DESCRIPTION

TITLE OF INVENTION

Antifouling Paint Composition, Antifouling Coating Film, and Method of Controlling Hydrolysis Rate of Antifouling Coating Film

TECHNICAL FIELD

The present invention relates to an antifouling paint composition, and more specifically to an antifouling paint composition that allows formation of an antifouling coating film having a constant hydrolysis rate in water. Furthermore, the present invention relates to an antifouling coating film formed from the antifouling paint composition and a method of controlling a hydrolysis rate of the antifouling coating film in water.

BACKGROUND ART

Underwater structures such as marine vessels, various fishnets including those for aquaculture, harbor facilities, oil fences, piping materials, bridges, buoyages, industrial water facilities, and sea bottom bases are exposed at all times in water where living organisms inhabit. Accordingly, as time passes, microorganisms such as bacteria adhere to these underwater structures while plants and animals such as acorn barnacles, sea mussels, sea lettuce, and diatoms that take lives of these bacteria for food also adhere to these underwater structures. When the surface of the underwater structure is covered with these microorganisms and plants and animals, there occur damages such as corrosion of the covered area, a decrease in fuel efficiency of vessels due to an increase in frictional resistance of vessels to seawater, massive death of fish and shellfishes due to clogging of fishnets, sinking of a buoyage due to reduced buoyancy, deterioration in operation efficiency, and the like.

In order to prevent adhesion of these harmful organisms, it is general to use a method of painting an antifouling paint containing one or more types of antifouling agents and a binder resin on the surface of the underwater structure to form an antifouling coating film on this surface. Various types of antifouling components

each effective as an antifouling agent have been found so far and put into practical use. Among others, cuprous oxide (Cu_2O) is known as an animal-resistant antifouling agent that can effectively prevent adhesion of animals such as acorn barnacles and regarded as one of frequently used antifouling agents. Various antifouling paints are proposed that include cuprous oxide as an antifouling agent or include a combination of cuprous oxide and another antifouling agent having an antifouling effect against algae.

For example, Japanese Patent Laying-Open No. 10-298455 (PTL 1) discloses an antifouling paint composition containing cuprous oxide; bis(2-pyridinethiol-1-oxide) copper salt; and one type of compounds selected from 2,4,5,6-tetrachloroisophthalonitrile, N,N-dimethyl-dichlorophenylurea, and zinc dimethyl dithiocarbamate. Furthermore, Japanese Patent Laying-Open No. 2001-342432 (PTL 2) discloses, as antifouling agents, 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; and a combination of cuprous oxide, 2-pyridinethiol-1-oxide copper salt and zinc ethylenebisdithiocarbamate, and the like.

On the other hand, as a binder resin used for an antifouling paint, a hydrolyzable resin having a hydrolyzable group such as, for example, a metal-containing group in a side chain of the resin has been used in recent years since an antifouling coating film of the hydrolyzable resin is self-polished by gradual hydrolysis due to immersion in water, which allows a long-term antifouling property to be exhibited (see PTL 1 and PTL 2 as described above).

CITATION LIST

PATENT LITERATURE

PTL 1: Japanese Patent Laying-Open No. 10-298455

PTL 2: Japanese Patent Laying-Open No. 2001-342432

SUMMARY OF INVENTION

TECHNICAL PROBLEM

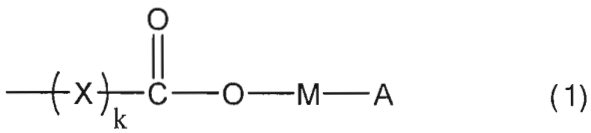
Although cuprous oxide (Cu_2O) is an effective antifouling component particularly as an animal-resistant antifouling agent, it is generally necessary to

increase the blending amount of cuprous oxide in order to obtain an antifouling paint composition having a sufficiently high antifouling property by using cuprous oxide. However, in the antifouling paint composition containing a large amount of cuprous oxide and a hydrolyzable resin as a binder resin, the hydrolysis rate of the formed antifouling coating film in water does not become constant, which causes a problem that a high antifouling property cannot be exhibited in a stable manner. Specifically, depending on the type of the hydrolyzable group contained in the hydrolyzable resin, even if the hydrolysis rate was relatively constant in the early stage of immersion in water, the hydrolysis rate sometimes rose rapidly after a lapse of a certain time period of immersion in water, or the hydrolysis rate was constant for a while after immersion in water, but the hydrolysis rate subsequently fell, and self-polishing of the coating film hardly progressed.

Accordingly, an object of the present invention is to provide an antifouling paint composition that allows formation of an antifouling coating film having a constant hydrolysis rate for a long period of time, thereby allowing a high antifouling property to be exhibited for a long period of time (for example, for the entire period during ship navigation) in a stable manner. Also, another object of the present invention is to provide an antifouling coating film formed from the antifouling paint composition, and a method of controlling the hydrolysis rate of the antifouling coating film in water by using the antifouling paint composition.

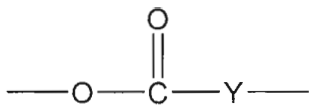
SOLUTION TO PROBLEM

The present invention provides an antifouling paint composition containing two or more types of antifouling agents containing 4-bromo-2-(4-chlorophenyl)-5-(trifluoromethyl)-1H-pyrrole-3-carbonitrile; and an acrylic resin having a group expressed in a general formula (1)



(1)

(where X is a group expressed in a general formula



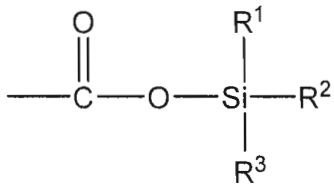
k is 0 or 1, Y is a hydrocarbon, M is a divalent metal, and A represents an organic acid residue of a monobasic acid) in a side chain.

It is preferable that the antifouling agents include a first antifouling agent that is 4-bromo-2-(4-chlorophenyl)-5-(trifluoromethyl)-1H-pyrrole-3-carbonitrile; and a second antifouling agent that is at least one type selected from the group consisting of zinc pyrithione, copper pyrithione, pyridine-triphenylborane, 1,1-dichloro-N-[(dimethylamino)sulfonyl]-1-fluoro-N-phenylmethanesulfenamide, 1,1-dichloro-N-[(dimethylamino)sulfonyl]-1-fluoro-N-(4-methylphenyl) methanesulfenamide, N'-(3,4-dichlorophenyl)-N,N'-dimethylurea, N'-tert-butyl-N-cyclopropyl-6-(methylthio)-1,3,5-triazine-2,4-diamine, and 4,5-dichloro-2-n-octyl-4-isothiazoline-3-one.

It is preferable that a ratio between a content of the first antifouling agent and a content of the second antifouling agent is within a range from 1/15 to 1/1 in a mass ratio.

The antifouling paint composition of the present invention does not need to contain cuprous oxide as the antifouling agent.

Furthermore, the acrylic resin may further have a group expressed in a general formula (2)



(2)

(where R^1, R^2 and R^3 are identical or different and each represent a hydrocarbon residue having a carbon number from 1 to 20) in a side chain.

Furthermore, the present invention provides an antifouling coating film formed using the antifouling paint composition of the present invention. Furthermore, the present invention provides a method of controlling a hydrolysis rate of an antifouling coating film in water that is formed on a surface of an object to be coated. The

controlling method of the present invention is characterized by using the antifouling paint composition of the present invention as a paint composition forming the antifouling coating film.

ADVANTAGEOUS EFFECTS OF INVENTION

According to the antifouling paint composition of the present invention, it becomes possible to form an antifouling coating film that is hydrolyzed at a constant rate for a long period of time, thereby allowing a long-term antifouling performance to be exhibited in a stable manner. Furthermore, according to the antifouling paint composition of the present invention, it becomes possible to form an antifouling coating film that is excellent in long-term antifouling property and also excellent in resistance to cracking. The antifouling paint composition of the present invention can be suitably used as an antifouling paint for preventing fouling on the surface of underwater structures such as marine vessels, various fishnets including those for aquaculture, harbor facilities, oil fences, piping materials, bridges, buoyages, industrial water facilities, and sea bottom bases.

Furthermore, according to the method of controlling the hydrolysis rate of the present invention, the hydrolysis rate of the antifouling coating film in water that is formed on the surface of an object to be coated can be rendered constant.

BRIEF DESCRIPTION OF DRAWINGS

Fig. 1 is a photograph showing an example of the state of the surface of a test plate after an antifouling property test (organism adhesion test) (24 months after immersion).

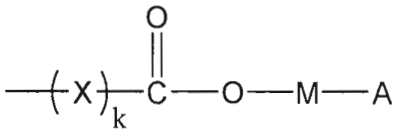
DESCRIPTION OF EMBODIMENTS

The antifouling paint composition of the present invention includes a hydrolyzable resin having a specific hydrolyzable group that is a binder resin, the first antifouling agent that is 4-bromo-2-(4-chlorophenyl)-5-(trifluoromethyl)-1H-pyrrole-3-carbonitrile, and one type or two or more types of antifouling agents different from the first antifouling agent. The antifouling coating film formed from such an antifouling paint composition hydrolyzes at a constant rate for a long period of time in

water, especially in seawater. Therefore, according to the antifouling paint composition of the present invention, it becomes possible to obtain a coating film that exhibits a high antifouling performance for a long period of time in a stable manner. Furthermore, the antifouling coating film formed from the antifouling paint composition of the present invention is excellent in long-term antifouling property and also in resistance to cracking. For example, when an antifouling paint composition is applied to a marine vessel and the like, an antifouling coating film is repeatedly exposed to a cycle of immersion in seawater for a certain time period and landing after this immersion in seawater. Therefore, the antifouling coating film is required to have flexibility sufficient to withstand such a condition. According to the present invention, it becomes possible to form an antifouling coating film that hardly undergoes cracking even after repetition of such a cycle. Each component contained in the antifouling paint composition of the present invention will be hereinafter described in detail.

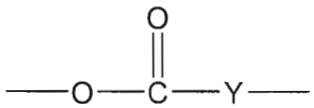
<Binder Resin>

The binder resin used for an antifouling paint composition of the present invention is an acrylic resin (hereinafter referred to as an acrylic resin (A)) having a group expressed in a general formula (1) below in a side chain.



(1)

Here, X is a group expressed in a general formula



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

Generally, acrylic resin (A) exhibits such a property as being gradually hydrolyzed in water (particularly, in sea water), owing to hydrolyzability of metal ester bond included in the group expressed in the general formula (1) above. Therefore, the antifouling coating film formed from such an antifouling paint composition containing

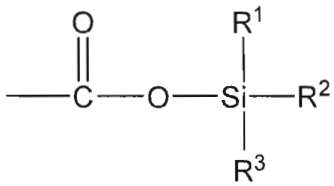
the acrylic resin as a binder resin has its surface self-polished by being immersed in water, thereby causing an antifouling component (antifouling agents, and a metal component and an organic acid component generated by hydrolysis of the metal ester bond) to be continuously released from the surface of the coating film. Therefore, antifouling performance is exhibited until the coating film is completely consumed.

However, the present inventors' studies showed that the antifouling coating film formed from an antifouling paint composition containing acrylic resin (A) as a binder resin and cuprous oxide as a main component of the antifouling agent exhibits a constant hydrolysis rate for a while after immersion in water, but the hydrolysis rate subsequently falls and self-polishing of the coating film hardly progresses, with the result that sufficiently high antifouling performance cannot be exhibited for a long period of time. It is considered that such a phenomenon is caused by interaction between the metal ester portion of the group expressed in the general formula (1) above and cuprous oxide. In other words, it is considered specifically as follows. Even if hydrolysis of the metal ester portion smoothly progresses in the early stage of immersion in water, when self-polishing of the coating film progresses to some extent, the ionized cuprous oxide comes to show a certain interaction with the side chain expressed in the general formula (1) above. This causes a stronger interaction between the metal ester portion and cuprous oxide, thereby making it less likely to cause hydrolysis of the metal ester portion. Consequently, renewability of the coating film by hydrolysis becomes poor.

In the present invention, in order to solve the above-described problems, the antifouling agent described below in detail is used together with acrylic resin (A). By using this antifouling agent, even when acrylic resin (A) is used as a binder resin, the hydrolysis rate of the antifouling coating film can be kept constant for a long period of time, so that high antifouling performance can be exhibited for a long period of time in a stable manner.

Examples of acrylic resin (A) used in the present invention may include an acrylic resin having a group expressed in the general formula (1) above as a

hydrolyzable group in a side chain and not having a group expressed in the general formula (2) below in a side chain (this acrylic resin will be hereinafter referred to as an acrylic resin (A1)); an acrylic resin having both of a group expressed in the general formula (1) above and a group expressed in the general formula (2) below as a hydrolyzable group in a side chain (this acrylic resin will be hereinafter referred to as an acrylic resin (A2)); and the like. Each of these resins may be used alone or in combination with two or more types of resins. Furthermore, acrylic resin (A1) and acrylic resin (A2) may be used together. In the present specification, the "acrylic resin" means a resin, at least a part of which is composed of a constitutional unit derived from a (meth)acrylic acid or a derivative thereof, or (meth)acrylic ester. The derivative of a (meth)acrylic acid also includes a (meth)acrylic acid metal salt.



(2)

(where R^1, R^2 and R^3 are identical or different and each represent a hydrocarbon residue having a carbon number from 1 to 20).

[Acrylic Resin (A1)]

Acrylic resin (A1) is an acrylic resin having a group expressed in the general formula (1) above as a hydrolyzable group in a side chain and not having a group expressed in the general formula (2) above in a side chain, which is typically an acrylic resin having only a group expressed in the general formula (1) above as a hydrolyzable group in a side chain. In the general formula (1) above, M is a divalent metal and, for example, may be 3A to 7A, 8 and 1B to 7B group elements in the periodic table. Among them, M is preferably copper or zinc.

In the general formula (1) above, A is an organic acid residue of a monobasic acid. Monobasic acid may be preferably, for example, a monobasic cyclic organic acid and the like. Monobasic cyclic organic acid is not particularly limited, but may be, for example, not only those having a cycloalkyl group such as naphthenic acid but

also a resin acid such as a tricyclic resin acid, a salt thereof, and the like. Tricyclic resin acid is not particularly limited, which may be, for example, a monobasic acid having a diterpene-based hydrocarbon skeleton and the like, and examples thereof may be a compound having an abietane, pimarane, isopimarane, or labdane skeleton, and more specifically, examples thereof may be abietic acid, neoabietic acid, dehydroabietic acid, hydrogenated abietic acid, palustric acid, pimaric acid, isopimaric acid, levopimaric acid, dextropimaric acid, sandaracopimaric acid, and a salt thereof, and the like. Among these, abietic acid, hydrogenated abietic acid, and a salt thereof are preferred, because hydrolysis moderately occurs, which leads to an excellent long-term antifouling property and also excellent resistance to cracking of a coating film and availability. Furthermore, a monobasic cyclic organic acid may preferably have an acid value of 120 to 220 mgKOH/g. By using a monobasic cyclic organic acid having an acid value of not more than 220 mgKOH/g, the viscosity of the obtained binder resin (A1) can be lowered, thereby reducing the solvent content in the paint to be obtained. This is because the viscosity of binder resin (A1) greatly depends on the interaction between functional groups expressed in general formula (1). Binder resin (A1) obtained by using a monobasic cyclic organic acid having an acid value of not more than 220 mgKOH/g tends to cause an increase in steric repulsion of the monobasic cyclic organic acid. In addition, it is considered that this steric repulsion acts to inhibit the interaction between the functional groups expressed in the general formula (1), with the result that the viscosity of binder resin (A1) can be lowered. Furthermore, when the acid value is less than 120, the binder resin (A1) to be obtained becomes too hydrophobic, thereby preventing hydrolysis of the obtained coating film, which is not preferable.

The monobasic cyclic organic acid described above does not have to be highly purified, and for example, turpentine, a resin acid of a pine, or the like can also be employed. Examples thereof can include rosin, hydrogenated rosin, disproportionated rosin, and the like, as well as naphthenic acid. The rosin herein refers to gum rosin, wood rosin, tall oil rosin, and the like. The rosin, the hydrogenated rosin, and the

disproportionated rosin are preferred because they are inexpensive and readily available and excellent in handleability, and they exhibit a long-term antifouling property. The above-described monobasic cyclic organic acid may be used alone or in combination of two or more types.

Monobasic acids that can be used in the present invention other than the above-described monobasic cyclic organic acids may be, for example, those having a carbon number from 1 to 20 such as acetic acid, propionic acid, butyric acid, lauryl acid, stearic acid, linolic acid, oleic acid, chloroacetic acid, fluoroacetic acid, and valeric acid. These monobasic acids may be used alone or in combination of two or more types.

Y in the general formula (1) above is not particularly limited as long as it is a hydrocarbon, and examples thereof may be a residue obtained when dibasic acid such as phthalic acid, succinic acid and maleic acid are added to a polymerizable unsaturated organic acid monomer.

A method of producing acrylic resin (A1) is not particularly limited, and examples thereof include (i) a method of causing reaction among a resin obtained by polymerization of a polymerizable unsaturated organic acid and another copolymerizable unsaturated monomer, a monobasic acid and a metal compound; and (ii) a method of causing reaction among a polymerizable unsaturated organic acid, a metal compound and a monobasic acid or causing reaction between a polymerizable unsaturated organic acid and a metal salt of a monobasic acid, and thereafter polymerizing the obtained metal containing unsaturated monomer and another copolymerizable unsaturated monomer; and the like. The same resin structure is provided in each of the resin obtained in the process of the method (i), that is, the resin obtained by polymerization of a polymerizable unsaturated organic acid and another copolymerizable unsaturated monomer; and the resin obtained by causing reaction among a polymerizable unsaturated organic acid, a metal compound and a monobasic acid or causing reaction between a polymerizable unsaturated organic acid and a metal salt of a monobasic acid, and thereafter polymerizing the obtained metal containing unsaturated monomer and another copolymerizable unsaturated monomer in

accordance with the method (ii), and further hydrolyzing its side chain expressed in the general formula (1). These resins are also collectively referred to as a "base acrylic resin (a1)" in the present specification.

Polymerizable unsaturated organic acid in the above-described methods (i) and (ii) is not particularly limited, and examples thereof include a polymerizable unsaturated organic acid having one or more carboxyl groups, and the like. More specifically, examples of the polymerizable unsaturated organic acid include an unsaturated monobasic acid such as (meth)acrylic acid; an unsaturated dibasic acid and monoalkyl ester thereof such as maleic acid and monoalkyl ester thereof, itaconic acid and monoalkyl ester thereof; a dibasic acid adduct of unsaturated-monobasic acid hydroxy alkyl 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. These polymerizable unsaturated organic acids may be used alone or in combination of two or more types. Furthermore, in the method (ii), a part or all of the metal containing unsaturated monomer may be replaced with a divalent metal di(meth)acrylate and then used. When divalent metal di(meth)acrylate is used, a resin has a cross-linking structure via the group expressed in the general formula (1), and this resin can also be used.

The above-described another copolymerizable unsaturated monomer is not particularly limited, and examples thereof may be, as (meth)acrylic esters, (meth)acrylic acid alkyl ester with an ester portion having a carbon number from 1 to 20 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 (meth)acrylic acid alkyl ester with an ester portion having a carbon number from 1 to 20 such as 2-hydroxypropyl (meth)acrylate and 2-hydroxyethyl (meth)acrylate; (meth)acrylic acid cyclic hydrocarbon ester such as phenyl (meth)acrylate and cyclohexyl (meth)acrylate; (meth)acrylic acid polyalkyleneglycol ester such as polyethyleneglycol mono(meth)acrylate and polyethyleneglycol mono

(meth)acrylate representing a degree of polymerization of 2 to 10; alkoxyalkyl (meth)acrylate having a carbon number from 1 to 3; (meth)acrylamide; a vinyl compound such as styrene, α-methylstyrene, vinyl acetate, vinyl propionate, vinyl benzoate, vinyltoluene, and acrylonitrile; crotonic acid esters; diester of unsaturated dibasic acid such as maleic acid diesters and itaconic acid diesters. The ester portion of (meth)acrylic esters described above is preferably an alkyl group having a carbon number from 1 to 8, and more preferably an alkyl group having a carbon number from 1 to 6, which is preferably methyl (meth)acrylate, ethyl (meth)acrylate, butyl (meth)acrylate, and cyclohexyl (meth)acrylate. These may be used alone or in combination of two or more types.

The above-described metal compound is not particularly limited, and examples thereof include metal oxide, metal hydroxide, metal chloride, metal sulfide, basic metal carbonate, acetic acid metal salt, and the like. Also, the monobasic acid described above is not particularly limited, and examples thereof may be those as described above.

Although the number average molecular weight (GPC, in terms of polystyrene) of base acrylic resin (a1) described above is not particularly limited, it is preferably 2000 or more and 100000 or less, and more preferably 3000 or more and 40000 or less. The number average molecular weight less than 2000 may cause deterioration in the film forming performance of the coating film while the number average molecular weight exceeding 100000 may cause deterioration in the storage stability of the obtained paint, which is not only suitable for practical use, but also not preferable in terms of public health and economical efficiency since a large amount of dilution solvents needs to be used during coating.

Acrylic resin (A1) contains at least one group expressed in general formula (1). By adjusting the content of the group expressed in the general formula (1), the elution rate of the coating film into water (hydrolysis rate of the coating film) can be controlled at a desirable elution rate. The content of the group expressed in the general formula (1) above can be mainly adjusted by adjusting the acid value of base acrylic resin (a1), and the acid value of base acrylic resin (a1) is preferably 100 to 250 mgKOH/g.

When the acid value is less than 100 mgKOH/g, the amount of metal salt bonded to a side chain is decreased, which may deteriorate the antifouling property. When the acid value exceeds 250 mgKOH/g, the elution rate becomes too high, and accordingly, a long-term antifouling property tends to be hardly achieved.

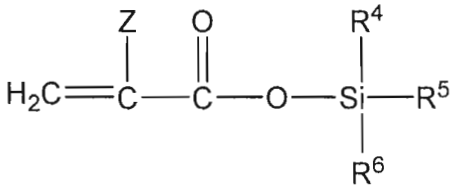
[Acrylic Resin (A2)]

Acrylic resin (A2) has both of a group expressed in the general formula (1) above and a group expressed in the general formula (2) above each as a hydrolyzable group in a side chain. In the general formula (2) above, R^1, R^2 and R^3 are identical or different and each represent a hydrocarbon residue having a carbon number from 1 to 20, and specific examples thereof include a linear or branched alkyl group having a carbon number not more than 20, such as a methyl group, an ethyl group, an 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; a cyclic alkyl group such as a cyclohexyl group and a substituted cyclohexyl group; an aryl group, a substituted aryl group, and the like. Examples of the substituted aryl group include an aryl group substituted with halogen, an alkyl group having a carbon number up to around 18, an acyl group, a nitro group, an amino group, or the like, and the like. Among these, since a stable polishing rate (polishing speed) can be exhibited in the obtained coating film and antifouling performance can be maintained in a stable manner for a long period, an isopropyl group and the like are preferable.

A method of producing acrylic resin (A2) is not particularly limited, and examples thereof include a method (I) of causing reaction among a resin obtained by polymerization of a polymerizable unsaturated organic acid, a monomer component having a triorganosilyl group and another copolymerizable unsaturated monomer, a monobasic acid and a metal compound; and a method (II) of polymerization of a metal-containing unsaturated monomer obtained by causing reaction among a polymerizable unsaturated organic acid, a metal compound and a monobasic acid or reaction between

a polymerizable unsaturated organic acid and a metal salt of a monobasic acid; a monomer component having a triorganosilyl group; and another copolymerizable unsaturated monomer; and the like. The same resin structure is provided in each of the resin obtained in the process of the method (I), that is, the resin obtained by polymerization of a polymerizable unsaturated organic acid, a monomer component having a triorganosilyl group and another copolymerizable unsaturated monomer, and the resin obtained by polymerization of a metal-containing unsaturated monomer obtained by causing reaction among a polymerizable unsaturated organic acid, a metal compound and a monobasic acid or reaction between a polymerizable unsaturated organic acid and a metal salt of a monobasic acid; a monomer component having a triorganosilyl group; and another copolymerizable unsaturated monomer in accordance with the method (II), and thereafter hydrolyzing its side chain expressed in the general formula (1). These resins are also collectively referred to as a "base acrylic resin (a2)" in the present specification.

As the monomer component having the triorganosilyl group described above, triorganosilyl (meth)acrylate expressed in a general formula (3) below can be preferably used.



(3)

In triorganosilyl (meth)acrylate expressed in the general formula (3), Z represents a hydrogen atom or a methyl group. The above-described R^4, R^5 and R^6 are identical or different and each represent a hydrocarbon residue having a carbon number from 1 to 20, and examples thereof may be a hydrocarbon residue similar to those of R^1, R^2 and R^3 described above.

Specific examples of triorganosilyl (meth)acrylate expressed in the general formula (3) above 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-hexyl silyl (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, dicyclohexyl-phenylsilyl (meth)acrylate, t-butyldiphenylsilyl (meth)acrylate, lauryl-diphenylsilyl (meth)acrylate, t-butyl-m-nitrophenylmethylsilyl (meth)acrylate, and the like. Among them, tri-i-propylsilyl (meth)acrylate is preferable since it can maintain a stable polishing rate (polishing speed) for a long period of time. These triorganosilyl (meth)acrylates may be used alone or in combination of two or more types.

Examples of polymerizable unsaturated organic acid, another copolymerizable unsaturated monomer, metal compound, and monobasic acid as described above may be those described with regard to acrylic resin (A1). These polymerizable unsaturated organic acid, another copolymerizable unsaturated monomer and the like may be used alone or in combination of two or more types.

The number average molecular weight (GPC, in terms of polystyrene) of the above-described base acrylic resin (a2) is not particularly limited, and is preferably 2000 or more and 100000 or less, and more preferably 3000 or more and 40000 or less. The number average molecular weight less than 2000 may cause deterioration in the film forming performance of the coating film while the number average molecular weight exceeding 100000 may cause deterioration in the storage stability of the obtained paint, which is not only suitable for practical use, but also not preferable in terms of public health and economical efficiency since a large amount of dilution solvents needs to be used during coating.

Acrylic resin (A2) has at least one group expressed in the general formula (1) above and at least one side chain expressed in the general formula (2) above. By adjusting the total content of the groups expressed in the general formula (1) and the

general formula (2), the elution rate of the coating film into water (hydrolysis rate of the coating film) can be controlled at a desirable elution rate. The total content of the groups expressed in the general formula (1) and the general formula (2) can be adjusted mainly by adjusting the acid value of base acrylic resin (a2), which is preferably set at 30 to 200 mgKOH/g. When the acid value is less than 30 mgKOH/g, the amount of metal salt to be bonded to a side chain is decreased, which may deteriorate the antifouling property. When the acid value exceeds 200 mgKOH/g, the elution rate becomes too high, and accordingly, a long-term antifouling property tends to be hardly achieved.

In the present invention, binder resins other than the above-described acrylic resin (A) may be used as a binder resin. By a combination use of other binder resins, the antifouling performance or resistance to cracking of a coating film may be further improved, and the physical properties and the consumption rate of the coating film can be more readily adjusted. Examples of other binder resins include chlorinated paraffin, polyvinyl ether, polypropylene sebacate, partially hydrogenated terphenyl, polyvinyl acetate, poly (meth)acrylic acid alkyl esters, polyether polyol, alkyd resin, polyester resin, polyvinyl chloride, silicone oil, wax; Vaseline; liquid paraffin, rosin, hydrogenated rosin, naphthenic acid, an aliphatic acid, a divalent metal salt thereof, and the like. Particularly, chlorinated paraffin, rosin and hydrogenated rosin are preferably used. Other binder resins may be used alone or in combination of two or more types.

The amount of use of other binder resins described above can be set at 0 to 150 parts by mass with respect to 100 parts by mass of acrylic resin (A) in a mass ratio based on the resin solid content. In consideration of improving effects for the antifouling performance and the resistance to cracking and the like, it is preferable to set the amount of use of other binder resins at 0 to 100 parts by mass with respect to 100 parts by mass of acrylic resin (A).

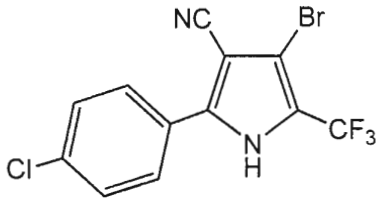
Furthermore, the antifouling paint composition of the present invention may contain a hydrolyzable resin other than acrylic resin (A) as a binder resin. Examples

of hydrolyzable resins other than acrylic resin (A) include an acrylic resin (B) having a group expressed in the general formula (2) above in a side chain and not having a group expressed in the general formula (1) above. Although the coating film containing acrylic resin (B) as a binder resin exhibits a relatively constant hydrolysis rate in the early stage of immersion in water, the hydrolysis rate tends to subsequently rise abruptly. Accordingly, in order to form an antifouling coating film that is hydrolyzed at a constant rate for a long period of time, the content of acrylic resin (B) is preferably not more than 50 parts by mass, and more preferably not more than 30 parts by mass, with respect to 100 parts by mass of acrylic resin (A) in a mass ratio based on the resin solid content.

In the antifouling paint composition of the present invention, the content of the binder resin is preferably 30 to 70 mass %, and more preferably 40 to 65 mass %, in the solid content contained in the antifouling paint composition. When the content is less than 30 mass %, defects such as cracks or peel-off may occur in the coating film. Furthermore, when the content exceeds 70 mass %, a desirable antifouling effect tends to be hardly achieved. It is to be noted that the solid content contained in the antifouling paint composition means the total components contained in the antifouling paint composition other than the solvent.

<Antifouling Agent>

The antifouling paint composition of the present invention contains two or more types of antifouling agents including 4-bromo-2-(4-chlorophenyl)-5-(trifluoromethyl)-1H-pyrrole-3-carbonitrile (which will be hereinafter referred to as the first antifouling agent) expressed in the formula (4) below.



(4)

The above-described first antifouling agent is an antifouling component that is effective as an animal-resistant antifouling agent. Therefore, by using the first

antifouling agent, use of cuprous oxide conventionally frequently used can be completely eliminated or significantly reduced. Consequently, the hydrolysis rate of the antifouling coating film containing an acrylic resin (A) as a binder resin can be set at a constant rate for a long period of time. Furthermore, as cuprous oxide is not used or reduced, the specific gravity of the antifouling paint can be lowered while limitation on the material of the object to be coated can be alleviated. Since the antifouling paint containing cuprous oxide causes corrosion of an aluminum base material, it could not be used for an aluminum object to be coated. The antifouling paint composition of the present invention however can be used also for such an object to be coated without limitation. Furthermore, the blending amount of cuprous oxide that shows redness is reduced, it becomes possible to adjust the color of a coating film to be obtained.

The antifouling paint composition of the present invention contains at least one type of the second antifouling agents in addition to the above-described first antifouling agent. This allows formation of an antifouling coating film exhibiting a high antifouling property against not only aquatic animals but also plants such as algae, and having an excellent antifouling performance against the entire aquatic organisms. As the second antifouling agent, it is preferable to employ an antifouling component that exhibits a high antifouling property against aquatic plants such as algae, and examples thereof include zinc pyrithione (2-pyridinethiol-1-oxide zinc salt); copper pyrithione (2-pyridinethiol-1-oxide copper salt); triphenylborane-amine complexes such as pyridine-triphenylborane; 1,1-dichloro-N-[(dimethylamino)sulfonyl]-1-fluoro-N-phenylmethanesulfenamide; 1,1-dichloro-N-[(dimethylamino)sulfonyl]-1-fluoro-N-(4-methylphenyl) methanesulfenamide; 4,5-dichloro-2-n-octyl-4-isothiazoline-3-one; N'-(3,4-dichlorophenyl)-N,N'-dimethylurea; and N'-tert-butyl-N-cyclopropyl-6-(methylthio)-1,3,5-triazine 2,4-diamine; and the like. These may be used alone or in combination of two or more types.

The triphenylborane-amine complex is a complex formed from triphenylborane and an amine. The amine is not particularly limited, and examples thereof include primary amine such as n-propylamine, n-butylamine, n-hexylamine, n-octylamine, n-

decylamine, n-dodecylamine, n-tridecylamine, n-tetradecylamine, n-hexadecylamine, n-octadecylamine, aniline, and toluidine; secondary amine 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, and diphenylamine; tertiary amine 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, and triphenylamine; pyridines such as pyridine or pyridine with a substituent on the ring, such as pyridine, 2-picoline, 3-picoline, 4-picoline, 2-chloropyridine, 3-chloropyridine, and 4-chloropyridine.

Among others, pyridine-triphenylborane containing pyridine as an amine is excellent in antifouling property, and therefore, preferably used.

The antifouling paint composition of the present invention can include, for example, cuprous oxide, cuprous thiocyanate (copper rhodanide) or the like as the second antifouling agent, in addition to the components described above. However, when cuprous oxide is used as a main component of the antifouling agent, the antifouling coating film that is hydrolyzed at a constant rate cannot be obtained as described above. Accordingly, when using cuprous oxide, it is preferable that the content of cuprous oxide is set at 15 mass % or less in the solid content contained in the antifouling paint composition, and more preferable that cuprous oxide is not contained. Furthermore, also when cuprous thiocyanate (copper rhodanide) is used in large amount, there occurs the same phenomenon as that in the case of cuprous oxide. Accordingly, when using cuprous thiocyanate, it is preferable that the content of cuprous thiocyanate is set at 15 mass % or less in the solid content contained in the antifouling paint composition, and more preferable that cuprous thiocyanate is not contained.

The content of the first antifouling agent is preferably 1 to 60 mass %, and more preferably 3 to 50 mass %, in the solid content contained in the antifouling paint composition. When the content is less than 3 mass %, sufficient antifouling

performance against aquatic animals tends to be hard to be achieved. When the content exceeds 60 mass %, defects such as cracks or peel-off may occur in the obtained coating film.

The content of the second antifouling agent (the total amount of antifouling agents other than the first antifouling agent) is preferably 5 to 60 mass %, and more preferably 10 to 55 mass %, in the solid content contained in the antifouling paint composition. When the content is less than 5 mass %, it is less likely to obtain an antifouling paint composition having excellent antifouling performance against the entire aquatic organisms. Furthermore, when the content exceeds 60 mass %, defects such as cracks or peel-off may occur in the obtained coating film.

The total content of the first antifouling agent and the second antifouling agent is preferably 5 to 70 mass %, and more preferably 10 to 60 mass %, in the solid content contained in the antifouling paint composition. When the total content is less than 5 mass %, it is less likely to obtain an antifouling paint composition excellent in long-term antifouling property. Furthermore, when the total content exceeds 60 mass %, defects such as cracks or peel-off may occur in the coating film.

The ratio (mass ratio) between the content of the first antifouling agent and the content of the second antifouling agent (the total amount of antifouling agents other than the first antifouling agent) is preferably 1/15 to 1/1, and more preferably 1/12 to 1/2. When the mass ratio is less than 1/15, the animal-resistant antifouling property tends to deteriorate. Furthermore, when the mass ratio exceeds 1/1, the algae-resistant antifouling property tends to deteriorate.

<Other Additives>

The antifouling paint composition of the present invention may contain commonly used additives such as a plasticizer, a pigment and a solvent. Examples of plasticizers include phthalate-ester-based plasticizers such as dioctyl phthalate, dimethyl phthalate and dicyclohexyl phthalate; an aliphatic-dibasic-acid-ester-based plasticizer such as isobutyl adipate and dibutyl sebacate; glycol-ester-based plasticizers such as diethylene glycol dibenzoate and pentaerythritol alkyl ester; phosphoric-ester-

based plasticizers such as tricresyl phosphate and trichloroethyl phosphate; epoxy-based plasticizers such as epoxy soybean oil and octyl epoxy stearate; organic-tin-based plasticizers such as dioctyltin laurate and dibutyltin laurate; trioctyl trimellitate, triacethylene, and the like. These plasticizers may be used alone or in combination of two or more types.

Examples of pigments include extenders such as precipitated barium, talc, clay, chalk, silica white, alumina white and bentonite; color pigments such as titanium oxide, zirconium oxide, basic lead sulfate, tin oxide, carbon black, graphite, red iron oxide (colcothar), chrome yellow, phthalocyanine green, phthalocyanine blue, and quinacridone. These pigments may be used alone or in combination of two or more types.

Examples of solvents include hydrocarbons such as toluene, xylene, ethylbenzene, cyclopentane, octane, heptane, cyclohexane, and white spirit; ethers such as dioxane, tetrahydrofuran, ethyleneglycol monomethyl ether, ethyleneglycol monoethyl ether, ethyleneglycol monobutyl ether, ethyleneglycol dibutyl ether, diethyleneglycol monomethyl ether, and diethyleneglycol monoethyl ether; esters such as butyl acetate, propyl acetate, benzyl acetate, ethyleneglycol monomethyl ether acetate, and ethyleneglycol monoethyl ether acetate; ketones such as ethyl isobutyl ketone and methyl isobutyl ketone; alcohols such as n-butanol and propyl alcohol; and the like. These solvents may be used alone or in combination of two or more types.

In addition to the above, for example, the following agents may be added, such as monoester of dicarboxylic acid such as monobutyl phthalate, monooctyl succinate, camphor, castor oil; a water binder, an anti-sagging agent, an anti-floating agent, an anti-settling agent, a defoaming agent, and the like.

The antifouling paint composition of the present invention can be prepared, for example, by adding, to the above-described binder resin, the above-described antifouling agent and, as required, commonly used additives such as a plasticizer, a coating film consumption control agent, a pigment, and a solvent, and mixing the resultant using a mixer such as a ball mill, a pebble mill, a roll mill, or a sand grind mill.

The antifouling coating film can be formed by applying the obtained antifouling paint composition to the surface of the object to be coated in accordance with an ordinary method, and then, volatilizing and removing a solvent at room temperature or under heating. Examples of objects to be coated are not particularly limited, but include underwater structures such as marine vessels, various fishnets, harbor facilities, oil fences, piping materials, bridges, and sea bottom bases. Since the antifouling coating film formed using the antifouling paint composition of the present invention is hydrolyzed at a constant rate for a long period of time, it can exhibit high antifouling performance for a long period of time in a stable manner. Furthermore, the antifouling coating film formed using the antifouling paint composition of the present invention has such an enhanced long-term antifouling property and is excellent in resistance to cracking.

Examples

Although the present invention will be hereinafter described in greater detail with reference to Examples and Comparative Examples, the present invention is not limited thereto.

(Production Example 1) Preparation of Acrylic Resin Varnish 1

In a four-neck flask including a stirrer, a cooler, a temperature control device, a nitrogen introduction pipe, and a dropping funnel, 64 parts by mass of xylene and 16 parts by mass of n-butanol were added, and a temperature thereof was kept at 100°C. In this solution, a mixture solution composed of monomers in accordance with a formulation (parts by mass) in Table 1 and 2 parts by mass of t-butylperoxy-2-ethylhexanoate was dropped at a constant velocity for 3 hours. After dropping ended, the temperature of the mixture solution was kept for 30 minutes. Thereafter, a mixture solution composed of 16 parts by mass of xylene, 4 parts by mass of n-butanol and 0.2 parts by mass of t-butylperoxy-2-ethylhexanoate was dropped at a constant velocity for 30 minutes. After dropping ended, the temperature of the mixture solution was kept for 1 hour and 30 minutes. A resin varnish I was thus obtained. The solid content of the obtained resin varnish I was 49.8 mass % and viscosity was 4.4

poises. Furthermore, the acid value of resin in this resin varnish I was 130. Table 1 summarizes the acid value of the obtained resin and the solid content of resin varnish I. The abbreviations of monomers described in Table 1 shows the following compounds.

(1) EA: ethyl acrylate

(2) CHMA: cyclohexyl methacrylate

(3) CHA: cyclohexyl acrylate

(4) M-90G: methoxypolyethyleneglycol methacrylate ester (NK ester M-90G, manufactured by Shin-Nakamura Chemical Co., Ltd.)

(5) MMA: methyl methacrylate

(6) AA: acrylic acid

(7) MAA: methacrylic acid

(8) TIPSA: triisopropylsilyl acrylate

Then, in a similar reaction vessel, 100 parts by mass of resin varnish I, 25.4 parts by mass of zinc acetate, 39.2 parts by mass of naphthenic acid (NA-165, acid value of 165, manufactured by Daiwa Yushi Kogyo), and 110 parts by mass of xylene were added, and the mixture was heated to 130°C to thereby remove acetic acid together with the solvent. Thus, an acrylic resin varnish 1 having a solid content of 41.5 mass % was obtained. Viscosity was 12.3 poises.

(Production Example 2) Preparation of Acrylic Resin Varnish 2

In the reaction vessel similar to that in production example 1 described above, 64 parts by mass of xylene and 16 parts by mass of n-butanol were added, and a temperature thereof was kept at 115°C. In this solution, a mixture solution composed of monomers in accordance with a formulation (parts by mass) in Table 1 and 3 parts by mass of t-butylperoxy-2-ethylhexanoate was dropped at a constant velocity for 3 hours. After dropping ended, the temperature of the mixture solution was kept for 30 minutes. Thereafter, a mixture solution composed of 16 parts by mass of xylene, 4 parts by mass of n-butanol and 0.2 parts by mass of t-butylperoxy-2-ethylhexanoate was dropped at a constant velocity for 30 minutes. After dropping ended, the temperature of the mixture solution was kept for 1 hour and 30 minutes. A resin

varnish II was thus obtained. The solid content of the obtained resin varnish II was 49.7 mass % and viscosity was 9.5 poises. Furthermore, the number average molecular weight (GPC, in terms of polystyrene) of the resin contained in resin varnish II was 6500 and the acid value was 160. Table 1 summarizes the acid value of the obtained resin and solid content of resin varnish II.

Then, reaction was conducted as in Production Example 1 above except that in a similar reaction vessel, 100 parts by mass of resin varnish II, 29.6 parts by mass of copper acetate, and 14.5 parts by mass of pivalic acid (acid value: 550 mgKOH/g) were added. Thus, an acrylic resin varnish 2 having a solid content of 45.2 mass % was obtained.

(Production Example 3) Preparation of Acrylic Resin Varnish 3

In the reaction vessel similar to that in Production Example 1 described above, 64 parts by mass of xylene and 16 parts by mass of n-butanol were added, and a temperature thereof was kept at 115°C. In this solution, a mixture solution composed of monomers in accordance with a formulation (parts by mass) in Table 1 and 2 parts by mass of t-butylperoxy-2-ethylhexanoate was dropped at a constant velocity for 3 hours. After dropping ended, the temperature of the mixture solution was kept for 30 minutes. Thereafter, a mixture solution composed of 16 parts by mass of xylene, 4 parts by mass of n-butanol and 0.2 parts by mass of t-butylperoxy-2-ethylhexanoate was dropped at a constant velocity for 30 minutes. After dropping ended, the temperature of the mixture solution was kept for 1 hour and 30 minutes. A resin varnish III was thus obtained. The solid content of the obtained resin varnish III was 49.6 mass % and viscosity was 6 poises. Furthermore, the number average molecular weight (GPC, in terms of polystyrene) of the resin contained in resin varnish III was 6000 and the acid value was 70 mgKOH/g. Table 1 summarizes the acid value of the obtained resin and solid content of resin varnish III.

Then, reaction was conducted as in Production Example 1 above except that in a similar reaction vessel, 100 parts by mass of resin varnish III, 12.9 parts by mass of copper acetate and 21.7 parts by mass of hydrogenated rosin (Hypale CH, acid value of

160, manufactured by Arakawa Chemical Industries, Ltd.) were added, and thus, an acrylic resin varnish 3 having a solid content of 50.6 mass % was obtained.

(Production Example 4) Preparation of Acrylic Resin Varnish 4

In a reaction vessel as in Production Example 1 above, 50 parts by mass of xylol was added, and a temperature thereof was kept at 90°C. In this solution, a mixture solution composed of monomers in accordance with a formulation (parts by mass) in Table 1 and 1 part by mass of t-butylperoxy-2-ethylhexanoate was dropped at a constant velocity for 3 hours. After dropping ended, the temperature of the mixture solution was kept for 30 minutes. Thereafter, a mixture solution composed of 7 parts by mass of xylol and 0.2 parts by mass of t-butylperoxy-2-ethylhexanoate was dropped at a constant velocity for 30 minutes. After dropping ended, the temperature of the mixture solution was kept for 1.5 hours, and cooled to 60 °C, to which 10 parts by mass of xylol was added. An acrylic resin varnish 4 was thus obtained. The solid content of the obtained acrylic resin varnish 4 was 60.0 mass % and viscosity was 7.5 poises. Furthermore, the number average molecular weight (GPC, in terms of polystyrene) of the resin contained in acrylic resin varnish 4 was 8000. Table 1 summarizes the solid content of acrylic resin varnish 4.

[Table 1]

		Production Example 1	Production Example 2	Production Example 3	Production Example 4
Resin Varnish		I	II	III	Acrylic Resin Varnish 4
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	-	-	40.00	65.0
Acid Value (mgKOH/g)		130	160	70	-
Solid Content (Mass %)		49.8	49.7	49.6	60.0

<Examples 1 to 41 and Comparative Examples 1 to 12>

Antifouling paint compositions were prepared by using acrylic resin varnishes 1 to 4 obtained in Production Examples 1 to 4 as described above and other components shown in Tables 2 to 6, and mixing the components with a high-speed disperser. Then, a long-term antifouling property, resistance to cracking, a state of the coating film, and a coating film consumption amount (polishing speed) were evaluated in accordance with the evaluation method below. Details of each component shown in Tables 2 to 6 are as follows.

(1) Cuprous oxide: "NC-301" manufactured by NC Tech

(2) Zinc white: "Zinc Oxide Type 2" manufactured by Sakai Chemical Industry Co., Ltd.

(3) Red iron oxide: "Toda Color KN-R" manufactured by Toda Kogyo Corp.

(4) Antifouling agent 1 (ECONEA): 4-bromo-2-(4-chlorophenyl)-5-(trifluoromethyl)-1H-pyrrole-3-carbonitrile ("ECONEA" manufactured by Janssen PMP)

(5) Antifouling agent 2 (ZPT): ZPT (zinc pyrithione) ("Zinc OMADINE" manufactured by Arch Chemicals)

(6) Antifouling agent 3 (CuPT): CuPT (copper pyrithione) "Copper OMADINE" manufactured by Arch Chemicals)

(7) Antifouling agent 4 (PK) : pyridine-triphenylborane ("PK" manufactured by Hokko Chemical Industry Co., Ltd.)

(8) Antifouling agent 5 (YN-18-20) : triphenylborane-n-octadecylamine complex ("YN-18-20" manufactured by Benny Toyama Corporation)

(9) Antifouling agent 6 (A4S): 1,1-dichloro-N-[(dimethylamino)sulfonyl]-1-fluoro-N-phenylmethanesulfenamide ("Preventol A4S" manufactured by Lanxess)

(10) Antifouling agent 7 (A5S): 1,1-dichloro-N-[(dimethylamino)sulfonyl]-1-fluoro-N-(4-methylphenyl)methanesulfenamide ("Preventol A5S" manufactured by Lanxess)

(11) Antifouling agent 8 (SN211): 4,5-dichloro-2-n-octyl-4-isothiazoline-3-

one(4,5-dichloro-2-n octyl-3(2H)isothiazolone) ("SeaNine 211" manufactured by Rohm and Haas Company)

(12) Antifouling agent 9 (A6): N'-(3,4-dichlorophenyl)-N,N'-dimethylurea ("Preventol A6-AF" manufactured by Lanxess)

(13) Antifouling agent 10 (I1051):N'-tert-butyl-N-cyclopropyl-6-(methylthio)-1,3,5-triazine-2,4-diamine ("Irgarol 1051" manufactured by Ciba Specialty Chemicals Inc.)

(14) Antifouling agent 11 (copper rhodanide): cuprous thiocyanate ("Copper Rhodanide" manufactured by Nihon Kagaku Sangyo Co., Ltd.)

(15) Chlorinated paraffin: ("Toyoparax A50" manufactured by Tosoh Corporation)

(16) Wood rosin : ("WW Rosin" manufactured by Arakawa Chemical Industries, Ltd.)

(17) Anti-sagging agent: "Disparlon A600-20X" manufactured by Kusumoto Chemicals, Ltd.

[Table 2]

Unit: Parts by Mass		Example											
		1	2	3	4	5	6	7	8	9	10	11	12
Acrylic Resin Varnish 1		38	49	38	51	37	38	36	38	37	39	36	37
Acrylic Resin Varnish 2													
Acrylic Resin Varnish 3													
Acrylic Resin Varnish 4													
Cuprous Oxide													
Zinc White		29		31	10	28	28	29	29	30	28	29	28
Red Iron Oxide		6		6	6	6	6	6	6	6	6	6	6
Antifouling Agent 1 (ECONEA)		3	3	0.5	5	3	4	3	3	3	3	4	3
Antifouling Agent 2 (ZPT)		9	31	9	14								
Antifouling Agent 3 (CuPT)						10							
Antifouling Agent 4 (PK)							9						
Antifouling Agent 5 (YN-18-20)								11					
Antifouling Agent 6 (A4S)									9				
Antifouling Agent 7 (A5S)										10			
Antifouling Agent 8 (SN211)											9		
Antifouling Agent 9 (A6)												10	
Antifouling Agent 10 (I1051)													11
Antifouling Agent 11 (copper rhodanide)													
Chlorinated Paraffin		1	1	1	1	1	1	1	1	1	1	1	1
Wood Rosin													
Anti-sagging Agent		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
Xylene		10	12	10	9	11	10	10	10	9	10	10	10
Total		100	100	100	100	100	100	100	100	100	100	100	100
Long-Term Antifouling Property Slime/Algae	3 Months	0	0	0	0	0	0	0	0	0	0	0	0
	6 Months	0	0	0	0	0	0	0	0	0	0	0	0
	12 Months	0	0	0	0	0	0	0	0	0	0	0	0
	18 Months	0	0	0	0	0	0	0	0	0	0	0	0
	24 Months	0	0	0	0	0	0	0	0	0	0	0	0
Long-Term Antifouling Property Animals	3 Months	0	0	0	0	0	0	0	0	0	0	0	0
	6 Months	0	0	0	0	0	0	0	0	0	0	0	0
	12 Months	0	0	0	0	0	0	0	0	0	0	0	0
	18 Months	0	0	0	0	0	0	0	0	0	0	0	0
	24 Months	0	0	1	0	0	0	0	0	0	0	0	0
State of Coating Film		A	A	A	A	A	A	A	A	A	A	A	A
Resistance to Cracking		A	A	A	A	A	A	A	A	A	A	A	A
Amount of Consumption of Coating Film (Total Amount of Decrease in Thickness of Coating Film [μm])	0 Month	0	0	0	0	0	0	0	0	0	0	0	0
	3 Months	18	22	17	20	17	19	19	20	19	21	18	19
	6 Months	34	43	33	41	32	34	35	36	34	36	37	39
	9 Months	51	60	49	59	50	54	56	53	51	54	56	58
	12 Months	70	81	68	80	68	69	70	71	70	74	74	78
	15 Months	88	103	87	101	87	88	90	90	89	90	91	94
	18 Months	107	122	108	120	107	109	111	112	109	113	110	113
	21 Months	126	146	125	142	126	127	128	129	126	130	128	132
	24 Months	142	169	140	163	141	144	147	145	142	142	145	150

[Table 3]

Unit: Parts by Mass		Example											
		13	14	15	16	17	18	19	20	21	22	23	24
Acrylic Resin Varnish 1		38	38	39	38	39	38	38	40	38	39	37	38
Acrylic Resin Varnish 2													
Acrylic Resin Varnish 3													
Acrylic Resin Varnish 4													
Cuprous Oxide													
Zinc White		29	29	26	29	27	28	28	27	29	27	29	28
Red Iron Oxide		6	6	6	6	6	6	6	6	6	6	6	6
Antifouling Agent 1 (ECONEA)		3	3	4	3	4	3	3	3	3	3	4	3
Antifouling Agent 2 (ZPT)		5		6		5					5		
Antifouling Agent 3 (CuPT)			4				5						
Antifouling Agent 4 (PK)		4											
Antifouling Agent 5 (YN-18-20)				5									
Antifouling Agent 6 (A4S)			5										
Antifouling Agent 7 (A5S)					4			5				5	
Antifouling Agent 8 (SN211)						6		5	6	6			
Antifouling Agent 9 (A6)							5		5			4	5
Antifouling Agent 10 (I1051)					5					4	4		4
Antifouling Agent 11 (copper rhodanide)													
Chlorinated Paraffin		1	1	1	1	1	1	1	1	1	1	1	1
Wood Rosin													
Anti-sagging Agent		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
Xylene		10	10	9	10	8	10	10	8	9	11	10	11
Total		100	100	100	100	100	100	100	100	100	100	100	100
Long-Term Antifouling Property Slime/Algae	3 Months	0	0	0	0	0	0	0	0	0	0	0	0
	6 Months	0	0	0	0	0	0	0	0	0	0	0	0
	12 Months	0	0	0	0	0	0	0	0	0	0	0	0
	18 Months	0	0	0	0	0	0	0	0	0	0	0	0
	24 Months	0	0	0	0	0	0	0	0	0	0	0	0
Long-Term Antifouling Property Animals	3 Months	0	0	0	0	0	0	0	0	0	0	0	0
	6 Months	0	0	0	0	0	0	0	0	0	0	0	0
	12 Months	0	0	0	0	0	0	0	0	0	0	0	0
	18 Months	0	0	0	0	0	0	0	0	0	0	0	0
	24 Months	0	0	0	0	0	0	0	0	0	0	0	0
State of Coating Film		A	A	A	A	A	A	A	A	A	A	A	A
Resistance to Cracking		A	A	A	A	A	A	A	A	A	A	A	A
Amount of Consumption of Coating Film (Total Amount of Decrease in Thickness of Coating Film [μm])	0 Month	0	0	0	0	0	0	0	0	0	0	0	0
	3 Months	17	17	18	18	19	18	19	18	18	17	20	17
	6 Months	33	32	35	34	34	36	37	36	34	34	39	32
	9 Months	50	55	50	49	52	51	54	55	50	51	56	50
	12 Months	69	68	70	69	70	71	70	71	68	69	75	68
	15 Months	87	88	89	89	89	90	88	89	90	89	92	87
	18 Months	109	109	111	110	111	109	107	111	109	111	114	107
	21 Months	127	128	129	128	129	127	127	128	129	129	131	126
	24 Months	142	144	143	143	144	143	146	144	146	144	148	141

[Table 4]

Unit: Parts by Mass		Example										
		25	26	27	28	29	30	31	32	33	34	35
Acrylic Resin Varnish 1		34					45	40				
Acrylic Resin Varnish 2			38	35					45	39		
Acrylic Resin Varnish 3					40	39					44	39
Acrylic Resin Varnish 4												
Cuprous Oxide							9	10	11	10	10	9
Zinc White		28	25	26	27	26	10	9	10	11	11	10
Red Iron Oxide		6	6	7	7	7	8	8	7	8	7	8
Antifouling Agent 1 (ECONEA)		4	4	4	3	3	4	3	4	4	3	4
Antifouling Agent 2 (ZPT)		11	12	10	10	9	12	11	10	12	10	9
Antifouling Agent 3 (CuPT)												
Antifouling Agent 4 (PK)												
Antifouling Agent 5 (YN-18-20)												
Antifouling Agent 6 (A4S)												
Antifouling Agent 7 (A5S)												
Antifouling Agent 8 (SN211)												
Antifouling Agent 9 (A6)												
Antifouling Agent 10 (I1051)												
Antifouling Agent 11 (copper rhodanide)												
Chlorinated Paraffin		2	2	2	2	1	1	2	1	2	1	2
Wood Rosin		3		2		2		3		2		2
Anti-sagging Agent		2	2	2	2	2	2	2	2	2	2	2
Butyl Cellosolve		2	2	2	1	1	1	1	1	1	1	1
Xylene		8	9	10	8	10	8	11	9	9	11	14
Total		100	100	100	100	100	100	100	100	100	100	100
Long-Term Antifouling Property Slime/Algae	3 Months	0	0	0	0	0	0	0	0	0	0	0
	6 Months	0	0	0	0	0	0	0	0	0	0	0
	12 Months	0	0	0	0	0	0	0	0	0	0	0
	18 Months	0	0	0	0	0	0	0	0	0	0	0
	24 Months	0	0	0	0	0	0	0	0	0	0	0
Long-Term Antifouling Property Animals	3 Months	0	0	0	0	0	0	0	0	0	0	0
	6 Months	0	0	0	0	0	0	0	0	0	0	0
	12 Months	0	0	0	0	0	0	0	0	0	0	0
	18 Months	0	0	0	0	0	0	0	0	0	0	0
	24 Months	0	0	0	0	0	0	0	0	0	0	0
State of Coating Film		A	A	A	A	A	A	A	A	A	A	A
Resistance to Cracking		A	A	A	A	A	A	A	A	A	A	A
Amount of Consumption of Coating Film (Total Amount of Decrease in Thickness of Coating Film [μm])	0 Month	0	0	0	0	0	0	0	0	0	0	0
	3 Months	22	25	26	12	15	18	22	28	29	11	15
	6 Months	43	49	53	25	31	35	42	51	55	24	31
	9 Months	63	74	78	36	44	51	63	75	81	36	45
	12 Months	84	98	100	49	60	71	85	100	102	48	59
	15 Months	103	122	127	60	74	89	104	124	130	61	75
	18 Months	122	149	155	71	92	107	122	152	159	73	93
	21 Months	141	172	180	86	107	128	140	175	184	85	108
	24 Months	162	198	203	99	124	143	163	201	208	98	126

[Table 5]

Unit: Parts by Mass		Example					
		36	37	38	39	40	41
Acrylic Resin Varnish 1		42	41				
Acrylic Resin Varnish 2				42	40		
Acrylic Resin Varnish 3						43	38
Acrylic Resin Varnish 4							
Cuprous Oxide							
Zinc White		11	10	14	11	10	9
Red Iron Oxide		7	6	6	7	8	8
Antifouling Agent 1 (ECONEA)		4	3	4	4	3	3
Antifouling Agent 2 (ZPT)		10	10	9	11	9	10
Antifouling Agent 3 (CuPT)							
Antifouling Agent 4 (PK)							
Antifouling Agent 5 (YN-18-20)							
Antifouling Agent 6 (A4S)							
Antifouling Agent 7 (A5S)							
Antifouling Agent 8 (SN211)							
Antifouling Agent 9 (A6)							
Antifouling Agent 10 (I1051)							
Antifouling Agent 11 (copper rhodanide)		10	11	10	9	11	10
Chlorinated Paraffin		1	2	1	2	1	2
Wood Rosin			3		2		2
Anti-sagging Agent		2	2	2	2	2	2
Butyl Cellosolve		1	1	1	1	1	1
Xylene		13	11	11	11	12	15
Total		100	100	100	100	100	100
Long-Term Antifouling Property Slime/Algae	3 Months	0	0	0	0	0	0
	6 Months	0	0	0	0	0	0
	12 Months	0	0	0	0	0	0
	18 Months	0	0	0	0	0	0
	24 Months	0	0	0	0	0	0
Long-Term Antifouling Property Animals	3 Months	0	0	0	0	0	0
	6 Months	0	0	0	0	0	0
	12 Months	0	0	0	0	0	0
	18 Months	0	0	0	0	0	0
	24 Months	0	0	0	0	0	0
State of Coating Film		A	A	A	A	A	A
Resistance to Cracking		A	A	A	A	A	A
Amount of Consumption of Coating Film (Total Amount of Decrease in Thickness of Coating Film [μm])	0 Month	0	0	0	0	0	0
	3 Months	18	22	28	29	11	15
	6 Months	36	41	51	55	23	32
	9 Months	52	63	74	86	35	45
	12 Months	71	86	99	110	48	60
	15 Months	90	106	124	131	62	74
	18 Months	107	123	153	158	74	91
	21 Months	129	141	175	183	85	108
	24 Months	144	164	200	208	99	126

[Table 6]

Unit: Parts by Mass		Comparative Example											
		1	2	3	4	5	6	7	8	9	10	11	12
Acrylic Resin Varnish 1		37	45	43					35	40			
Acrylic Resin Varnish 2								33					
Acrylic Resin Varnish 3											34		43
Acrylic Resin Varnish 4						41	32						
Cuprous Oxide							38	40	40		39	40	12
Zinc White		29	29	20	27	24	4	5	4	10	4	4	9
Red Iron Oxide		7	8	8	8	7	3	3	3	3	3	3	3
Antifouling Agent 1 (ECONEA)			3	14	5	3							
Antifouling Agent 2 (ZPT)		3				9		9		10		10	
Antifouling Agent 3 (CuPT)							10		10		9		12
Antifouling Agent 4 (PK)		7											
Antifouling Agent 5 (YN-18-20)													
Antifouling Agent 6 (A4S)													
Antifouling Agent 7 (A5S)													
Antifouling Agent 8 (SN211)													
Antifouling Agent 9 (A6)													
Antifouling Agent 10 (I1051)													
Antifouling Agent 11 (copper rhodanide)										25			
Chlorinated Paraffin		1	1	1	4	3	2	3	1	1	1	4	1
Wood Rosin					18	2	4				3	13	3
Anti-sagging Agent		2	2	2	2	2	2	2	2	2	2	2	2
Butyl Cellosolve		2	2	2	2	1	1	1	1	1	1	1	1
Xylene		12	10	10	34	8	4	4	4	8	4	23	14
Total		100	100	100	100	100	100	100	100	100	100	100	100
Long-Term Antifouling Property Slime/Algae	3 Months	0	1	2	3	0	0	0	0	0	0	0	0
	6 Months	1	3	3	4	0	0	0	0	1	0	1	1
	12 Months	3	5	5	5	0	0	1	2	3	0	3	2
	18 Months	2	5	5	5	0	2	3	4	2	2	2	3
	24 Months	0	5	5	5	4	3	4	2	0	2	0	1
Long-Term Antifouling Property Animals	3 Months	0	0	0	0	0	0	0	0	0	0	0	1
	6 Months	2	0	0	0	0	0	0	0	3	0	0	2
	12 Months	3	0	0	0	0	0	0	2	4	0	2	3
	18 Months	4	0	0	0	0	3	2	3	5	1	4	4
	24 Months	5	1	0	2	3	4	2	5	5	2	5	5
State of Coating Film		A	A	A	B	A	A	B	B	A	B	B	A
Resistance to Cracking		A	A	A	7	A	A	7	13	A	16	3	A
Amount of Consumption of Coating Film (Total Amount of Decrease in Thickness of Coating Film [μm])	0 Month	0	0	0	0	0	0	0	0	0	0	0	0
	3 Months	19	16	18	30	11	12	81	42	39	11	27	12
	6 Months	35	31	36	55	23	22	105	58	54	24	53	25
	9 Months	51	48	53	80	33	33	115	72	67	37	75	39
	12 Months	71	67	73	101	46	45	121	80	78	48	99	49
	15 Months	89	85	92	122	71	59	126	85	84	61	120	63
	18 Months	107	104	110	139	111	103	129	88	87	72	135	73
	21 Months	127	122	130	155	195	184	133	90	89	85	148	86
	24 Months	144	139	149	169	300	291	135	91	90	99	165	101

(Evaluation)

(1) Long-term Antifouling Property

The obtained antifouling paint composition was applied to a blast plate, to which a rustproof paint had been applied in advance so that a dry film thickness of a coating film is 300 μm, and the blast plate was left in a room for 2 days and nights for drying. The test plate having the antifouling coating film was thus obtained. The obtained test plate was subjected to an organism adhesion test by using an experimental raft installed in Marine Research Laboratory of Nippon Paint Marine Coatings Co., Ltd. in Tamano, Okayama Prefecture and an antifouling property was evaluated. The results are shown in Tables 2 to 6. The number of months in the tables shows a period during which the raft was immersed. In addition, numeric values in the tables each show a proportion (%) of an organism adhering area to an area of the coating film (determination by visual inspection) and are rated based on the following criteria, and a ratio not higher than 1 was determined as pass.

Evaluation score 0: Proportion of the organism adhering area to the coating film area 0%

Evaluation score 1: Proportion of the organism adhering area to the coating film area more than 0% and less than 20%

Evaluation score 2: Proportion of the organism adhering area to the coating film area not less than 20% and less than 40%

Evaluation score 3: Proportion of the organism adhering area to the coating film area not less than 40% and less than 60%

Evaluation score 4: Proportion of the organism adhering area to the coating film area not less than 60% and less than 80%

Evaluation score 5: Proportion of the organism adhering area to the coating film area 80% to 100%

Fig. 1 is a photograph showing an example of the state of the test plate surface after an antifouling property test (organism adhesion test) (24 months after immersion). In Fig. 1, the left photograph shows an example in the case where the evaluation score

of animal adhesion is 5 while the evaluation score of slime/algae adhesion is 0 (for example, Comparative Example 1). The center photograph shows an example in the case where the evaluation score of animal adhesion is 0 while the evaluation score of slime/algae adhesion is 5 (for example, Comparative Example 3). The right photograph shows an example in the case where both animals and slime/algae adhere, in which the evaluation score of animal adhesion is 3 while the evaluation score of slime/algae adhesion is 3.

(2) State of Coating Film

A state of the coating film on the test plate after 6 months of a raft immersion period in the long-term antifouling property test above was observed visually and with rubbing, and then evaluated. The results thereof are shown in Tables 2 to 6. A coating film in which no crack was observed was evaluated as A and a coating film in which a crack was observed was evaluated as B.

Test for Resistance to Cracking (Dry and Wet Alternating Test)

A test plate having the antifouling coating film was obtained by applying the obtained antifouling paint composition to a blast plate, to which a rustproof paint had been applied in advance so that a dry film thickness of a coating film is 300 μm and leaving the blast plate in a room for 2 days and nights for drying. The obtained test plate was immersed for 1 week in seawater at 40°C followed by drying in a room for 1 week, and a dry and wet alternating test with this procedure being defined as 1 cycle was conducted 20 cycles at the maximum. If a crack is generated in the coating film during the test, the test was terminated at the time point of generation of a crack and the number of cycles at that time point is shown in the tables. A plate having no crack after 20 cycles was evaluated as A.

(4) Coating Film Consumption Amount (Polishing Speed) Test

A test plate having the antifouling coating film was obtained by applying the obtained antifouling paint composition to a blast plate, to which a rustproof paint had been applied in advance so that a dry film thickness of a coating film is 300 μm and leaving the blast plate in a room for 2 days and nights for drying. This test plate was

bonded to a side surface of a cylinder having a diameter of 750 mm and a length of 1200 mm, the cylinder was continuously turned in seawater for 24 months at a peripheral speed of 15 knots, and an amount of consumption of the coating film on the test plate (a total amount of decrease in thickness of the coating film [μm]) was measured every three months. The test results are shown in Tables 2 to 6.

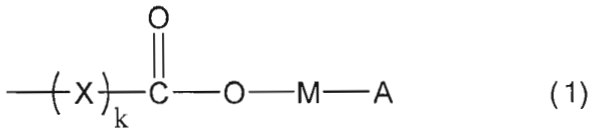
As shown in Tables 2 to 6, the hydrolysis rate (polishing speed) of the antifouling coating film obtained from the antifouling paint composition of each Example is almost constant for 24 months, so that a relatively high antifouling property can be exhibited against aquatic animals and slime/algae for a long period of time in a stable manner. Furthermore, it is also found that a long-term antifouling property and excellent resistance to cracking can be achieved. In addition, the state of the coating film is also excellent for a long period of time.

CLAIMS

1. An antifouling paint composition comprising:

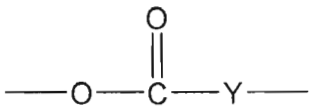
two or more types of antifouling agents containing 4-bromo-2-(4-chlorophenyl)-5-(trifluoromethyl)-1H-pyrrole-3-carbonitrile; and

an acrylic resin having a group expressed in a general formula (1)



(1)

(where X is a group expressed in a general formula



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

2. The antifouling paint composition according to claim 1, wherein

said antifouling agents include

a first antifouling agent that is 4-bromo-2-(4-chlorophenyl)-5-(trifluoromethyl)-1H-pyrrole-3-carbonitrile, and

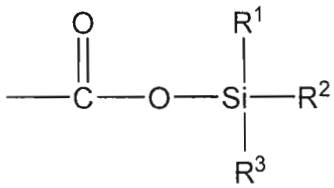
a second antifouling agent that is at least one type selected from the group consisting of zinc pyrithione, copper pyrithione, pyridine-triphenylborane, 1,1-dichloro-N-[(dimethylamino)sulfonyl]-1-fluoro-N-phenylmethanesulfenamide, 1,1-dichloro-N-[(dimethylamino)sulfonyl]-1-fluoro-N-(4-methylphenyl) methanesulfenamide, N'-(3,4-dichlorophenyl)-N,N'-dimethylurea, N'-tert-butyl-N-cyclopropyl-6-(methylthio)-1,3,5-triazine-2,4-diamine, and 4,5-dichloro-2-n-octyl-4-isothiazoline-3-one.

3. The antifouling paint composition according to claim 2, wherein a ratio between a content of said first antifouling agent and a content of said second

antifouling agent is within a range from 1/15 to 1/1 in a mass ratio.

4. The antifouling paint composition according to claim 1, wherein said antifouling paint composition does not include cuprous oxide.

5. The antifouling paint composition according to claim 1, wherein said acrylic resin further has a group expressed in a general formula (2)



(2)

(where R^1, R^2 and R^3 are identical or different and each represent a hydrocarbon residue having a carbon number from 1 to 20) in a side chain.

6. An antifouling coating film formed using the antifouling paint composition according to claim 1.

7. A method of controlling a hydrolysis rate of an antifouling coating film in water that is formed on a surface of an object to be coated, wherein

the antifouling paint composition according to claim 1 is used as a paint composition forming said antifouling coating film.