

DESCRIPTION

Antifouling Coating Composition, Antifouling Coating Film as well as Marine Vessel
and Underwater Structure

5

TECHNICAL FIELD

The present invention relates to an antifouling coating composition, and more specifically, it relates to an antifouling coating composition capable of forming an antifouling coating film which is excellent in a long-term antifouling property and crack
10 resistance. The present invention also relates to an antifouling coating film formed from this antifouling coating composition, as well as a marine vessel and an underwater structure each having this antifouling coating film.

BACKGROUND ART

A marine vessel or an underwater structure such various fishnets for aquaculture
15 or the like, harbor facilities, an oil fence, a piping material, a bridge, a buoy, industrial water facilities or a submarine base is regularly exposed to seawater inhabited by organisms, and hence microorganisms such as bacteria adhere thereto with the lapse of time, and animals and plants such as barnacles, mussels, sea lettuces and diatoms, for example, eating the microorganisms adhere thereto. When the surface of the marine
20 vessel or the underwater structure is covered with these microorganisms, animals and plants, damage such as corrosion of this portion, reduction of fuel consumption in marine vessels resulting from increase in seawater friction resistance of the marine vessel, mass mortality of fish and shellfish resulting from clogging of the fishnet, subsidence of the buoy resulting from buoyancy reduction or reduction of working efficiency takes
25 place.

In an industrial water system of cooling water or the like utilizing natural water such as river water or lake water and a circular cooling apparatus using intermediate or service water, an impediment such as deterioration of the water quality, reduction of

cooling efficiency resulting from adherence to the apparatus wall, blocking of a water pipe or flow rate reduction results from proliferation of bacteria, diatoms, blue-green algae and the like.

5 As a method of preventing adherence of these harmful organisms, a method of applying an antifouling paint has generally been employed, and an organotin compound has been mainly employed for this antifouling paint as an antifouling agent. In recent years, however, use of such an antifouling agent has been in the process of prohibition, in view of safety to the ecosystem.

10 For example, Japanese Patent Laying-Open No. 11-29725 (Patent Document 1), Japanese Patent Laying-Open No. 11-172159 (Patent Document 2), Japanese Patent Laying-Open No. 2002-265849 (Patent Document 3) and Japanese Patent Laying-Open No. 11-29747 (Patent Document 4) list cuprous oxide, copper thiocyanate (copper rhodanide), manganese ethylene bisdithiocarbamate, N,N-dimethyldichlorophenylurea, 4,5-dichloro-2-n-octyl-3(2H)-isothiazoline, 2-pyridinethiol-1-oxide zinc salt (zinc
15 pyrithione), N,N'-dimethyl-N'-phenyl-(N-fluorodichloromethylthio) sulfamide, pyridine-triphenylborane and the like, for example, as usable antifouling agents substituting for the organotin compound.

Employment of the aforementioned antifouling agents in combination is also generally performed. For example, Japanese Patent Laying-Open No. 2001-329228
20 (Patent Document 5) and Japanese Patent Laying-Open No. 11-323209 (Patent Document 6) disclose antifouling coating compositions each employing pyridine-triphenylborane and at least any one of 2-pyridinethiol-1-oxide zinc salt (zinc pyrithione), 2-pyridinethiol-1-oxide copper salt (copper pyrithione), cuprous oxide, copper thiocyanate (copper rhodanide) and 4,5-dichloro-2-n-octyl-3(2H)-isothiazoline as
25 antifouling agents.

Japanese Patent Laying-Open No. 9-3366 (Patent Document 7) discloses an antifouling paint containing pyridine-triphenylborane as a first antifouling effective component and containing any one compound selected from manganese ethylene

bisdithiocarbamate, zinc ethylene bisdithiocarbamate, bisdimethyl dithiocarbamoyl zinc ethylene bisdithiocarbamate, cuprous oxide, copper thiocyanate, copper or zinc bis(2-pyridylthio-1-oxide), N-(fluorodichloromethylthio)-phthalimide, N-(dichlorofluoromethylthio)-N',N'-dimethyl-N-phenylsulfamide, 4,5-dichloro-2-n-octyl-
5 isothiazoline-3-one, 2,3,5,6-tetrachloro-4-methylsulfonylpyridine and 3-iodo-2-propynylbutylcarbamate as a second antifouling effective component.

Japanese Patent Laying-Open No. 10-298455 (Patent Document 8) discloses an antifouling coating composition containing cuprous oxide, bis(2-pyridinethiol-1-oxide) copper salt and any one compound selected from 2,4,5,6-tetrachloroisophthalonitrile,
10 N,N-dimethyl-dichlorophenylurea and zinc dimethyl dithiocarbamate.

Japanese Patent Laying-Open No. 2001-342432 (Patent Document 9) discloses a combination of cuprous oxide and 4,5-dichloro-2-n-octyl-3(2H)-isothiazoline, a combination of cuprous oxide and 2-pyridinethiol-1-oxide zinc salt, a combination of cuprous oxide, 2-pyridinethiol-1-oxide copper salt and zinc ethylene bisdithiocarbamate
15 and the like.

However, all of the aforementioned antifouling coating compositions have required improvements in view of the antifouling property, particularly the long-term antifouling property. Further, large quantities of antifouling agents must be blended in order to attain sufficient antifouling effects, and improvements have been required also
20 in view of countermeasures against environmental pollution. In addition, a marine vessel or the like provided with an antifouling coating film repeats such a cycle that the same is landed after dipped in seawater for a constant period and hence flexibility capable of withstanding such conditions is required to the antifouling coating film, while it cannot be said that an antifouling coating film formed from the aforementioned
25 antifouling coating compositions has sufficient flexibility, but the coating film may be cracked when the aforementioned cycle is repeated a plurality of times.

Patent Document 1: Japanese Patent Laying-Open No. 11-29725

Patent Document 2: Japanese Patent Laying-Open No. 11-172159

Patent Document 3: Japanese Patent Laying-Open No. 2002-265849

Patent Document 4: Japanese Patent Laying-Open No. 11-29747

Patent Document 5: Japanese Patent Laying-Open No. 2001-329228

Patent Document 6: Japanese Patent Laying-Open No. 11-323209

5 Patent Document 7: Japanese Patent Laying-Open No. 9-3366

Patent Document 8: Japanese Patent Laying-Open No. 10-298455

Patent Document 9: Japanese Patent Laying-Open No. 2001-342432

DISCLOSURE OF THE INVENTION

PROBLEMS TO BE SOLVED BY THE INVENTION

10 The present invention has been proposed in order to solve the aforementioned problems, and an object thereof is to provide an antifouling coating composition capable of forming an antifouling coating film capable of sustaining a high antifouling property over a long period even if the loading of an antifouling agent is smaller than that in the conventional antifouling coating composition and excellent in crack resistance, i.e.,

15 hardly cracked even if a cycle of seawater dipping/landing is repetitively carried out. Another object of the present invention is to provide an antifouling coating film formed from this antifouling coating composition, as well as a marine vessel and an underwater structure each having this antifouling coating film.

MEANS FOR SOLVING THE PROBLEMS

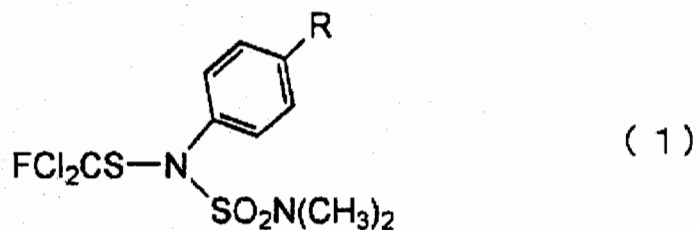
20 The inventors have made deep studies as to the types of antifouling agents and combinations thereof in order to solve the aforementioned problems, to find such an extremely specific effect that an antifouling coating film having an extremely high long-term antifouling property with a small loading of an antifouling agent and provided with excellent crack resistance is obtained according to an antifouling coating composition

25 employing certain specific antifouling agents. In other words, the present invention is as follows:

The present invention is an antifouling coating composition containing binder resin (A) and an antifouling agent (B), wherein the antifouling agent (B) contains metal

pyrithione (B1), triphenylborane amine salt (B2) and a sulfamide-based compound (B3) expressed by the following general formula (1):

[Chemical Formula 1]

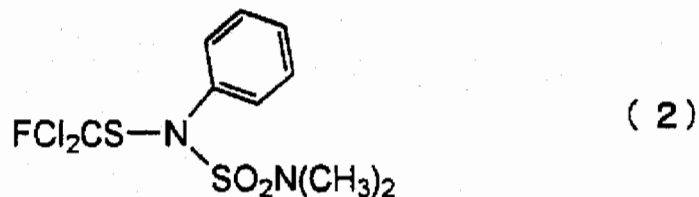


- 5 (in the above general formula (1), R represents a hydrogen atom or a linear or branched alkyl group having 1-10 carbon atoms).

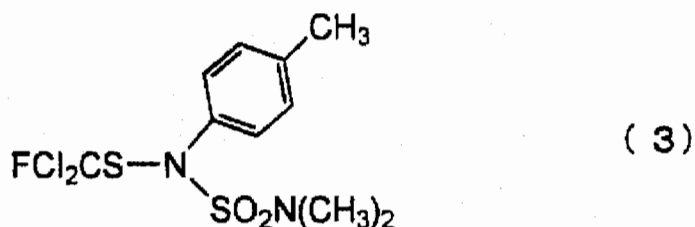
Preferably, the aforementioned triphenylborane amine salt (B2) includes pyridine triphenylborane. Preferably, the aforementioned sulfamide-based compound (B3) includes at least one compound selected from compounds expressed by the following

10 formula (2) and the following formula (3):

[Chemical Formula 2]

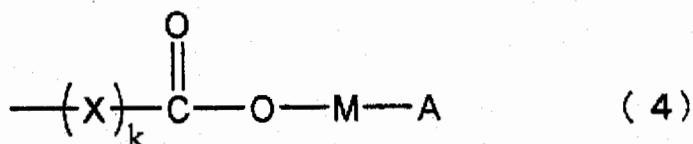


[Chemical Formula 3]

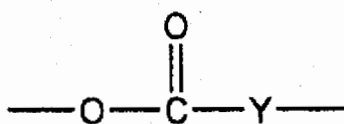


- 15 Preferably, the aforementioned binder resin (A) includes resin having, in a side chain thereof, at least one group expressed by the following general formula (4):

[Chemical Formula 4]



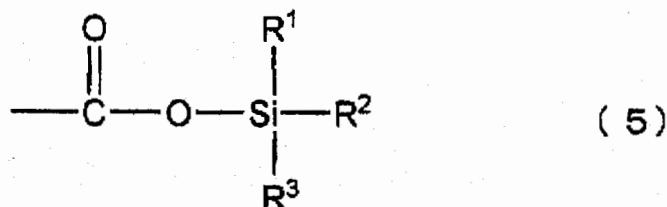
(in the above general formula (4), X represents a group expressed by:
[Chemical Formula 5])



- 5 k represents 0 or 1, Y represents hydrocarbon, M represents a divalent metal, and A represents an organic acid residue of a monobasic acid).

Preferably, the aforementioned binder resin (A) includes resin having, in a side chain thereof, at least one group expressed by the following general formula (5):

[Chemical Formula 6]



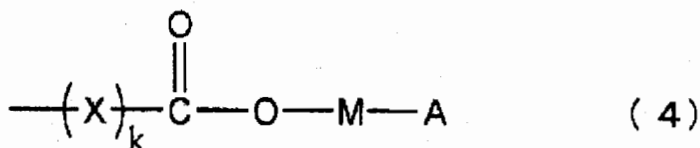
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(in the above general formula (5), R¹, R² and R³ are the same or different from one another and represent a hydrocarbon residue having 1-20 carbon atoms).

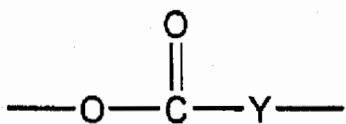
Preferably, the aforementioned binder resin (A) includes resin having, in a side chain thereof, at least one group expressed by the following general formula (4):

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[Chemical Formula 7]

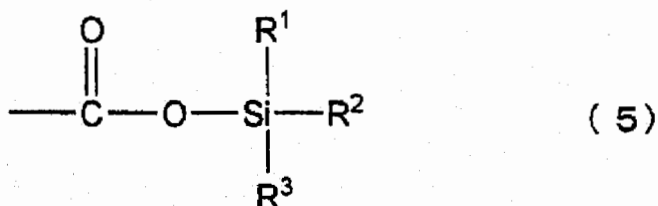


(in the above general formula (4), X represents a group expressed by:
[Chemical Formula 8])



k represents 0 or 1, Y represents hydrocarbon, M represents a divalent metal, and A represents an organic acid residue of a monobasic acid), and at least one group expressed by the following general formula (5):

5 [Chemical Formula 9]



(in the above general formula (5), R^1 , R^2 and R^3 are the same or different from one another and represent a hydrocarbon residue having 1-20 carbon atoms.)

Preferably, the aforementioned monobasic acid is monobasic cyclic organic acid.

10 Preferably, the aforementioned monobasic acid is at least one type selected from the group consisting of rosins, hydrogenated rosins, disproportionated rosins, naphthenic acid, abietic acid, dehydroabietic acid and hydrogenated abietic acid. In the antifouling coating composition according to the present invention, the binder resin (A) may include, along with the aforementioned hydrolyzable resin or in place of the hydrolyzable resin,
15 another binder resin other than the hydrolyzable resin. Chlorinated paraffin, rosins and hydrogenated rosins can be preferably employed as another binder resin.

The present invention also provides an antifouling coating film formed by employing the antifouling coating composition according to any of the above, as well as a marine vessel and an underwater structure each having this antifouling coating film.

20 EFFECTS OF THE INVENTION

According to the antifouling coating composition of the present invention, an antifouling coating film capable of sustaining an extremely high antifouling property over a long period with a small loading of an antifouling agent and excellent in crack

resistance can be formed. The antifouling coating composition according to the present invention can be preferably employed as an antifouling paint for preventing the surface of a marine vessel or an underwater structure such as various fishnets for aquaculture or the like, harbor facilities, an oil fence, a piping material, a bridge, a buoy, industrial water facilities or a submarine base from fouling.

BEST MODES FOR CARRYING OUT THE INVENTION

The antifouling coating composition according to the present invention is an antifouling coating composition containing the binder resin (A) and the antifouling agent (B), and this antifouling agent (B) contains the metal pyrithione (B1), the triphenylborane amine salt (B2) and the sulfamide-based compound (B3). According to such coating composition, an antifouling coating film extremely high in antifouling property and excellent in crack resistance can be formed. The components contained in the antifouling coating composition according to the present invention are now described in detail.

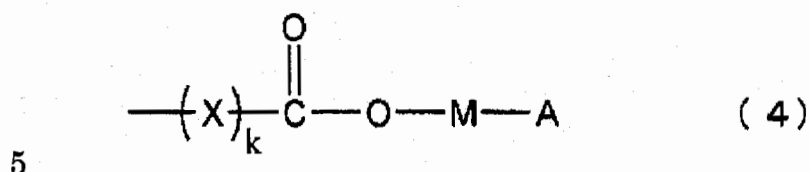
<Binder Resin (A)>

While a known binder resin can be employed as the binder resin employed for the antifouling coating composition according to the present invention, hydrolyzable resin is preferable in particular. The hydrolyzable resin is so employed as the binder resin that the high antifouling property with the antifouling agent can be sustained over a longer period.

While resin generally used for an antifouling paint can be employed as the hydrolyzable resin, acrylic resin can be preferably employed in particular, and (i) acrylic resin having a group expressed by the following general formula (4), (ii) acrylic resin having a group expressed by the following general formula (5), and (iii) acrylic resin having both of the group expressed by the following general formula (4) and the group expressed by the following general formula (5) can be listed as the acrylic resin. These may be singly employed, or at least two types may be employed together. In this specification, "acrylic resin" denotes such resin that at least part of the resin consists of a

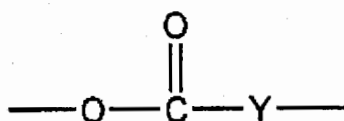
constitutional unit derived from (meth)acrylic acid or a derivative thereof or (meth)acrylate. (Meth)acrylic acid metal salt is also included in the derivative of (meth)acrylic acid.

[Chemical Formula 10]



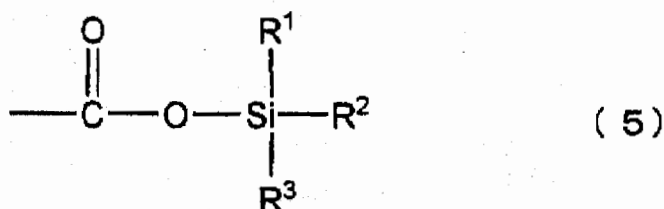
(in the above general formula (4), X represents a group expressed by:

[Chemical Formula 11]



k represents 0 or 1, Y represents hydrocarbon, M represents a divalent metal, and A represents an organic acid residue of a monobasic acid).

[Chemical Formula 12]



(in the above general formula (5), R^1 , R^2 and R^3 are the same or different from one another and represent a hydrocarbon residue having 1-20 carbon atoms).

Preferable examples of the above acrylic resin (i) include acrylic resin (hereinafter referred to also as acrylic resin (A1)) having at least one group expressed by the above general formula (4) on the side chain. Thus, the obtained coating film can maintain a stable polishing rate over a long period, whereby a superior long-term antifouling property can be exhibited.

In the above general formula (4), M represents a divalent metal, and elements of

the groups 3A to 7A, 8 and 1B to 7B in the periodic table can be listed, for example. Preferably, M is copper or zinc.

In the above general formula (4), A represents an organic acid residue of a monobasic acid. As preferable monobasic acid, monobasic cyclic organic acid or the like can be listed, for example. The monobasic cyclic organic acid is not particularly limited, and includes an acid having a cycloalkyl group such as naphthenic acid, as well as a resin acid such as tricyclic resin acid and salts thereof, for example. The tricyclic resin acid is not particularly limited and includes a monobasic acid having a diterpene-based hydrocarbon structure, for example, and as such a compound, a compound having a structure of abietane, pimarane, isopimarane and rhabdane can be listed. More specifically, abietic acid, neoabietic acid, dehydroabietic acid, hydrogenated abietic acid, parastrinic acid, pimaric acid, isopimaric acid, levopimaric acid, dextropimaric acid, sandaracopimaric acid and salts of these can be listed, for example. Among these, abietic acid, hydrogenated abietic acid and salts of these are preferable, since the same are excellent in long-term antifouling property due to properly performed hydrolysis and also excellent in crack resistance of a coating film and ease of availability. Further, that having an acid value of not more than 220 mgKOH/g can be listed as preferable monobasic cyclic organic acid. Monobasic cyclic organic acid having an acid value of not more than 220 mgKOH/g is so employed that the viscosity of the obtained binder resin (A) can be reduced, and a solvent content of the obtained paint can be reduced. This is because the viscosity of the binder resin (A) remarkably depends on interaction between functional groups expressed by the general formula (4). The binder resin (A) obtained by employing the monobasic cyclic organic acid having the acid value of not more than 220 mgKOH/g has such a tendency that steric repulsion of the monobasic cyclic organic acid increases, this steric repulsion conceivably acts to inhibit the interaction between the functional groups expressed by the general formula (4), and the viscosity of the binder resin (A) can be reduced as a result.

The aforementioned monobasic cyclic organic acid may not be highly purified,

and turpentine or a resin acid of pine can also be used, for example. Examples of such a substance include rosins, hydrogenated rosins, disproportionated rosins, for example. The term rosins refers to gum rosin, wood rosin, tall oil rosin or the like. Rosins, hydrogenated rosins and disproportionated rosins are preferable in such points that they are low-priced and easy to obtain, excellent in handleability and exhibit long-term antifouling properties. These monobasic cyclic organic acids may be singly employed, or at least two types may be employed together.

Examples of a monobasic acid other than the above monobasic cyclic organic acids among monobasic acids usable in the present invention include monobasic acids having 1-20 carbon atoms such as acetic acid, propionic acid, butyric acid, lauryl acid, stearic acid, linoleic acid, oleic acid, chloroacetic acid, fluoroacetic acid and valeric acid, for example. These monobasic acids may be singly employed, or at least two types may be employed together.

Y in the above general formula (4) is not particularly restricted so far as the same is hydrocarbon, and includes a residue in a case of adding dibasic acid such as phthalic acid, succinic acid or maleic acid to a polymerizable unsaturated organic acid monomer, for example.

A method of preparing the acrylic resin (A1) is not particularly restricted, but (a) a method of reacting resin obtained by polymerizing polymerizable unsaturated organic acid and another copolymerizable unsaturated monomer with monobasic acid and a metal compound, (b) a method of reacting polymerizable unsaturated organic acid, a metal compound and monobasic acid with each other or reacting polymerizable unsaturated organic acid and metal salt of monobasic acid with each other and polymerizing the obtained metal-containing unsaturated monomer with another copolymerizable unsaturated monomer or the like can be listed.

The polymerizable unsaturated organic acid in the above methods (a) and (b) is not particularly limited and includes polymerizable unsaturated organic acid having at least one carboxyl group, for example. More specifically, unsaturated monobasic acid

such as (meth)acrylic acid; unsaturated dibasic acid and monoalkyl ester thereof such as maleic acid and monoalkyl ester thereof, itaconic acid and monoalkyl ester thereof or the like; a dibasic acid adduct of unsaturated monobasic acid hydroxyalkyl ester such as a maleic acid adduct of 2-hydroxyethyl (meth)acrylate, a phthalic acid adduct of 2-hydroxyethyl (meth)acrylate, a succinic acid adduct of 2-hydroxyethyl (meth)acrylate or the like can be listed, for example. These polymerizable unsaturated organic acids may be singly employed, or at least two types may be employed together. In the method (b), the metal-containing unsaturated monomer may be partially or entirely replaced with divalent metal di(meth)acrylate. While the resin is brought into a bridged structure through the group expressed by the general formula (4) when employing divalent metal di(meth)acrylate, it is also possible to employ such resin.

The aforementioned another copolymerizable unsaturated monomer is not particularly limited and as (meth)acrylates include alkyl (meth)acrylate in which an ester portion has 1-20 carbon atoms such as methyl (meth)acrylate, ethyl (meth)acrylate, i-propyl (meth)acrylate, n-butyl (meth)acrylate, i-butyl (meth)acrylate, t-butyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, lauryl (meth)acrylate and stearyl (meth)acrylate; hydroxyl group-containing alkyl (meth)acrylate in which an ester portion has 1-20 carbon atoms such as 2-hydroxypropyl (meth)acrylate and 2-hydroxyethyl (meth)acrylate; cyclic hydrocarbon (meth)acrylate such as phenyl (meth)acrylate and cyclohexyl (meth)acrylate; polyalkylene glycol (meth)acrylate such as (poly)ethylene glycol mono(meth)acrylate and polyethylene glycol mono(meth)acrylate having a polymerization degree of 2 to 10; and alkoxyalkyl (meth)acrylate having 1-3 carbon atoms as well as (meth)acrylamide; a vinyl compound such as styrene, α -methyl styrene, vinyl acetate, vinyl propionate, vinyl benzoate, vinyl toluene and acrylonitrile; crotonate; and diester of unsaturated dibasic acid such as dimaleate or diitaconate, for example. The ester portion of the aforementioned (meth)acrylate is preferably an alkyl group having 1-8 carbon atoms, more preferably an alkyl group having 1-6 carbon atoms. Methyl (meth)acrylate, ethyl (meth)acrylate, butyl (meth)acrylate and cyclohexyl

(meth)acrylate are preferable. These may be singly employed, or at least two types may be employed together.

5 The aforementioned metal compound is not particularly limited and includes a metal oxide, a hydroxide, a chloride, a sulfide, a basic carbonate, or metal acetate can be listed, for example. The aforementioned monobasic acid is not particularly limited and the aforementioned one can be listed, for example.

10 The number-average molecular weight (GPC, in terms of polystyrene) of the acrylic resin (A1) is not particularly limited, but preferably at least 2000 and not more than 100000, more preferably at least 3000 and not more than 40000. The film forming property of the coating film may be deteriorated if the number-average molecular weight is less than 2000, while not only the obtained paint is deteriorated in storage stability and unsuitable for practical use but also it is unpreferable in view of public health and economy due to the use of a large quantity of a dilutive solvent in coating process.

15 While the acrylic acid (A1) must contain at least one group expressed by the general formula (4), a coating film elution speed into water can be controlled to a desired elution speed by adjusting the content of the group expressed in the general formula (4). The acrylic resin (A1) preferably has an acid value of 100 to 250 mgKOH/g. The quantity of the metal salt bonded to the side chain may be so reduced
20 that the coating composition is inferior in antifouling property if the acid value is less than 100 mgKOH/g, while the elution speed tends to be so high that a long-term antifouling property is hard to obtain if the acid value exceeds 250 mgKOH/g.

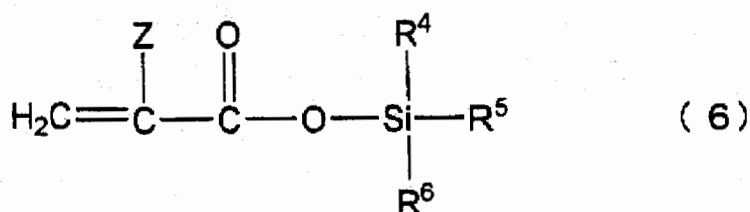
25 Preferable examples of the aforementioned acrylic resin (ii) include acrylic resin (hereinafter referred to also as acrylic resin (A2)) having at least one group expressed by the above general formula (5) on the side chain. Thus, the obtained coating film can maintain a stable polishing rate over a long period, whereby a superior long-term antifouling property can be exhibited.

In the above general formula (5), R^1 , R^2 and R^3 are the same or different from

one another and represent a hydrocarbon residue having 1-20 carbon atoms, and more specifically, linear or branched alkyl groups having carbon numbers of not more than 20 such as a methyl group, an ethyl group, a propyl group, an isopropyl group, an n-butyl group, an isobutyl group, a sec-butyl group, a t-butyl group, a pentyl group, a hexyl group, a heptyl group, an octyl group, a nonyl group, a decyl group, an undecyl group, a dodecyl group, a tridecyl group and a tetradecyl group; cyclic alkyl groups such as a cyclohexyl group and a substituted cyclohexyl group; an aryl group, a substituted aryl group and the like can be listed. As the substituted aryl group, an aryl group substituted by halogen, an alkyl group having a carbon number of up to about 18, an acyl group, a nitro group or an amino group can be listed. In particular, the isopropyl group or the like is preferable in such a point of view that the obtained coating film exhibits a stable polishing rate and stably maintains antifouling performance over a long period.

While a resin obtained by a method of copolymerizing a polymerizable unsaturated monomer and a monomer component partially having a triorganosilyl group or the like can be listed as the acrylic resin (A2), for example, a resin obtained by copolymerizing triorganosilyl (meth)acrylate expressed by the following general formula (6):

[Chemical Formula 13]



and another copolymerizable unsaturated monomer is preferable in particular. The aforementioned another copolymerizable unsaturated monomer is not particularly limited and those mentioned as to the aforementioned acrylic resin (A1) and the polymerizable unsaturated organic acid mentioned as to the aforementioned acrylic resin (A1) can be listed. These polymerizable unsaturated organic acids and another

copolymerizable unsaturated monomer may be singly employed, or at least two types may be employed together.

5 In the triorganosilyl (meth)acrylate expressed by the above general formula (6), Z represents a hydrogen atom or a methyl group. The aforementioned R^4 , R^5 and R^6 are the same or different from one another and express a hydrocarbon residue having 1-20 carbon atoms, and hydrocarbon residues similar to the aforementioned R^1 , R^2 and R^3 can be listed, for example.

Specific examples of triorganosilyl (meth)acrylate expressed by the above general formula (6) are not particularly limited and include trimethylsilyl (meth)acrylate, triethylsilyl (meth)acrylate, tri-n-propylsilyl (meth)acrylate, tri-i-propylsilyl (meth)acrylate, tri-n-butylsilyl (meth)acrylate, tri-i-butylsilyl (meth)acrylate, tri-s-butylsilyl (meth)acrylate, tri-n-amylsilyl (meth)acrylate, tri-n-hexylsilyl (meth)acrylate, tri-n-octylsilyl (meth)acrylate, tri-n-dodecylsilyl (meth)acrylate, triphenylsilyl (meth)acrylate, tri-p-methylphenylsilyl (meth)acrylate, tribenzylsilyl (meth)acrylate, ethyldimethylsilyl (meth)acrylate, n-butyldimethylsilyl (meth)acrylate, di-i-propyl-n-butylsilyl (meth)acrylate, n-octyldi-n-butylsilyl (meth)acrylate, di-i-propylstearylsilyl (meth)acrylate, dicyclohexylphenylsilyl (meth)acrylate, t-butyl diphenylsilyl (meth)acrylate, lauryldiphenylsilyl (meth)acrylate, t-butyl-m-nitrophenylmethylsilyl (meth)acrylate. In particular, tri-i-propylsilyl (meth)acrylate is preferable in a point maintaining a stable polishing rate over a long period. These triorganosilyl (meth)acrylates may be singly employed, or at least two types may be employed together.

25 The number-average molecular weight of the acrylic resin (A2) is not particularly limited, but preferably at least 2000 and not more than 100000, more preferably at least 3000 and not more than 40000. The film forming property of the coating film may be deteriorated if the number-average molecular weight is less than 2000, while not only the obtained paint is deteriorated in storage stability and unsuitable for practical use but also it is unpreferable in view of public health and economy due to the use of a large quantity of a dilutive solvent in coating process.

Preferable examples of the aforementioned acrylic resin (iii) include acrylic resin (hereinafter referred to also as acrylic resin (A3)) having at least one group expressed by the above general formula (4) and having at least one group expressed by the above general formula (5) on the side chain. The polishing rate can be changed to a desired rate by adjusting the content of the group expressed by the general formula (5), whereby a superior long-term antifouling property can be exhibited.

A method of preparing the acrylic resin (A3) is not particularly limited and (I) a method of reacting a resin obtained by polymerizing polymerizable unsaturated organic acid, triorganosilyl (meth)acrylate expressed by the above general formula (6) and another copolymerizable unsaturated monomer with monobasic acid and a metal compound, (II) a method of reacting polymerizable unsaturated organic acid, a metal compound and monobasic acid with each other or reacting polymerizable unsaturated organic acid and a metal salt of monobasic acid with each other and polymerizing the obtained metal-containing unsaturated monomer with triorganosilyl (meth)acrylate expressed by the above general formula (6) and another copolymerizable unsaturated monomer or the like can be listed, for example.

The acrylic resin (A3) has at least one side chain expressed by the above general formula (5) (side chain derived from triorganosilyl (meth)acrylate expressed by the above general formula (6), for example) and at least one side chain expressed by the above general formula (4). The polishing rate of the obtained coating film can be changed to a desired rate by varying the total content of the groups expressed by the general formula (4) and the general formula (5).

In the present invention, another binder resin other than the aforementioned hydrolyzable resin may be employed as the binder resin (A). An excellent antifouling property and crack resistance can be attained also by employing another binder resin. As another binder resin, chlorinated paraffin, polyvinyl ether, polypropylene sebacate, partially hydrogenated terphenyl, polyvinyl acetate, alkyl poly(meth)acrylate, polyether polyol, alkyd resin, polyester resin, polyvinyl chloride, silicon oil, wax, Vaseline, liquid

paraffin, rosin, hydrogenated rosin, naphthenic acid, aliphatic acid and divalent metal salts thereof can be listed, for example. In particular, chlorinated paraffin, rosin and hydrogenated rosin are preferably employed. As to another binder resin, only one type may be singly employed, or at least two types may be employed together.

5 While the binder resin (A) may contain only the aforementioned hydrolyzable resin or may contain only the aforementioned another binder resin, or hydrolyzable resin and another binder resin may be employed together, a particularly excellent long-term antifouling property can be obtained when the binder resin (A) contains hydrolyzable resin and another binder resin at a ratio of 100:0 to 50:50 ([hydrolyzable resin]:[another
10 binder resin]) in a mass ratio based on resin solid contents. Further, the physical properties of the coating film and the consumption speed of the coating film can be more easily adjusted when employing the aforementioned another binder resin along with hydrolyzable resin.

 In the antifouling coating composition according to the present invention, the
15 content of the binder resin (A) is preferably 30 to 70 mass % in the solid content contained in the antifouling coating composition, more preferably 40 to 65 mass %. If the content is less than 30 mass %, a defect such as cracking/separation tends to take place in the coating film. If the content exceeds 70 mass %, a desirable antifouling effect tends to be hardly attained. The solid content contained in the antifouling
20 coating composition denotes the sum of components other than a solvent contained in the antifouling coating composition.

<Antifouling Agent (B)>

 The antifouling coating composition according to the present invention contains metal pyrithione (B1), triphenylborane amine salt (B2) and a sulfamide-based compound
25 (B3) as the antifouling agent (B). According to such a combination of antifouling agents, a remarkably high long-term antifouling property can be provided as compared with generally known single use and combinational use of antifouling agents. In particular, it has been found that such an unexpected effect is attained that an antifouling

property exceeding a level equivalent to a conventional one can be exhibited due to such a combination of the antifouling agents even if the loadings of the antifouling agents are reduced below heretofore known levels. While largeness of loadings of antifouling agents having been generally blended in order to increase the antifouling property of the obtained coating film has been one of the factors deteriorating crack resistance of the coating film in long-term use, such a problem has been solved by the present invention, and it has been made possible to obtain an antifouling coating film excellent in antifouling property and having excellent crack resistance as a result.

The metal pyrrhithione (B1) contained in the antifouling coating composition according to the present invention includes pyrrhithiones such as sodium pyrrhithione, magnesium pyrrhithione, calcium pyrrhithione, barium pyrrhithione, aluminum pyrrhithione, copper pyrrhithione, zinc pyrrhithione, iron pyrrhithione, lead pyrrhithione, for example. In particular, 2-pyridinethiol-1-oxide zinc salt (zinc pyrrhithione), 2-pyridinethiol-1-oxide copper salt (copper pyrrhithione) and the like are preferable. These may be singly employed, or may be employed in combination.

The content of the metal pyrrhithione (B1) (when a plurality of pyrrhithiones are employed, the total content thereof) is preferably 3 to 20 mass % in the solid content contained in the antifouling coating composition, more preferably 5 to 15 mass %. If the content is less than 3 mass %, a desirable antifouling effect tends to be hardly attained. If the content exceeds 20 mass %, a defect such as cracking/separation tends to take place in the coating film.

The triphenylborane amine salt (B2) contained in the antifouling coating composition according to the present invention is a complex formed by triphenylborane and amine. The amine is not particularly limited and includes primary amines such as n-propylamine, n-butylamine, n-hexylamine, n-octylamine, n-decylamine, n-dodecylamine, n-tridecylamine, n-tetradecylamine, n-hexadecylamine, n-octadecylamine, aniline, toluidine or the like; secondary amines such as di-n-butylamine, di-n-hexylamine, di-n-octylamine, di-n-decylamine, di-n-dodecylamine, di-n-tridecylamine, di-n-

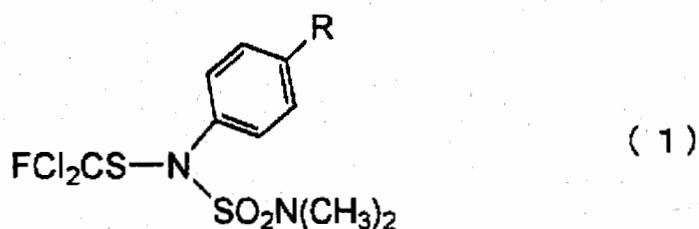
tetradecylamine, di-n-hexadecylamine, di-n-octadecylamine, diphenylamine or the like; tertiary amines such as tri-n-propylamine, tri-n-hexylamine, tri-n-octylamine, tri-n-decylamine, tri-n-dodecylamine, tri-n-tridecylamine, tri-n-tetradecylamine, tri-n-hexadecylamine, tri-n-octadecylamine, triphenylamine or the like; pyridines such as
5 pyridine or a nuclear substitute thereof (for example, 2-picoline, 3-picoline, 4-picoline, 2-chloropyridine, 3-chloropyridine and 4-chloropyridine), for example. As to these triphenylborane amine salts, only one type may be employed, or at least two types may be employed together.

Among the above, pyridinetriphenylborane in which the amine is pyridine is
10 excellent in antifouling performance, and preferably employed.

The content of the triphenylborane amine salt (B2) (when a plurality of triphenylborane amine salts are employed, the total content thereof) is preferably 3 to 30 mass % in the solid content contained in the antifouling coating composition, more preferably 5 to 25 mass %. If the content is less than 3 mass %, a desirable antifouling
15 effect tends to be hardly attained. If the content exceeds 30 mass %, a defect such as cracking/separation tends to take place in the coating film.

The sulfamide-based compound (B3) contained in the antifouling coating composition according to the present invention is a compound expressed by the following general formula (1):

20 [Chemical Formula 14]

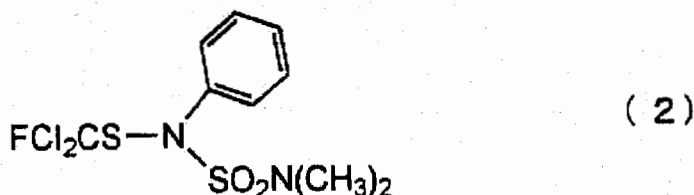


(in the above general formula (1), R represents a hydrogen atom or a linear or branched alkyl group having 1-10 carbon atoms).

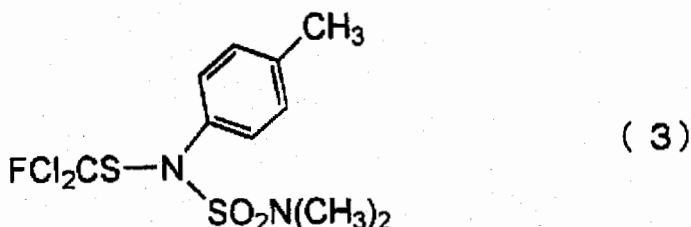
Among these, such a sulfamide-based compound of the following formula (2) or

(3) that R in the above general formula (1) is a hydrogen atom or a methyl group is preferable.

[Chemical Formula 15]



5 [Chemical Formula 16]



The compound of the above formula (2) is a compound referred to as N-(dichlorofluoromethylthio)-N',N'-dimethyl-N-phenylsulfamide or 1,1-dichloro-N-
 10 [(dimethylamino)sulfonyl]-1-fluoro-N-phenylmethane sulfenamide, and may be referred to as N,N'-dimethyl-N'-phenyl-(N-fluorodichloromethylthio) sulfamide or N-(dichlorofluoromethylthio)-N',N'-dimethyl-N-phenylsulfamide. The compound of the above formula (3) is a compound referred to as N-(dichlorofluoromethylthio)-N',N'-
 15 dimethyl-N-(4-methylphenyl) sulfamide or 1,1-dichloro-N-[(dimethylamino) sulfonyl]-1-fluoro-N-(4-methylphenyl) methane sulfenamide.

The compounds of the above formula (2) and the formula (3) may be singly employed respectively, or may be employed together.

The content of the sulfamide-based compound (B3) (when a plurality of compounds are employed, the total content thereof) is preferably 3 to 20 mass % in the
 20 solid content contained in the antifouling coating composition, more preferably 5 to 15 mass %. If the content is less than 3 mass %, a desirable antifouling effect tends to be

hardly attained. If the content exceeds 20 mass %, a defect such as cracking/separation tends to take place in the coating film.

5 The total content of the aforementioned metal pyrithione (B1), the triphenylboraneamine salt (B2) and the sulfamide-based compound (B3) is preferably 10 to 50 mass % in the solid content contained in the antifouling coating composition, more preferably 15 to 45 mass %. If the total content is less than 10 mass %, an antifouling effect tends to be hardly attained. If the total content exceeds 50 mass %, a defect such as cracking/separation tends to take place in the coating film.

10 The ratio (mass ratio) of the content of the triphenylborane amine salt (B2) (when a plurality of triphenylborane amine salts are employed, the total content thereof) to the content of the metal pyrithione (B1) (when a plurality of metal pyrithiones are employed, the total content thereof) is preferably 0.5/1 to 10/1, more preferably 1/1 to 5/1. If this mass ratio is less than 0.5/1, an animal-resistant antifouling property tends to lower. If the mass ratio exceeds 10/1, an algae-resistant antifouling property tends to lower.

15 The antifouling coating composition according to the present invention may further contain another antifouling agent other than the aforementioned (B1) to (B3). Another antifouling agent is not particularly limited and a known one can be used, and an inorganic compound, an organic compound containing metal and an organic compound containing no metal can be listed, for example.

20 Specific examples of another antifouling agent are not particularly limited and include cuprous oxide, manganese ethylene bisdithiocarbamate, zinc dimethylcarbamate, 2-methylthio-4-t-butylamino-6-cyclopropylamino-s-triazine, 2,4,6-tetrachloroisophthalonitrile, N,N-dimethyldichlorophenylurea, zinc ethylene bisdithiocarbamate, copper rhodanide (copper thiocyanate), 4,5-dichloro-2-n-octyl-3(2H) isothiazolone, N-(fluorodichloromethylthio) phthalimide, tetramethylthiuram disulfide, 2,4,6-trichlorophenyl maleimide, 2,3,5,6-tetrachloro-4-(methylsulfonyl) pyridine, 3-iodo-2-propylbutyl carbamate, diiodomethyl paratrisulfone,

phenyl(bispyridyl) bismuth dichloride, 2-(4-thiazolyl)-benzimidazole, for example.

These antifouling agents may be singly employed, or at least two types may be employed together.

When employing another antifouling agent, the ratio of another antifouling agent occupying the total content of all antifouling agents is preferably set to not more than 55 mass %, more preferably set to not more than 50 mass %. When the content of another antifouling agent exceeds 55 mass %, the effect resulting from the addition of the aforementioned antifouling agents (B1) to (B3) is not sufficiently attained, and compatibility of the long-term antifouling property and crack resistance tends to be insufficient as a result.

<Other Additives>

The antifouling coating composition according to the present invention may contain conventional additives such as a plasticizer, a pigment and a solvent. Examples of the plasticizers include phthalate-based plasticizers such as dioctyl phthalate, dimethyl phthalate, dicyclohexyl phthalate and the like; aliphatic dibasic ester-based plasticizers such as isobutyl adipate, dibutyl sebacate and the like; glycol ester-based plasticizers such as diethylene glycol dibenzoate, pentaerythritol alkyl ester and the like; phosphate-based plasticizers such as trichlene diphosphate, trichloroethyl phosphate and the like; epoxy-based plasticizers such as epoxy soybean oil and octyl epoxystearate; organic tin-based plasticizers such as dioctyltin laurylate, dibutyltin laurylate and the like; trioctyl trimellitate, triacetylene, for example. These plasticizers may be singly employed, or at least two types may be employed together.

Examples of the pigments include extenders such as precipitated barium, talc, clay, chalk, silica white, alumina white, bentonite and the like; and coloring pigments such as titanium oxide, zircon oxide, basic lead sulfate, tin oxide, carbon black, graphite, red iron oxide (colcothar), chrome yellow, phthalocyanine green, phthalocyanine blue and quinacridone, for example. These pigments may be singly employed, or at least two types may be employed together.

Examples of the solvents include hydrocarbons such as toluene, xylene, ethylbenzene, cyclopentane, octane, heptane, cyclohexane, white spirit and the like; ethers such as dioxane, tetrahydrofuran, ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol monobutyl ether, ethylene glycol dibutyl ether, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether and the like; esters such as butyl acetate, propyl acetate, benzyl acetate, ethylene glycol monomethyl ether acetate, ethylene glycol monoethyl ether acetate and the like; ketones such as ethyl isobutyl ketone, methyl isobutyl ketone and the like; and alcohols such as n-butanol, propyl alcohol and the like, for example. These solvents may be singly employed, or at least two types may be employed together.

Other than the above, monoester of dicarboxylic acid such as monobutyl phthalate, monooctyl succinate and the like, camphor and castor oil; a water binder and an anti-sagging agent; an anti-flooding agent; an anti-settling agent; an antifoaming agent and the like may be added, for example.

The antifouling coating composition according to the present invention can be prepared by adding the aforementioned antifouling agents (B1) to (B3) as well as conventional additives such as another antifouling agent, a plasticizer, a compensating agent for coating film attrition, a pigment, a solvent and the like if necessary and mixing the same with a mixer such as a ball mill, a pebble mill, a roll mill, a sand grind mill or the like.

The antifouling coating film can be formed by applying the obtained antifouling coating composition to the surface of a substance to be coated according to an ordinary method and thereafter evaporating/removing the solvent under room temperature or under heating. The substance to be coated is not particularly limited and a marine vessel and underwater structures such as various fishnets, harbor facilities, an oil fence, a piping material, a bridge, a submarine base and the like can be listed, for example. The antifouling coating film formed from the antifouling coating composition according to the present invention can sustain a high antifouling property over a long period and has

excellent crack resistance, and such an antifouling coating film compatibly attaining a remarkably excellent long-term antifouling property and crack resistance is implemented by the constitution specific to the antifouling coating composition according to the present invention.

5 While the present invention is now described in more detail with reference to Examples and Comparative Examples, the present invention is not limited to these.

(Manufactural Example 1) Preparation of Acrylic Resin Varnish 1

64 parts by mass of xylene and 16 parts by mass of n-butanol were added to a four-necked flask equipped with a stirrer, a condenser, a temperature controller, a
10 nitrogen inlet tube and a dropping funnel and kept at 100°C. Into this solution, a mixed liquid consisting of monomers according to blending (parts by mass) shown in Table 1 and 2 parts by mass of t-butylperoxy-2-ethyl hexanoate was isokinetically dropped over 3 hours, and the temperature of the mixture was maintained for 30 minutes after termination of the dropping. Thereafter resin varnish I was obtained by
15 isokinetically dropping a mixed liquid consisting of 16 parts by mass of xylene, 4 parts by mass of n-butanol and 0.2 parts by mass of t-butylperoxy-2-ethyl hexanoate over 30 minutes and maintaining the temperature of the mixture for 1 hour and 30 minutes after termination of the dropping. The solid content in the obtained resin varnish I was 49.8 mass %, and the viscosity was 4.4 poises. The acid value of resin in this resin varnish I
20 was 130. The acid value of the obtained resin and the solid content in the resin varnish I were listed in Table 1. Abbreviations of monomers described in Table 1 denote the following compounds:

(1) EA: ethyl acrylate

(2) CHMA: cyclohexyl methacrylate

25 (3) CHA: cyclohexyl acrylate

(4) M-90G: methoxypolyethylene glycol methacrylate (NK Ester M-90G by Shin-Nakamura Chemical Co., Ltd.)

(5) MMA: methyl methacrylate

(6) AA: acrylic acid

(7) MAA: methacrylic acid

(8) TIPSI: triisopropylsilyl acrylate

Then, acrylic resin varnish 1 having a solid content of 41.5 mass % was obtained
5 by adding 100 parts by mass of the resin varnish I, 25.4 parts by mass of zinc acetate,
32.4 parts by mass of naphthenic acid (NA-165, acid value 165, by Daiwa Yushi Kogyo)
and 110 parts by mass of xylene to a similar reaction vessel, heating the same to 130°C
and removing acetic acid along with the solvent. The viscosity was 12.3 poises.

(Manufactural Example 2) Preparation of Acrylic Resin Varnish 2

10 64 parts by mass of xylene and 16 parts by mass of n-butanol were added to a
reaction vessel similar to that in the aforementioned Manufactural Example 1 and kept at
115°C. Into this solution, a mixed liquid consisting of monomers according to
blending (parts by mass) shown in Table 1 and 3 parts by mass of t-butylperoxy-2-ethyl
hexanoate was isokinetically dropped over 3 hours, and the temperature of the mixture
15 was maintained for 30 minutes after termination of the dropping. Thereafter resin
varnish II was obtained by isokinetically dropping a mixed liquid consisting of 16 parts
by mass of xylene, 4 parts by mass of n-butanol and 0.2 parts by mass of t-butylperoxy-
2-ethyl hexanoate and maintaining the temperature of the mixture for 1.5 hours after
termination of the dropping. The solid content in the obtained resin varnish II was 49.7
20 mass %, and the viscosity was 9.5 poises. The number-average molecular weight
(GPC, in terms of polystyrene) of the resin in this resin varnish II was 6500, and the acid
value was 160. The acid value of the obtained resin and the solid content in the resin
varnish II were listed in Table 1.

Then, acrylic resin varnish 2 having a solid content of 45.2 mass % was obtained
25 by performing reaction similarly to the aforementioned Manufactural Example 1 except
that 100 parts by mass of the resin varnish II, 29.6 parts by mass of copper acetate and
12.6 parts by mass of pivalic acid were added to a similar reaction vessel.

(Manufactural Example 3) Preparation of Acrylic Resin Varnish 3

50 parts by mass of xylol was added to a reaction vessel similar to that in the
aforementioned Manufactural Example 1 and kept at 90°C. Into this solution, a mixed
liquid consisting of monomers according to blending (parts by mass) shown in Table 1
and 1 part by mass of t-butylperoxy-2-ethyl hexanoate was isokinetically dropped and
5 the temperature of the mixture was maintained for 30 minutes after termination of the
dropping. Thereafter a mixed liquid consisting of 7 parts by mass of xylol and 0.2 parts
by mass of t-butylperoxy-2-ethyl hexanoate was isokinetically dropped over 30 minutes,
and the temperature of the mixture was maintained for 1.5 hours after termination of the
dropping. Thereafter acrylic resin varnish 3 was obtained by cooling the mixed liquid
10 up to 60°C and adding 10 parts by mass of xylol. The solid content in the obtained
acrylic resin varnish 3 was 60.0 mass %, and the viscosity was 7.5 poises. The
number-average molecular weight (GPC, in terms of polystyrene) of the resin in the
acrylic resin varnish 3 was 8000. The solid content in the acrylic resin varnish 3 and
the Gardner viscosity (25°C) of the acrylic resin varnish 3 were listed in Table 1.

15 (Manufactural Example 4) Preparation of Acrylic Resin Varnish 4

64 parts by mass of xylene and 16 parts by mass of n-butanol were added to a
reaction vessel similar to that in the aforementioned Manufactural Example 1 and kept at
115°C. Into this solution, a mixed liquid consisting of monomers according to
blending (parts by mass) shown in Table 1 and 2 parts by mass of t-butylperoxy-2-ethyl
20 hexanoate was isokinetically dropped over 3 hours, and the temperature of the mixture
was maintained for 30 minutes after termination of the dropping. Thereafter resin
varnish IV was obtained by isokinetically dropping a mixed liquid consisting of 16 parts
by mass of xylene, 4 parts by mass of n-butanol and 0.2 parts by mass of t-butylperoxy-
2-ethyl hexanoate over 30 minutes and maintaining the temperature of the mixture for
25 1.5 hours after termination of the dropping. The solid content in the obtained resin
varnish IV was 49.6 mass %, and the viscosity was 6 poises. The number-average
molecular weight (GPC, in terms of polystyrene) of the resin in the resin varnish IV was
6000, and the acid value was 70 mgKOH/g. The acid value of the obtained resin and

the solid content in the resin varnish IV were listed in Table 1.

Then, acrylic resin varnish 4 having a solid content of 50.6 mass % was obtained by performing reaction similarly to the aforementioned Manufactural Example 1 except that 100 parts by mass of the resin varnish IV, 37.06 parts by mass of copper acetate and 60.6 parts by mass of naphthenic acid (NA-165, acid value 165, by Daiwa Yushi Kogyo) were added to a similar reaction vessel.

[Table 1]

		Manufactural Example1	Manufactural Example2	Manufactural Example3	Manufactural Example4
Resin Varnish		I	II	Acrylic Resin Varnish3	IV
Monomer (parts by mass)	EA	58.3	16.30	-	26.02
	CHMA	15.0	15.00	-	15.00
	CHA	-	15.00	-	-
	M-90G	10.0	20.00	-	10.00
	MMA	-	11.17	35.0	-
	AA	16.7	10.27	-	8.98
	MAA	-	12.26	-	-
	TIPSI	-	-	65.0	40.00
Acid Value (mgKOH/g)		130	160	-	70
Solid Content (mass%)		49.8	49.7	60.0	49.6

<Examples 1 to 35 and Comparative Examples 1 to 11>

Antifouling coating compositions were prepared by using the acrylic resin varnishes 1 to 4 obtained in the aforementioned Manufactural Examples 1 to 4 and other components shown in Table 2 to 5 and mixing the same with a high-speed disperser, and long-term antifouling properties, crack resistance and the conditions of the coating films were evaluated according to the following evaluation method. The details of the respective components described in Table 2 to 5 are as follows:

(1) cuprous oxide: "NC-301" by NC Tech

- (2) zinc oxide: "Zinc Oxide Type 2" by Sakai Chemical Industry Co., Ltd.
- (3) colcothar: "Toda Color KN-R" by Toda Kogyo Corporation
- (4) antifouling agent 1: ZPT (zinc pyrithione) ("Zinc Omagin" by Arch Chemicals Co., Ltd.)
- 5 (5) antifouling agent 2: CuPT (copper pyrithione) ("Copper Omagin" by Arch Chemicals Co., Ltd.)
- (6) antifouling agent 3: pyridine triphenylborane ("PK" by Hokko Chemical Industry Co., Ltd.)
- (7) antifouling agent 4: triphenylborane-n-octadecylamine complex ("YN-18-20" by Benny-Toyama Corporation)
- 10 (8) antifouling agent 5: 1,1-dichloro-N-[(dimethylamino)sulfonyl]-1-fluoro-N-phenylmethane sulfenamide ("Preventol A4S" by Lanxes)
- (9) antifouling agent 6: 1,1-dichloro-N-[(dimethylamino)sulfonyl]-1-fluoro-N-(4-methylphenyl)methane sulfenamide ("Preventol A5S" by Lanxes)
- 15 (10) antifouling agent 7: 4,5-dichloro-2-n-octyl-4-isothiazoline-3-one(4,5-dichloro-2-n-octyl-3(2H)isothiazolone) ("Sea-Nine 211" by Rohm and Haas)
- (11) chlorinated paraffin: "Toyoparax A50" by Tosoh Corporation
- (12) wood rosin: "WW Rosin" by Arakawa Chemical Industries, Ltd.
- (13) anti-sagging agent: "Disperon A600-20X" by Kusumoto Chemicals, Ltd.

[Table 2]

Unit:parts by mass		Example												
		1	2	3	4	5	6	7	8	9	10	11	12	13
Acrylic Resin Varnish1		38	38	44	58	38	38	37	39	45	43		7	17
Acrylic Resin Varnish2														
Acrylic Resin Varnish3														
Acrylic Resin Varnish4														
Cuprous Oxide														
Zinc Oxide		29	29	29		29	29	29	23	13	31	31	31	31
Colcothar		6	6			6	6	6	6	6	6	6	6	6
Antifouling Agent1		2	2	2	3		2	2	4	3	0.5	2	2	2
Antifouling Agent2						3								
Antifouling Agent3		6	6	6	12	7		6	8	12	2	7	7	7
Antifouling Agent4							6							
Antifouling Agent5		2												
Antifouling Agent6			2	2	3	3	2	2	3	3	0.5	2	2	2
Antifouling Agent7														
Chlorinated Paraffin		1	1	1		1	1	1	1	1	1	4	2	2
Wood Rosin								3				15	12	6
Anti-Sagging Agent		2	2	2	2	2	2	2	2	2	2	2	2	2
Butyl Cellosolve		2	2	2	2	2	2	2	2	2	2	2	2	2
Xylene		12	12	12	20	9	12	10	12	13	12	29	27	23
Total		100	100	100	100	100	100	100	100	100	100	100	100	100
Long-Term Antifouling Property	3Months	0	0	0	0	0	0	0	0	0	0	0	0	0
	6Months	0	0	0	0	0	0	0	0	0	0	0	0	0
	12Months	0	0	0	0	0	0	0	0	0	5	10	5	0
	18Months	0	0	0	0	0	0	0	0	0	10	20	10	0
	24Months	0	0	0	0	0	0	0	0	0	20	30	20	0
Condition of Coating Film		A	A	A	A	A	A	A	A	A	A	A	A	A
Crack Resistance		A	A	A	A	A	A	A	A	A	A	17	A	A

[Table 3]

Unit:parts by mass		Example								
		14	15	16	17	18	19	20	21	22
Acrylic Resin Varnish1										
Acrylic Resin Varnish2		40	8	18						
Acrylic Resin Varnish3					41	7	17			
Acrylic Resin Varnish4								44	8	19
Cuprous Oxide										
Zinc Oxide		20	20	20	20	20	20	20	20	20
Colcothar		7	7	7	7	7	7	7	7	7
Antifouling Agent1										
Antifouling Agent2		3	3	3	3	3	3	3	3	3
Antifouling Agent3		10	10	10	9	9	9	9	9	9
Antifouling Agent4										
Antifouling Agent5										
Antifouling Agent6		3	3	3	3	3	3	3	3	3
Antifouling Agent7										
Chlorinated Paraffin		2	2	2	3	3	2	3	3	2
Wood Rosin			12	6	2	12	6	2	12	6
Anti-Sagging Agent		2	2	2	2	2	2	2	2	2
Butyl Cellosolve		2	2	2	1	1	1	1	1	1
Xylene		11	31	27	9	33	30	6	32	28
Total		100	100	100	100	100	100	100	100	100
Long-Term Antifouling Property	3Months	0	0	0	0	0	0	0	0	0
	6Months	0	0	0	0	0	0	0	0	0
	12Months	0	5	0	0	0	0	0	0	0
	18Months	0	10	0	0	5	0	0	5	0
	24Months	0	20	0	0	10	0	0	10	0
Condition of Coating Film		A	A	A	A	A	A	A	A	A
Crack Resistance		A	A	A	A	A	A	A	A	A

[Table 4]

Unit:parts by mass		Example												
		23	24	25	26	27	28	29	30	31	32	33	34	35
Acrylic Resin Varnish1			46	8	18									
Acrylic Resin Varnish2						45	8	18						
Acrylic Resin Varnish3									43	7	17			
Acrylic Resin Varnish4												44	8	19
Cuprous Oxide		10	10	10	10	10	10	10	10	10	10	10	10	10
Zinc Oxide		10	10	10	10	10	10	10	10	10	10	10	10	10
Colcothar		8	8	8	8	8	8	8	8	8	8	8	8	8
Antifouling Agent1														
Antifouling Agent2		2	2	2	2	2	2	2	2	2	2	2	2	2
Antifouling Agent3		7	7	7	7	7	7	7	6	6	6	6	6	6
Antifouling Agent4														
Antifouling Agent5														
Antifouling Agent6		2	2	2	2	2	2	2	2	2	2	2	2	2
Antifouling Agent7														
Chlorinated Paraffin		4	1	2	2	1	2	2	1	3	2	1	3	2
Wood Rosin		16		12	6		12	6	2	12	6	2	12	6
Anti-Sagging Agent		2	2	2	2	2	2	2	2	2	2	2	2	2
Butyl Cellosolve		1	1	1	1	1	1	1	1	1	1	1	1	1
Xylene		38	11	36	32	12	36	32	13	37	34	12	36	32
Total		100	100	100	100	100	100	100	100	100	100	100	100	100
Long-Term Antifouling Property	3Months	0	0	0	0	0	0	0	0	0	0	0	0	0
	6Months	0	0	0	0	0	0	0	0	0	0	0	0	0
	12Months	5	0	5	0	0	5	0	0	0	0	0	0	0
	18Months	15	0	10	0	0	10	0	0	5	0	0	5	0
	24Months	25	0	20	0	0	20	0	0	10	0	0	10	0
Condition of Coating Film		A	A	A	A	A	A	A	A	A	A	A	A	A
Crack Resistance		15	A	A	A	A	A	A	A	A	A	A	A	A

[Table 5]

Unit:parts by mass		Comparative Example										
		1	2	3	4	5	6	7	8	9	10	11
Acrylic Resin Varnish1		43	43	43	38				37			
Acrylic Resin Varnish2							36	38				
Acrylic Resin Varnish3											35	
Acrylic Resin Varnish4										37		
Cuprous Oxide							35	35	35	35	35	35
Zinc Oxide		6	6	6	29	18						
Colcothar		7	7	7	6	6	4	5	4	2	2	2
Antifouling Agent1		10		13	2	10	15	6				10
Antifouling Agent2									15	15	15	
Antifouling Agent3		16	16		6							
Antifouling Agent4												
Antifouling Agent5			10	13		13		4				
Antifouling Agent6												
Antifouling Agent7					2							
Chlorinated Paraffin		1	1	1	1	4	3	4	1	1	2	4
Wood Rosin						15				3	4	15
Anti-Sagging Agent		2	2	2	2	2	2	2	2	2	2	2
Butyl Cellosolve		2	2	2	2	2	1	1	1	1	1	1
Xylene		13	13	13	12	30	4	5	5	4	4	31
Total		100	100	100	100	100	100	100	100	100	100	100
Long-Term Antifouling Property	3Months	0	0	0	0	20	0	0	0	0	0	0
	6Months	30	30	40	50	70	40	50	40	0	30	30
	12Months	50	60	70	80	100	60	80	60	10	50	60
	18Months	70	80	90	100	100	80	100	80	40	70	100
	24Months	100	100	100	100	100	100	100	100	60	90	100
Condition of Coating Film		A	A	A	A	B	B	B	B	B	B	B
Crack Resistance		A	A	A	A	7	10	15	12	13	14	5

(Evaluation)

(1) Long-Term Antifouling Property

5

Test plates having antifouling coating films were obtained by applying the antifouling coating compositions according to Examples 1 to 35 and Comparative

Examples 1 to 11 to blast plates previously coated with anticorrosive paints, so that dried film thicknesses were 300 μm and drying the same by being left standing the same indoors for two days and two nights. The obtained test plates were subjected to an organism adherence test with an experimental raft set in Seaside Laboratory of Nippon Paint Marine Coats Co., Ltd. located in Tamano-Shi, Okayama-Ken, and antifouling properties were evaluated. Tables 2 to 5 show the results. Months in Tables 2 to 5 show raft dipping periods. Numerical values show rates (%) (visual determination) of organism adherence areas occupying coating film areas, and those of not more than 15 % were evaluated as acceptable.

(2) Condition of Coating Film

The conditions of the coating films in the test plates of the raft dipping periods of 6 months in the aforementioned long-term antifouling property test were observed by visual recognition and rubbing, and evaluated. Tables 2 to 5 show the results. Those in which no cracks were confirmed were evaluated as A, and those in which cracks were confirmed were evaluated as B.

(3) Crack Resistance Test (Alternate Immersion Test)

Test plates having antifouling coating films were obtained by applying the antifouling coating compositions according to Examples 1 to 35 and Comparative Examples 1 to 11 to blast plates previously coated with anticorrosive paints, so that dried film thicknesses were 300 μm and drying the same by being left standing the same indoors for two days and two nights. The obtained test plates were dipped in seawater of 40°C for one week and thereafter subjected to indoor drying for one week, and an alternate immersion test regarding this as one cycle was executed up to 20 cycles at the maximum. When any coating film was cracked in an intermediate stage, the test was terminated at the time when the crack took place, and the cycle number at this point of time was described in Tables 2 to 5. Those not cracked upon execution of 20 cycles were evaluated as A.

As shown in Tables 2 to 5, it is understood that the antifouling coating films

obtained from the antifouling coating compositions according to Examples can maintain remarkably excellent antifouling properties over a long period and are also excellent in crack resistance. It has been recognized that the conditions of the coating films are also excellent over a long period. In particular, it is understood that an excellent
5 antifouling property can be exhibited over a longer period when employing any of the acrylic resin varnishes 1 to 4 containing hydrolyzable resin and chlorinated paraffin and/or rosin in the ratio of 100:0 to 50:50.

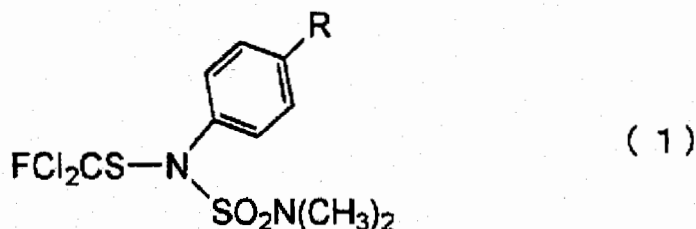
The embodiment and Examples disclosed this time are to be considered as illustrative in all points and not restrictive. The range of the present invention is shown
10 not by the above description but by the scope of claims for patent, and it is intended that all modifications within the meaning and range equivalent to the scope of claims for patent are included.

CLAIMS

1. An antifouling coating composition containing binder resin (A) and an antifouling agent (B), wherein

5 said antifouling agent (B) contains metal pyrithione (B1), triphenylborane amine salt (B2) and a sulfamide-based compound (B3) expressed by the following general formula (1):

[Chemical Formula 1]



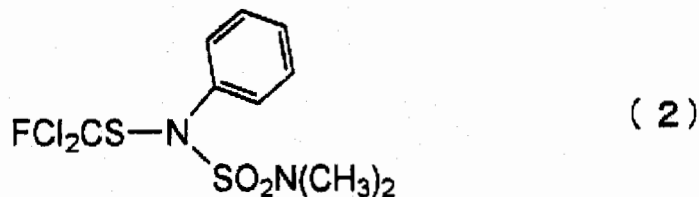
10 (in the above general formula (1), R represents a hydrogen atom or a linear or branched alkyl group having 1-10 carbon atoms).

2. The antifouling coating composition according to claim 1, wherein said triphenylborane amine salt (B2) includes pyridine triphenylborane.

15

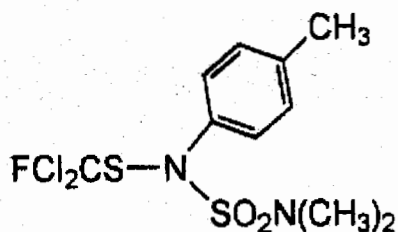
3. The antifouling coating composition according to claim 1, wherein said sulfamide-based compound (B3) includes at least one compound selected from compounds expressed by the following formula (2) and the following formula (3):

[Chemical Formula 2]



20

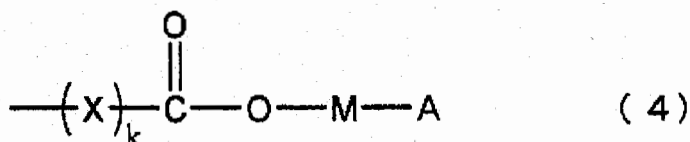
[Chemical Formula 3]



(3)

4. The antifouling coating composition according to claim 1, wherein
5 said binder resin (A) includes resin having, in a side chain thereof, at least one group expressed by the following general formula (4):

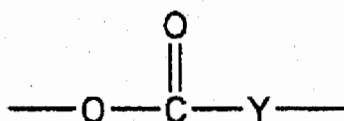
[Chemical Formula 4]



(4)

(in the above general formula (4), X represents a group expressed by:

- 10 [Chemical Formula 5]

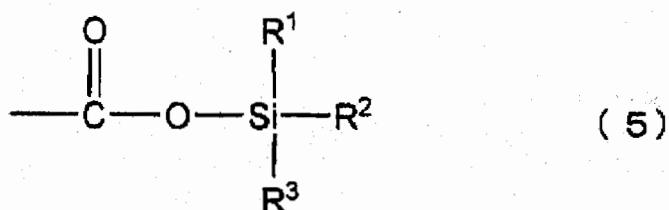


k represents 0 or 1, Y represents hydrocarbon, M represents a divalent metal, and A represents an organic acid residue of a monobasic acid).

15

5. The antifouling coating composition according to claim 1, wherein
said binder resin (A) includes resin having, in a side chain thereof, at least one group expressed by the following general formula (5):

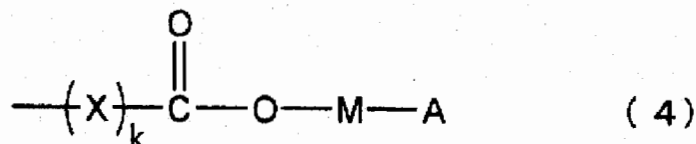
[Chemical Formula 6]



(in the above general formula (5), R^1 , R^2 and R^3 are the same or different from one another and represent a hydrocarbon residue having 1-20 carbon atoms).

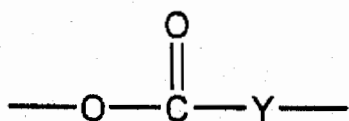
- 5 6. The antifouling coating composition according to claim 1, wherein said binder resin (A) includes resin, in a side chain thereof, having at least one group expressed by the following general formula (4):

[Chemical Formula 7]



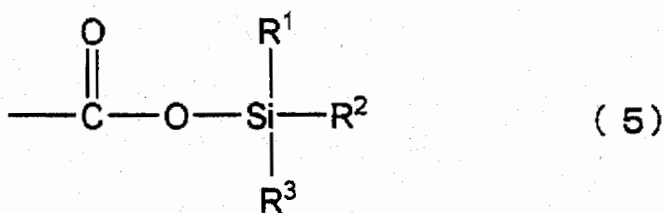
- 10 (in the above general formula (4), X represents a group expressed by:

[Chemical Formula 8]



- 15 k represents 0 or 1, Y represents hydrocarbon, M represents a divalent metal, and A represents an organic acid residue of a monobasic acid), and at least one group expressed by the following general formula (5):

[Chemical Formula 9]



(in the above general formula (5), R^1 , R^2 and R^3 are the same or different from one another and represent a hydrocarbon residue having 1-20 carbon atoms).

5

7. The antifouling coating composition according to claim 4 or 6, wherein said monobasic acid is monobasic cyclic organic acid.

10

8. The antifouling coating composition according to claim 4 or 6, wherein said monobasic acid is at least one type selected from the group consisting of rosins, hydrogenated rosins, disproportionated rosins, naphthenic acid, abietic acid, dehydroabietic acid and hydrogenated abietic acid.

15

9. The antifouling coating composition according to claim 1, wherein said binder resin (A) contains at least one selected from the group consisting of chlorinated paraffin, rosins and hydrogenated rosins.

20

10. An antifouling coating film formed with the antifouling coating composition according to claim 1.

11. A marine vessel or an underwater structure having the antifouling coating film according to claim 10.