

DESCRIPTION

ANTIFOULING COATING COMPOSITION

Technical Field

5 [0001]

The present invention relates to an antifouling coating composition, an antifouling coating film, a substrate with an antifouling coating film, a method for producing a substrate with an antifouling coating film, and
10 an antifouling method for a substrate. More specifically, the present invention relates to, for example, an antifouling coating composition containing specific components such as a hydrolyzable polymer and an antifouling agent.

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Background Art

[0002]

As a method for preventing fouling of a substrate such as a ship by an aquatic organism or the like, a method
20 for forming an antifouling coating film containing a hydrolyzable polymer on the surface of the substrate is widely used. As such an antifouling coating film, various antifouling coating materials that contain a polymer containing a metal ester group have been studied.

25 [0003]

For example, Patent Literature 1 discloses an antifouling coating composition that contains a polymer containing a metal ester group and an antifouling agent containing at least medetomidine and optionally further
5 containing copper pyrithione, 2-(p-chlorophenyl)-3-cyano-4-bromo-5-trifluoromethylpyrrole (also known as tralopyril), or the like (claims and the like), and describes that "an antifouling coating film having a stable coating film depletion degree in a ship, an underwater structure, or the
10 like and exhibiting an excellent antifouling property over a long period of time" can be formed from such an antifouling coating composition.

[0004]

Patent Literature 2 discloses an antifouling coating
15 composition that contains a hydrolyzable polymer containing a metal ester group, a tertiary carboxylic acid component containing versatic acid, and an antifouling agent component, for example, 4-bromo-2-(4-chlorophenyl)-5-(trifluoromethyl)-1H-pyrrole-3-carbonitrile (also known as
20 tralopyril) (claims and the like), and describes that "an antifouling coating film which has an excellent coating film depletion degree and an excellent antifouling property over a long period of time, is excellent in coating film physical properties such as weather resistance, and does
25 not easily cause foaming (blister) even when formed on a

deteriorated coating film" can be formed from such an antifouling coating composition.

[0005]

Patent Literature 3 discloses an antifouling coating
5 composition that contains a hydrolyzable polymer containing
a metal ester group, a specific amount of zinc oxide, and
medetomidine (claims and the like), and describes that "an
antifouling coating film which maintains a high antifouling
property over a long period of time and is excellent in
10 damage resistance" can be formed from such an antifouling
coating composition.

[0006]

Patent Literature 4 discloses an antifouling coating
composition that contains a specific amount of a resin
15 having a specific metal carboxylate structure and a
specific amount of an antifouling agent containing at least
medetomidine and 4-bromo-2-(4-chlorophenyl)-5-
(trifluoromethyl)-1H-pyrrole-3-carbonitrile (also known as
tralopyril) and that may optionally further contain copper
20 pyrithione or the like (claims and the like), and describes
that a coating film "capable of ensuring a long-term
antifouling property without using cuprous oxide" can be
formed from such an antifouling coating composition.

25 Citation List

Patent Literature

[0007]

Patent Literature 1: WO 2011/118526 A

Patent Literature 2: WO 2016/084769 A

5 Patent Literature 3: WO 2018/003135 A

Patent Literature 4: JP 2020-100794 A

Summary of Invention

Technical Problem

10 [0008]

In recent years, there has been reported a case where even in a conventional hydrolyzable antifouling coating film (for example, a hydrolyzable antifouling coating film containing medetomidine described in Patent Literature 1), which has been considered to have a certain level of antifouling performance as described in Patent Literatures 1 to 4, adhesion of animal species such as barnacles, Bryozoa, and Serpula is observed during a low speed and low working operation in a highly fouling sea area or during mooring at the quay waiting for docking. Therefore, in particular, in an outfitting process when a new ship is built, a coating material having both a static antifouling property and an antifouling property at anchorage after operation (a static antifouling property after long-term dynamic immersion) has been required.

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Furthermore, due to the influence of the COVID-19 pandemic, not only the number of ships that are anchored for a long period of time and ships whose operation rate is lowered is increasing, but also the risk of fouling of ships is

5 increasing due to abnormal weather and changes in the marine environment. In order to cope with such a risk of fouling of ships, there has been a strong demand for the development of a coating composition having an excellent antifouling property for ships anchored for a long period
10 of time and also long-term ships anchored after operation.
[0009]

On the other hand, a hull block construction method is generally used for building a new ship. When the surface of the coating film is roughened with a power tool
15 around the welded seam in the erection step (a joining step of a hull block) and the like, a conventional antifouling coating film has a problem that peeling and scattering of coating film pieces occur, which is presumed to be due to adhesiveness to the primer anticorrosive coating film, the
20 coating film physical properties (hardness), and the like. In addition, generally, the antifouling coating film whose service life has elapsed is repair (mend)-painted by pulling up a structure such as a ship to the land (for example, a ship dock). However, during this repair
25 painting, not only a ship cannot be used, but also a usage

fee of a dock or the like is high, and thus it is economically strongly required to complete the repair painting in a short period of time. Therefore, it is important to have not only adhesiveness to a sound primer
5 such as an anticorrosive coating film before use but also excellent adhesiveness that enables direct painting on a deteriorated antifouling coating film (old antifouling coating film) to be repaired (that is, it is not necessary to remove the old antifouling coating film).

10 [0010]

An object of the present invention is to provide an antifouling coating composition which enables the formation of an antifouling coating film that is (1) excellent in both a static antifouling property generally required for
15 an antifouling coating film and a static antifouling property after long-term dynamic immersion required for a ship or the like (deteriorated, altered, or depleted antifouling coating film) at anchorage after operation as an antifouling property, and that is (2) excellent in any
20 of adhesiveness to a sound anticorrosive coating film or the like (primer coating film or intermediate coating film) before use (before seawater immersion) and peel resistance of a coating film during a power tool treatment, and adhesiveness to an old antifouling coating film after use
25 (after seawater immersion).

Solution to Problem

[0011]

The present inventors have found that an antifouling
5 coating composition that can achieve the above object can
be prepared by incorporating a hydrolyzable polymer
containing a specific metal ester group, three specific
antifouling agents, that is, medetomidine, tralopyril, and
copper pyrithione, and a specific alkyl carboxylic acid,
10 for example versatic acid, as essential components, and
have completed the present invention. Although these
components are also used in conventional antifouling
coating compositions individually or in partial
combination, it was a surprising and unpredictable matter
15 that the use of all these components in combination
provides an antifouling coating composition, which
satisfies various performance as described above in a well-
balanced manner and can achieve the new object,
particularly that even similar components that are treated
20 as equivalents or alternatives in conventional antifouling
coating compositions can achieve effects, which are not
exhibited when other components are selected, by selecting
specific components. Although it may be possible to
satisfy individual performance or several performance with
25 a collection of prior arts, the antifouling coating

composition of the present invention, which can simultaneously satisfy various performance in a well-balanced manner without impairing specific performance by selecting and combining specific components, would not have
5 been easily accomplished by anyone skilled in the art other than the present inventor.

[0012]

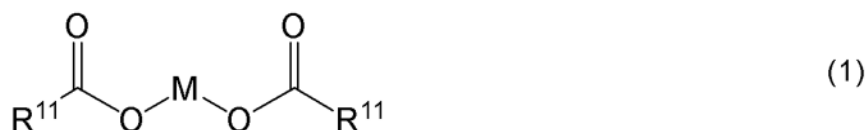
That is, the present invention includes at least the following items.

10 [Item 1]

An antifouling coating composition containing a hydrolyzable polymer (A) containing a metal ester group, medetomidine (B), tralopyril (C), copper pyrithione (D), and a linear or branched alkyl carboxylic acid (E) having 4
15 to 30 carbon atoms, in which

the polymer (A) includes a constituent unit derived from a metal ester group-containing monomer (a1) represented by formula (1) below and/or a constituent unit derived from a metal ester group-containing monomer (a2)
20 represented by formula (2) below.

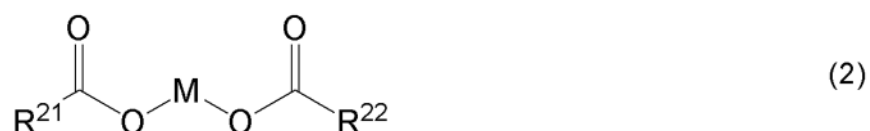
[Chem. 1]



In formula (1), R¹¹'s each independently represent a

monovalent group containing a terminal ethylenically unsaturated group, and M represents a copper atom or a zinc atom.

[Chem. 2]

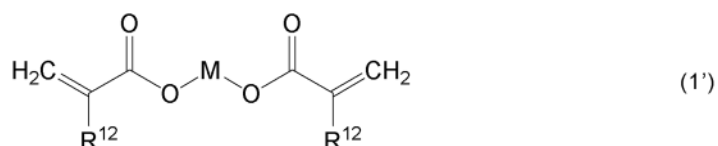


In formula (2), R²¹ represents a monovalent group containing a terminal ethylenically unsaturated group, R²² represents a monovalent organic group containing no terminal ethylenically unsaturated group and having 1 to 30 carbon atoms, and M represents a copper atom or a zinc atom.

[Item 2]

The antifouling coating composition according to item 1, in which the polymer (A) contains a metal ester group-containing monomer (a1) represented by formula (1') below.

[Chem. 3]



In formula (1'), R¹²'s each independently represent a hydrogen atom or a methyl group, and M represents a copper atom or a zinc atom.

[Item 3]

The antifouling coating composition according to item 1 or 2, in which the alkyl carboxylic acid (E) is versatic acid.

5 [Item 4]

The antifouling coating composition according to any one of items 1 to 3, in which

a content of the medetomidine (B) is 0.1 to 100 mass% and a content of the tralopyril (C) is 10 to 1,700 mass% with respect to 100 mass% of the copper pyrithione (D), and

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a content of the copper pyrithione (D) is 0.5 to 12 mass% with respect to 100 mass% of a solid content of the antifouling coating composition.

15 [Item 5]

An antifouling coating film, formed from the antifouling coating composition according to any one of items 1 to 4.

[Item 6]

20 A substrate with an antifouling coating film, including a substrate and the antifouling coating film according to item 5.

[Item 7]

The substrate with an antifouling coating film according to item 6, in which the substrate is selected

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from a group consisting of a ship, an underwater structure,
and a fishery material.

[Item 8]

A method for producing a substrate with an
5 antifouling coating film, the method including a step (1)
of coating or impregnating a substrate with the antifouling
coating composition according to any one of items 1 to 4 to
obtain a coated body or an impregnated body, and a step (2)
of drying the coated body or the impregnated body.

10 [Item 9]

An antifouling method for a substrate, including a
step of forming the antifouling coating film according to
item 5 on at least a part of a substrate.

15 Advantageous Effects of Invention

[0013]

The antifouling coating composition of the present
invention enables the formation of an antifouling coating
film that is excellent in both a general static antifouling
20 property and a static antifouling property after long-term
dynamic immersion and that is excellent in any of
adhesiveness and peel resistance to a primer coating film
and an intermediate coating film, and adhesiveness to an
old antifouling coating film. This makes it possible to
25 also cope with the performance newly required for an

antifouling coating film in a ship or the like, which has become apparent due to recent environmental changes.

Description of Embodiments

5 [0014]

As used herein, “(meth)acrylic acid” means “acrylic acid or methacrylic acid” or “acrylic acid and methacrylic acid” depending on the context, and “(meth)acrylate” means “acrylate or methacrylate” or “acrylate and methacrylate”
10 depending on the context.

[0015]

An upper limit and a lower limit described in the present description (regarding, for example, the content of a component) can be arbitrarily combined to set a numerical
15 range.

[0016]

In the present description (particularly, examples), “part(s)” as a unit added after a numerical value denotes “part(s) by mass” unless otherwise specified.

20 [0017]

-Antifouling coating composition-

The antifouling coating composition of the present invention contains a hydrolyzable polymer (A) containing a metal ester group (sometimes referred to as “polymer (A)”
25 or “component (A)” in the present description),

medetomidine (B) (sometimes referred to as "component (B)" in the present description), tralopyril (C) (sometimes referred to as "component (C)" in the present description), copper pyrithione (D) (sometimes referred to as "component (D)" in the present description), and a linear or branched alkyl carboxylic acid (E) having 4 to 30 carbon atoms (sometimes referred to as "alkyl carboxylic acid (E)" or "component (E)" in the present description).

[0018]

<Polymer (A)>

The polymer (A) contains a constituent unit derived from a metal ester group-containing monomer (a1) (sometimes referred to as "monomer (a1) in the present description) and/or a constituent unit derived from a metal ester group-containing monomer (a2) (sometimes referred to as "monomer (a2) in the present description). In the polymer (A), any one type may be used, or two or more types of constituent units derived from the monomer (a1) and/or constituent units derived from the monomer (a2) having different structures, proportions, or the like may be used. It is preferable that the polymer (A) contains at least a constituent unit derived from the monomer (a1), that is, contains a constituent unit derived from the monomer (a1), or contains both a constituent unit derived from the monomer (a1) and a constituent unit derived from the

monomer (a2).

[0019]

· Monomer (a1)

The metal ester group-containing monomer (a1) is a
5 monomer represented by the following formula (1). The
monomer (a1) may be any one type or two or more types.

[0020]

[Chem. 4]



10 [0021]

In formula (1), R^{11} 's each independently represent a monovalent group containing a terminal ethylenically unsaturated group ($\text{CH}_2=\text{C}<$), and M represents a copper atom or a zinc atom.

15 [0022]

The number of carbon atoms in the terminal ethylenically unsaturated group of R^{11} is preferably 2 to 50, more preferably 2 to 30, still more preferably 2 to 10, and particularly preferably 2 to 6.

20 [0023]

R^{11} may further contain an ethylenically unsaturated group other than at the terminal, but more preferably contains an ethylenically unsaturated group only at the

terminal.

[0024]

R^{11} is preferably an organic group containing a terminal ethylenically unsaturated group (referred to as a "terminal ethylenically unsaturated organic group" in the present description). Examples of the terminal ethylenically unsaturated organic group include an unsaturated aliphatic hydrocarbon group in which a part of the structure may be substituted with an ester bond, an amide bond, or an ether bond. Specific examples of such a terminal ethylenically unsaturated organic group include a group obtained by removing a carboxy group from an aliphatic unsaturated monocarboxylic acid containing a terminal ethylenically unsaturated group such as acrylic acid (also known as 2-propenoic acid), methacrylic acid (also known as 2-methyl-2-propenoic acid), 3-butenic acid, 4-pentenoic acid, 10-undecenoic acid, or a (meth)acryloyloxyalkylcarboxylic acid [for example, 3-(meth)acryloyloxypropionic acid, or 3-(meth)acryloyloxy-2-methylpropionic acid]; and a group obtained by removing one carboxy group from an aliphatic unsaturated dicarboxylic acid having a terminal ethylenically unsaturated group such as itaconic acid. The terminal ethylenically unsaturated organic group is more preferably a group obtained by removing a carboxy group from an aliphatic unsaturated

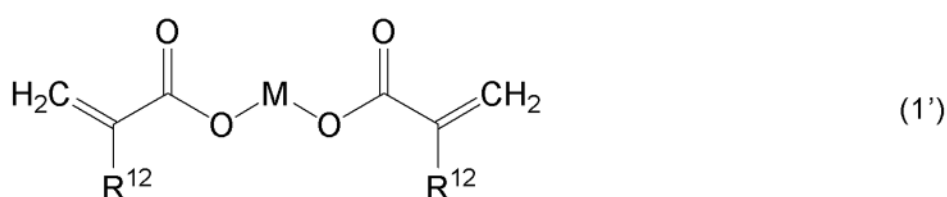
monocarboxylic acid containing a terminal ethylenically unsaturated group, still more preferably a group obtained by removing a carboxy group from acrylic acid, methacrylic acid, or a (meth)acryloyloxyalkylcarboxylic acid, and particularly preferably a group obtained by removing a carboxy group from acrylic acid or methacrylic acid.

[0025]

The monomer (a1) is preferably a monomer represented by the following formula (1') (sometimes referred to as "monomer (a1') in the present description). The monomer (a1') corresponds to a case where, in the monomer (1), both of the terminal ethylenically unsaturated organic groups of two R¹¹'s are groups obtained by removing a carboxy group from acrylic acid or methacrylic acid.

[0026]

[Chem. 5]



[0027]

In formula (1'), R¹²'s each independently represent a hydrogen atom or a methyl group, and M represents a copper atom or a zinc atom.

[0028]

Examples of the monomer (a1) include zinc

diacrylate, zinc dimethacrylate, zinc acrylate methacrylate, zinc di(3-acryloyloxypropionate), zinc di(3-methacryloyloxypropionate), zinc di(3-(meth)acryloyloxy-2-methylpropionate), copper diacrylate, copper dimethacrylate, copper acrylate methacrylate, copper di(3-acryloyloxypropionate), copper di(3-methacryloyloxypropionate), and copper di(3-(meth)acryloyloxy-2-methylpropionate), and among these, zinc diacrylate, zinc dimethacrylate, or zinc acrylate methacrylate is preferable from the viewpoint that an antifouling coating film having a sufficient antifouling property can be easily obtained. Zinc diacrylate, zinc dimethacrylate, zinc acrylate methacrylate, copper diacrylate, copper dimethacrylate, and copper acrylate methacrylate correspond to the monomer (a1').

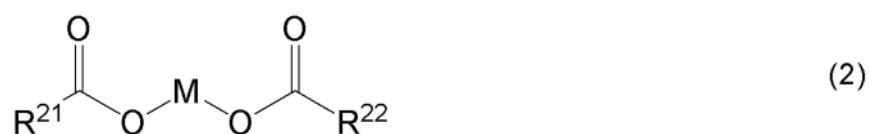
[0029]

· Monomer (a2)

The metal ester group-containing monomer (a2) is a monomer represented by the following formula (2). The monomer (a2) may be any one type or two or more types.

[0030]

[Chem. 6]



[0031]

In formula (2), R^{21} represents a monovalent group containing a terminal ethylenically unsaturated group ($CH_2=C<$), R^{22} represents a monovalent organic group
5 containing no terminal ethylenically unsaturated group and having 1 to 30 carbon atoms, and M represents a copper atom or a zinc atom.

[0032]

With respect to technical matters regarding the
10 terminal ethylenically unsaturated group of R^{21} , the technical matters regarding the terminal ethylenically unsaturated group of R^{11} described in the relationship with formula (1) can be directly referred to in the present description.

15 [0033]

Examples of R^{22} include an organic group containing no terminal ethylenically unsaturated group (referred to as "non-terminal ethylenically unsaturated organic group" in the present description) such as an aliphatic hydrocarbon
20 group having 1 to 30 carbon atoms, an alicyclic hydrocarbon group having 3 to 30 carbon atoms, or an aromatic hydrocarbon group having 6 to 30 carbon atoms. The non-terminal ethylenically unsaturated organic group may further contain a substituent (for example, a hydroxy
25 group).

[0034]

The aliphatic hydrocarbon group in the non-terminal ethylenically unsaturated organic group may be either linear or branched, and may be a saturated aliphatic hydrocarbon group or an unsaturated aliphatic hydrocarbon group (limited to those not containing a terminal ethylenically unsaturated group). The number of carbon atoms in the aliphatic hydrocarbon group is 1 to 30, preferably 1 to 28, more preferably 1 to 26, and still more preferably 1 to 24. The aliphatic hydrocarbon group may be substituted with an alicyclic hydrocarbon group or an aromatic hydrocarbon group.

[0035]

The alicyclic hydrocarbon group in the non-terminal ethylenically unsaturated organic group may be a saturated alicyclic hydrocarbon group or an unsaturated alicyclic hydrocarbon group. The number of carbon atoms in the alicyclic hydrocarbon group is 3 to 30, preferably 4 to 20, more preferably 5 to 16, and still more preferably 6 to 12. The alicyclic hydrocarbon group may be substituted with an aliphatic hydrocarbon group or an aromatic hydrocarbon group.

[0036]

The number of carbon atoms in the aromatic hydrocarbon group in the non-terminal ethylenically

unsaturated organic group is 6 to 30, preferably 6 to 24,
more preferably 6 to 18, and still more preferably 6 to 10.
The aromatic hydrocarbon group may be substituted with an
aliphatic hydrocarbon group or an alicyclic hydrocarbon
5 group.

[0037]

R^{22} is preferably an organic acid residue derived
from a monobasic acid, and specific examples thereof
include a group obtained by removing a carboxy group from
10 an organic acid such as versatic acid, palmitic acid,
stearic acid, isostearic acid, oleic acid, linoleic acid,
linolenic acid, abietic acid, neoabietic acid, pimaric
acid, dehydroabietic acid, 12-hydroxystearic acid, or
naphthenic acid. Among these, a group obtained by removing
15 a carboxy group from abietic acid, versatic acid, or
naphthenic acid is preferable, and a group obtained by
removing a carboxy group from abietic acid or versatic acid
is more preferable. Versatic acid is a generic term for a
mixture of highly branched carboxylic acids having 9 to 11
20 carbon atoms, mainly 10 carbon atoms.

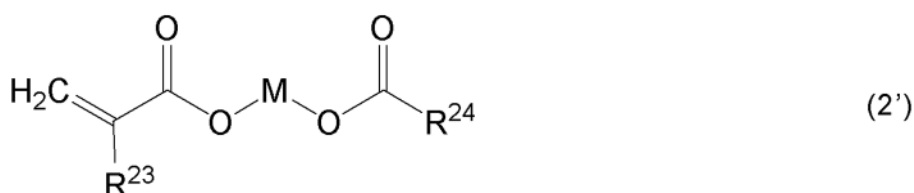
[0038]

The monomer (a2) is preferably a monomer represented
by the following formula (2') (sometimes referred to as
"monomer (a2') in the present description). The monomer
25 (a2') corresponds to a monomer (2) in which the terminal

ethylenically unsaturated organic group of R^{22} is a group obtained by removing a carboxy group from acrylic acid or methacrylic acid.

[0039]

5 [Chem. 7]



[0040]

In formula (2'), R^{23} represents a hydrogen atom or a methyl group, R^{24} has the same meaning as R^{22} in formula
 10 (2), and M represents a copper atom or a zinc atom.

[0041]

Examples of the monomer (a2) include zinc 3-(meth)acryloyloxypropionate rosin, zinc 3-(meth)acryloyloxypropionate versatate, zinc (meth)acrylate
 15 rosin, zinc (meth)acrylate versatate, zinc (meth)acrylate naphthenate, copper 3-(meth)acryloyloxypropionate rosin, copper 3-(meth)acryloyloxypropionate versatate, copper (meth)acrylate rosin, copper (meth)acrylate versatate, and copper (meth)acrylate naphthenate. Note that zinc
 20 (meth)acrylate rosin, zinc (meth)acrylate versatate, zinc (meth)acrylate naphthenate, copper (meth)acrylate rosin, copper (meth)acrylate versatate, and copper (meth)acrylate naphthenate correspond to the monomer (a2').

[0042]

· Other monomers

If necessary, the polymer (A) may further contain a monomer other than the monomer (a1) and the monomer (a2) copolymerizable with the monomer (a1) and/or the monomer (a2). Examples of such an optional monomer include a monomer which does not contain a metal ester group but has an ethylenically unsaturated group, for example, an organosiloxane block-containing monomer (a3) (sometimes referred to as "monomer (a3) in the present description); (meth)acrylate or an ester thereof (a4) (sometimes referred to as "monomer (a4) in the present description); and a vinyl compound (a5) (sometimes referred to as "monomer (a5) in the present description).

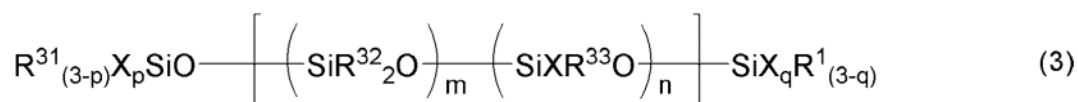
[0043]

· Monomer (a3)

The monomer (a3), that is, the organosiloxane block-containing monomer (a3) is a monomer represented by the following formula (3). The monomer (a3) may be any one type or two or more types.

[0044]

[Chem. 8]



[0045]

In formula (3), R^{31} , R^{32} , and R^{33} each independently represent a monovalent hydrocarbon group, X's each independently represent a (meth)acryloyloxyalkyl group or a mercaptoalkyl group, m is 1 or more, n is 0 or more, p and q are each independently 0 or 1, and $n + p + q$ is 1 or more.

[0046]

Examples of the hydrocarbon group in R^{31} , R^{32} , and R^{33} include a linear, branched, or cyclic alkyl group and an aryl group. The number of carbon atoms in the alkyl group is preferably 1 to 12, more preferably 1 to 8, and still more preferably 1 to 4. The number of carbon atoms in the aryl group is preferably 6 to 14 and more preferably 6 to 10. R^{31} , R^{32} , and R^{33} are each independently preferably an alkyl group such as a methyl group or a butyl group from the viewpoint of ease of polymerization.

[0047]

Examples of X include (meth)acryloyloxyalkyl groups such as a (meth)acryloyloxyethyl group, a (meth)acryloyloxypropyl group, and a (meth)acryloyloxybutyl group; and mercaptoalkyl groups such as a mercaptomethyl group, a mercaptoethyl group, a mercaptopropyl group, and a mercaptobutyl group. X is preferably a (meth)acryloyloxyalkyl group from the viewpoint of uniform progress of polymerization, and is preferably a

mercaptoalkyl group from the viewpoint of reducing the viscosity of the copolymer (A) and facilitating handling.

[0048]

m and n denote the average number of added moles of
5 (SiR³²₂O) and the average number of added moles of
(SiXR³³O), respectively. m + n is preferably 2 or more.
That is, the organosiloxane block-containing monomer (a3)
is preferably a polyorganosiloxane block-containing
monomer.

10 [0049]

In the present description, when two or more
different repeating units are described in parallel between
[] as in formula (3), it indicates that these repeating
units may be repeated in any order of a random shape, an
15 alternating shape, or a block shape. That is, for example,
in the case of a formula -[Y₃-Z₃]- (here, Y and Z each
represent a repeating unit), it may be in a random shape
such as -YYZYZZ-, an alternating shape such as -YZYZYZ-, or
a block shape such as -YYYZZZ- or -ZZZYYY-.

20 [0050]

A first embodiment of the monomer (a3) includes a
monomer (a31) in which n is 0, p is 1, and q is 0. It is
preferable that the copolymer (A) contains a constituent
unit derived from such a monomer (a31) because, for
25 example, the antifouling coating composition facilitates

the formation of an antifouling coating film excellent in antifouling property. m in the monomer (a31) is preferably 3 or more, more preferably 5 or more, and is preferably 200 or less, more preferably 70 or less from the viewpoint of ease of polymerization and the like.

[0051]

As the monomer (a31), for example, commercially available products manufactured by JNC Corporation "FM-0711" (one-terminal methacryloyloxyalkyl-modified organopolysiloxane, number average molecular weight: 1,000), "FM-0721" (one-terminal methacryloyloxyalkyl-modified organopolysiloxane, number average molecular weight: 5,000), and "FM-0725" (one-terminal methacryloyloxyalkyl-modified organopolysiloxane, number average molecular weight: 10,000); commercially available products manufactured by Shin-Etsu Chemical Co., Ltd. "X-22-174ASX" (one-terminal methacryloyloxyalkyl-modified organopolysiloxane, functional group equivalent: 900 g/mol), "KF-2012" (one-terminal methacryloyloxyalkyl-modified organopolysiloxane, functional group equivalent: 4,600 g/mol), and X-22-2426 (one-terminal methacryloyloxyalkyl-modified organopolysiloxane, functional group equivalent: 12,000 g/mol); and the like can be used.

[0052]

A second embodiment of the monomer (a3) includes a monomer (a32) in which n is 0 and p and q are 1. It is preferable that the copolymer (A) contains a constituent unit derived from such a monomer (a32) because, for
5 example, the antifouling coating composition facilitates the formation of an antifouling coating film excellent in repairability, that is, excellent in adhesiveness to an old antifouling coating film after use (after seawater immersion). m in the monomer (a32) is preferably 3 or
10 more, more preferably 5 or more, and is preferably 200 or less, more preferably 70 or less from the viewpoint of ease of polymerization and the like.

[0053]

As the monomer (a32), for example, commercially
15 available products manufactured by JNC Corporation "FM-7711" (both-terminal methacryloyloxyalkyl-modified organopolysiloxane, number average molecular weight: 1,000), "FM-7721" (both-terminal methacryloyloxyalkyl-modified organopolysiloxane, number average molecular
20 weight: 5,000), and "FM-7725" (both-terminal methacryloyloxyalkyl-modified organopolysiloxane, number average molecular weight: 10,000); commercially available products manufactured by Shin-Etsu Chemical Co., Ltd. "X-22-164" (both-terminal methacryloyloxyalkyl-modified
25 organopolysiloxane, functional group equivalent: 190

g/mol), "X-22-164AS" (both-terminal methacryloyloxyalkyl-modified organopolysiloxane, functional group equivalent: 450 g/mol), "X-22-164A" (both-terminal methacryloyloxyalkyl-modified organopolysiloxane,

functional group equivalent: 860 g/mol), "X-22-164B" (both-terminal methacryloyloxyalkyl-modified organopolysiloxane, functional group equivalent: 1,630 g/mol), "X-22-164 C" (both-terminal methacryloyloxyalkyl-modified organopolysiloxane, functional group equivalent: 2,370

g/mol), "X-22-164E" (both-terminal methacryloyloxyalkyl-modified organopolysiloxane, functional group equivalent: 3,900 g/mol), and "X-22-167B" (both-terminal mercaptoalkyl-modified organopolysiloxane, functional group equivalent: 1,670 g/mol); and the like can be used.

[0054]

A third embodiment of the monomer (a3) includes a monomer (a33) in which n is 1 or more. It is preferable that the copolymer (A) contains a constituent unit derived from such a monomer (a33) because, for example, the viscosity of the antifouling coating composition tends to decrease to facilitate the handling. m in the monomer (a33) is preferably 50 to 1,000, and n is preferably 1 to 30.

[0055]

As the monomer (a33), for example, commercially

available products manufactured by Shin-Etsu Chemical Co.,
Ltd. "KF-2001" (side chain mercaptoalkyl-modified
organopolysiloxane, functional group equivalent: 1,900
g/mol) and "KF-2004" (side chain mercaptoalkyl-modified
5 organopolysiloxane, functional group equivalent: 30,000
g/mol); and the like can be used.

[0056]

· Monomer (a4)

The monomer (a4), that is, the (meth)acrylate or an
10 ester thereof (a4) is a compound represented by the
following formula (4). The monomer (a4) may be any one
type or two or more types.

[0057]

[Chem. 9]



[0058]

In formula (4), R^{41} represents a monovalent group
containing an ethylenically unsaturated group, and R^{42}
represents a hydrogen atom, an alkyl group, an aryl group,
20 an alkoxyalkyl group, a hydroxyalkyl group, or a glycidyl
group.

[0059]

A first embodiment of the monomer (a4) includes a

monomer (a41) in which R^{42} is a hydrogen atom, for example, (meth)acrylic acid. When the copolymer (A) contains such a monomer (a41), the resulting antifouling coating composition tends to have excellent adhesiveness to an old antifouling coating film after use (after seawater immersion), a low viscosity, and excellent paint workability, and an antifouling coating film to be formed tends to have a high coating film depletion degree.

[0060]

A second embodiment of the monomer (a4) includes a monomer (a42) in which R^{42} is an alkyl group or an aryl group. The alkyl group as R^{42} may have any of a linear, branched, and cyclic structure, and the number of carbon atoms is preferably 1 to 20, more preferably 1 to 12, and still more preferably 1 to 6. When the copolymer (A) contains such a monomer (a42), an antifouling coating film formed from the obtained antifouling coating composition tends to have a coating film depletion degree kept at an appropriate update rate without significantly impairing the antifouling property, and tends to be excellent in damage resistance and/or crack resistance.

[0061]

Specific examples of the monomer (a42) include methyl (meth)acrylate, ethyl (meth)acrylate, n-propyl (meth)acrylate, isopropyl (meth)acrylate, n-butyl

(meth)acrylate, isobutyl (meth)acrylate, tert-butyl
(meth)acrylate, pentyl (meth)acrylate, hexyl
(meth)acrylate, cyclohexyl (meth)acrylate, n-octyl
(meth)acrylate, isooctyl (meth)acrylate, 2-ethylhexyl
5 (meth)acrylate, 3,5,5-trimethylhexyl (meth)acrylate, lauryl
(meth)acrylate, cetyl (meth)acrylate, stearyl
(meth)acrylate, phenyl (meth)acrylate, and benzyl
(meth)acrylate. For example, it is preferable to use at
least one selected from the group consisting of methyl
10 (meth)acrylate, ethyl (meth)acrylate, n-butyl
(meth)acrylate, and cyclohexyl (meth)acrylate as the
monomer (a42).

[0062]

A third embodiment of the monomer (a4) includes a
15 monomer (a43) in which R^{42} is an alkoxyalkyl group. The
alkoxyalkyl group as R^{42} may have any of a linear,
branched, and cyclic structure, and the number of carbon
atoms (the sum of the number of carbon atoms contained in
the alkyl group in the alkoxy group and the number of
20 carbon atoms contained in the alkyl group) is preferably 1
to 20, more preferably 1 to 12, and still more preferably 1
to 6. When the copolymer (A) contains such a monomer
(a43), an antifouling coating film formed from the obtained
antifouling coating composition tends to maintain an
25 appropriate coating film depletion degree over a long

period of time.

[0063]

Specific examples of the monomer (a43) include 2-methoxyethyl (meth)acrylate, 2-ethoxyethyl (meth)acrylate, 3-methoxybutyl (meth)acrylate, 4-methoxybutyl (meth)acrylate, 3-methoxy-n-propyl (meth)acrylate, 2-propoxyethyl (meth)acrylate, 2-butoxyethyl (meth)acrylate, isobutoxybutyl diglycol (meth)acrylate, 2-phenoxyethyl (meth)acrylate, methoxy polyethylene glycol (meth)acrylate, ethoxy polyethylene glycol (meth)acrylate, butoxy polyethylene glycol (meth)acrylate, and phenoxy polyethylene glycol (meth)acrylate. For example, it is preferable to use 2-methoxyethyl (meth)acrylate as the monomer (a43).

[0064]

A fourth embodiment of the monomer (a4) includes a monomer (a44) in which R^{42} is a hydroxyalkyl group. The hydroxyalkyl group as R^{42} may have any of a linear, branched, and cyclic structure, and the number of carbon atoms is preferably 1 to 20, more preferably 1 to 12, and still more preferably 1 to 6. When the copolymer (A) contains such a monomer (a44), an antifouling coating film formed from the obtained antifouling coating composition tends to have a high coating film depletion degree.

[0065]

Specific examples of the monomer (a44) include hydroxymethyl (meth)acrylate, 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, 4-hydroxybutyl (meth)acrylate, and 2-hydroxy-3-phenoxypropyl (meth)acrylate.

[0066]

A fifth embodiment of the monomer (a4) includes a monomer (a45) in which R^{42} is a glycidyl group, for example, glycidyl (meth)acrylate. When the copolymer (A) contains such a monomer (a44), an antifouling coating film formed from the obtained antifouling coating composition tends to have a high coating film depletion degree.

[0067]

The polymer (A) preferably contains the monomer (a42) and/or the monomer (a43) among the monomers (a4) from the viewpoint that an antifouling coating film formed from the obtained antifouling coating composition can appropriately adjust the coating film depletion degree and tends to be excellent in damage resistance and/or crack resistance.

[0068]

· Monomer (a5)

Examples of the monomer (a5), that is, the vinyl compound include styrene, α -methylstyrene, vinyl acetate, vinyl benzoate, vinyl toluene, acrylonitrile,

vinylpyridine, vinylpyrrolidone, and vinyl chloride. The monomer (a5) may be any one type or two or more types.

[0069]

· Proportions of constituent units

5 The type and proportion of the constituent unit derived from each of the monomer (a1) and/or the monomer (a2) contained in the polymer (A) and other monomers used as necessary can be appropriately adjusted in consideration of the effect of the present invention, other technical
10 matters, and the like.

[0070]

For example, the proportion of the constituent unit derived from the monomer (a1) and/or the constituent unit derived from the monomer (a2) is preferably 5 mass% or
15 more, more preferably 7 mass% or more, still more preferably 9 mass% or more, and is preferably 50 mass% or less, more preferably 40 mass% or less, still more preferably 30 mass% or less with respect to 100 mass% of all the constituent units in the copolymer (A).

20 [0071]

In addition, the polymer (A) preferably contains at least a constituent unit derived from (meth)acrylate or an ester thereof (a4) in addition to the constituent unit derived from the monomer (a1) and/or the constituent unit
25 derived from the monomer (a2), and may further contain a

constituent unit derived from the organosiloxane block-containing monomer (a3).

[0072]

When the polymer (A) contains a constituent unit
5 derived from the organosiloxane block-containing monomer
(a3), the proportion thereof is preferably 5 mass% or more,
more preferably 8 mass% or more, and is preferably 20 mass%
or less, more preferably 15 mass% or less with respect to
100 mass% of all the constituent units in the copolymer
10 (A).

[0073]

When the polymer (A) contains a constituent unit
derived from a (meth)acrylate or an ester thereof (a4), the
proportion thereof is preferably 3 mass% or more, more
15 preferably 5 mass% or more, and is preferably 95 mass% or
less, more preferably 80 mass% or less, particularly
preferably 70 mass% or less with respect to 100 mass% of
all the constituent units in the copolymer (A).

[0074]

20 When the polymer (A) contains a constituent unit
derived from the vinyl compound (a4), the proportion
thereof is preferably 3 mass% or more, more preferably 5
mass% or more, and is preferably 50 mass% or less, more
preferably 40 mass% or less, particularly preferably 30
25 mass% or less with respect to 100 mass% of all the

constituent units in the copolymer (A).

[0075]

The proportion of each constituent unit in the copolymer (A) can be measured by nuclear magnetic resonance spectroscopy (NMR), gas chromatography-mass spectrometry (GC-MS), or the like according to a conventional method, and can also be calculated from the amount of each monomer used when the copolymer (A) is synthesized. All the constituent units in the copolymer (A) do not include constituent units derived from a polymerization initiator and a chain transfer agent.

[0076]

The number average molecular weight (M_n) and the weight average molecular weight (M_w) of the polymer (A) can be appropriately adjusted so that the effect of the present invention reaches a desired degree in consideration of the viscosity and storage stability of the resulting antifouling coating composition, the coating film depletion degree (elution rate, updateability) of the resulting antifouling coating film, and the like. The M_n of the polymer (A) is preferably 500 or more, more preferably 700 or more, and is preferably 100,000 or less, more preferably 50,000 or less. The M_w of the copolymer (A) is preferably 1,000 or more, more preferably 1,200 or more, particularly preferably 1,500 or more, and is preferably 150,000 or

less, more preferably 10,000 or less, particularly preferably 7,000 or less.

[0077]

Note that Mn and Mw can be determined by performing measurement by gel permeation chromatography according to a conventional method, followed by conversion with standard polystyrene. For more specific measurement methods, conditions, and the like for Mn and Mw, the following examples can be referred to.

[0078]

· Content of component (A)

The content of the polymer (A) can be appropriately adjusted according to the type, characteristics, and the like of the component so that the effect of the present invention reaches a desired degree in consideration of the paint workability of the resulting antifouling coating composition and other technical matters. The content of the polymer (A) is, for example, preferably 10 mass% or more, more preferably 15 mass% or more, and is preferably 40 mass% or less, more preferably 35 mass% or less with respect to 100 mass% of the solid content of the antifouling coating composition.

[0079]

In the present description, the "solid content" of each component (for example, the components (A) to (E), an

oxidized polyethylene wax as an anti-sagging agent/anti-settling agent (G), a fatty acid amide wax, and the like) or the antifouling coating composition of the present invention or each component contained therein refers to a component obtained by removing a volatile component contained as a solvent in each component or the antifouling coating composition of the present invention. Such a solid content can be calculated as a proportion of the mass of a substance obtained by drying each component or the antifouling coating composition of the present invention in a hot air dryer at 108°C for 3 hours to the mass of each component or the antifouling coating composition of the present invention according to a conventional method. More specifically, according to JIS K 5601-1-2:2008, 1 ± 0.1 g of an object to be measured is weighed on a flat bottom dish, uniformly spread on the bottom surface using a wire having a known mass, dried at 108°C for 3 hours at 1 atm, and the mass of the wire is subtracted from the obtained heating residue, followed by calculation to obtain a value of a mass percentage. When a numerical value as a solid content is shown in a label, a catalog, or the like for a product of each component, the numerical value can be regarded as the solid content of the component. When the compounding formulation (type and amount of each component and solid content of each component) of the antifouling

coating composition of the present invention is known by the above-described measurement method, a numerical value calculated based on the compounding formulation can be regarded as the solid content of the antifouling coating composition of the present invention.

[0080]

<Medetomidine (B)>

Medetomidine (B), systematic name (+/-) 4-[1-(2,3-dimethylphenyl)ethyl]-1H-imidazole is a compound

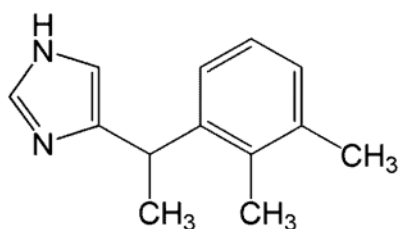
represented by the following structural formula. The medetomidine (B) is a racemate (a mixture of any proportion, for example, approximately equal amounts) of (+)4-[1-(2,3-dimethylphenyl)ethyl]-1H-imidazole and (-)4-[1-(2,3-dimethylphenyl)ethyl]-1H-imidazole. The

medetomidine (B) has optical isomerism, but may be one isomer thereof or a mixture in any ratio. As a part or the whole of the medetomidine (B), an adduct to an imidazolium salt, a metal, or the like may be used. In this case, as a raw material for preparing the antifouling coating

composition of the present invention, an adduct to an imidazolium salt, a metal, or the like may be used, or an adduct to an imidazolium salt, a metal, or the like may be formed in the antifouling coating composition or the antifouling coating film of the present invention.

[0081]

[Chem. 10]



(B)

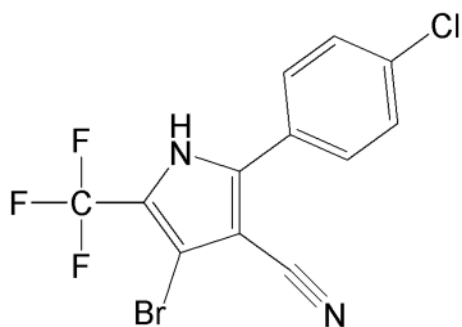
[0082]

<Tralopyril (C)>

5 Tralopyril (C), systematic name 4-bromo-2-(4-chlorophenyl)-5-(trifluoromethyl)-1H-pyrrole-3-carbonitrile, 2-(p-chlorophenyl)-3-cyano-4-bromo-5-trifluoromethylpyrrole is a compound represented by the following structural formula.

10 [0083]

[Chem. 11]



(C)

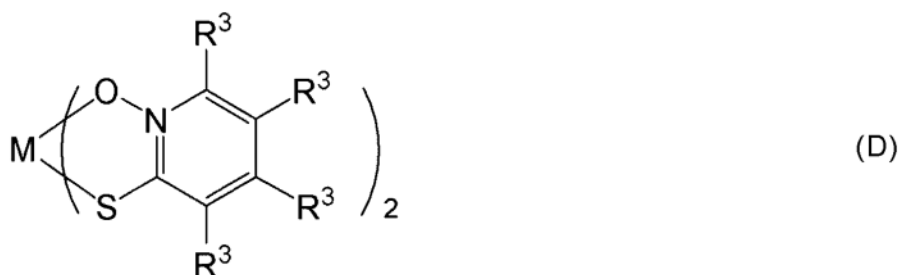
[0084]

<Copper pyriithione (D)>

15 Copper pyriithione (D), systematic name copper(II) bis[1,2-dihydro-2-thioxopyridine-1-olate] is a compound represented by the following structural formula.

[0085]

[Chem. 12]



[0086]

In formula (D), R³'s each independently represent a
5 hydrogen atom or an alkyl group having 1 to 6 carbon atoms,
a cyclic alkyl group, an alkenyl group, an aryl group, an
alkoxy group, or a halogenated alkyl group, and M is a
copper atom. R³ is preferably a hydrogen atom.

[0087]

10 The antifouling coating composition of the present
invention contains at least the medetomidine (B), the
tralopyril (C), and the copper pyrimithione (D) as
antifouling agents, and even when only these three
antifouling agents are used, a certain level of excellent
15 antifouling performance can be exhibited, but if necessary,
one or more other antifouling agents can be additionally
used in an appropriate amount. Examples of the antifouling
agent other than the medetomidine (B), the tralopyril (C),
and the copper pyrimithione (D) include cuprous oxide, a
20 metal pyrimithione other than the copper pyrimithione (D) (for
example, zinc pyrimithione), 4,5-dichloro-2-n-octyl-4-

isothiazolin-3-one (also known as DC0IT), pyridine triphenylborane, 4-isopropylpyridine diphenylmethylborane, N,N-dimethyl-N'-(3,4-dichlorophenyl)urea (also known as diuron), N-(2,4,6-trichlorophenyl)maleimide, 2,4,5,6-tetrachloroisophthalnitrile, 2-methylthio-4-tert-butylamino-6-cyclopropylamino-1,3,5-triazine (also known as cybutrin), bisdimethyldithiocarbamoyl zinc ethylenebisdithiocarbamate (also known as polycarbamate), chloromethyl-n-octyl disulfide, N,N'-dimethyl-N'-phenyl-(N-fluorodichloromethylthio)sulfamide (also known as diclofluanide), tetraalkylthiuram disulfide (also known as TMTD), zinc dimethyl dithiocarbamate (also known as Ziram), zinc ethylene bisdithiocarbamate, 2,3-dichloro-N-(2',6'-diethylphenyl)maleimide, and 2,3-dichloro-N-(2'-ethyl-6'-methylphenyl)maleimide.

[0088]

However, cuprous oxide is an antifouling agent having a high environmental load, and the antifouling coating composition of the present invention can exhibit an excellent antifouling property over a long period of time without using cuprous oxide. The content of cuprous oxide in the solid content of the antifouling coating composition of the present invention is preferably 10 mass% or less, more preferably 5 mass% or less, still more preferably 1 mass% or less, and still more preferably 0.5 mass% or less,

and it is particularly preferable that cuprous oxide is substantially not contained. The phrase "cuprous oxide is substantially not contained" means that cuprous oxide is not intentionally added, and it is not excluded that a small amount of cuprous oxide is contained as an impurity.

[0089]

· Contents of components (B), (C), and (D)

The contents of the medetomidine (B), the tralopyril (C), and the copper pyrithione (D) can be appropriately adjusted so that the effect of the present invention reaches a desired degree in consideration of the paint workability of the resulting antifouling coating composition and other technical matters.

[0090]

For example, the content of the medetomidine (B) is preferably 0.1 mass% or more, more preferably 1 mass% or more, and is preferably 100 mass% or less, more preferably 80 mass% or less, still more preferably 50 mass% or less, particularly preferably 10 mass% or less with respect to 100 mass% of the copper pyrithione (D).

[0091]

The content of the tralopyril (C) is preferably 10 mass% or more, more preferably 25 mass% or more, and is preferably 1,700 mass% or less, more preferably 1,500 mass% or less, still more preferably 1,200 mass% or less, still

more preferably 1,000 mass% or less, particularly preferably 100 mass% or less with respect to 100 mass% of the copper pyrithione (D).

[0092]

5 The content of the copper pyrithione (D) is preferably 0.5 mass% or more, more preferably 1.0 mass% or more, still more preferably 3.0 mass% or more, and is preferably 12 mass% or less, more preferably 11 mass% or less, still more preferably 10 mass% or less, particularly
10 preferably 8 mass% or less with respect to 100 mass% of the solid content of the antifouling coating composition.

[0093]

<Alkyl carboxylic acid (E)>

 Examples of the linear or branched alkyl carboxylic
15 acid (E) having 4 to 30 carbon atoms include versatic acid, palmitic acid, stearic acid, and isostearic acid, and among these, versatic acid is preferable. The versatic acid is a mixture containing branched alkyl carboxylic acids having 5 to 15 carbon atoms, mainly 9 to 11 carbon atoms, in
20 particular 10 carbon atoms. As the alkyl carboxylic acid (E), any one type may be used alone, or two or more types may be used.

[0094]

 The alkyl carboxylic acid (E) may form a metal ester
25 (for example, a copper ester). The metal ester may be

formed in advance before the production of the antifouling coating composition, or may be formed by a reaction with another coating component during the production of the antifouling coating composition.

5 [0095]

Rosin (rosin such as gum rosin, wood rosin, or tall oil rosin, a rosin derivative such as hydrogenated rosin or disproportionated rosin) is a mixture of abietic acid, which has a carboxy group and a three ring structures
10 including a conjugated double bond, and isomers thereof, and is a monocarboxylic acid but does not correspond to "a linear or branched alkyl carboxylic acid having 4 to 30 carbon atoms". Naphthenic acid, salicylic acid, and the like are also compounds having a ring structure and a
15 carboxyl group, and are monocarboxylic acids but do not correspond to "a linear or branched alkyl carboxylic acid having 4 to 30 carbon atoms".

[0096]

· Content of component (E)

20 The content of the alkyl carboxylic acid (E) can be appropriately adjusted according to the type, characteristics, and the like of the component in consideration of the effect of the present invention and the like. The content of the alkyl carboxylic acid (E) is
25 preferably 0.1 mass% or more, more preferably 0.2 mass% or

more, and is preferably 10 mass% or less, more preferably 7 mass% or less with respect to 100 mass% of the solid content of the antifouling coating composition.

[0097]

5 <Optional component>

The antifouling coating composition of the present invention may further contain a component other than the polymer (A), the medetomidine (B), the tralopyril (C), the copper pyrithione (D), and the alkyl carboxylic acid (E) as
10 necessary. Examples of such an optional component include a pigment (F), an anti-sagging agent/anti-settling agent (G), a solvent (H), a plasticizer (I), and a binder component (J). Additional examples of such an optional component include a wet dispersant, a dehydrating agent,
15 and a plasticizer. These optional components are not essential for exhibiting the effect of the present invention, but can be components that are naturally required or commonly used for carrying out as an antifouling coating composition, components that can
20 facilitate or enhance the effect of the present invention, or components for exhibiting effects other than the present invention.

[0098]

<Pigment (F)>

25 The antifouling coating composition of the present

invention can contain a pigment (F) for the purpose of coloring the coating film and hiding the base and/or for the purpose of adjusting the coating film strength to an appropriate level. As the pigment (F), any one type may be
5 used alone, or two or more types may be used.

[0099]

Examples of the pigment (F) include extender pigments such as zinc oxide, zinc phosphate, talc, mica, clay, potassium feldspar, calcium carbonate, kaolin,
10 alumina white, white carbon, aluminum hydroxide, magnesium carbonate, barium carbonate, barium sulfate (for example, precipitated barium sulfate), calcium sulfate (for example, calcined plaster), and zinc sulfide; and color pigments such as Bengal red (red iron oxide), titanium white
15 (titanium oxide), yellow iron oxide, carbon black, naphthol red, and phthalocyanine blue.

[0100]

When the antifouling coating composition of the present invention contains the pigment (F), the content
20 thereof can be appropriately adjusted according to the purpose, the type of the component, and the like, and is, for example, preferably 1 to 40 mass% with respect to 100 mass% of the solid content of the composition.

[0101]

25 <Anti-sagging agent/anti-settling agent (G)>

The antifouling coating composition of the present invention can contain an anti-sagging agent/anti-settling agent (G) for the purpose of, for example, adjusting the viscosity of the composition. As the anti-sagging

5 agent/anti-settling agent (G), any one type may be used alone, or two or more types may be used.

[0102]

Examples of the anti-sagging agent/anti-settling agent (G) include organic clay-based waxes (for example,
10 stearate, lecithin, and alkylsulfonate salts of Al, Ca, Zn), organic waxes (for example, polyethylene wax, oxidized polyethylene wax, fatty acid amide wax, and hydrogenated castor oil wax), a mixture of an organic clay-based wax and an organic wax, and synthetic fine powder silica. As such
15 an anti-sagging agent/anti-settling agent (H), for example, a commercially available product such as "DISPARLON 305", "DISPARLON 4200-20", "DISPARLON A630-20X", or "DISPARLON 6900-20X" manufactured by Kusumoto Chemicals, Ltd.; or "A-S-A D-120" manufactured by Itoh Oil Chemicals Co., Ltd. can
20 be used.

[0103]

When the antifouling coating composition of the present invention contains the anti-sagging agent/anti-settling agent (G), the content thereof can be
25 appropriately adjusted according to the purpose, the type

of the component, and the like, and is, for example,
preferably 0.01 mass% or more, more preferably 0.1 mass% or
more, and is preferably 10 mass% or less, more preferably 3
mass% or less with respect to 100 mass% of the solid

5 content of the composition.

[0104]

<Solvent (H)>

The antifouling coating composition of the present
invention can contain a solvent (H) such as water or an
10 organic solvent for the purpose of, for example, adjusting
the viscosity of the composition. The antifouling coating
composition of the present invention can be prepared using
a liquid containing the copolymer (A) obtained when the
copolymer (A) is synthesized, and in this case, a solvent
15 contained in the liquid, a solvent separately added when
the copolymer (A) is mixed with other essential components
(B) to (E) and an optional component as necessary, and the
like correspond to the solvent (H). As the solvent (H),
any one type may be used alone, or two or more types may be
20 used. The solvent (H) is preferably an organic solvent.

[0105]

Examples of the organic solvent include aromatic
organic solvents such as xylene, toluene, and ethylbenzene;
ketones such as methyl ethyl ketone, methyl isobutyl
25 ketone, and cyclohexanone; aliphatic (about 1 to 10,

preferably 2 to 5 carbon atoms) monohydric alcohols such as ethanol, isopropyl alcohol, n-butanol, isobutanol, and propylene glycol monomethyl ether; and ester-based solvents such as ethyl acetate and butyl acetate.

5 [0106]

When the antifouling coating composition of the present invention contains the solvent (H), the content thereof can be appropriately adjusted according to the purpose, the type of the component, and the like, and is,
10 for example, preferably 0 to 50 mass% with respect to 100 mass% of the composition.

[0107]

<Plasticizer (I)>

The antifouling coating composition of the present
15 invention may contain a plasticizer (I) for the purpose of, for example, imparting plasticity to an antifouling coating film to be formed. As the plasticizer (I), only one type may be used, or two or more types may be used.

[0108]

20 Examples of the plasticizer (I) include chlorinated paraffin, n-paraffin, tricresyl phosphate (TCP), dioctyl phthalate (DOP), and diisodecyl phthalate (DIDP), and chlorinated paraffin and TCP are preferable.

[0109]

25 The chlorinated paraffin may have either a linear or

branched molecular structure, and may be liquid or solid (for example, powdery) under conditions of room temperature (for example, 23°C).

[0110]

5 The average number of carbon atoms in one molecule of the chlorinated paraffin is preferably 8 or more, more preferably 10 or more, and is preferably 30 or less, more preferably 26 or less. If the average number of carbon atoms is less than 8, the effect of preventing the
10 occurrence of cracking in an antifouling coating film to be formed may be insufficient, whereas if the average number of carbon atoms exceeds 30, the hydrolyzability (coating film depletion degree, updateability, and abrasiveness) of an antifouling coating film to be formed may excessively
15 become low, as a result, the antifouling property may be poor.

[0111]

 The viscosity (unit: poise, measurement temperature: 25°C) of the chlorinated paraffin is preferably 1 or more, and more preferably 1.2 or more. The specific gravity
20 (25°C) thereof is preferably 1.05 g/cm³ or more, more preferably 1.10 g/cm³ or more, and is preferably 1.80 g/cm³ or less, more preferably 1.70 g/cm³ or less.

[0112]

25 The chlorination rate (chlorine content) of the

chlorinated paraffin is usually 35 to 70 mass%, and preferably 35 to 65 mass% with respect to 100 mass% of the chlorinated paraffin.

[0113]

5 When the antifouling coating composition of the present invention contains the plasticizer (I), the content thereof is preferably 0.1 mass% or more, more preferably 0.5 mass% or more, and is preferably 10 mass% or less, more preferably 5 mass% or less with respect to 100 mass% of the
10 solid content of the antifouling coating composition of the present invention from the viewpoint that the plasticity of the antifouling coating film can be maintained well.

[0114]

<Binder component (J)>

15 The antifouling coating composition of the present invention can contain a binder component (J) for the purpose of, for example, imparting water resistance, crack resistance, and strength to an antifouling coating film to be formed. The binder component (J) refers to a binder
20 component other than the polymer (A). As the binder component (J), any one type may be used alone, or two or more types may be used.

[0115]

 Examples of the binder component (J) include a
25 polyester-based polymer, a (meth)acrylic (co)polymer, a

vinyl-based (co)polymer, a terpene phenol resin, a petroleum resin, and a ketone resin. Among these, a polyester-based polymer, a (meth)acrylic (co)polymer, a vinyl-based (co)polymer, and a petroleum resin are preferable, and a polyester-based polymer and a petroleum resin are more preferable.

[0116]

When the antifouling coating composition of the present invention contains the binder component (J), the content thereof can be appropriately adjusted according to the purpose, the type of the component, and the like, and is, for example, preferably 0.1 to 40 mass% with respect to 100 mass% of the solid content of the composition.

[0117]

<Method for preparing antifouling coating composition>

The antifouling coating composition of the present invention can be prepared by means (apparatus, method, condition, and the like) similar to those for a general antifouling coating composition using the components (A) to (E) and other optional components as necessary.

Specifically, after the copolymer (A) is synthesized, (a solution of) the obtained copolymer (A), the medetomidine (B), the tralopyril (C), the copper pyrithione (D), and the alkyl carboxylic acid (E), and other optional components as necessary are added at once or sequentially to a container,

and stirred and mixed, whereby the preparation can be carried out.

[0118]

-Antifouling coating film-

5 The antifouling coating film of the present invention is formed from the antifouling coating composition of the present invention. The antifouling coating film of the present invention is formed by drying the antifouling coating composition of the present
10 invention in the same manner as in the case of forming a conventional antifouling coating film from a conventional antifouling coating composition. However, the antifouling coating film of the present invention is not limited to one immediately after being formed from the antifouling coating
15 composition of the present invention in this manner, and the antifouling coating film of the present invention also includes one after being deteriorated by use. The antifouling coating film of the present invention immediately after formation contains substances similar to
20 the antifouling coating composition of the present invention, except that a volatile component such as a solvent is lost by drying or the like, and the antifouling coating film after use contains substances similar to the antifouling coating composition of the present invention,
25 except that some components are lost (released) by

exhibiting antifouling performance in addition to the volatile component.

[0119]

The thickness of the antifouling coating film of the present invention is not particularly limited, and can be set within an appropriate range according to the characteristics (for example, a coating film depletion rate) and applications (such as type of substrate, and period of use) of the antifouling coating film of the present invention, and for example, the thickness in a state immediately after formation is preferably 30 to 1,000 μm .

[0120]

-Substrate with antifouling coating film-

The substrate with an antifouling coating film of the present invention has a substrate and the antifouling coating film of the present invention. The antifouling coating film of the present invention is usually formed on a substrate, which is used as the substrate with an antifouling coating film.

[0121]

The substrate is not particularly limited as long as the antifouling coating film of the present invention can be formed and a function can be exhibited, and examples thereof include a ship (for example, a hull outer plate of

a large steel ship such as a container ship, a tanker, or a bulker, a fishing ship, an FRP ship, a wooden ship, a yacht, or the like including both a newly built ship and a repair ship), a fishery or another marine material (for
5 example, a rope, a fishing net, a fishing gear, a float, a buoy, a diver suit, underwater glasses, an oxygen cylinder, a swimming suit, a torpedo), and an underwater structure (for example, a structure such as an oil pipeline, a water conduit, a circulating water pipe, or a water
10 supply/discharge port of a thermal/nuclear power plant, or a submarine cable, seawater utilization equipment (such as a seawater pump), a mega-float, a coastal road, a submarine tunnel, a harbor facility, a structure for underwater civil engineering works in a canal/waterway, or the like). In
15 view of the effect of the present invention, a ship (a newly built ship or a ship after operation) is preferable as the substrate, and a large steel ship such as a container ship, a tanker, or a bulker, or the like, which repeatedly sails on the open sea and anchors for a long
20 period of time, is particularly preferable.

[0122]

The substrate may be a substrate treated with an antirust agent or another treatment agent, or a substrate having a coating film other than an antifouling coating
25 film (non-antifouling coating film) such as an antirust

coating film (for example, zinc rich paint), an anticorrosive coating film (for example, an epoxy-based heavy anticorrosive coating material), or a binder coating film, or the antifouling coating film of the present

5 invention which has been deteriorated, altered, or depleted, or an antifouling coating film (old antifouling coating film) formed from another antifouling coating composition, formed on the surface thereof. In the substrate with an antifouling coating film of the present
10 invention, the antifouling coating film does not need to be formed in direct contact with the surface of the substrate, and may be formed on the substrate via a treatment agent, another coating film, or the like. Therefore, the substrate with an antifouling coating film of the present
15 invention may further contain another treatment agent, a coating film, or the like in addition to the substrate and the antifouling coating film of the present invention. The antifouling coating film of the present invention can be formed on various non-antifouling coating films,
20 deteriorated antifouling coating films, and the like.

[0123]

The "non-antifouling coating film" of the substrate refers to a coating film other than an antifouling coating film, such as a primer coating film or an intermediate
25 coating film, which is formed on the substrate in advance

before the antifouling coating film of the present invention is formed, depending on the type and application of the substrate. The type of the non-antifouling coating film is not particularly limited, and examples thereof

5 include an antirust coating film formed from an antirust coating material, an anticorrosive coating film formed from an anticorrosive coating material, and a binder coating film formed from a binder coating material. Examples of the anticorrosive coating film include those formed from an

10 anticorrosive coating material containing an epoxy-based resin. Examples of the binder coating film include those formed from a binder coating material containing one type or two or more types of resins such as an epoxy-based resin, a vinyl-based resin, and a (meth)acrylic resin. In

15 the case of application to a substrate such as a ship, there is no clear distinction between an anticorrosive coating film (primer coating film) and a binder coating film (intermediate coating film), and a coating film that serves as both is sometimes used. However, the "non-

20 antifouling coating film" may be a binder coating film that also has a function of such an anticorrosive coating film.

[0124]

The "old antifouling coating film" of the substrate is an antifouling coating film after being used in contact

25 with water (seawater) for a certain period of time (for

example, the service life of the antifouling coating film), and refers to an antifouling coating film which is in a deteriorated, altered, or depleted state as compared with a sound antifouling coating film before use (before seawater immersion). The degree of deterioration, alteration, or depletion of the antifouling coating film is not particularly limited, and may be any degree as long as it is recognized that the antifouling coating film of the present invention needs to be formed or is preferably formed. The type of the antifouling coating film is not particularly limited, and may be the antifouling coating film of the present invention or another antifouling coating film. Examples of the antifouling coating film include a hydrolyzable type (for example, a coating film formed from a silyl ester resin-based antifouling coating material) and a hydration-decomposable type (for example, a coating film formed from a vinyl chloride-isobutyl vinyl ether resin-based antifouling coating material).

[0125]

-Method for producing substrate with antifouling coating film-

The method for producing a substrate with an antifouling coating film of the present invention includes the following steps (1) and (2):

(1) a step of coating or impregnating a substrate

with the antifouling coating composition of the present invention to obtain a coated body or an impregnated body; and

(2) a step of drying the coated body or the
5 impregnated body.

[0126]

The coating in the step (1) can be performed according to a general method, and for example, a method of coating a substrate with the antifouling coating
10 composition using an airless spray, an air spray, a brush, a roller, or the like can be used. The impregnation in the step (1) can also be performed according to a general method, and for example, a method of immersing a substrate in the antifouling coating composition can be used.

15 [0127]

The conditions for coating or impregnation can be adjusted so that an antifouling coating film having a desired thickness can be formed also in consideration of the drying conditions in the step (2). For example, the
20 substrate can be coated or impregnated with an appropriate amount of the antifouling coating composition per unit area of the substrate so that the thickness of the dry coating film after the step (2) is 10 to 300 μm , preferably 30 to 200 μm .

25 [0128]

The drying in the step (2) may be performed according to a general method at an appropriate temperature or in another environment for an appropriate time. For example, a method of leaving the coated body or the
5 impregnated body obtained in the step (1) at normal temperature (for example, 25°C), preferably for 0.5 to 14 days, and more preferably for 1 to 7 days can be mentioned. The drying in this step may be performed under heating or may be performed while blowing air.

10 [0129]

The steps (1) and (2) can be repeated as necessary. For example, when an antifouling coating film having a desired thickness cannot be formed by performing the steps (1) and (2) only once, the steps (1) and (2) at the second
15 time can be performed after the steps (1) and (2) at the first time, and the steps (1) and (2) can be further performed as many times as necessary.

[0130]

In an embodiment of the present invention, the
20 method for producing a substrate with an antifouling coating film of the present invention includes, as the step (1), a step of coating or impregnating a substrate having an old antifouling coating film with the antifouling coating composition of the present invention to obtain a
25 coated body or an impregnated body. In the present

embodiment, a necessary step, for example, a step of removing dirt on the surface of the old antifouling coating film by water washing or the like, followed by drying may be further included before the step (1). When a

5 conventional antifouling coating composition is used, the adhesion to an old antifouling coating film is poor, so that a step of removing the old antifouling coating film may be required. However, since the antifouling coating composition of the present invention is excellent in

10 bondability to various old antifouling coating films, such a removal step can be omitted.

[0131]

-Antifouling method for substrate-

The antifouling method for a substrate of the
15 present invention includes a step of forming the antifouling coating film of the present invention on at least a part of a substrate.

[0132]

In the substrate, a portion in which the antifouling
20 coating film of the present invention is formed is not particularly limited, and can be appropriately selected according to the application. For example, when the substrate is a ship, a ship bottom part (permanently submerged part) or a water line part (dry-wet alternating
25 part) exposed to a biological fouling environment can be a

portion (a part of the substrate) in which the antifouling coating film of the present invention is formed.

[0133]

The "step of forming an antifouling coating film" in the "antifouling method for a substrate" is basically similar to the steps (1) and (2) in the "method for producing a substrate with an antifouling coating film".

That is, the antifouling method for a substrate of the present invention can be rephrased as one that includes

(1') a step of coating or impregnating at least a part of a substrate with the antifouling coating composition of the present invention to obtain a coated body or an impregnated body; and (2') a step of drying the coated body or the impregnated body.

[0134]

In addition, the technical matters described regarding the "method for producing a substrate with an antifouling coating film" in the present description can be appropriately replaced with the technical matters regarding the "antifouling method for a substrate". For example, in accordance with an embodiment in which the substrate has a deteriorated antifouling coating film, the "antifouling method for a substrate" of the present invention can be replaced with a "method for repairing a substrate with a deteriorated antifouling coating film".

Examples

[0135]

(1) Production Example for synthesis of metal ester group-
5 containing monomer

[Production Example M1] Production of metal ester group-
containing monomer mixture solution (M-1)

A four-necked flask equipped with a condenser, a
thermometer, a dropping funnel, and a stirrer was charged
10 with 85.4 parts of PGM (propylene glycol monomethyl ether)
and 40.7 parts of zinc oxide, and the temperature was
raised to 75°C with stirring. Subsequently, a mixture of
43.1 parts of methacrylic acid, 36.1 parts of acrylic acid,
and 5 parts of water was added dropwise thereto through the
15 dropping funnel at a constant dropping rate over 3 hours.
After further stirring for 2 hours, 36 parts of PGM was
added thereto to obtain a transparent metal ester group-
containing monomer mixture solution (M-1). The solid
content in the solution (M-1) was 44.8 mass%. The solution
20 (M-1) contains zinc diacrylate, zinc dimethacrylate, and
zinc acrylate methacrylate corresponding to the compound
(1') as a mixture of the metal ester group-containing
monomer (a1).

[0136]

25 [Production Example M2] Production of metal ester group-

containing monomer mixture solution (M-2)

A four-necked flask equipped with a condenser, a thermometer, a dropping funnel, and a stirrer was charged with 72.4 parts of PGM and 40.7 parts of zinc oxide, and
5 the temperature was raised to 75°C with stirring.

Subsequently, a mixture of 30.1 parts of methacrylic acid, 25.2 parts of acrylic acid, and 51.6 parts by mass of versatic acid was added dropwise thereto through the dropping funnel at a constant dropping rate over 3 hours.

10 After further stirring for 2 hours, 11 parts of PGM was added thereto to obtain a transparent metal ester group-containing monomer mixture solution (M-2). The solid content in the solution (M-2) was 59.6 mass%. The solution (M-2) contains zinc diacrylate, zinc dimethacrylate, and
15 zinc acrylate methacrylate corresponding to the compound (1') and zinc (meth)acrylate versatate corresponding to the monomer (2') as a mixture of the metal ester group-containing monomers (a1) and (a2).

[0137]

20 [Production Example M3] Production of metal ester group-containing monomer mixture solution (M-3)

A four-necked flask equipped with a condenser, a thermometer, a dropping funnel, and a stirrer was charged with 59.9 parts of PGM and 40.7 parts of zinc oxide, and
25 the temperature was raised to 75°C with stirring.

Subsequently, a mixture of 43 parts of methacrylic acid, 36 parts of acrylic acid, and 5 parts of water was added dropwise thereto through the dropping funnel at a constant dropping rate over 3 hours. After further stirring for 2 hours, 29.4 parts of PGM was added thereto to obtain a transparent metal ester group-containing monomer mixture solution (M-3). The solid content in the solution (M-3) was 55.1 mass%. The solution (M-3) contains zinc diacrylate, zinc dimethacrylate, and zinc acrylate methacrylate corresponding to the compound (1') as a mixture of the metal ester group-containing monomer (a1). [0138]

(2) Production Example for synthesis of metal ester group-containing hydrolyzable copolymer

[Production Example A1] Production of hydrolyzable copolymer solution (A-1)

A four-necked flask equipped with a condenser, a thermometer, a dropping funnel, and a stirrer was charged with 15 parts of PGM, 57 parts of xylene, and 4 parts of ethyl acrylate (EA), and the temperature was raised to 100 ± 5°C with stirring. While the temperature was maintained, 52 parts of the metal ester group-containing monomer mixture solution (M-1), 1 part of methyl methacrylate (MMA), 66.2 parts of ethyl acrylate (EA), and 5.4 parts of 2-methoxyethyl acrylate (MEA), and 2.5 parts of a

polymerization initiator 2,2'-azobisisobutyronitrile, 7 parts of a polymerization initiator 2,2'-azobis(2-methylbutyronitrile), 1 part of a chain transfer agent "NOFMER MSD" (product name, manufactured by NOF

5 CORPORATION, α -methylstyrene dimer), and 10 parts of xylene were added dropwise thereto through the dropping funnel over 6 hours. After completion of the dropwise addition, 0.5 parts of a polymerization initiator tert-butyl peroctoate (TBPO) and 7.0 parts of xylene were added
10 dropwise thereto over 30 minutes, and the mixture was further stirred for 1 hour and 30 minutes, and then 4.4 parts of xylene was added thereto to obtain a pale yellow transparent hydrolyzable copolymer solution (A-1).

[0139]

15 [Production Example A2] Production of hydrolyzable copolymer solution (A-2)

A four-necked flask equipped with a condenser, a thermometer, a dropping funnel, and a stirrer was charged with 10 parts of PGM, 63 parts of xylene, and 3 parts of
20 ethyl acrylate (EA), and the temperature was raised to 100 $\pm$ 5°C with stirring. While the temperature was maintained, 50.3 parts of the metal ester group-containing monomer mixture solution (M-2), 9 parts of methyl methacrylate (MMA), 58 parts of ethyl acrylate (EA), 5 parts of 2,2'-
25 azobis(2-methylbutyronitrile) (AMBN) and 10 parts of PGM

were added dropwise thereto through the dropping funnel over 4 hours. After completion of the dropwise addition, 0.5 parts of a polymerization initiator tert-butyl peroctoate and 7 parts of xylene were added dropwise thereto over 30 minutes, and the mixture was further stirred for 1 hour and 30 minutes, and then 12 parts of xylene was added thereto to obtain a pale yellow transparent hydrolyzable copolymer solution (A-2).

[0140]

[Production Example A3] Production of hydrolyzable copolymer solution (A-3)

An autoclave capable of pressure polymerization and equipped with a condenser, a thermometer, a dropping tank, and a stirrer was charged with 10 parts of PGM, 35 parts of xylene, and 4 parts of ethyl acrylate (EA), and the autoclave was pressurized to 350 kPa and heated to 135°C with stirring. Subsequently, 15 parts of methyl methacrylate (MMA), 48 parts of ethyl acrylate (EA), 15 parts of n-butyl acrylate (n-BA), 40 parts of the metal ester group-containing monomer mixture solution (M-3), 10 parts of xylene, 1.8 parts of "NOFMER MSD", 4 parts of 2,2'-azobisisobutyronitrile (AIBN), and 2 parts of 2,2'-azobis(2-methylbutyronitrile) (AMBN) were added dropwise thereto through the dropping tank at a constant dropping rate over 2.5 hours. After completion of the dropwise

addition, the temperature was lowered to 110°C over 30 minutes, 0.5 parts of t-butylperoxyoctoate and 5 parts of xylene were added dropwise thereto over 30 minutes, and the mixture was further stirred for 1 hour and 30 minutes, and then 3 parts of xylene was added thereto. The resulting mixture was filtered through 300 mesh to obtain a hydrolyzable copolymer solution (A-3) as a pale yellow transparent filtrate containing no insoluble matter.

[0141]

[Production Example A4] Production of hydrolyzable copolymer solution (A-4)

A four-necked flask equipped with a condenser, a thermometer, a dropping funnel, and a stirrer was charged with 15 parts of n-butanol, 56 parts of xylene, and 4 parts of ethyl acrylate (EA), and the temperature was raised to 100°C with stirring. Subsequently, 12.5 parts of n-butyl acrylate (BA), 30.2 parts of methyl methacrylate (MMA), 23.2 parts of ethyl acrylate, 6 parts of 2-methoxyethyl acrylate (2-MEA), 10 parts of "X-22-174ASX" (product name, manufactured by Shin-Etsu Chemical Co., Ltd.), 31.3 parts of the metal ester group-containing monomer mixture solution (M-1), 10 parts of xylene, 0.8 parts of "NOFMER MSD", 1 part of 2,2'-azobisisobutyronitrile (AIBN), and 8 parts of 2,2'-azobis(2-methylbutyronitrile) (AMBN) were added dropwise thereto through the dropping funnel at a

constant dropping rate over 6 hours. After completion of the dropwise addition, 2 parts of tert-butyl peroxyoctoate (TBPO) and 7 parts of xylene were added dropwise thereto over 90 minutes, the mixture was further stirred for 60 minutes, and then 7.5 parts of xylene was added thereto to obtain a colorless and transparent hydrolyzable copolymer solution (A-4).

[0142]

[Production Example A5] Production of hydrolyzable copolymer solution (A-5)

A four-necked flask equipped with a condenser, a thermometer, a dropping funnel, and a stirrer was charged with 15 parts of n-butanol, 56 parts of xylene, and 4 parts of ethyl acrylate (EA), and the temperature was raised to 100°C with stirring. Subsequently, 7.5 parts of n-butyl acrylate (n-BA), 37 parts of methyl methacrylate (MMA), 32 parts of ethyl acrylate (EA), 10 parts of "X-22-174ASX", 21.5 parts of the metal ester group-containing monomer mixture solution (M-1), 10 parts of xylene, 0.8 parts of "NOFMER MSD", 1 part of 2,2'-azobisisobutyronitrile (AIBN) and 8 parts of 2,2'-azobis (2-methylbutyronitrile) (AMBN) were added dropwise thereto through the dropping funnel at a constant dropping rate over 6 hours. After completion of the dropwise addition, 2 parts of tert-butyl peroxyoctoate (TBPO) and 7 parts of xylene were added dropwise thereto

over 90 minutes, the mixture was further stirred for 60 minutes, and then 13 parts of xylene was added thereto to obtain a colorless and transparent hydrolyzable copolymer solution (A-5).

5 [0143]

[Production Example A6] Production of hydrolyzable copolymer solution (A-6)

A four-necked flask equipped with a condenser, a thermometer, a dropping funnel, and a stirrer was charged
10 with 15 parts of n-butanol, 36 parts of xylene, and 4 parts of ethyl acrylate (EA), and the temperature was raised to 100°C with stirring. Subsequently, 7.5 parts of n-butyl acrylate (n-BA), 21 parts of methyl methacrylate (MMA), 30.9 parts of ethyl acrylate (EA), 12.5 parts of cyclohexyl
15 methacrylate (CHMA), 10 parts of "X-22-174ASX", 31.3 parts of the metal ester group-containing monomer mixture solution (M-1), 0.8 parts of "NOFMER MSD", 1 part of 2,2'-azobisisobutyronitrile (AIBN) and 10 parts of 2,2'-azobis(2-methylbutyronitrile) (AMBN) were added dropwise
20 thereto through the dropping funnel at a constant dropping rate over 6 hours. After completion of the dropwise addition, 2 parts of tert-butyl peroxyoctoate (TBPO) and 7 parts of xylene were added dropwise thereto over 90 minutes, the mixture was further stirred for 60 minutes,
25 and then 13.5 parts of xylene was added thereto to obtain a

colorless and transparent hydrolyzable copolymer solution (A-6).

[0144]

<Measurement of number average molecular weight (Mn) and weight average molecular weight (Mw) of copolymer>

The number average molecular weight (Mn) and the weight average molecular weight (Mw) of the copolymers contained in the hydrolyzable copolymer solutions (A-1) to (A-6) were measured by gel permeation chromatography (GPC) under the following conditions.

[0145]

Apparatus: "HLC-8320GPC" (manufactured by TOSOH CORPORATION)

Column: "TSKgelG4000HXL*G2000HXL" (manufactured by TOSOH CORPORATION, size 7.8 mm ID × 30 cm L)

Eluent: THF (1 mmol citric acid)

Flow rate: 1.000 ml/min

Detector: RI

Column thermostat temperature: 40°C

Standard substance: polystyrene

Sample preparation method: THF (tetrahydrofuran) containing 1 mmol of citric acid was added to the copolymer solution prepared in each production example for dilution so that the solid content concentration of the copolymer was 0.4 wt%, and then the mixture was filtered through a

membrane filter, and the resulting filtrate was used as a GPC measurement sample.

[0146]

Information (monomers and characteristics) on the hydrolyzable copolymer solutions (A-1) to (A-6) is shown in Table 1.

[0147]

[Table 1]

			Production Example A1	Production Example A2	Production Example A3	Production Example A4	Production Example A5	Production Example A6
			Solution (A-1)	Solution (A-2)	Solution (A-3)	Solution (A-4)	Solution (A-5)	Solution (A-6)
Monomer	(a1)	Metal ester group-containing monomer mixture solution (M-1)	52			31.3	21.5	31.3
	(a2)	Metal ester group-containing monomer mixture solution (M-2)		50.3				
	(a1)	Metal ester group-containing monomer mixture solution (M-3)			40			
	(a3)	X-22-174ASX				10	10	10
	(a4)	Cyclohexyl methacrylate (CHMA)						12.5
	(a4)	Methyl methacrylate	1	9	15	30.2	37	21
	(a4)	Ethyl acrylate (EA)	66.2	61	52	27.2	36	34.9
	(a4)	n-butyl acrylate (n-BA)			15	12.5	7.5	7.5
	(a4)	2-methoxyethyl acrylate (MEA)	5.4			6		
Characteristics		Solid content (mass%)	45.6	45.0	55.3	48.4	48.5	54.2
		Number average molecular weight (Mn)	1,950	1,100	1,150	1,900	2,100	2,000
		Weight average molecular weight (Mw)	5,200	5,900	3,200	4,300	4,500	4,200

10 [0148]

(3) Preparation of antifouling coating composition of Examples 1 to 23 and Comparative Examples 1 to 6

In a plastic container, 6.5 parts of xylene as a solvent, 3 parts of "propylene glycol monomethyl ether" (product name, propylene glycol monomethyl ether), 0.5 parts of versatic acid, 1 part of chlorinated paraffin, and 5 35 parts of the hydrolyzable polymer solution (A-3) were added and mixed using a paint shaker until each component was uniformly dispersed or dissolved. Thereafter, 10 parts of talc, 25 parts of zinc oxide, 2 parts of Bengal red, 5 parts of precipitated barium sulfate, 2 parts of calcined 10 plaster, 5 parts of copper pyrithione, 0.5 parts of medetomidine, 2.5 parts of tralopyril, and 1 part of an oxidized polyethylene wax were further added to the plastic container, and the mixture was stirred using a paint shaker for 1 hour to disperse these components. After the 15 dispersion, 1 part of a fatty acid amide wax was further added thereto, and the mixture was stirred using a paint shaker for 20 minutes, and then the mixture was filtered through a filtration net (mesh opening: 80 mesh) to remove a residue, and a metal ester-based antifouling coating 20 composition of Example 1 was obtained as a filtrate.

[0149]

Metal ester-based antifouling coating compositions of Examples 2 to 23 and Comparative Examples 1 to 6 were obtained by a preparation method similar to the above 25 except that the blending amounts of the respective

components were changed as shown in Table 2.

[0150]

The blending amounts of the respective components shown in Table 2 each indicate the blending amount as it is. For example, in Example 1, since the blending amount of the fatty acid amide wax as it is (as a whole) is 1 part and the solid content is 20 mass%, the blending amount of the fatty acid amide wax is 0.2 parts.

[0151]

(4) Evaluation test

(4-1) Static antifouling performance after operation (dynamic immersion)

A sandblasted steel plate (length 170 mm × width 70 mm × thickness 2.3 mm) which was bent so as to be attachable to a side surface of a rotary drum placed in a test raft moored in Kure Bay, Hiroshima Prefecture was prepared. An epoxy-based anticorrosive coating material ("BANNOH 500" manufactured by CHUGOKU MARINE PAINTS, LTD.) was applied to the sandblasted steel plate so as to have a dry film thickness of 150 μm, and dried at room temperature for 1 day to form a coating film. An epoxy-based binder coating material ("BANNOH 500N" manufactured by CHUGOKU MARINE PAINTS, LTD.) was applied to the surface of the anticorrosive coating film so as to have a dry film

thickness of 100 μm, and dried at room temperature for 1

day. Furthermore, each of the antifouling coating compositions prepared in examples and comparative examples was applied onto the coating film so as to have a dry film thickness of 100 μm , and dried at room temperature for 7 days to prepare a test plate 1 with an antifouling coating film.

[0152]

First, in accordance with a dynamic antifouling property test, the test plate 1 with an antifouling coating film was attached to the rotary drum, and the test plate was continuously rotated for 6 months at a peripheral speed of 10 kt assuming an actual ship operation, and the entire test plate was dynamically immersed in seawater.

Subsequently, the test plate 1 with an antifouling coating film after dynamic immersion was placed in a test raft in Hiroshima Bay so that the entire test plate was immersed in seawater, and a static antifouling property test was performed for 6 months and 12 months. The aquatic organism adhesion area on the antifouling coating film after 6 months and 12 months was measured, and the static antifouling property of the antifouling coating film after operation (dynamic immersion) was evaluated according to the following evaluation criteria for antifouling performance.

[0153]

(4-2) Static antifouling performance of dry-wet alternating part

An epoxy-based anticorrosive coating material ("BANNOH 500" manufactured by CHUGOKU MARINE PAINTS, LTD.) was applied to a sandblasted steel plate (length 300 mm × width 100 mm × thickness 2.3 mm) so as to have a dry film thickness of 150 μm, and then dried at room temperature for 1 day to form a coating film. An epoxy-based binder coating material ("BANNOH 500N" manufactured by CHUGOKU MARINE PAINTS, LTD.) was applied to the surface of the anticorrosive coating film so as to have a dry film thickness of 100 μm, and dried at room temperature for 1 day. Furthermore, each of the antifouling coating compositions prepared in examples and comparative examples was applied onto the coating film so as to have a dry film thickness of 100 μm, and dried at room temperature for 7 days to prepare a test plate 2 with an antifouling coating film.

[0154]

The test plate 2 with an antifouling coating film was placed in a test raft in Hiroshima Bay so that half of the test plate was immersed in seawater, and a static antifouling property test was performed for 6 months and 12 months. The aquatic organism adhesion area on the antifouling coating film after 6 months and 12 months was

measured, and the static antifouling property of the antifouling coating film of the dry-wet alternating part was evaluated according to the following evaluation criteria for the antifouling performance.

5 [0155]

<Evaluation criteria for antifouling performance/scores of 0, 1, and 2 are passing scores>

0: No adhesion of marine organisms

1: The adhesion area of marine organisms is less
10 than 1% of the total area.

2: The adhesion area of marine organisms is 1% or more and less than 10% of the total area.

3: The adhesion area of marine organisms is 10% or more and less than 30% of the total area.

15 4: The adhesion area of marine organisms is 30% or more and less than 70% of the total area.

5: The adhesion area of marine organisms is 70% or more of the total area.

[0156]

20 (4-3) Adhesion performance on binder coating film (dried at 60°C for 2 days)

An epoxy-based anticorrosive coating material ("BANNOH 500" manufactured by CHUGOKU MARINE PAINTS, LTD.) was applied to a sandblasted steel plate (length 150 mm ×
25 width 70 mm × thickness 2.3 mm) so as to have a dry film

thickness of 150 μm , and then dried at room temperature for 1 day to form a coating film. An epoxy-based binder coating material ("BANNOH 500N" manufactured by CHUGOKU MARINE PAINTS, LTD.) was applied to the surface of the anticorrosive coating film so as to have a dry film thickness of 100 μm , and dried in an environment of 40°C for 1 day. Furthermore, each of the antifouling coating compositions prepared in examples and comparative examples was applied onto the coating film so as to have a dry film thickness of 100 μm , and dried in an environment at 60°C for 2 days to prepare a test plate 3 with an antifouling coating film.

[0157]

A 1,000 g weight was allowed to fall from a falling height of 50 cm on the test plate 3 with an antifouling coating film based on the 6. DuPont method in JIS K 5600-5-3:1999. Cracking and peeling on the coating film surface after the weight fell were evaluated by visual inspection according to the following evaluation criteria for adhesion performance.

[0158]

<Evaluation criteria for adhesion performance/scores of 0, 1, and 2 are passing scores>

0: No cracking or peeling occurred on the coating film surface

1: Peeling occurred on the coating film surface, and the maximum length of peeling measured through the center point where the weight was allowed to fall was less than 10 mm.

5 2: Peeling occurred on the coating film surface, and the maximum length was 10 mm or more and less than 20 mm.

3: Peeling occurred on the coating film surface, and the maximum length was 20 mm or more and less than 30 mm.

4: Peeling occurred on the coating film surface, and
10 the maximum length was 30 mm or more and less than 40 mm.

5: Peeling occurred on the coating film surface, and the maximum length was 40 mm or more.

[0159]

(4-4) Adhesion performance on binder substrate (immersion
15 in seawater at 40°C for 3 months)

The test plate 2 with an antifouling coating film was immersed in natural seawater at 40°C for 3 months, and then cuts were made at intervals of 5 mm by a method in accordance with JIS K 5600-5-6:1999, followed by evaluation
20 according to the following evaluation criteria for adhesion performance.

[0160]

<Evaluation criteria for adhesion performance/scores of 0, 1, and 2 are passing scores>

25 0: No peeling

1: The peeled area is less than 5% of the total area.

2: The peeled area is 5% or more and less than 10% of the total area.

5 3: The peeled area is 10% or more and less than 30% of the total area.

4: The peeled area is 30% or more and less than 70% of the total area.

5: The peeled area is 70% or more of the total area.

10 [0161]

(4-5) Adhesion performance on deteriorated coating film

An epoxy-based anticorrosive coating material ("BANNOH 500" manufactured by CHUGOKU MARINE PAINTS, LTD.) was applied to a sandblasted steel plate (length 300 mm × width 100 mm × thickness 2.3 mm) so as to have a dry film thickness of 150 μm, and then dried at room temperature for 1 day to form a coating film. An epoxy-based binder coating material ("BANNOH 500N" manufactured by CHUGOKU MARINE PAINTS, LTD.) was applied to the surface of the anticorrosive coating film so as to have a dry film thickness of 100 μm, and dried at room temperature for 1 day. Furthermore, each of the silyl ester resin-based antifouling coating composition, the vinyl chloride-isobutyl vinyl ether resin-based antifouling coating composition, and the antifouling coating compositions

15
20
25

prepared in examples and comparative examples was applied onto the coating film so as to have a dry film thickness of 100 μm , and dried at room temperature for 7 days, and then immersed in natural seawater at 40°C for 3 months to

5 prepare test plates 1 to 3 with a deteriorated coating film.

[0162]

The test plates 1 to 3 with a deteriorated coating film was washed with water at a pressure of 80 kgf/cm² and
10 dried at room temperature for 7 days. Thereafter, each of the coating compositions of examples and comparative examples was applied onto each deteriorated coating film, and dried at room temperature for 7 days to prepare a test plate with an antifouling coating film on the deteriorated
15 coating film. These test plates were immersed in seawater at 40°C for 3 months, and then cuts were made at intervals of 5 mm by a method in accordance with JIS K 5600-5-6:1999, followed by evaluation according to the following evaluation criteria for adhesion performance.

20 [0163]

<Evaluation criteria for adhesion performance/scores of 0, 1, and 2 are passing scores>

0: No peeling

1: The peeled area is less than 5% of the total

25 area.

2: The peeled area is 5% or more and less than 10% of the total area.

3: The peeled area is 10% or more and less than 30% of the total area.

5 4: The peeled area is 30% or more and less than 70% of the total area.

5: The peeled area is 70% or more of the total area.

[0164]

The silyl ester resin-based antifouling coating
10 composition was prepared according to the following
Production Example X, and the vinyl chloride-isobutyl vinyl
ether resin-based antifouling coating composition was
prepared according to the following Production Example Y.
The test plate 1 with a deteriorated coating film refers to
15 a test plate on which a silyl ester resin-based antifouling
coating film was formed, the test plate 2 with a
deteriorated coating film refers to a test plate on which a
vinyl chloride-isobutyl vinyl ether resin-based antifouling
coating film was formed, and the test plate 3 with a
20 deteriorated coating film refers to a test plate on which
each of the antifouling coating films described in examples
and comparative examples was formed.

[0165]

[Production Example X] Silyl ester resin-based antifouling
25 coating composition

The following reaction was performed under normal pressure in a nitrogen atmosphere. A reaction vessel equipped with a stirrer, a reflux condenser, a thermometer, a nitrogen inlet tube, and a dropping funnel was charged with 428.6 parts of xylene and 100 parts of triisopropylsilyl methacrylate (TIPSMA), and heated to a liquid temperature of 80°C with stirring with a stirrer. A mixture of 500 parts of triisopropylsilyl methacrylate (TIPSMA), 250 parts of 2-methoxyethyl methacrylate (MEMA), 100 parts of methyl methacrylate (MMA), 50 parts of butyl acrylate (BA) and 13 parts of 2,2'-azobisisobutyronitrile (AIBN) was added dropwise to the reaction vessel through the dropping funnel over 2 hours while the liquid temperature in the reaction vessel was maintained at 80 ± 5°C. After completion of the dropwise addition, the reaction liquid was stirred at 80°C for 1 hour and at 80 to 95°C for 1 hour and 30 minutes. Thereafter, 1 part of AIBN was added to the reaction liquid 4 times every 30 minutes while the temperature was maintained at 95°C, and the liquid temperature was raised to 105°C to complete the polymerization reaction. Subsequently, 238 parts of xylene was added to the reaction vessel, and the mixture was stirred until the liquid became uniform to obtain a copolymer solution (X1) having a solid content of 61.1 mass% and a viscosity of 1,498 mPa·s. The copolymer

contained in the copolymer solution (X1) had a Mw of 31,213.

[0166]

In a plastic container, 8.5 parts of xylene as a solvent, 1 part of an aromatic hydrocarbon solvent (Solvesso No. 100, manufactured by Exxon Mobil Corporation), 2.5 parts of rosin, 0.5 parts of alkoxysilane (Ethyl Silicate 28, manufactured by COLCOAT CO., LTD.), and 21 parts of a copolymer solution (X1) were added and mixed using a paint shaker until each component was uniformly dispersed or dissolved. Thereafter, 4 parts of talc, 4 parts of zinc oxide, 50 parts of cuprous oxide (NC-301), 1.5 parts of Bengal red, 2.5 parts of titanium oxide (Tipaque PFC105, manufactured by ISHIHARA SANGYO KAISHA, LTD.), 2 parts of copper pyrithione, and 1 part of an oxidized polyethylene wax were further added to the plastic container, and the mixture was stirred using a paint shaker for 1 hour to disperse these components. After the dispersion, 1.5 parts of a fatty acid amide wax was further added thereto, and the mixture was stirred using a paint shaker for 20 minutes, and then the mixture was filtered through a filtration net (mesh opening: 80 mesh) to remove a residue, and a silyl ester-based antifouling coating composition was obtained as a filtrate.

[0167]

[Production Example Y] Vinyl chloride-isobutyl vinyl ether resin-based antifouling coating composition

In a plastic container, 13 parts of xylene as a solvent, 3 parts of 2-heptanone, 9 parts of rosin, 3 parts of tricresyl phosphate (TCP, manufactured by Kyowa Hakko Kogyo Co., Ltd.), and 5 parts of a vinyl chloride-isobutyl vinyl ether copolymer (Laroflex MP 25, manufactured by BASF SE) were added and mixed using a paint shaker until each component was uniformly dispersed or dissolved.

Thereafter, 10 parts of talc, 3 parts of zinc oxide, 42 parts of cuprous oxide (Red Copp 97N Premium, manufactured by American Chemet Corp.), 4 parts of titanium oxide, and 5 parts of DCOIT (SEA NINE 211 N, manufactured by Rohm and Haas Japan Co., Ltd., solid content: 30%) were further added to the plastic container, and the mixture was stirred using a paint shaker for 1 hour to disperse these components. After the dispersion, 3 parts of a fatty acid amide wax was further added thereto, and the mixture was stirred using a paint shaker for 20 minutes, and then the mixture was filtered through a filtration net (mesh opening: 80 mesh) to remove a residue, and a vinyl chloride-isobutyl vinyl ether-based antifouling coating composition was obtained as a filtrate.

[0168]

Information (formulation and evaluation test

results) on the antifouling coating compositions of Examples 1 to 23 and Comparative Examples 1 to 6 is shown in Table 2. In addition, the details of the components (products) shown in Table 2 used for the preparation of these antifouling coating compositions are shown in Table 3.

[0169]

[Table 2-1]

		Example							
Coating material formulation number		1	2	3	4	5	6	7	8
A	Hydrolyzable polymer solution (A-1)								
	Hydrolyzable polymer solution (A-2)								
	Hydrolyzable polymer solution (A-3)	35	35	35	35	35	35	35	35
	Hydrolyzable polymer solution (A-4)								
	Hydrolyzable polymer solution (A-5)								
	Hydrolyzable polymer solution (A-6)								
B	Medetomidine	0.5	0.1	0.1	0.01	0.1	0.1	0.1	0.1
C	Tralopyril	2.5	2.5	2.5	2.5	2.5	2.5	5	0.5
D	Copper pyrithione	5	5	5	5	8	1	5	5
	Zinc pyrithione								
E	Versatic acid	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
	Rosin								
F	Zinc oxide	25	25	25	25	25	25	25	25
	Bengal red	2	2	2	2	2	2	2	2
	Precipitated barium sulfate	5	5	5	5	5	5	5	5
	Talc	10	10	10	10	10	10	10	10
	Calcined plaster	2	2	2	2	2	2	2	2
G	Fatty acid amide wax (solid content: 20%)	1	1	1	1	1	1	1	1
	Oxidized polyethylene wax (solid content: 20%)	1	1	1	1	1	1	1	1
H	Xylene	6.5	6.9	7.9	6.99	4.4	10.9	4.4	8.9
	Propylene glycol monomethyl ether	3	3	3	3	3	3	3	3
I	Chlorinated paraffin	1	1	0	1	1	1	1	1
Total		100	100	100	100	100.5	100	100	100
Coating material solid content (mass%)		73.3	72.9	71.9	72.8	75.5	68.9	75.4	70.9
Content of (B) with respect to 100 mass% of (D)		10.0%	2.0%	2.0%	0.20%	1.3%	10.0%	2.0%	2.0%
Content of (C) with respect to 100 mass% of (D)		50.0%	50.0%	50.0%	50.0%	31.3%	250.0 %	100.0 %	10.0%
Content of (D) with respect to 100 mass% of coating material solid content		6.8%	6.9%	7.0%	6.9%	10.6%	1.5%	6.6%	7.1%
Static antifouling property after operation (dynamic immersion)	6 months	0	0	0	0	0	0	0	0
	12 months	0	0	0	0	0	1	0	0

Static antifouling property of dry-wet alternating part	6 months	0	0	0	0	0	0	0	0
	12 months	0	0	0	0	0	1	0	1
Adhesiveness on deteriorated coating film 1 (silyl ester resin-based)		0	0	0	0	0	0	0	0
Adhesiveness on deteriorated coating film 2 (vinyl chloride-isobutyl vinyl ether resin-based)		0	0	0	0	0	0	0	0
Adhesiveness on deteriorated coating film 3 (same antifouling coating film)		0	0	0	0	0	0	0	0
Adhesiveness on binder substrate (dried at 60°C for 2 days)		0	0	0	0	0	0	0	0
Adhesiveness on binder substrate (immersion in seawater at 40°C for 6 months)		0	0	0	0	0	0	0	0

[Table 2-2]

		Example							
Coating material formulation number		9	10	11	12	13	14	15	16
A	Hydrolyzable polymer solution (A-1)			35					
	Hydrolyzable polymer solution (A-2)				35				
	Hydrolyzable polymer solution (A-3)	35	35						35
	Hydrolyzable polymer solution (A-4)					35			
	Hydrolyzable polymer solution (A-5)						35		
	Hydrolyzable polymer solution (A-6)							35	
B	Medetomidine	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.2
C	Tralopyril	2.5	2.5	2.5	2.5	2.5	2.5	2.5	0.5
D	Copper pyrithione	5	5	5	5	5	5	5	0.5
	Zinc pyrithione								
E	Versatic acid	4	0.25	0.5	0.5	0.5	0.5	0.5	0.5
	Rosin								
F	Zinc oxide	25	25	25	25	25	25	25	25
	Bengal red	2	2	2	2	2	2	2	2
	Precipitated barium sulfate	5	7	5	5	5	5	5	5
	Talc	10	10	10	10	10	10	10	10
	Calcined plaster	2	2	2	2	2	2	2	2
G	Fatty acid amide wax (solid content: 20%)	1	1	1	1	1	1	1	1
	Oxidized polyethylene wax (solid content: 20%)	1	1	1	1	1	1	1	1
H	Xylene	4.4	5.15	6.9	6.9	6.9	6.9	6.9	13.3
	Propylene glycol monomethyl ether	3	3	3	3	3	3	3	3
I	Chlorinated paraffin	1	1	1	1	1	1	1	1
Total		101	100	100	100	100	100	100	100
Coating material solid content (mass%)		75.6	74.6	69.5	69.3	70.4	70.5	72.5	66.5
Content of (B) with respect to 100 mass% of (D)		2.0%	2.0%	2.0%	2.0%	2.0%	2.0%	2.0%	40.0%
Content of (C) with respect to 100 mass% of (D)		50.0%	50.0%	50.0%	50.0%	50.0%	50.0%	50.0%	100.0%
of (D) with respect to 100 mass% of coating material solid content		6.6%	6.7%	7.2%	7.2%	7.1%	7.1%	6.9%	0.8%
Static antifouling property after operation	6 months	0	0	0	0	0	0	0	0

(dynamic immersion)	12 months	0	0	0	0	0	0	0	1
Static antifouling property of dry-wet alternating part	6 months	0	0	0	0	0	0	0	1
	12 months	0	0	0	0	0	0	0	2
Adhesiveness on deteriorated coating film 1 (silyl ester resin-based)		0	0	0	0	0	0	0	0
Adhesiveness on deteriorated coating film 2 (vinyl chloride-isobutyl vinyl ether resin-based)		0	0	0	0	0	0	0	0
Adhesiveness on deteriorated coating film 3 (same antifouling coating film)		0	0	0	0	0	0	0	0
Adhesiveness on binder substrate (dried at 60°C for 2 days)		0	0	0	0	0	0	0	0
Adhesiveness on binder substrate (immersion in seawater at 40°C for 6 months)		0	0	0	0	0	0	0	0

[Table 2-3]

		Example						
Coating material formulation number		17	18	19	20	21	22	23
A	Hydrolyzable polymer solution (A-1)							
	Hydrolyzable polymer solution (A-2)							
	Hydrolyzable polymer solution (A-3)	35	35	35				
	Hydrolyzable polymer solution (A-4)							
	Hydrolyzable polymer solution (A-5)							
	Hydrolyzable polymer solution (A-6)				35	35	35	35
B	Medetomidine	0.3	0.2	0.2	0.2	0.3	0.2	0.2
C	Tralopyril	0.5	5	7.5	0.5	0.5	5	7.5
D	Copper pyrithione	0.5	0.5	0.5	0.5	0.5	0.5	0.5
	Zinc pyrithione							
E	Versatic acid	0.5	0.5	0.5	0.5	0.5	0.5	0.5
	Rosin							
F	Zinc oxide	25	25	25	25	25	25	25
	Bengal red	2	2	2	2	2	2	2
	Precipitated barium sulfate	5	5	5	5	5	5	5
	Talc	10	10	10	10	10	10	10
	Calcined plaster	2	2	2	2	2	2	2
G	Fatty acid amide wax (solid content: 20%)	1	1	1	1	1	1	1
	Oxidized polyethylene wax (solid content: 20%)	1	1	1	1	1	1	1
H	Xylene	13.2	8.8	6.3	13.3	13.2	8.8	6.3
	Propylene glycol monomethyl ether	3	3	3	3	3	3	3
I	Chlorinated paraffin	1	1	1	1	1	1	1
	Total	100	100	100	100	100	100	100
	Coating material solid content (mass%)	66.6	71.0	73.5	66.1	66.2	70.6	73.1
	Content of (B) with respect to 100 mass% of (D)	60.0%	40.0%	40.0%	40.0%	60.0%	40.0%	40.0%
	Content of (C) with respect to 100 mass% of (D)	100.0%	1000.0%	1500.0%	100.0%	100.0%	1000.0%	1500.0%
	of (D) with respect to 100 mass% of coating material solid content	0.8%	0.7%	0.7%	0.8%	0.8%	0.7%	0.7%

Static antifouling property after operation (dynamic immersion)	6 months	0	0	0	0	0	0	0
	12 months	0	1	0	1	0	1	0
Static antifouling property of dry-wet alternating part	6 months	0	0	0	1	0	0	0
	12 months	1	0	0	2	1	0	0
Adhesiveness on deteriorated coating film 1 (silyl ester resin-based)		0	0	0	0	0	0	0
Adhesiveness on deteriorated coating film 2 (vinyl chloride-isobutyl vinyl ether resin-based)		0	0	0	0	0	0	0
Adhesiveness on deteriorated coating film 3 (same antifouling coating film)		0	0	0	0	0	0	0
Adhesiveness on binder substrate (dried at 60°C for 2 days)		0	0	0	0	0	0	0
Adhesiveness on binder substrate (immersion in seawater at 40°C for 6 months)		0	0	0	0	0	0	0

[Table 2-4]

		Comparative Example					
Coating material formulation number		1	2	3	4	5	6
A	Hydrolyzable polymer solution (A-1)						
	Hydrolyzable polymer solution (A-2)						
	Hydrolyzable polymer solution (A-3)	35	35	35	35	35	35
	Hydrolyzable polymer solution (A-4)						
	Hydrolyzable polymer solution (A-5)						
	Hydrolyzable polymer solution (A-6)						
B	Medetomidine		0.1	0.1	0.1	0.1	0.1
C	Tralopyril	2.5	2.5	2.5		2.5	2.5
D	Copper pyrithione	5			5	5	5
	Zinc pyrithione			5			
E	Versatic acid	0.5	0.5	0.5	0.5		
	Rosin						0.5
F	Zinc oxide	25	25	25	25	25	25
	Bengal red	2	2	2	2	2	2
	Precipitated barium sulfate	5	5	5	5	5	5
	Talc	10	10	10	10	10	10
	Calcined plaster	2	2	2	2	2	2
G	Fatty acid amide wax (solid content: 20%)	1	1	1	1	1	1
	Oxidized polyethylene wax (solid content: 20%)	1	1	1	1	1	1
H	Xylene	7	11.9	6.9	9.4	7.4	6.9
	Propylene glycol monomethyl ether	3	3	3	3	3	3
I	Chlorinated paraffin	1	1	1	1	1	1
Total		100	100	100	100	100	100
Coating material solid content (mass%)		72.8	67.9	72.9	70.4	72.4	72.9
Content of (B) with respect to 100 mass% of (D)		0.0%	-	-	2.0%	2.0%	2.0%
Content of (C) with respect to 100 mass% of (D)		50.0%	-	-	0.0%	50.0%	50.0%
of (D) with respect to 100 mass% of coating material solid		6.9%	0.0%	0.0%	7.1%	6.9%	6.9%

content							
Static antifouling property after operation (dynamic immersion)	6 months	3	2	0	0	0	0
	12 months	4	3	0	1	0	0
Static antifouling property of dry-wet alternating part	6 months	2	1	0	2	0	0
	12 months	3	2	0	3	0	0
Adhesiveness on deteriorated coating film 1 (silyl ester resin-based)		0	0	2	0	3	4
Adhesiveness on deteriorated coating film 2 (vinyl chloride-isobutyl vinyl ether resin-based)		2	2	3	2	4	5
Adhesiveness on deteriorated coating film 3 (same antifouling coating film)		0	0	0	0	0	1
Adhesiveness on binder substrate (dried at 60°C for 2 days)		0	0	4	0	4	4
Adhesiveness on binder substrate (immersion in seawater at 40°C for 6 months)		0	0	2	0	2	4

[0170]

[Table 3]

	Product name	Details
B	Medetomidine	"Selektope" manufactured by I-tech AB, chemical name: (+/-) -4-[1-(2,3-dimethylphenyl)ethyl]-1H-imidazole
C	Tralopyril	"ECONEA technical" manufactured by Janssen PMP, chemical name: 4-bromo-2-(4-chlorophenyl)-5-(trifluoromethyl)-1H-pyrrole-3-carbonitrile
D	Copper pyrrhione	"Copper Omadine Powder" manufactured by Arch UK Biocides Ltd., chemical formula: Cu(-S-C ₅ H ₄ N-O-) ₂
	Zinc pyrrhione	"Zinc Omadine Powder" manufactured by Arch UK Biocides Ltd., chemical formula: Zn(-S-C ₅ H ₄ N-O-) ₂
E	Versatic acid	"Versatic 10" manufactured by Japan Epoxy Resin Co., Ltd., neodecanoic acid
	Rosin	WW rosin (made in China)
F	Zinc oxide	"Zinc Oxide Grade 2" manufactured by Hokusui Tech Co., Ltd.
	Bengal red	"TODA COLOR NM-50" manufactured by Morishita Bengara Kogyo Co., Ltd.
	Precipitated barium sulfate	"Precipitated barium sulfate 100" manufactured by Sakai Chemical Industry Co., Ltd.
	Talc	"TTK Talc" manufactured by Takehara Kagaku Kogyo Co., Ltd.
	Calcined plaster	"Calcined Plaster FT-2" manufactured by Noritake Company Limited.
G	Fatty acid amide wax (solid content: 20%)	"DISPARLON A630-20X" manufactured by Kusumoto Chemicals, Ltd. (solid content: 20 mass%)
	Oxidized polyethylene wax (solid content: 20%)	"A-S-A D-120" manufactured by Itoh Oil Chemicals, Co., Ltd. (solid content: 20 mass%)
I	Chlorinated paraffin	"Toyoparax 150" manufactured by TOSOH CHEMICAL CO., LTD. (viscosity (25°C): 12 poise, specific gravity (25°C) = 1.24 g/cm ³ , chlorine content = 50%)

[0171]

examples and comparative examples shown in Table 2, for example, the following can be said.

[0172]

(1) From the comparison of Comparative Example 1 in which, as antifouling agents, tralopyril (C) and copper pyrithione (D) are contained, but medetomidine (B) is not contained with Examples 1, 2 and 4 in which all of medetomidine (B), tralopyril (C) and copper pyrithione (D) are contained, and the other components are equivalent to the components of Comparative Example 1, the antifouling coating composition of the present invention that satisfies the configuration requirement such as the latter enables the formation of an antifouling coating film that is particularly excellent in static antifouling property after long-term dynamic immersion and is also excellent in static antifouling property of a dry-wet alternating part without impairing the performance related to the other evaluation tests as compared with a conventional antifouling coating composition such as the former. In addition, as compared with the former antifouling coating film, the latter antifouling coating film is also excellent in adhesiveness to a vinyl chloride-isobutyl vinyl ether resin-based deteriorated antifouling coating film.

[0173]

(2) From the comparison of Comparative Example 4 in

which, as antifouling agents, medetomidine (B) and copper pyrithione (D) are contained but tralopyril (C) is not contained with Examples 2, 5 and 6 in which all of medetomidine (B), tralopyril (C) and copper pyrithione (D) are contained, and the other components are equivalent to the components of Comparative Example 4, the antifouling coating composition of the present invention that satisfies the configuration requirement such as the latter enables the formation of an antifouling coating film excellent in static antifouling property after long-term dynamic immersion and excellent in static antifouling property of a dry-wet alternating part without impairing the performance related to the other evaluation tests as compared with a conventional antifouling coating composition such as the former. In addition, as compared with the former antifouling coating film, the latter antifouling coating film is also excellent in adhesiveness to a vinyl chloride-isobutyl vinyl ether resin-based deteriorated antifouling coating film.

[0174]

(3) From the comparison of Comparative Example 5 in which the linear or branched alkyl carboxylic acid (E) having 4 to 30 carbon atoms (versatic acid as a representative example thereof) is not contained with Examples 2, 9 and 10 in which the alkyl carboxylic acid (E)

is contained, and the other components are equivalent to the components of Comparative Example 9, the antifouling coating composition of the present invention that satisfies the configuration requirement such as the latter enables the formation of an antifouling coating film excellent in adhesiveness to a silyl ester resin-based deteriorated antifouling coating film and a vinyl chloride-isobutyl vinyl ether resin-based deteriorated antifouling coating film (that is, an old antifouling coating film other than the same antifouling coating film) and also excellent in adhesiveness to an epoxy-based binder coating film without impairing the performance related to the other evaluation tests as compared with a conventional antifouling coating composition such as the former.

[0175]

(4) From the comparison of Comparative Example 3 in which copper pyrithione (C) is not contained, but zinc pyrithione is contained instead with Example 2 in which copper pyrithione (C) is contained, but zinc pyrithione is not contained, and the other components are equivalent to the components of Comparative Example 3, the antifouling coating composition of the present invention that satisfies the configuration requirement such as the latter enables the formation of an antifouling coating film excellent in adhesiveness to a silyl ester resin-based deteriorated

antifouling coating film and a vinyl chloride-isobutyl vinyl ether resin-based deteriorated antifouling coating film (that is, an old antifouling coating film other than the same antifouling coating film) and also excellent in adhesiveness to an epoxy-based binder coating film without impairing the performance related to the other evaluation tests as compared with a conventional antifouling coating composition such as the former.

[0176]

(5) From the comparison of Comparative Example 6 in which the linear or branched alkyl carboxylic acid (E) having 4 to 30 carbon atoms (versatic acid as a representative example thereof) is not contained, but rosin is contained instead with Example 2 in which the linear or branched alkyl carboxylic acid (E) having 4 to 30 carbon atoms (versatic acid as a representative example thereof) is contained, but rosin is not contained, and the other components are equivalent to the components of Comparative Example 6, the antifouling coating composition of the present invention that satisfies the configuration requirement such as the latter enables the formation of an antifouling coating film excellent in adhesiveness to a silyl ester resin-based deteriorated antifouling coating film and a vinyl chloride-isobutyl vinyl ether resin-based deteriorated antifouling coating film (that is, an old

antifouling coating film other than the same antifouling coating film) and also excellent in adhesiveness to an epoxy-based binder coating film without impairing the performance related to the other evaluation tests as
5 compared with a conventional antifouling coating composition such as the former.

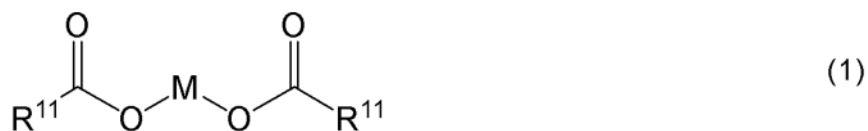
CLAIMS

1. An antifouling coating composition comprising a hydrolyzable polymer (A) containing a metal ester group,
5 medetomidine (B), tralopyril (C), copper pyrithione (D), and a linear or branched alkyl carboxylic acid (E) having 4 to 30 carbon atoms, wherein

the polymer (A) includes a constituent unit derived from a metal ester group-containing monomer (a1)

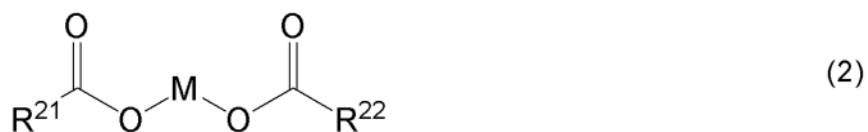
10 represented by formula (1) below and/or a constituent unit derived from a metal ester group-containing monomer (a2) represented by formula (2) below:

[Chem. 1]



15 wherein R¹¹'s each independently represent a monovalent group containing a terminal ethylenically unsaturated group, and M represents a copper atom or a zinc atom; and

[Chem. 2]



20

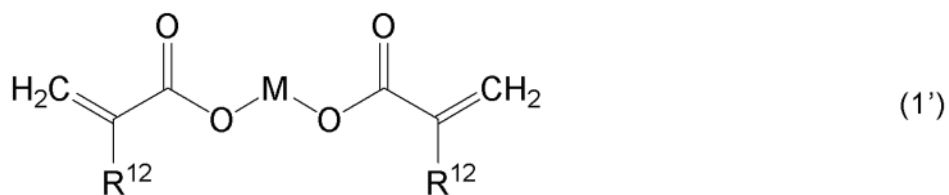
wherein R²¹ represents a monovalent group containing

a terminal ethylenically unsaturated group, R^{22} represents a monovalent organic group containing no terminal ethylenically unsaturated group and having 1 to 30 carbon atoms, and M represents a copper atom or a zinc atom.

5

2. The antifouling coating composition according to claim 1, wherein the polymer (A) contains a metal ester group-containing monomer (a1) represented by formula (1') below:

10 [Chem. 3]



wherein R^{12} 's each independently represent a hydrogen atom or a methyl group, and M represents a copper atom or a zinc atom.

15

3. The antifouling coating composition according to claim 1 or 2, wherein the alkyl carboxylic acid (E) is versatic acid.

20

4. The antifouling coating composition according to claim 1 or 2, wherein

a content of the medetomidine (B) is 0.1 to 100 mass% and a content of the tralopyril (C) is 10 to 1,700

mass% with respect to 100 mass% of the copper pyrithione (D), and

a content of the copper pyrithione (D) is 0.5 to 12 mass% with respect to 100 mass% of a solid content of the antifouling coating composition.

5. An antifouling coating film, formed from the antifouling coating composition according to claim 1 or 2.

10 6. A substrate with an antifouling coating film, comprising a substrate and the antifouling coating film according to claim 5.

7. The substrate with an antifouling coating film according to claim 6, wherein the substrate is selected from a group consisting of a ship, an underwater structure, and a fishery material.

8. A method for producing a substrate with an antifouling coating film, the method comprising a step (1) of coating or impregnating a substrate with the antifouling coating composition according to claim 1 or 2 to obtain a coated body or an impregnated body, and a step (2) of drying the coated body or the impregnated body.

25

9. An antifouling method for a substrate, comprising a step of forming the antifouling coating film according to claim 5 on at least a part of a substrate.