkyl (meth)acrylates; 2-methoxyethyl (meth)acrylate, 2-methoxypropyl (meth)acrylate, 4-methoxybutyl (meth)acrylate, 2-ethoxyethyl (meth)acrylate and like alkoxyalkyl (meth)acrylates; ethylene glycol monomethyl (meth)acrylate, propylene glycol monomethyl (meth)acrylate and like alkylene glycol monomethyl (meth)acrylates; 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate and like hydroxyalkyl (meth)acrylates; dimethylaminoethyl (meth)acrylate, diethylaminoethyl (meth)acrylate and like dialkylaminoethyl (meth)acrylates; and tri-*n*-butylsilyl (meth)acrylate, triisobutylsilyl (meth)acrylate, tri-*s*-butylsilyl (meth)acrylate, triphenylsilyl (meth)acrylate, *t*-butyldiphenylsilyl (meth)acrylate and like triorganosilyl (meth)acrylates other than Monomer (a). In addition, benzyl (meth)acrylate, phenyl (meth)acrylate, etc., may also be used. The above-mentioned examples of Monomer (c) may be used as a monomer component of Copolymer (A) singly or in combination. Among these, ethyl (meth)acrylate, *n*-butyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, 2-methoxyethyl (meth)acrylate, 2-methoxypropyl (meth)acrylate, etc., are particularly preferable as Monomer (c).

[0044]

In synthesizing Copolymer (A), any monomers other than the above-mentioned Monomers (a), (b) and (c) may be added in an amount that does not adversely affect the water resistance and

35

resolvability of the coating film.

[0045]

Examples of usable monomers include vinyl compounds having a functional group, aromatic compounds, acrylic acid and methacrylic acid. Examples of vinyl compounds having a functional group include vinyl chloride, vinylidene chloride, (meth)acrylonitrile, vinyl acetate, butyl vinyl ether, lauryl vinyl ether, *N*-vinyl pyrrolidone, etc. Examples of aromatic compounds include styrene, vinyl toluene, α -methyl styrene, etc.

10 [0046]

In particular, Copolymer (A) is preferably a copolymer of triisopropylsilyl (meth)acrylate (Monomer (a)), methyl methacrylate (Monomer (b)), and at least one monomer selected from the group consisting of ethyl (meth)acrylate, *n*-butyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, 2-methoxyethyl (meth)acrylate and 2-methoxypropyl (meth)acrylate (Monomer (c)).

[0047]

Polymer (A) may be a random copolymer, an alternating copolymer, a periodic copolymer, or a block copolymer.

20 [0048]

Polymer (A) may be obtained by, for example, polymerizing Monomer (a), Monomer (b) and Monomer (c) in the presence of a polymerization initiator.

[0049]

25 Examples of polymerization initiators used in the polymerization reaction include 2,2'-azobisisobutyronitrile (AIBN), 2,2'-azobis-2-methylbutyronitrile, dimethyl-2,2'-azobisisobutyrate and like azo compounds; dibenzoyl peroxide, di(3-methylbenzoyl) peroxide, benzoyl (3-methylbenzoyl) peroxide, dilauryl peroxide and like diacyl peroxide compounds; di-*t*-butyl peroxide, *t*-butyl peroxybenzoate, *t*-butyl peroxyisopropylcarbonate, *t*-butyl peroxyoctoate and like *t*-butyl peroxide compounds; *t*-amyl peroxy-2-ethylhexanoate, *t*-amyl peroxyacetate, *t*-amyl peroxyisononanoate, *t*-amyl peroxybenzoate, 30 *t*-amyl peroxyacetate, *t*-amyl peroxyoctoate, di(*t*-amyl peroxide), 35

1,1-di(*t*-amyl peroxy)cyclohexane and like *t*-amyl peroxide compounds; and *t*-hexyl peroxy-2-ethylhexanoate, *t*-hexyl peroxybenzoate, *t*-hexyl peroxy-isopropylmonocarbonate, *t*-hexyl peroxy-pivalate, *t*-hexyl peroxyoctoate, *t*-hexyl peroxyneodecanoate and like *t*-hexyl peroxide compounds. These polymerization initiators may be used singly or in combination. Preferable examples of the polymerization initiators include diacylperoxide compounds, *t*-butylperoxide compounds, *t*-amylperoxide compounds and *t*-hexylperoxide compounds. Among these, *t*-amylperoxide compounds and *t*-hexylperoxide compounds are more preferable. By using *t*-amylperoxide compounds or *t*-hexylperoxide compounds as the polymerization initiator, a polymer having a narrower molecular weight distribution, and a lower viscosity can be obtained compared to the case of using another polymerization initiator.

[0050]

By suitably selecting the amount of the polymerization initiator used, the molecular weight of Polymer (A) can be suitably adjusted.

[0051]

Examples of polymerization methods include solution polymerization, bulk polymerization, emulsion polymerization, suspension polymerization, etc. Among these, solution polymerization is preferable, because it allows Polymer (A) to be prepared easily and accurately.

[0052]

In the polymerization reaction, an organic solvent may be added, if necessary. Examples of organic solvents include xylene, toluene and like aromatic hydrocarbon-based solvents; hexane, heptane and like aliphatic hydrocarbon-based solvents; ethyl acetate, butyl acetate, isobutyl acetate, methoxypropyl acetate and like ester-based solvents; isopropyl alcohol, butyl alcohol and like alcohol-based solvents; dioxane, diethyl ether, dibutyl ether and like ether-based solvents; methyl ethyl ketone, methyl isobutyl ketone and like ketone-based solvents; etc. Among

these, aromatic hydrocarbon-based solvents are preferable, and xylene is more preferable. These solvents may be used singly or in combination.

[0053]

5 The reaction temperature in the polymerization reaction may be suitably selected depending on the type of the polymerization initiator, etc., but is generally 70 to 140°C, and preferably 80 to 120°C. The time necessary for the polymerization reaction may be suitably selected depending on the reaction
10 temperature, etc., but is generally about 4 to 8 hours.

[0054]

The polymerization reaction is preferably conducted in inert gas atmospheres, such as nitrogen gas and argon gas.

[0055]

15 Zinc Salt (B)

The antifouling coating composition of the present invention contains at least one zinc salt (Zinc Salt (B)) selected from the group consisting of rosin zinc salts and zinc salts of rosin derivatives. Because zinc salts mentioned above
20 have a high compatibility with Polymer (A), they can stably exist in the coating film. Therefore, the composition of the present invention has excellent long-term storageability.

[0056]

When sodium salt, calcium salt, magnesium salt, etc.,
25 other than the zinc salts mentioned above are used as metal salts of rosin (or rosin derivatives), because sodium salt and the like have an overly high hydrophilicity, although not as high as that of rosin (or rosin derivatives) having free carboxylic acid, there is a risk that the water resistance of the coating film may
30 be lowered.

[0057]

Examples of rosin zinc salts include gum rosin zinc salt, wood rosin zinc salt, tall oil rosin zinc salt, etc. These salts may be used singly or in combination.

35 [0058]

Examples of zinc salts of rosin derivatives include maleinized rosin zinc salts, formylated rosin zinc salts, polymerized rosin zinc salts, hydrogenated rosin zinc salts, disproportionated rosin zinc salts, etc. These salts may be used
5 singly or in combination.
[0059]

In the present invention, it is preferable that the rosin zinc salt be at least one member selected from the group consisting of gum rosin zinc salts, wood rosin zinc salts and
10 tall oil rosin zinc salts; and that the zinc salt of a rosin derivative be at least one member selected from the group consisting of hydrogenated rosin zinc salts and disproportionated rosin zinc salts.
[0060]

15 The rosin salts and the rosin derivative salts may be commercially available ones. Alternatively, the rosin salts and the rosin derivative salts may be produced by a known method. For example, the rosin (or the rosin derivative) zinc salts can be prepared by reacting rosin (or a rosin derivative) having a free
20 carboxyl group (COO^- group) with a zinc oxide while heating in a solution.
[0061]

One of the major features of the composition of the present invention is that it contains a relatively large amount
25 of Zinc Salt (B). The weight ratio of the content of Polymer (A) to that of Zinc Salt (B) in the composition ((A)/(B)) is preferably 45/55 to 10/90, and more preferably 40/60 to 20/80. When the weight ratio falls within the range of 45/55 to 10/90, the resulting coating film will have excellent hardness and
30 strength, allowing the dissolving amount of the coating film to be desirably controlled and the coating film to exhibit a long-term antifouling effect.
[0062]

Furthermore, rosin zinc salts and zinc salts of rosin
35 derivatives have a lower viscosity than Polymer (A) and copper

salts and like metal salts other than rosin zinc salts and zinc salts of rosin derivatives. Therefore, by using a relatively large amount of rosin zinc salts and zinc salts of rosin derivatives, i.e., within the weight ratio range as mentioned
5 above, the viscosity of the coating composition can be lowered. In this case, because the resulting coating composition has a low viscosity, the amount of solvent can be reduced when the composition is used as a coating material. This results in desirably obtaining an antifouling coating material containing a
10 large volume of nonvolatile matter content and a small percentage of volatile organic compounds (VOCs), i.e., a low-VOC antifouling coating material.

[0063]

The composition of the present invention is
15 substantially free from rosin and rosin derivatives that contain free carboxyl groups. Specifically, the content of the rosin and rosin derivative in the composition of the present invention is preferably not higher than 1 weight%, and more preferably 0 to 0.1 weight%. The rosin and rosin derivatives that contain free
20 carboxyl groups have high hydrophilicity. Therefore, when the coating film contains such rosins and rosin derivatives, the water resistance of the coating film will be lowered, which may cause blisters, cracking and like defects on the coating film.

[0064]

25 Cuprous Oxide

It is preferable that the antifouling coating composition of the present invention further contain a cuprous oxide. The cuprous oxide can function as an antifoulant. By containing the cuprous oxide, the resulting coating film can
30 effectively exhibit the antifouling effect.

[0065]

There is no limitation to the form of the cuprous oxide, as long as it does not adversely affect the effect of the invention. For example, the cuprous oxide may take a form of a
35 particle.

[0066]

The average particle diameter of the particulate cuprous oxide is preferably 3 to 20 μm and more preferably 8 to 20 μm . When the composition of the present invention contains the
5 cuprous oxide having an average particle diameter of 3 to 20 μm , the dissolving rate of the coating film can be desirably controlled so that a long-term antifouling effect can be exhibited. When the cuprous oxide has an average particle diameter that falls within the range of 8 to 20 μm , the viscosity
10 of the coating composition of the present invention can be further lowered, desirably producing a low-VOC antifouling coating material.

[0067]

A preferable example of the form of the cuprous oxide
15 is a cuprous oxide whose surface is covered with a coating agent. When a particulate cuprous oxide is used, it is preferable that the surface of each particle be covered with a coating agent. By covering with a coating agent, oxidation of the cuprous oxide can be desirably prevented.

20 [0068]

Examples of the usable coating agents include stearic acid, lauric acid, glycerol, sucrose, lecithin, etc. These coating agents may be used singly or in combination.

[0069]

25 It is preferable that the composition of the present invention contain 100 to 400 parts by weight, and more preferably 200 to 300 parts by weight of cuprous oxide per 100 parts by weight of total amount of Polymer (A) and Zinc Salt (B). When the content of the cuprous oxide is 100 to 400 parts by weight per
30 100 parts by weight of total amount of Polymer (A) and Zinc Salt (B), the coating film can exhibit an excellent antifouling effect.

[0070]

It is desirable that cuprous oxide contained in the composition be covered with Polymer (A), Zinc Salt (B), an
35 organic solvent to be described later, etc. When the cuprous

oxide is not satisfactorily covered with Polymer (A), etc., the cuprous oxide cannot be satisfactorily dispersed in the composition and may exhibit aggregation. When the cuprous oxide aggregates, cracking or peeling easily occurs in the resulting coating film.

[0071]

The composition of the present invention may further contain any other inorganic antifoulants, in addition to the cuprous oxide, in such an amount that does not adversely affect the antifouling effect. Examples of usable inorganic antifoulants include copper thiocyanate (general name: copper rhodanide), cupronickel, copper powder, etc. These inorganic antifoulants may be used singly or in combination.

[0072]

15 Pigment

The antifouling coating composition of the present invention may contain various pigments. By adding one or more pigments, the strength, the weather resistance, the water resistance, and the dissolvability of the coating film can be improved.

[0073]

In particular, it is preferable that the composition of the present invention further comprise a zinc oxide. By adding a zinc oxide, the dissolution of the resulting coating film in seawater is accelerated, and the antifouling effect can be effectively exhibited. The form of zinc oxide is not particularly limited. For example, a particulate zinc oxide can be used.

[0074]

When a particulate zinc oxide is used, the particle diameter thereof is not particularly limited and may be selected from the range that does not adversely affect the effects of the invention.

[0075]

The zinc oxide content in the composition of the present invention is preferably 10 to 100 parts by weight, and

more preferably 20 to 50 parts by weight per 100 parts by weight of total amount of Polymer (A) and Zinc Salt (B). When the zinc oxide content falls within the range of 10 to 100 parts by weight per 100 parts by weight of total amount of Polymer (A) and Zinc Salt (B), the dissolving rate of the coating film can be suitably controlled. When the zinc oxide content is less than 10 parts by weight per 100 parts by weight of total amount of Polymer (A) and Zinc Salt (B), it is impossible to satisfactorily accelerate the dissolution of the coating film in the seawater. When the zinc oxide content exceeds 100 parts by weight per 100 parts by weight of total amount of Polymer (A) and Zinc Salt (B), the solubility of the coating film excessively increases. This makes it difficult to control the dissolving rate of the coating film.

[0076]

Other than the zinc oxides mentioned above, known water-soluble pigments and water-insoluble pigments may be used as the pigments.

[0077]

Examples of water-soluble pigments include cuprous oxide, copper oxide, copper thiocyanate, zinc carbonate, zinc sulfide, calcium hydrogenphosphate, calcium phosphate, calcium silicate, iron carbonate, iron carbonyl, magnesium hydroxide, magnesium carbonate, etc. These water-soluble pigments may be used singly or in combination. In particular, it is preferable that at least one member selected from the group consisting of cuprous oxides and cuprous thiocyanates be used as a water-soluble pigment.

[0078]

The cuprous oxide mentioned as an example of a water-soluble pigment may be the same or different from those listed in the above description of cuprous oxide.

[0079]

Examples of water-insoluble pigments include titanium oxide, iron oxide, talc, calcium carbonate, silica, kaolin, perlite, mica, barium sulfate, graphite, carbon black, etc. These

may be used singly or in combination. In particular, it is preferable to use at least one member selected from the group consisting of titanium oxides, iron oxides, talc, calcium carbonates, silica, kaolin and barium sulfates as a water-
5 insoluble pigment.

[0080]

The water-soluble pigments exhibit the effect of increasing the solubility of the coating film in seawater. Zinc oxide is a compound that belongs to the water-soluble pigment
10 category. The water-insoluble pigments exhibit the effect of reducing the solubility of the coating film in seawater. Therefore, by suitably selecting the types and amounts of water-soluble pigment and water-insoluble pigment, the physical properties and solubility of the coating film can be suitably
15 controlled.

[0081]

There is no limitation to the content of the pigment in the composition of the present invention. However, it is desirable that the content of the pigment be selected so that the
20 resulting coating film has a pigment volume concentration (PVC) of 20 to 50% and more preferably 25 to 45%.

[0082]

A coating film having a PVC of less than 20% will be too soft and have insufficient strength. A coating film having a
25 PVC of exceeding 50% will be brittle and easily crack.

[0083]

The PVC can be obtained by the following calculation.

[0084]

$$\text{PVC (\%)} = \frac{\text{Total volume (ml) of the pigments (including pigments that are not dissolved in the solvent)}}{\text{Total volume (ml) of the solid components}} \times 100$$

[0085]

In the calculation, the expression "Total volume (ml) of the solid components" refers to the sum of the volumes of the
35 pigments, Polymer (A), Zinc Salt (B) and the like. When the

composition of the present invention contains the cuprous oxides listed in the above description of cuprous oxide, and organic antifoulants, plasticizers, dewatering agents, dispersants and the like, which are described later, the volumes of those

5 components are included in the "Total volume (ml) of the solid components".

[0086]

Similar to the cuprous oxides, it is desirable that the pigments contained in the composition be covered with Polymer (A) and the like. When the pigment is satisfactorily covered with Polymer (A) and the like, cracking or peeling in the resulting coating film can be effectively prevented.

[0087]

Organic antifoulant

15 The antifouling coating composition of the present invention may further contain any organic antifoulant.

[0088]

There is no limitation to the organic antifoulants as long as they have a killing or repelling effect against aquatic fouling organisms. Examples of the organic antifoulants include 2-mercaptopyridine-*N*-oxide copper (general name: copper pyrithione) and like organic copper compounds; 2-mercaptopyridine-*N*-oxide zinc (general name: zinc pyrithione), zinc ethylenebisdithiocarbamate (general name: zineb), zinc bis(dimethyldithiocarbamate) (general name: ziram), bis(dimethyl dithiocarbamoyl) zinc ethylene bis(dithio carbamate) (general name: polycarbamate) and like organic zinc compounds; pyridine-triphenylborane, 4-isopropyl pyridyl-diphenylmethyl borane, 4-phenyl pyridiyl-diphenyl borane, triphenylboron-*n*-octadecyl amine, triphenyl[3-(2-ethylhexyloxy)propyl amine]boron and like organic boron compounds; and 2,4,6-trichloromaleimide, *N*-(2,6-diethylphenyl)-2,3-dichloromaleimide and like maleimide compounds. Other examples of the organic antifoulants include 4,5-dichloro-2-*n*-octyl-3-isothiazolone (general name: Sea-Nine 211), 3,4-dichlorophenyl-*N,N*-dimethylurea (general name: diuron), 2-

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methythio-4-t-butylamino-6-cyclopropylamino-s-triazine (general name: Irgarol 1051), 2,4,5,6-tetrachloroisophthalonitrile (general name: chlorothalonil), N-dichlorofluoromethylthio-N',N'-dimethyl-N-p-tolylsulfamide (general name: tolylfluand), N-dichloromethylthio-N',N'-dimethyl-N-phenylsulfamide (general name: dichlofluand), 2-(4-thiazolyl)benzimidazole (general name: thiabendazole), 3-(benzo[b]thien-2-yl)-5,6-dihydro-1,4,2-oxathiazine-4-oxide (general name: bethoxazine), 2-(p-chlorophenyl)-3-cyano-4-bromo-5-trifluoromethyl pyrrole (general name: Econe 028), etc. Among these, zinc pyrithione, copper pyrithione, pyridine-triphenylborane, 4-isopropylpyridyl-diphenylmethyl borane, bethoxazine, zineb, Sea-Nine 211 and Irgarol 1051 are preferable. Copper pyrithione, zinc pyrithione, pyridine-triphenylborane and bethoxazine are more preferable. These organic antifoulants may be used singly or in combination. [0089]

The content of the organic antifoulants in the composition of the present invention is preferably 1 to 50 parts by weight, and more preferably 10 to 30 parts by weight per 100 parts by weight of total amount of Polymer (A) and Zinc Salt (B). If the content of the organic antifoulants is less than one part by weight per 100 parts by weight of total amount of Polymer (A) and Zinc Salt (B), the antifouling effect of the organic antifoulant cannot satisfactorily be exhibited. If the content exceeds 50 parts by weight per 100 parts by weight of total amount of Polymer (A) and Zinc Salt (B), no improvement in the antifouling effect can be observed in proportion to the increase in the amount of the organic antifoulant; this is thus uneconomical.

[0090]

Plasticizer

The antifouling coating composition of the present invention may further contain a plasticizer. By containing the plasticizer, the plasticity of the composition can be enhanced, allowing an preferably strong coating film to be obtained. This

also improves the adhesiveness of the coating film to an object to be coated.

[0091]

Examples of the usable plasticizers include tricresyl
5 phosphate, trioctyl phosphate, triphenyl phosphate and like
phosphate esters; dibutyl phthalate, dioctyl phthalate and like
phthalate esters; dibutyl adipate, dioctyl adipate and like
adipate esters; dibutyl sebacate, dioctyl sebacate and like
sebacate esters; epoxidized soybean oil, epoxidized linseed oil
10 and like epoxidized oils and fats; methyl vinyl ether polymer,
ethyl vinyl ether polymer and like alkyl vinyl ether polymers;
and polyethylene glycol, polypropylene glycol and like
polyalkylene glycols. Other examples of the plasticizers include
t-nonylpentasulfide, vaseline, polybutene, tris(2-ethyl hexyl)
15 trimellitate, silicone oil, liquid paraffin, chlorinated paraffin,
polymeric plasticizers formed of ethylenically unsaturated
carboxylic ester polymer having Tg of not higher than -20°C, etc.
These plasticizers may be used singly or in combination.

[0092]

20 In the present invention, it is preferable that the
plasticizer is at least one member selected from the group
consisting of phosphate esters, epoxidized oils and fats and
ethylenically unsaturated carboxylic ester polymers having Tg of
not higher than -20°C. Among these, epoxidized oils and fats are
25 more preferable.

[0093]

The content of the plasticizer in the composition of
the present invention depends on the content of the rosin zinc
salt and/or zinc salt of rosin derivative in the composition, but
30 is preferably 1 to 50 parts by weight, and more preferably 5 to
30 parts by weight per 100 parts by weight of total amount of
Polymer (A) and Zinc Salt (B). If the content of the plasticizer
is less than one part by weight per 100 parts by weight of total
amount of Polymer (A) and Zinc Salt (B), satisfactory improvement
35 in the physical properties (strength and adhesiveness) cannot be

obtained. If it exceeds 50 parts by weight per 100 parts by weight of total amount of Polymer (A) and Zinc Salt (B), the coating film becomes too soft, and is practically unusable.

[0094]

5 Dewatering agent

It is preferable that the antifouling coating composition of the present invention further contain a dewatering agent. The dewatering agent is an agent that removes water in the composition. Examples of usable dewatering agents include

10 dehumidifiers and dehydrating agents. The dehumidifiers and the dehydrating agents may be used singly, or both the dehumidifier and the dehydrating agent may be used in combination.

[0095]

The dehumidifier is a compound that can remove water in
15 the coating composition by reacting with water. Examples of the dehumidifiers include methyl orthoformate, ethyl orthoformate and like alkyl orthoformates; tetraethoxysilane, tetrabutoxysilane, tetraphenoxysilane, tetrakis(2-ethoxybutoxy)silane, methyltrimethoxysilane, methyltriethoxysilane,
20 dimethyldiethoxysilane, trimethylethoxysilane, diphenyldiethoxysilane and like alkoxysilanes; and maleic anhydride, phthalic anhydride and like acid anhydrides.

[0096]

The dehydrating agent is a compound that can remove
25 water in the composition by incorporating the water into the dehydrating agent as crystallization water. Examples of dehydrating agents include anhydrous gypsum, molecular sieves, magnesium sulfate, sodium sulfate, etc.

[0097]

30 A dehumidifier is preferably used as the dewatering agent. A preferable dehumidifier is at least one member selected from the group consisting of alkoxysilanes and alkyl orthoformates, and a particularly preferable dehumidifier is tetraethoxysilane.

35 [0098]

There is no limitation to the content of the dewatering agent in the composition of the present invention, but it is preferably 1 to 50 parts by weight, and more preferably 2 to 30 parts by weight per 100 parts by weight of total amount of Polymer (A) and Zinc Salt (B). If the content of the dewatering agent is less than one part by weight per 100 parts by weight of total amount of Polymer (A) and Zinc Salt (B), the composition of the present invention may not be able to attain satisfactory storage stability. If the content of the dewatering agent exceeds 50 parts by weight per 100 parts by weight of total amount of Polymer (A) and Zinc Salt (B), the coating film may become too brittle. In particular, dehumidifiers easily volatilize into the air. Therefore, when a dehumidifier is used as the dewatering agent, in order to reduce the adverse affect on the environment, it is preferable that the amount of the dehumidifier be not higher than 30 parts by weight per 100 parts by weight of total amount of Polymer (A) and Zinc Salt (B).

[0099]

Dispersant

The composition of the present invention preferably further contains a dispersant (an anti-settling agent). By containing a dispersant, sedimentation of the components (e.g., pigment, cuprous oxide, zinc oxide, titanium oxide, red iron oxide, talc, etc.) of the composition of the present invention, as well as the formation of a hard cake (a hard precipitate), can be prevented during storage of the composition of the present invention. This also effectively solves the problem of dripping of the composition (the coating material) when a coating film is formed on the surface of an object to be coated by using the composition of the present invention.

[0100]

Examples of dispersants include oxidized polyethylene-based dispersants, fatty acid amide-based dispersants, fatty acid ester-based dispersants, hydrogenated castor oil-based dispersants, vegetable polymerized oil-based dispersants,

polyether ester-type surfactants, sulfate ester-type anionic surfactants, polycarboxylic acid amine salt-based dispersants, polycarboxylic acid-based dispersants, high-molecular-weight polyether-based dispersants, acrylic polymer-based dispersants, 5 special silicon-based dispersants, talc-based dispersants, bentonite-based dispersants, kaolinite-based dispersants, silica gel-based dispersants, etc. These dispersants may be used singly or in combination. The composition of the present invention preferably contains a fatty acid amide-based dispersant as a 10 dispersant. The composition of the present invention can be produced by, for example, preparing a mixed solution containing Polymer (A) and other components, and then mixing and dispersing the mixed solution. When the mixed solution contains the fatty acid amide-based dispersant, the storage stability of the mixed 15 solution can be enhanced, and the composition of the present invention can be obtained more easily and reliably.

[0101]

In the present invention, commercially available dispersants may be used. Examples of the fatty acid amide-based 20 dispersants include Dispalon A603-10X (or 20X), Dispalon 6900-10X (or 20X), and Dispalon 6810-10X (or 20X) (all products of Kusumoto Chemicals, Ltd.); Talen 7500-20 and Flownon SP-1000 (both products of Kyoeisha Chemical Co., Ltd.); etc.

[0102]

25 The dispersants may be used after being dispersed in an organic solvent, such as xylene. There is no limitation to the content of the dispersant in the composition of the present invention; however, the content is preferably 1 to 50 parts by weight, and more preferably 2 to 30 parts by weight per 100 parts 30 by weight of total amount of Polymer (A) and Zinc Salt (B). If the content of the dispersant is less than one part by weight per 100 parts by weight of total amount of Polymer (A) and Zinc Salt (B), the effects of the dispersant (i.e., preventing the formation of a hard cake) may not be exhibited. Specifically, the 35 storage stability of the composition of the present invention may

become inadequate. If the content of the dispersant exceeds 50 parts by weight per 100 parts by weight of total amount of Polymer (A) and Zinc Salt (B), viscosity of the composition becomes too high, which may make the conduction of coating
5 difficult. Furthermore, no improvement in the prevention of hard cake formation will be obtained by the increase of the content of the dispersant, and is therefore uneconomical.

[0103]

Other additives and the like

10 The composition of the present invention may further contain dyes, antissettling agents, antifoaming agents, etc.

[0104]

 The composition of the present invention is usually dissolved or dispersed in an organic solvent. This makes the
15 coating material desirably usable. Examples of the usable organic solvents include xylene, toluene, mineral spirit, MIBK, butyl acetate, etc. Among these, xylene and MIBK are particularly preferable. These organic solvents may be used singly or in combination.

20 [0105]

 In particular, when the composition of the present invention is used, the amount of the organic solvent used can be reduced. This is attributable to the low viscosity of the composition of the present invention. A coating material using
25 such a composition is sometimes referred to as a "high-solids coating material" in the art.

[0106]

 To be more specific, the composition of the present invention can be used as a low-VOC antifouling coating
30 composition. The coating material obtained by using the composition of the present invention releases a smaller amount of volatile organic compounds into the air, reducing adverse effects on the environment.

[0107]

35 It is preferable that the VOC content of the

composition of the present invention be less than 400 g/L and more preferably within the range of 300 to 350 g/L.

[0108]

5 The nonvolatile matter content of the composition of the present invention is generally not less than 75 weight%, preferably not less than 80 weight%, and more preferably not less than 85 weight%.

[0109]

10 The composition of the present invention has a viscosity of preferably 70 to 100 KU measured at 25°C using a Stormer viscometer, and more preferably 80 to 100 KU. When the composition has a viscosity within the range of 70 to 100 KU measured at 25°C using a Stormer viscometer, a sufficiently thick coating film can be readily obtained using the coating
15 composition of the present invention with a small amount of solvent. Furthermore, when the composition has a viscosity within that range, sedimentation of the components (for example pigment, cuprous oxide, zinc oxide, titanium oxide, red iron oxide, talc, etc.) of the composition of the present invention
20 can be effectively prevented and long-term storage becomes possible.

[0110]

The viscosity can be measured in accordance with JIS-5400 (or ASTM D562-01). A commercially available Stormer
25 viscometer may be used.

[0111]

The composition of the present invention exhibits excellent storage stability, with almost no gelling or solidifying even after long-term storage.

30 [0112]

Production method of the antifouling coating composition

The method for producing the antifouling coating composition of the present invention comprises the steps of:

35 mixing (A) a polymer (Polymer (A)) having a number average molecular weight of 1,000 to 20,000 that is obtained by

polymerizing a polymerizable triorganosilyl unsaturated carboxylate with (B) at least one zinc salt (Zinc Salt (B)) selected from the group consisting of rosin zinc salts and zinc salts of rosin derivatives.

5 The antifouling coating composition obtained by this production method has the following characteristics.

(1) The weight ratio of the content of Polymer (A) to the content of Zinc Salt (B) ((A)/(B)) is 45/55 to 10/90.

(2) The nonvolatile matter content is not less than 75
10 weight%.

(3) The antifouling coating composition is substantially free from a rosin or rosin derivative containing a free carboxyl group.

[0113]

15 The above-described production method of the present invention allows the antifouling coating composition of the present invention to be effectively obtained.

[0114]

The polymers and zinc salts listed under the subtitles
20 of Polymer (A) and Zinc Salt (B) above may be used as Polymer (A) and Zinc Salt (B). If necessary, pigments, cuprous oxides, organic antifoulants, dewatering agents, dispersants and other additives listed above may be added.

[0115]

25 The amounts of Polymer (A), Zinc Salt (B), and other components may be suitably selected so that the resulting antifouling coating composition contains Polymer (A), Zinc Salt (B), etc., in acceptable content ranges as described above.

[0116]

30 It is preferable that these components be mixed in such a manner that Polymer (A) and like various materials are dissolved or dispersed in a solvent. For example, Polymer (A) and Zinc Salt (B) may be dissolved or dispersed in a solvent first, and then mixed with other materials (such as organic
35 antifoulants). Examples of the usable solvents include xylene,

toluene, mineral spirit, MIBK, butyl acetate, etc. Among these, xylene is particularly preferable. They may be used singly or in combination.

[0117]

5 When the antifouling coating composition of the present invention is produced using cuprous oxide, it is preferable to suitably select Production Method 1 or Production Method 2, depending on the average particle diameter of the cuprous oxide used.

10 [0118]

 Specifically, when a cuprous oxide having an average particle diameter of 3 to 10 μm , preferably 3 to 8 μm is used, Production Method 1 is preferably selected.

[0119]

15 Production Method 1

 The antifouling coating composition can be produced by adding a cuprous oxide having an average particle diameter of 3 to 10 μm and preferably 3 to 8 μm to a mixture of Polymer (A) and Zinc Salt (B), and mixing and dispersing the resulting mixture
20 using a disperser.

[0120]

 The cuprous oxide having an average particle diameter of 3 to 10 μm tends to form secondary aggregation. Therefore, when only a cuprous oxide-containing material is added, the
25 obtained composition may have lumps. This may cause cracking or the like in the resulting coating film. In Production Method 1, a mixed substance that contains cuprous oxide having an average particle diameter of 3 to 10 μm is mixed and dispersed using a disperser so that the secondary-aggregated cuprous oxide can be
30 broken down. This makes it possible to obtain an antifouling coating composition with the cuprous oxide desirably dispersed therein.

[0121]

 Production Method 1 allows the antifouling coating
35 composition to be produced by mixing and dispersing, using a

disperser, a mixed substance that contains Polymer (A), Zinc Salt (B), and the cuprous oxide having an average particle diameter of 3 to 10 μ m.

[0122]

5 The mixed substance may further contain, if necessary, pigments, organic antifoulants, dewatering agents, dispersants and like various additives mentioned above.

[0123]

10 The contents of Polymer (A), Zinc Salt (B), the cuprous oxide, etc. in the mixed substance may be suitably selected so that the resulting antifouling coating composition contains Polymer (A), Zinc Salt (B), the cuprous oxide, etc. in acceptable contents ranges as described above.

[0124]

15 It is preferable that the mixed substance be prepared by dissolving or dispersing Polymer (A) and like various materials in a solvent. One example of the method for preparing the mixed substance is that Polymer (A) and Zinc Salt (B) are dissolved or dispersed in a solvent, and then mixed with other
20 materials (such as the above-mentioned organic antifoulants, etc.). Examples of the usable solvents are the same as those mentioned above.

[0125]

25 The disperser may be desirably selected from those that can be used as micro-pulverizers. Specific examples thereof include mills and dissolvers.

[0126]

30 Examples of usable mills include ball mills, sand mills, bead mills, pearl mills, Dyno mills, Cowles mills, basket mills, attritors and like mills generally used for mixing and dispersing coating materials.

[0127]

35 A dissolver is a disperser having a rotary vane-type grinder. The mixed solution can be mixed and dispersed by rotating the grinder. When a dissolver is used as the disperser,

it is preferable that the grinder of the dissolver be rotated at high speed. By making the grinder rotate at a high speed, the secondary-aggregated cuprous oxide can be desirably broken down.
[0128]

5 The dissolver may also be called a disperser.
[0129]

When a cuprous oxide having an average particle diameter of 10 to 20 μm , preferably 13 to 20 μm is used as the cuprous oxide, it is preferable to select Production Method 2,
10 described below.
[0130]

Production Method 2

The antifouling coating composition can be produced by using a disperser to mix and disperse a mixture that has been
15 obtained by mixing Polymer (A) with Zinc Salt (B), and then adding thereto and mixing a cuprous oxide having an average particle diameter of 10 to 20 μm and preferably 13 to 20 μm .
[0131]

The cuprous oxide having an average particle diameter
20 of 10 to 20 μm barely forms secondary aggregation. Therefore, the composition of the present invention can be produced by mixing and dispersing a mixed substance that contains Polymer (A) and Zinc Salt (B) using a disperser, adding the cuprous oxide to the resulting mixed dispersion, and then mixing the mixture using
25 mixing equipment in such a manner that the cuprous oxide particles will be ground as little as possible. In this method, the cuprous oxide will be ground very little, therefore allowing the surface area of the cuprous oxide in the resulting composition to be limited to a relatively small range. For
30 example, the surface area of the cuprous oxide can be not higher than $1.3 \times 10^{-3} \text{ mm}^2$, and is preferably in the range of 3.0×10^{-4} to $1.3 \times 10^{-3} \text{ mm}^2$.
[0132]

As described above, it is desirable that the cuprous
35 oxide contained in the composition be satisfactorily covered with

Polymer (A) and the like.

[0133]

When the cuprous oxide has a small surface area, the amounts of Polymer (A), Zinc Salt (B), organic solvent and the like used to cover the surface of the cuprous oxide can be reduced. As a result, a low-VOC antifouling coating material can desirably be obtained.

[0134]

As for an antifouling coating film, when the surface area of the cuprous oxide is small, even if the temperature of the seawater is high, specifically not lower than 30°C, the dissolving rate of the coating film can be effectively controlled. Production Method 2 can shorten the time for the process conducted using the disperser, reducing the production cost of the composition of the present invention.

[0135]

The mixed substance is the same as that used in Production Method 1, except that it does not contain the cuprous oxide.

[0136]

The amount of the cuprous oxide added may be suitably selected so that the resulting antifouling coating composition contains the cuprous oxide in acceptable content ranges.

[0137]

The disperser may be the same as that used in Production Method 1.

[0138]

There is no limitation to the mixing equipment, and any known mixing equipment may be used. For example, the above-mentioned dissolver may be used. When the dissolver is used, it is preferable that the rotation speed of the grinder be set to medium or low. By setting the rotation speed of the grinder to medium or low, crushing of the cuprous oxide can be effectively prevented.

[0139]

Antifouling Treatment Method, Antifouling Coating Film, and
Coated Object

The antifouling treatment method of the present invention is characterized in that an antifouling coating film is
5 formed on the surface of the object to be coated using the above-
explained antifouling coating composition. The antifouling
treatment method of the present invention can prevent adhesion of
aquatic fouling organisms by the gradual dissolution of the
surface of the antifouling coating film, so as to continually
10 renew the surface of the coating film. After the dissolution of
the coating film, the antifouling effect can be continuously
exhibited by recoating the composition.

[0140]

Examples of objects on which a coating film can be
15 formed include ships (in particular, ship bottoms), fishing tools,
structures submerged in seawater, etc. Examples of the fishing
tools include fishing nets for use in aquaculture or in fixed
netting, and fishing net accessories such as floats attached to
fishing nets, ropes, etc. Examples of structures submerged in
20 seawater include power plant aqueducts, bridges, port facilities,
etc.

[0141]

The antifouling coating film of the present invention
can be formed by applying the antifouling coating composition to
25 the surface (entirely or partially) of an object on which a
coating film is to be formed.

[0142]

Examples of the coating method include brush coating,
spray coating, dipping, flow coating, spin coating, etc. These
30 coating methods may be employed singly or in combination.

[0143]

The coating composition is dried after application. The
drying temperature may be room temperature. The drying time may
be suitably selected depending on the thickness of the coating
35 film, etc. The thickness of the antifouling coating film may be

suitably selected depending on the type of object on which the coating film is to be formed, the sailing speed of the ship, the seawater temperature, etc. For example, when the object on which the coating film is to be formed is a ship bottom, the thickness
5 of the antifouling coating film is generally 50 to 500 μm , and preferably 100 to 400 μm .

[0144]

The antifouling coating film of the present invention has the following advantages.

10 1) The coating film dissolves in seawater in a stable manner for a long period of time, thereby constantly replacing the coating film surface, which enables an excellent antifouling effect to be achieved and prevents the attachment of aquatic fouling organisms to the surface of the coating film.

15 2) The coating film has excellent water resistance, preventing the occurrence of blisters, swelling, cracking or other defects on the surface of the coating film even after being in seawater for a long period of time.

 3) The coating film has a desirable hardness, which
20 resists cold flow and other defects.

 4) The coating film is highly adhesive to the object on which the coating film is to be formed, which makes the application thereon easier.

[0145]

25 The coated object of the present invention has the antifouling coating film on its surface. The coated object of the present invention may have the antifouling coating film on the entire surface thereof, or a part thereof.

[0146]

30 The coated object of the present invention is covered with the antifouling coating film having the characteristics of Items 1 to 4 described above. Therefore, it can be desirably applied to ships (in particular, ship bottoms), fishing tools, structures submerged in seawater, etc.

35 [0147]

For example, when the antifouling coating film is to be formed on the surface of a ship bottom, the antifouling coating film gradually dissolves from the surface, so that the coating film surface is always renewed. This prevents the adhesion of aquatic fouling organisms.

[0148]

Furthermore, the hydrolysis rate of the antifouling coating film in seawater is desirably controlled. Therefore, ships benefit from the antifouling effect for a long period of time; additionally, even when the ships are not moving, for example, during anchorage, rigging, etc., the adhesion and incrustation of aquatic fouling organisms is barely observed, and the antifouling effect is exhibited for a long time.

[0149]

The surface of the antifouling coating film is basically free from cracking or peeling even after a long period of time. Therefore, it is unnecessary to re-form a new coating film after completely removing the existing coating film. Therefore, by directly recoating the antifouling coating film composition thereon, the antifouling coating film can be effectively formed. This makes it possible to continuously maintain the antifouling effect easily and at low cost.

EFFECTS OF INVENTION

[0150]

The antifouling coating composition of the present invention can reduce the content of volatile organic compounds (organic solvent, etc.) in the resulting coating material. This reduces the emission of organic compounds into the air that can occur when forming an antifouling coating film having a sufficient thickness, and accordingly reduces the adverse effects on the environment.

[0151]

The composition of the present invention has excellent long-term storageability. Specifically, the composition of the

present invention thickens, gels or solidifies very little even after long-term storage. Furthermore, the antifouling coating composition of the present invention is highly environmentally safe, and is substantially free from marine pollution, even if dissolved in seawater.

[0152]

The antifouling coating film that is formed using the antifouling coating composition of the present invention has the following advantages.

1) The coating film dissolves in seawater in a stable manner for a long period of time, thereby constantly replacing the coating film surface, which enables an excellent antifouling effect to be achieved and prevents the attachment of aquatic fouling organisms to the surface of the coating film.

2) The coating film has excellent water resistance, preventing the occurrence of blisters, swelling, cracking or other defects on the surface of the coating film even after being in seawater for a long period of time.

3) The coating film has a desirable hardness, which resists cold flow and other defects.

4) The coating film is highly adhesive to the object on which the coating film is to be formed, which makes the application thereon easier. The coated object of the present invention is covered with the antifouling coating film having the characteristics of Items 1 to 4 described above. Therefore, it can be desirably applied to ships (in particular, ship bottoms), fishing tools, structures submerged in seawater, etc. For example, when the antifouling coating film is to be formed on the surface of a ship bottom, the antifouling coating film gradually dissolves from the surface, so that the coating film surface is always renewed. This prevents the adhesion of aquatic fouling organisms.

Furthermore, the antifouling coating film has a suitable solubility. Therefore, when the ships are not moving, for example, during anchorage, rigging, etc., the adhesion and

incrustation of aquatic fouling organisms is barely observed, and the antifouling effect is exhibited for a long time. This reduces the frictional resistance of the ships, and accordingly reduces the fuel cost while sailing.

5 [0153]

Furthermore, the surface of the antifouling coating film is basically free from coating film defects, even after a long period of time. Therefore, after using the coated object for a predetermined period, a new antifouling coating film can be
10 desirably formed by directly recoating the antifouling coating film composition thereon. This makes it possible to continuously maintain the antifouling effect in a simple and inexpensive manner.

Examples

15 [0154]

Features of the invention will be further clarified by referring to the Examples etc. shown below. The invention, however, is not limited by the Examples etc.

[0155]

20 In each of the Production Examples, Comparative Production Examples, Examples, and Comparative Examples, "%" denotes "% by weight".

[0156]

The viscosity of Copolymer (A) Solution was determined
25 at 25°C using a Brookfield viscometer.

[0157]

The nonvolatile residue was determined by heating at 125°C for 1 hour in accordance with JIS K5601-1-2 (or ISO 3251) Standard.

30 [0158]

The number average molecular weight (Mn) was determined by gel permeation chromatography (GPC) (using a polystyrene standard).

[0159]

35 The GPC conditions were as follows:

Equipment: HLC-8220GPC; Tosoh Corporation

Column: TSK-gel Super HZM-M, two

Flow rate: 0.35 mL/min

Detector: RI

5 Column thermostat temperature: 40°C

Eluate: THF

The degree of dispersion of molecular weight was determined by dividing by M_n the weight average molecular weight (M_w) determined by GPC under the foregoing conditions.

10 [0160]

The glass transition temperature (T_g) of the copolymer was determined in accordance with JIS K 7121 Standard, using a Seiko Instruments SSC/5200 differential scanning calorimeter.

[0161]

15 The viscosity of the coating composition was determined in accordance with JIS K 5400 Standard, using a Stormer viscometer at 25°C. The measurement conditions were as follows:

Stormer viscometer: Stormer viscometer NO.453, manufactured by Coating Tester Co., Ltd.

20 Measurement temperature: 25 ± 0.5°C

Sample amount: 500 ml (a 500 ml sample can is filled with the sample up to the marked line)

Weight: 75 to 1,000 g

Measurement method: The time required for the rotor to produce 100 revolutions was measured. Measurements were conducted while changing the weight. Among the values ranging from 27 to 33 seconds required to produce 100 revolutions, the value closest to 30 seconds was selected, and the KU value was determined from the mass of the weight used and the time in seconds required to produce 100 revolutions, using charts for conversion to KU units.

30 [0162]

The amounts of each ingredient shown in Table 1 are represented in grams.

[0163]

35 Production Example 1 (Production of Copolymer (A) Solution)

330 grams of xylene was charged to a 1,000 ml flask fitted with a thermometer, a reflux condenser, a stirrer, and a dropping funnel; subsequently, a mixed solution of 150 g of triisopropylsilyl acrylate, 150 g of methyl methacrylate, 50 g of n-butyl acrylate, 150 g of 2-methoxyethyl methacrylate, and 5 g of t-butyl peroctoate was added dropwise into the flask over a period of 3 hours, while stirring at 115 to 120°C in a nitrogen atmosphere. After the dropwise addition, the polymerization reaction was performed for 2 hours at 115 to 120°C. 2 grams of t-butyl peroctoate (additional) was subsequently added to the resulting reaction solution to further continue the polymerization reaction for 2 hours at 115 to 120°C, thus producing Copolymer (A) Solution S-1. Table 1 shows the viscosity, nonvolatile residue, number average molecular weight (Mn), degree of dispersion of molecular weight (Mw/Mn), and glass transition temperature (Tg) of Copolymer Solution S-1.

[0164]

Production Examples 2 to 6 (Production of Copolymer (A) Solutions)

Polymerization reactions were performed according to the same procedure as in Production Example 1, using the solvent, monomers, and polymerization initiators shown in Table 1, thus producing Copolymer (A) Solutions S-2 to S-6. Table 1 shows the viscosity, nonvolatile residue, number average molecular weight (Mn), degree of dispersion of molecular weight (Mw/Mn), and glass transition temperature (Tg) of each of the resulting copolymer solutions.

[0165]

Comparative Production Example 1 (Production of Copolymer Solution H-1)

A polymerization reaction was performed according to the same procedure as in Production Example 1, using the organic solvent, monomers, polymerization initiator, and reaction temperature shown in Table 1, thus producing Copolymer Solution H-1. Table 1 shows the viscosity, nonvolatile residue, number

average molecular weight (M_n), degree of dispersion of molecular weight (M_w/M_n), and glass transition temperature (T_g) of the resulting copolymer solution.

[0166]

5 Comparative Production Example 2 (Production of Copolymer Solution H-2)

330 grams of xylene was charged to a 1,000 ml flask fitted with a thermometer, a reflux condenser, a stirrer, and a dropping funnel; subsequently, a mixed solution of 150 g of
10 triisopropylsilyl methacrylate, 150 g of methyl methacrylate, 50 g of n-butyl acrylate, 100 g of n-butyl methacrylate, 50 g of 2-methoxyethyl methacrylate, and 1 g of t-butyl peroctoate was added dropwise into the flask over a period of 2 hours, while stirring at 90 to 100°C in a nitrogen atmosphere. After the
15 dropwise addition, the polymerization reaction was performed for 2 hours at 90 to 100°C. 2 grams of t-butyl peroctoate (additional) was subsequently added to the resulting reaction solution to further continue the polymerization reaction for 2 hours at 90 to 100°C, thus producing Copolymer Solution H-2.
20 Table 1 shows the viscosity, nonvolatile residue, number average molecular weight (M_n), degree of dispersion of molecular weight (M_w/M_n), and glass transition temperature (T_g) of Copolymer Solution H-2.

[0167]

25 Table 1-1

Classification of Ingredients	Ingredient Name	Production Examples					
		1	2	3	4	5	6
Initially Charged Solvent	Xylene	330	330	330	330	330	330
Monomer (a)	Triisopropylsilyl Acrylate	150	200	225	250		
	Triisopropylsilyl Methacrylate					150	250
Monomer (b)	Methyl Methacrylate	150	175	200	200	150	125
	Ethyl Acrylate						25
Monomer (c)	n-Butyl Acrylate	50	50	50	25	50	25
	n-Butyl Methacrylate				25		
	2-Methoxyethyl Acrylate		50	25			
	2-Methoxyethyl Methacrylate	150	25			150	75
	t-Butyl Peroxyoctoate	5	5				
	t-Amyl Peroxyoctoate			5	5	5	
Initially Added	t-Hexyl Peroxyoctoate						5
	t-Butyl Peroxyoctoate	2	2				
Additional	t-Amyl Peroxyoctoate			2	2	2	
	t-Hexyl Peroxyoctoate						2
Additional Solvent	Xylene						
Physical Properties of Copolymer	Reaction Temperature (°C)	115-120	115-120	115-120	115-120	115-120	115-120
	Viscosity (mPa · S/25°C)	710	680	980	970	1050	880
	Nonvolatile Residue (% 125°C, 1 hr)	60.0	59.8	60.2	60.5	60.3	60.6
	Number Average Molecular Weight (Mn)	8,300	7,900	7,500	7,800	8,100	7,700
	Degree of dispersion of molecular weight (Mw/Mn)	2.7	2.8	2.3	2.4	2.4	2.2
	Glass Transition Temperature (T _g , °C)	33	29	39	51	45	57
	Copolymer Name	S-1	S-2	S-3	S-4	S-5	S-6

[0168]
Table 1-2

[0169]

Classification of Ingredients		Ingredient Name	Comparative Production Examples	
			1	2
Initially Charged Solvent		Xylene	330	330
Monomer (a)		Triisopropylsilyl Acrylate	100	
		Triisopropylsilyl Methacrylate		150
Monomer (b)		Methyl Methacrylate	200	150
Monomer (c)		Ethyl Acrylate		
		n-Butyl Acrylate	50	50
		n-Butyl Methacrylate	50	100
		2-Methoxyethyl Acrylate		
		2-Methoxyethyl Methacrylate	50	50
Polymerization Initiator	Initially Added	t-Butyl Peroxyoctoate	3	1
		t-Amyl Peroxyoctoate		
		t-Hexyl Peroxyoctoate		
	Additional	t-Butyl Peroxyoctoate	2	2
		t-Amyl Peroxyoctoate		
		t-Hexyl Peroxyoctoate		
Additional Solvent		Xylene		170
Reaction Temperature (°C)			115–120	90–100
Physical Properties of Copolymer		Viscosity (mPa·S/25°C)	1150	2280
		Nonvolatile Residue (% , 125°C, 1 hr)	60.7	49.6
		Number Average Molecular Weight (Mn)	12,300	22,300
		Degree of dispersion of molecular weight (Mw/Mn)	3.2	3.7
		Glass Transition Temperature (T _g , °C)	77	46
		Copolymer Name	H-1	H-2

Examples 1 and 2 and Comparative Examples 1 to 5 (Production of Coating Compositions)

Each of Copolymer (A) Solutions S-1 to S-6 (solids content: about 60%) obtained in Production Examples 1 to 6, or each of Copolymer Solutions H-1 and H-2 (solids content: about 60%) obtained in Comparative Production Examples 1 and 2 for use as a copolymer was blended with a xylene solution of a gum rosin zinc salt (solids content: about 60%) or a xylene solution of a hydrogenated rosin zinc salt (solids content: about 60%) for use as a rosin zinc salt, and a xylene solution of gum rosin (solids content: about 60%) or a xylene solution of hydrogenated rosin (solids content: about 60%) for use as rosin; cuprous oxide having an average particle diameter of 3 or 6 μm for use as cuprous oxide; and additionally, any of the organic antifoulants, pigments, additives, and solvent listed in Table 2 in the proportions (wt%) shown in Table 2. The above ingredients were mixed and dispersed with a small desktop laboratory sandmill (using glass beads with a diameter of 1.5 to 2.5 mm) to produce a coating composition. The nonvolatile matter content, VOC content, PVC, and coating material viscosity of each of the resulting coating compositions are shown in Table 2.

[0170]

Examples 3 to 8 (Production of Coating Compositions)

Each of Copolymer (A) Solutions S-3 to S-6 obtained in Production Examples 3 to 6 for use as a copolymer was blended with a xylene solution of a gum rosin zinc salt (solids content: about 60%) or a xylene solution of a hydrogenated rosin zinc salt (solids content: about 60%) for use as a rosin zinc salt; and additionally, any of the antifoulants, pigments, additives, and solvent listed in Table 2 in the proportions (wt%) shown in Table 2. The above ingredients were mixed and dispersed with a small desktop laboratory sandmill (using glass beads with a diameter of 1.5 to 2.5 mm), and the resulting mixture was removed. Cuprous oxide with an average particle diameter of 13 or 19 μm was subsequently added to the mixture and slowly stirred with a stirring blade, thus producing a coating composition. The nonvolatile matter content, VOC content, PVC, and coating material viscosity of each of the resulting coating compositions are shown in Table 2.

[0171]

Table 2-1

Ingredient Name		Examples							
		1	2	3	4	5	6	7	8
Copolymer	S-1	7.5						5	
	S-2		7.5						5
	S-3			7.5					
	S-4				5				
	S-5					5			
	S-6						5		
	H-1								
	H-2								
Resin	Gum Rosin Zinc Salt Solution (Xylene Solution, Solids Content: About 60%)	17.5	17.5	17.5				20	
	Hydrogenated Rosin Zinc Salt Solution (Xylene Solution, Solids Content: About 60%)				20	20	20		20
	Gum Rosin Solution (Xylene Solution, Solids Content: About 60%)								
	Hydrogenated Rosin Solution (Xylene Solution, Solids Content: About 60%)								
Plasticizer	Tricresyl Phosphate							1	1
	ARUFON UP-1080	3	3	3	3	3	3	2	2
	Lutonal A25								
	Sansooizer E-2000	1	1	1	1	1	1	1	1
	Chlorinated Paraffin								
Cuprous Oxide	NC-301 (Nisshin Chemco, Ltd., Average Particle Diameter: 3 μm)	45							
	RED COP 97N PREMIUM (American Chemet Corporation, Average Particle Diameter: 6 μm)		45						
	PURPLE COPP (American Chemet Corporation, Average Particle Diameter: 13 μm)			45	45	45			
	LOLO-TINT97 (American Chemet Corporation, Average Particle Diameter: 19 μm)						45	45	45
Organic Antifoulant	Copper Pyrrhione	3	3	2	3	3	3	3	3
	Dichlofluamid						1		
	Tolyfluamid			1					
	Irgarol 1051							1	
	Zineb								1
Pigment	Red Iron Oxide	3.5	3.5	3.5	2.5	2.5	3	3	3
	Talc	2	2	2	2	2	2	2	2
	Zinc Oxide	5	5	5	5	5	5	5	5
	Titanium Oxide	1	1	1	1	1	1	1	1
	Fuji Red	1	1	1	1	1	1	1	1
Other Additives	Anhydrous Gypsum (Dehydrating Agent)								
	Tetraethoxysilane (Dehumidifier)	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
	Disparlon A603-20x (Dispersant, Kusumoto Chemicals, Ltd.)	2	2	2			2	2	2
	Talen 7500-20 (Dispersant, Kyoeisha Yushi Chemical Industry Co., Ltd)				2	2			
	Bentone #38				1	1			
Solvent	Xylene	8	8	8	8	8	7.5	7.5	7.5
Total		100	100	100	100	100	100	100	100
Nonvolatile Matter Content (wt%)		80	80	80	80	80	80	80	80
Volatile Matter Content (g/L)		376	376	376	376	376	367	367	367
PVC (Pigment Volume Concentration %)		41	41	39	42	42	40	42	42
Coating Composition Viscosity (KU Value/25°C)		95	93	89	85	86	86	84	85

[0172]
Table 2-2

Ingredient Name		Comparative Examples				
		1	2	3	4	5
Copolymer	S-1	17.5				
	S-2		17.5			
	S-3			17.5		
	S-4					
	S-5					
	S-6					
	H-1				20	
	H-2					17.5
Resin	Gum Rosin Zinc Salt Solution (Xylene Solution, Solids Content: About 60%)	7.5	5		7.5	7.5
	Hydrogenated Rosin Zinc Salt Solution (Xylene Solution, Solids Content: About 60%)			6		
	Gum Rosin Solution (Xylene Solution, Solids Content: About 60%)		2.5			
	Hydrogenated Rosin Solution (Xylene Solution, Solids Content: About 60%)			1.5		
Plasticizer	Tricresyl Phosphate					
	ARUFON UP-1080					
	Lutonal A25	3	3	3	3	2
	Sansocizer E-2000					
	Chlorinated Paraffin					1
Cuprous Oxide	NC-301 (Nisshin Chemco, Ltd., Average Particle Diameter: 3 μm)	45	45	45	45	45
	RED COP 97N PREMIUM (American Chemet Corporation, Average Particle Diameter: 6 μm)					
	PURPLE COPP (American Chemet Corporation, Average Particle Diameter: 13 μm)					
	LOLO-TINT97 (American Chemet Corporation, Average Particle Diameter: 19 μm)					
Organic Antifoulant	Copper Pyrrhione	3	3	3	2	2
	Dichlofluonid					
	Tolyfluonid					
	Irgarol 1051					
	Zineb					1
Pigment	Red Iron Oxide	2	2	2	2	2
	Talc	2	2	2	2	2
	Zinc Oxide	5	5	5	5	5
	Titanium Oxide	1	1	1	1	1
	Fuji Red	1	1	1	1	1
Other Additives	Anhydrous Gypsum (Dehydrating Agent)	0.5	0.5	0.5		
	Tetraethoxysilane (Dehumidifier)				0.5	0.5
	Disparlon A603-20x (Dispersant, Kusumoto Chemicals, Ltd.)	2	2	2	2	2
	Tafen 7500-20 (Dispersant, Kyoeisha Yushi Chemical Industry Co., Ltd)					
	Bentone #38					
Solvent	Xylene	10.5	10.5	10.5	9	10.5
Total		100	100	100	100	100
Nonvolatile Matter Content (wt%)		78	78	78	78	77
Volatile Matter Content (g/L)		413	413	409	413	423
PVC (Pigment Volume Concentration %)		42	42	42	39	41
Coating Composition Viscosity (KU Value/25°C)		116	110	112	115	125

[0173]

Test Example 1 (Spray Coatability)

Each of the coating compositions obtained in Examples 1 to 8 and Comparative Examples 1 to 5 was spray-coated to a blast-finished tin plate (75 x 150 mm) so that the dry coating film thickness would be about 100 μm . Coating compositions that were capable of being spray-coated were rated as "A", and coating compositions that were not capable of being spray-coated were rated as "B".

[0174]

Test Example 2 (Stability Test for Coating Compositions)

Each of the coating compositions obtained in Examples 1 to 8 and Comparative Examples 1 to 5 was sealed in a 100 ml wide-mouth tin can and stored in a thermostat at 40°C for 1 month, after which the viscosity of the coating composition was measured using a Brookfield viscometer.

[0175]

The viscosity of the coating composition was evaluated as follows:

A: a change in viscosity of less than 500 mPa·s/25°C (substantially no change in the coating composition)

B: a change in viscosity of 500 to 5,000 mPa·s/25°C (a slight increase in viscosity)

C: a change in viscosity of 5,000 to 100,000 mPa·s/25°C (a significant increase in viscosity)

D: a change so significant that the viscosity was unmeasurable (the coating composition turned into a gel, or solidified)

[0176]

The results are shown in Table 3.

[0177]

It is seen from Table 3 that the compositions containing rosin (or a rosin derivative) having free carboxy groups (Comparative Examples 2 and 3) lack long-term stability.

[0178]

Test Example 3 (Coating Film Hardness)

Each of the antifouling coating compositions obtained in Examples 1 to 8 and Comparative Examples 1 to 5 was applied to a transparent glass plate (75 x 150 x 1 mm) so that the dry coating film thickness would be about 100 μm , and dried at 40°C for 1 day. The coating film hardness of the resulting dry coating film was measured at 25°C using a pendulum hardness tester. The results (count number) are shown in Table 3. A count number of 20 to 50 is preferable for practical purposes.

[0179]

It is seen from Table 3 that the coating films

formed using the coating compositions of the invention (Examples 1 to 8) have a suitable hardness.

[0180]

Test Example 4 (Adhesion Test for Coating Films)

5 The adhesion of each coating film was tested in accordance with JIS K-5600-5-6 Standard. Specifically, tests were conducted according to the following method. Each of the coating compositions obtained in Examples 1 to 8 and Comparative Examples 1 to 5 was first applied to a blast-
10 finished fiber-reinforced plastic plate (FRP plate) (75 x 150 x 2 mm) and a tin plate (75 x 150 x 2 mm) so that the dry coating film thickness would be about 100 μ m. The applied coating was then dried at 40°C for 1 day to prepare a dry coating film with a thickness of about 100 μ m. The adhesion
15 test was conducted on the dry coating film (2 x 2 mm, the number of squares in the crosshatch = 100).

[0181]

The adhesion was evaluated as follows:

20 A: the number of the squares that did not peel off is from 70 to 100.

 B: the number of the squares that did not peel off is from 40 to 69.

 C: the number of the squares that did not peel off is from 20 to 39.

25 D: the number of the squares that did not peel off is from 0 to 19.

[0182]

The results are shown in Table 3.

[0183]

30 It is seen from Table 3 that the coating films formed using the coating compositions of the invention (Examples 1 to 8) strongly adhere to both the FRP plate and the tin plate.

[0184]

35 Test Example 5 (Flexibility Test for Coating Films)

 Each of the coating compositions obtained in Examples 1 to 8 and Comparative Examples 1 to 5 was applied to a blast-finished tin plate (75 x 150 mm) so that the dry coating film thickness would be about 100 μ m. The applied
40 coating was then dried at 40°C for 1 day to prepare a dry coating film with a thickness of about 100 μ m. The tin plate coated with the dry coating film was bent 90°, and the condition of the bent coating film was visually inspected.

[0185]

45 The flexibility was evaluated as follows:

 A: substantially free of cracks

 B: contained minute cracks

 C: contained large cracks

 D: a portion of the coating film easily peeled

[0186]

The results are shown in Table 3.

[0187]

5 It is seen from Table 3 that the coating films formed using the coating compositions of the invention (Examples 1 to 8) are strong and resistant to embrittlement.

[0188]

Test Example 6 (Water Resistance Test for Coating Films)

10 An anti-corrosive coating film was formed by applying an anti-corrosive coating material (a vinyl-based A/C) to a ground glass plate (75 x 150 x 1 mm) so that the thickness after drying would be about 50 μm , followed by drying. Each of the coating compositions obtained in Examples 1 to 8 and Comparative Examples 1 to 5 was
15 subsequently applied to the anti-corrosive coating film so that the dry coating film thickness would be about 100 μm . The applied coating was dried at 40°C for 1 day, thus preparing a specimen with a dry coating film thickness of about 100 μm . The specimen was immersed in natural seawater
20 at 35°C for 3 months, after which the condition of the coating film was visually inspected.

[0189]

The water resistance was evaluated as follows:

25 A: the coating film underwent no change
B: the coating film slightly changed color
C: the coating film was slightly blistered
D: defects such as cracks, swelling, and peeling were observed in the coating film

[0190]

30 The results are shown in Table 3.

[0191]

It is seen from Table 3 that the coating films formed using the coating film compositions of the invention (Examples 1 to 8) have excellent resistance to water.

35 [0192]

Table 3

Examples/ Comparative Examples		Spray Coatability	Coating Composition Stability	Adhesion Test		Flexibility Test	Water Resistance Test
			40°C After 1 Month	FRP Plate	Tin Plate		35°C After 3 Months
Examples	1	A	A	A	A	A	A
	2	A	A	A	A	A	A
	3	A	A	A	A	A	A
	4	A	A	A	A	A	A
	5	A	A	A	A	A	A
	6	A	A	A	A	A	A
	7	A	A	A	A	A	A
	8	A	A	A	A	A	A
Comparative Examples	1	B	A	C	A	B	C
	2	B	D	A	A	A	D
	3	B	C	A	A	A	D
	4	B	A	C	A	C	C
	5	B	A	B	A	A	C

[0193]

Test Example 7 (Solubility Test (Rotary Test) for Coating Films)

5 A tank was centrally provided with a rotating drum with a diameter of 515 mm and a height of 440 mm to cause the rotation of the drum via a motor. The tank was also provided with a cooling apparatus for keeping the seawater temperature constant, and a pH automatic controller for keeping the pH of
10 the seawater constant.

[0194]

Two test plates were prepared according to the following method.

[0195]

15 An anti-corrosive coating film was formed by applying an anti-corrosive coating material (a vinyl-based A/C) to a hard vinyl chloride plate (75 x 150 x 1 mm) so that the thickness after drying would be about 50 μm , followed by drying. Each of the antifouling coating compositions
20 obtained in Examples 1 to 8 and Comparative Examples 1 to 5 was applied to the anti-corrosive coating film so that the thickness after drying would be about 300 μm . The applied coating was dried at 40°C for 3 days, thus preparing a test plate having a dry coating film with a thickness of about 300
25 μm .

[0196]

One of the thus-prepared test plates was secured to the rotating drum of the rotary apparatus of the above-mentioned equipment so that the test plate contacted seawater,
30 and the rotating drum was rotated at a speed of 20 knots. During the test, the seawater temperature was maintained at 25°C, and the pH at 8.0 to 8.2; the seawater was replaced once every week.

[0197]

35 The initial coating film thickness and the remaining coating film thicknesses after 1 month, 3 months, and 6 months were measured for each test plate, using a laser focus displacement gauge; and the thickness of the dissolved coating film was calculated from the difference between the
40 initial coating film thickness and the remaining coating film thickness, thereby determining the amount of the coating film dissolved in the initial 6 months.

[0198]

45 The dissolving amount of the coating film is represented in terms of the total dissolving amount (μm) of the coating film during the period. The results are shown in Table 4.

[0199]

It is seen from Table 4 that the coating films

formed using the coating compositions of the invention (Examples 1 to 8) are dissolved in sufficiently large amounts from the initial period, revealing that these coating films provide good initial antifouling effects.

5 [0200]

It is seen that the coating films formed using the coating compositions of Comparative Examples 1 to 5 are not easily dissolved in seawater during the initial period, and cannot exhibit effective antifouling effects. It is understood that the coating films formed using the coating compositions of Comparative Examples 2 and 3 have low water resistance, causing cracking and/or peeling during the test.

10 [0201]

Table 4

Coating Composition Name		Dissolving Amount (μm) of Coating Film			
		After 1 Month	After 2 Months	After 3 Months	After 6 Months
Examples	1	8	15	20	36
	2	7	13	18	31
	3	6	11	16	28
	4	7	12	17	30
	5	5	10	14	26
	6	6	12	17	29
	7	5	11	16	31
	8	6	10	15	30
Comparative Examples	1	2	4	5	11
	2	3	5	8	15
	3	2	4	7	13
	4	1	2	3	7
	5	0	1	2	5

[0202]

Test Example 8 (Slime Attachment Test)

Each of the coating compositions obtained in Examples 1 to 8 and Comparative Examples 1 to 5 was applied to both surfaces of a hard vinyl chloride plate (100 x 200 x 2 mm) so that the dry coating film thickness would be about 100 μm . The applied coating was dried at room temperature (25°C) for 3 days, thus preparing a test plate having a dry coating film with a thickness of about 100 μm . This test plate was immersed at 1.5 m below sea level in Kushimoto City, Wakayama Prefecture, Japan. After 1 month, 2 months, and 3 months of immersion, the attachment of slime to the test plate was visually inspected.

[0203]

The results are shown in Table 5.

15 [0204]

The figures in Table 5 represent the degrees of the attachment of slime. The degree of the attachment of slime was evaluated as follows:

0: Substantially no slime was observed.

20 1: A small amount of slime attached to the test plate.

2: Slime attached thickly on the entire surface of the test plate, but could easily be removed with a brush.

3: Slime attached thickly on the entire surface of the test plate, and could not be easily removed with a brush.

25 [0205]

It is seen from Table 5 that the coating films formed using the coating compositions of the invention (Examples 1 to 8) are substantially free of slime attachment, compared to the coating films formed using the coating compositions of Comparative Examples 1 to 5. This is because the coating films formed using the coating compositions of the invention are sufficiently dissolved from the initial period.

[0206]

Test Example 9 (Recoating Test)

35 Each of the test plates subjected to the slime

attachment test of Test Example 8 was washed by pouring ion exchange water thereon, and dried at room temperature (25°C) for 1 day. Each of the coating compositions obtained in Examples 1 to 8 and Comparative Examples 1 to 5 was subsequently applied to one
5 surface of the test plate so that the dry coating film thickness would be about 100 μm . The applied coating was dried at room temperature (25°C) for 3 days, thus preparing a test plate on which a new coating film having a thickness of about 100 μm had been formed over the old coating film. A test for determining the
10 adhesion of the coating film was conducted on the test plate according to JIS K-5600-5-6 (2 x 2 mm, the number of squares in the crosshatch = 100).

[0207]

The adhesion was evaluated as follows:

15 A: the number of squares that did not peel off is from 70 to 100.

B: the number of squares that did not peel off is from 40 to 69.

20 C: the number of squares that did not peel off is from 20 to 39.

D: the number of squares that did not peel off is from 0 to 19.

[0208]

The results are shown in Table 5.

25 [0209]

It is seen from Table 5 that the coating films formed using the coating compositions of the invention (Examples 1 to 8) exhibit sufficient adhesion of the new coating films to the older films, compared to the coating films formed using the coating
30 compositions of Comparative Examples 1 to 5. This is because the coating films formed using the coating compositions of Comparative Examples 1 to 5 have poor initial coating film solubility, causing slime to attach to these coating films in a short period of time. In contrast, the coating films formed using
35 the coating compositions of the invention exhibit sufficiently

high initial coating film solubility, allowing the coating film surfaces to be renewed, resulting in the attachment of little slime.

[0210]

5 Table 5

Coating Composition		Slime Attachment Test			Recoating Test
		After 1 Month	After 2 Months	After 3 Months	
Examples	1	0	0	0	A
	2	0	0	0	A
	3	0	0	0	A
	4	0	0	0	A
	5	0	0	0	A
	6	0	0	0	A
	7	0	0	0	A
	8	0	0	0	A
Comparative Examples	1	0	1	2	D
	2	0	1	2	D
	3	0	1	2	D
	4	1	2	3	D
	5	2	3	3	D

[0211]

Test Example 10 (Antifouling Test)

Each of the coating compositions obtained in Examples 1 to 8 and Comparative Examples 1 to 5 was applied to both surfaces of a hard vinyl chloride plate (100 x 200 x 2 mm) so that the dry coating film thickness would be about 200 μm . The applied coating was dried at room temperature (25°C) for 3 days, thus preparing a test plate having a dry coating film with a thickness of about 200 μm . This test plate was immersed at 1.5 m below sea level in Owase City, Mie Prefecture, Japan, and fouling of the test plate was examined for 24 months.

[0212]

The results are shown in Table 6.

[0213]

The figures in Table 6 represent the areas (%) to which
5 fouling organisms were attached.

[0214]

It is seen from Table 6 that the coating films formed
using the coating compositions of the invention (Examples 1 to 8)
are substantially free of the adhesion of aquatic fouling
10 organisms, compared to the coating films formed using the coating
film compositions of Comparative Examples 1 to 5. This is because
the coating films formed using the coating compositions of the
invention exhibit somewhat reduced hydrolysis rates, allowing
them to be stably dissolved at a constant rate for an extended
15 period of time.

[0215]

Table 6

Coating Composition		Test Duration				Fouling Organisms
		After 6 Months	After 12 Months	After 18 Months	After 24 Months	
Examples	1	0	0	0	0	None (Small Amount of Slime)
	2	0	0	0	0	None (Small Amount of Slime)
	3	0	0	0	0	None (Small Amount of Slime)
	4	0	0	0	5	None (Small Amount of Slime)
	5	0	0	0	0	None (Small Amount of Slime)
	6	0	0	0	0	None (Small Amount of Slime)
	7	0	0	0	0	None (Small Amount of Slime)
	8	0	0	0	0	None (Small Amount of Slime)
Comparative Examples	1	0	0	0	0	None (Large Amount of Slime)
	2	0	0	0	0	None (Large Amount of Slime)
	3	0	0	0	0	None (Large Amount of Slime)
	4	0	0	20	50	<i>Tubeworms</i> Barnacles
	5	0	10	50	100	<i>Tubeworms</i> Barnacles

CLAIMS

1. An antifouling coating composition comprising:

Polymer (A), which is a polymer having a number average molecular weight of 1,000 to 20,000 that is obtained by
5 polymerizing a polymerizable triorganosilyl unsaturated carboxylate; and

Zinc Salt (B), which is at least one zinc salt selected from the group consisting of rosin zinc salts and zinc salts of rosin derivatives;

10 the antifouling coating composition (1) having the weight ratio of the content of Polymer (A) to that of Zinc Salt (B) ((A)/(B)) of 45/55 to 10/90;

(2) having the nonvolatile matter content of not less than 75 weight%; and

15 (3) substantially being free from a rosin or rosin derivative containing a free carboxyl group.

2. The antifouling coating composition according to claim 1, wherein Polymer (A) has a number average molecular
20 weight of 2,000 to 15,000, and a degree of dispersion of molecular weight of less than 2.5.

3. The antifouling coating composition according to claim 1 or 2, wherein Polymer (A) has a glass transition
25 temperature of 20 to 70°C.

4. The antifouling coating composition according to claim 1, wherein Polymer (A) is triisopropylsilyl (meth)acrylate copolymer.

30

5. The antifouling coating composition according to claim 3, wherein the triisopropylsilyl (meth)acrylate copolymer is obtained by copolymerizing (a) 30 to 60 weight% of triisopropylsilyl (meth)acrylate, (b) 10 to 50 weight% of methyl
35 methacrylate, and (c) 0 to 60 weight% of (meth)acrylic ester

other than those defined in (a) and (b).

6. The antifouling coating composition according to claim 1, wherein the rosin zinc salt is at least one zinc salt
5 selected from the group consisting of gum rosin zinc salts, wood rosin zinc salts and tall oil rosin zinc salts, and the zinc salt of the rosin derivative is at least one zinc salt selected from the group consisting of hydrogenated rosin zinc salts and disproportionated rosin zinc salts.

10

7. The antifouling coating composition according to claim 1, wherein the nonvolatile matter content is not less than 80 weight% and viscosity is 80 to 100 KU measured using a Stormer viscometer at 25°C.

15

8. The antifouling coating composition according to claim 1, wherein the content of the volatile organic compound is less than 400 g/L.

20

9. The antifouling coating composition according to claim 1, which further comprises 10 to 100 parts by weight of zinc oxide per 100 parts by weight of total amount of Polymer (A) and Zinc Salt (B).

25

10. The antifouling coating composition according to claim 1, which further comprises 100 to 400 parts by weight of cuprous oxide per 100 parts by weight of total amount of Polymer (A) and Zinc Salt (B).

30

11. The antifouling coating composition according to claim 10, wherein the cuprous oxide has an average particle diameter of 8 to 20 μm .

12. The antifouling coating composition according to
35 claim 1, which further comprises 1 to 100 parts by weight of

organic antifoulant per 100 parts by weight of total amount of Polymer (A) and Zinc Salt (B).

13. The antifouling coating composition according to
5 claim 1, which further comprises 1 to 50 parts by weight of plasticizer per 100 parts by weight of total amount of Polymer (A) and Zinc Salt (B).

14. The antifouling coating composition according to
10 claim 13, wherein the plasticizer is an epoxidized oil or fat.

15. The antifouling coating composition according to
claim 1, which comprises 1 to 50 parts by weight of dewatering agent per 100 parts by weight of total amount of Polymer (A) and
15 Zinc Salt (B).

16. The antifouling coating composition according to
claim 15, wherein the dewatering agent is at least one
dehumidifier selected from the group consisting of alkoxysilanes
20 and alkyl orthoformates.

17. The antifouling coating composition according to
claim 1, which further comprises 1 to 50 parts by weight of fatty acid amide-based dispersant per 100 parts by weight of total
25 amount of Polymer (A) and Zinc Salt (B).

18. An antifouling treatment method conducted using the
antifouling coating composition of any one of claims 1 to 17
comprising a step of forming an antifouling coating film on the
30 surface of an object to be coated.

19. An antifouling coating film formed by using the
antifouling coating composition of any one of claims 1 to 17.

35 20. A coated object having the antifouling coating

film of claim 19 on its surface.

21. A method for producing an antifouling coating composition comprising the steps of:

5 mixing Polymer (A), which is a polymer having a number average molecular weight of 1,000 to 20,000 that is obtained by polymerizing a polymerizable triorganosilyl unsaturated carboxylate with Zinc Salt (B), which is at least one zinc salt selected from the group consisting of rosin zinc salts and zinc
10 salts of rosin derivatives;

 the antifouling coating composition (1) having the weight ratio of the content of Polymer (A) to that of Zinc Salt (B) ((A)/(B)) of 45/55 to 10/90;

 (2) having the nonvolatile matter content of not less
15 than 75 weight%; and

 (3) substantially being free from a rosin or rosin derivative containing a free carboxyl group.

22. The method for producing an antifouling coating
20 composition according to claim 21, which comprises the steps of:

 mixing Polymer (A) with Zinc Salt (B);

 adding a cuprous oxide having an average particle diameter of 3 to 10 μm to the mixture of Polymer (A) and Zinc Salt (B); and

25 mixing and dispersing the resulting mixture using a disperser.

23. The method for producing an antifouling coating composition according to claim 21, which comprises the steps of:

30 mixing Polymer (A) with Zinc Salt (B);

 dispersing the mixture using a disperser while mixing;
and

 adding and mixing a cuprous oxide having an average particle diameter of 10 to 20 μm .