

SPECIFICATION

TITLE OF INVENTION: ANTIFOULING COATING COMPOSITION, COPOLYMER FOR ANTIFOULING COATING COMPOSITION, AND COATED ARTICLE HAVING SURFACE THAT IS PROVIDED WITH ANTIFOULING COATING FILM WHICH IS FORMED USING THE COMPOSITION

TECHNICAL FIELD

[0001]

The present invention relates to an antifouling coating composition, a copolymer for the antifouling coating composition, and an object coated on its surface with an antifouling coating film using the composition.

BACKGROUND ART

[0002]

Aquatic fouling organisms such as barnacles, tubeworms, common mussels, *Bugula neritina*, sea squirts, green laver, sea lettuce, and slimes attach to ships (especially the ship bottoms), fishing tools such as fishing nets and fishing net accessories, and structures submerged in seawater such as power plant aqueducts, leading to dysfunction, impaired appearances, and other problems of the ships and so on. Since a conventional organic tin-containing copolymer has been banned, triorganosilyl group-containing copolymers which have low toxicity and are environment-friendly have been developed, and have been used for antifouling coating materials.

[0003]

When copolymers, such as tri-n-butylsilyl ester-containing copolymers, which are obtained by copolymerizing silyl ester-containing monomers having straight-chain alkyl groups, are used as the above triorganosilyl group-containing copolymer, the hydrolysis rate of the coating film is very large

and water resistance is low, and therefore, it is difficult to control the coating film dissolving rate (Patent Document 3).

[0004]

When a tri-isopropylsilyl ester-containing copolymer, which is produced by
5 copolymerizing triorganosilyl ester-containing monomers having branched alkyl
groups, is used as the triorganosilyl group-containing copolymer, the copolymer
dissolves in seawater at a constant rate at the initial stage. Its coating film
dissolving rate, however, gradually becomes large. After a certain long term has
passed, the coating film dissolving rate becomes too large, so that the design of
10 the coating material is unfortunately difficult. The coating film undergoing
long-term seawater treatment may cause coating film defects such as cracks.
Regarding the coating material containing the tri-isopropylsilyl ester-containing
copolymer, however, there is a problem that water contained in the raw materials
of the coating materials or water generated during manufacturing of the coating
15 material easily causes hydrolysis of the resin component during the storage, and
thus induces thickening, gelation, and the like of the coating materials.
Addition of a dehydrating agent has been proposed to solve the problem.
However, although the dehydrating agent exhibits some effect, it does not solve
the problem completely, and thus there's still some concern of thickening,
20 gelation, and the like in the case of long-term storage. In addition, in handling
the raw materials, caution to water is required, which deteriorates the work
efficiency (Patent Documents 1, 2, and 4 to 7).

[0005]

Using t-butyldiphenylsilyl methacrylate copolymer as the triorganosilyl
25 ester-containing copolymer has been disclosed. The copolymer, however, has a
much lower coating film dissolving rate in seawater. Consequently, a desired
antifouling effect cannot be obtained and its coating film hardness becomes too
large, which causes coating film defects such as cracks and poor attachment to
structures submerged in seawater (Patent Documents 1, 2, and 4 to 7).

So far, there is no antifouling coating composition which keeps suitable hydrolyzability without causing the coating film defects such as cracks during long-term seawater treatment and which is excellent in stability during long-term storage.

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PRIOR ART REFERENCE

PATENT DOCUMENT

[0006]

[Patent Document 1] JP-A-Hei7-102193

10 [Patent Document 2] JP-A-Hei8-269390

[Patent Document 3] JP-A-Hei9-194790

[Patent Document 4] JP-A-Hei10-30071

[Patent Document 5] JP-A-2001-226440

[Patent Document 6] JP-A-2003-261816

15 [Patent Document 7] JP-A-2005-082725

SUMMARY OF THE INVENTION

PROBLEMS TO BE SOLVED BY THE INVENTION

[0007]

20 It is an object of the present invention to provide an antifouling coating composition having excellent stability in long-term storage and to provide a copolymer which can maintain stable coating film solubility and antifouling performance without causing coating film defects such as cracks during long-term seawater treatment and which has a certain specific structure in order
25 to produce an antifouling coating film having increased environment safety.

MEANS FOR SOLVING THE PROBLEMS

[0008]

An aspect of the present invention provides an antifouling coating

composition, comprising a copolymer A obtainable by copolymerizing (a) 55 to 80% by mass of a t-butyldiphenylsilyl acrylate monomer and (b) 20 to 45% by mass of an ethylenically unsaturated monomer other than the monomer (a), wherein the monomer (b) is at least one monomer selected from the group consisting of methyl methacrylate, butyl (meth)acrylate, and 2-methoxyethyl (meth)acrylate.

[0009]

Unfortunately, an antifouling coating film as produced using an antifouling coating material containing a t-butyldiphenylsilyl methacrylate copolymer has coating film defects such as cracks and poor attachment to structures submerged in seawater. In order to solve these problems, the present inventors have conceived use of acrylate having increased flexibility as an alternative for methacrylate. Then, a t-butyldiphenylsilyl acrylate copolymer-containing antifouling coating material has been used to produce an antifouling coating film, and its performance has been evaluated. The results have demonstrated a remarkable outcome in attachment and flexibility tests. When a coating film condition is observed after an extended period of time, no coating film defects such as cracks occur. Use of acrylate as an alternative for methacrylate is found to resolve many problems with the t-butyldiphenylsilyl methacrylate copolymer.

While further details have been investigated regarding the antifouling coating film as produced using an antifouling coating material containing a t-butyldiphenylsilyl acrylate copolymer, antifouling performance of this antifouling coating film has been found to decrease within a relatively short period. Such problems have not previously been recognized, and what is responsible for the decrease in the antifouling performance has been unclear.

The present inventors have conducted intensive research to solve these problems, and found out a strong correlation of the long-term antifouling performance with a proportion of t-butyldiphenylsilyl acrylate in the copolymer.

Then, the present inventors further found that the duration to maintain the antifouling performance can be remarkably improved by setting the proportion of t-butyldiphenylsilyl acrylate in the copolymer to 55% by mass or higher. Why such an excellent effect can be achieved by having 55% by mass or higher is not completely unveiled. Meanwhile, the dissolving rate of the coating film has been tested. When the proportion of t-butyldiphenylsilyl acrylate is equal to or greater than 55% by mass, the dissolving rate of the coating film remains constant over a long period. In contrast, when the proportion is equal to or less than 54% by mass, the dissolving rate of the coating film has been found to decrease as the time has passed. This suggests that in order to stably hydrolyze the t-butyldiphenylsilyl acrylate copolymer, it is essential to set a proportion of t-butyldiphenylsilyl acrylate in the copolymer at 55% by mass or higher; and when the proportion is lower than the above proportion, the hydrolysis rate of the t-butyldiphenylsilyl acrylate copolymer is unstable, which results in a relatively rapid decrease in its antifouling performance.

In addition, the present inventors have examined how the antifouling coating film performance is altered as the proportion of t-butyldiphenylsilyl acrylate in the copolymer is further increased. The results have demonstrated that when the proportion of t-butyldiphenylsilyl acrylate in the copolymer is from 55 to 80% by mass, excellent performance can be achieved. When the proportion exceeds 80% by mass, however, the duration to maintain the antifouling performance becomes short. The present inventors have investigated the cause and found out that when the proportion of t-butyldiphenylsilyl acrylate in the copolymer exceeds 80% by mass, the dissolving rate of the coating film increases as the time has passed, which leads to an early loss of an agent of the coating film.

The above findings have revealed that use of an antifouling coating composition containing a copolymer A obtainable by copolymerizing (a) 55 to 80% by mass of a t-butyldiphenylsilyl acrylate monomer and (b) 20 to 45% by

mass of an ethylenically unsaturated monomer other than the monomer (a) can produce an antifouling coating film which can keep its antifouling performance for an extended period of time.

In addition, an antifouling coating composition of the present invention has much better coating material storage stability than conventional antifouling coating compositions containing, for example, a tri-isopropylsilyl ester-containing copolymer. This seems to be because the monomer (a) in the copolymer A has a slow hydrolysis rate from an acidic to about neutral pH but has a rapid hydrolysis rate at alkaline conditions that are equal to or greater than a weak alkaline condition (from pH 8 to 9). These particular characteristics make the antifouling coating material unlikely to be hydrolyzed when water is mixed during manufacture or storage of the antifouling coating material. In addition, its storage stability is superb. Then, the above coating material exhibits a suitable hydrolysis rate in seawater under an alkaline condition which is equal to or more alkaline than weak alkaline conditions (pH 8 to 9), and is thus able to exert an excellent long-term antifouling effect.

ADVANTAGEOUS EFFECTS OF THE INVENTION

[0010]

Embodiments of the present invention provide an antifouling coating composition which can produce an antifouling coating film having excellent storage stability and increased antifouling performance maintained for an extended period of time.

DESCRIPTION OF EMBODIMENTS

[0011]

The following details the present invention.

Antifouling Coating Composition

An antifouling coating composition according to an embodiment of the

present invention comprises a copolymer A obtainable by copolymerizing (a) 55 to 80% by mass of a t-butyldiphenylsilyl acrylate monomer and (b) 20 to 45% by mass of an ethylenically unsaturated monomer other than the monomer (a).

[0012]

5 **<Copolymer A>**

The copolymer A can be produced by copolymerizing (a) 55 to 80% by mass of a t-butyldiphenylsilyl acrylate monomer and (b) 20 to 45% by mass of an ethylenically unsaturated monomer other than the monomer (a).

[0013]

10 The monomer (a) can be readily obtained as follows. First, readily available diphenyldichlorosilane is reacted with, for example, a Grignard reagent. After the reaction, the reaction solution is filtered, and the generated magnesium salt is removed to yield t-butyldiphenylchlorosilane. Then, the t-butyldiphenylchlorosilane is reacted with, for example, acrylic acid under basic
15 conditions, followed by a process according to common procedure to yield the monomer (a). An intermediate of t-butyldiphenylchlorosilane and the monomer (a) can be purified as needed before use, by distillation under reduced pressure. In addition, the monomer (a) can include a general polymerization inhibitor such as hydroquinone, p-methoxyphenol, or BHT so as to retain its storage stability.

20 [0014]

The ethylenically unsaturated monomer (b) other than the monomer (a) is at least one monomer selected from the group consisting of methyl methacrylate, butyl (meth)acrylate, and 2-methoxyethyl (meth)acrylate.

[0015]

25 In addition, when used in combination of two or more kinds, the monomer (b) preferably contains methyl methacrylate. The proportion of the methyl methacrylate in the ethylenically unsaturated monomer is preferably from 15 to 90% by mass and more preferably from 30 to 90% by mass. This proportion is, for example, 15, 20, 30, 40, 50, 60, 70, 80, or 90% by mass, or may be between

any two of the above-described numbers. In addition, the monomer (b) preferably contains 2-methoxyethyl (meth)acrylate, and its proportion is preferably from 10 to 85% by mass in the ethylenically unsaturated monomer and more preferably from 10 to 60% by mass. This proportion is, for example,
5 10, 20, 30, 40, 50, 60, 70, 80, or 85% by mass, or may be between any two of the above-described numbers. The monomer (b) may contain either 2-methoxyethyl acrylate or 2-methoxyethyl methacrylate, or may contain both. In the case of inclusion of the both, the proportion of 2-methoxyethyl methacrylate is preferably from 80 to 95 parts by mass when the total amount of
10 methoxyethyl acrylate and methoxyethyl methacrylate is 100 parts by mass. This proportion is, for example, 80, 85, 90, or 95% by mass, or may be between any two of the above-described numbers.

[0016]

A preferable embodiment of the copolymer A included in the composition
15 according to the present invention is a copolymer of (a) 55 to 80% by mass of a t-butyldiphenylsilyl acrylate monomer with (b) 20 to 45% by mass of at least one monomer selected from methyl methacrylate, butyl (meth)acrylate, and 2-methoxyethyl (meth)acrylate. A further preferable embodiment is a copolymer of (a) 55 to 70% by mass of a t-butyldiphenylsilyl acrylate monomer
20 with (b) 30 to 45% by mass of at least one monomer selected from methyl methacrylate, butyl (meth)acrylate, and 2-methoxyethyl (meth)acrylate. The proportion of the monomer (a) in the copolymer is, for example, 55, 58, 60, 65, 70, 75, or 80% by mass, or may be between any two of the above-described numbers.

[0017]

25 The copolymer A has a weight-average molecular weight (Mw) of preferably from 10,000 to 100,000 and more preferably from 20,000 to 70,000. When the Mw is from 10,000 to 100,000, the coating films are not brittle and have a suitable dissolving rate, so that a desired antifouling effect can be effectively exerted. One example of the method for measuring the Mw is gel permeation

chromatography (GPC).

[0018]

The copolymer A may be any copolymer of random copolymer, alternate copolymer, periodical copolymer, and block copolymer between the monomer (a) and the monomer (b). The copolymer A can be prepared by polymerizing the monomer (a) and the monomer (b) under the presence of, for example, a polymerization initiator.

[0019]

With regard to the polymerization initiator used in the polymerization reaction, those similar to the above-described polymerization initiator can be used singly or in combination. Examples of the preferable polymerization initiator include AIBN, in particular, and t-butyl peroxy-2-ethyl hexanoate. The molecular weight of the copolymer A can be adjusted by suitably selecting the amount of the polymerization initiator used.

[0020]

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

[0021]

In the polymerization reaction, an organic solvent may be added, if necessary. Examples of the organic solvent include aromatic hydrocarbon-based solvents (e.g., xylene, toluene); aliphatic hydrocarbon-based solvents (e.g., hexane, heptane); ester-based solvents (e.g., ethyl acetate, butyl acetate, isobutyl acetate, methoxypropyl acetate); alcohol-based solvents (e.g., isopropyl alcohol, butyl alcohol); ether-based solvents (e.g., dioxane, diethyl ether, dibutyl ether); and ketone-based solvents (e.g., methyl ethyl ketone, methyl isobutyl ketone). Among them, aromatic hydrocarbon-based solvents are preferable, and xylene is particularly preferable. These solvents may be

used singly or in combination.

[0022]

The reaction temperature in the polymerization reaction may be suitably selected depending on the type of the polymerization initiator, etc., but is usually about 70 to 140°C, and preferably about 80 to 120°C. The time necessary for the polymerization reaction may be suitably selected depending on the reaction temperature, etc., but is usually about 4 to 8 hours. The polymerization reaction is preferably conducted in an inert gas (e.g. nitrogen gas and argon gas) atmosphere.

[0023]

The amount of the copolymer A in the composition of the present invention is not particularly limited, but it is usually 20 to 70% by mass and preferably 40 to 60% by mass with respect to the solid content of the composition of the present invention. When the amount of the copolymer A is from 20 to 70% by mass, a suitable dissolving rate and property of the coating film in seawater can be achieved. In addition, a long-term stable surface renewal can remain constant and a desired antifouling effect can be effectively exerted. Also, the coating film can exert excellent recoating performance.

[0024]

The antifouling coating composition of the present invention may further contain, as necessary, an antifoulant B, a release modifier C, a plasticizer D, another resin E, and the like in addition to the copolymer A. The addition can improve the antifouling effect.

[0025]

<Antifoulant B>

There is no limitation to the antifoulants B as long as they have a killing or repelling effect against aquatic fouling organisms. Examples can include inorganic and organic antifoulants.

[0026]

Examples of the inorganic antifoulants include, cuprous oxide, copper thiocyanate (general name: copper rhodanide), cupronickel, and copper powder. Among them, cuprous oxide and copper rhodanide are particularly preferred.

[0027]

5 Examples of the organic antifoulants include 2-mercaptopyridine-N-oxide copper (general name: copper pyrithione) and like organic copper compounds; 2-mercaptopyridine-N-oxide zinc (general name : zinc pyrithione), zinc ethylene bis(dithiocarbamate) (general name : zineb), zinc bis(dimethyldithiocarbamate) (general name : ziram), dizinc
10 bis(dimethyldithiocarbamate)ethylenebis(dithiocarbamate) (general name : polycarbamate) and like organic zinc compounds; pyridine-triphenylborane, 4-isopropyl pyridyl-diphenylmethyl borane, 4-phenyl pyridyl-diphenyl borane, triphenylboron-n-octadecyl amine, triphenyl[3-(2-ethylhexyloxy) propyl amine]boron and like organic boron compounds; 2,4,6-trichloromaleimide,
15 N-(2,6-diethylphenyl)-2,3-dichloromaleimide and like maleimide compounds; and, 4,5-dichloro-2-n-octyl-3-isothiazolone (general name : Sea-Nine 211), 3,4-dichlorophenyl-N-N-dimethylurea (general name : diuron), 2-methylthio-4-t-butylamino-6-cyclopropylamino-s-triazine (general name : Irgarol 1051), 2,4,5,6-tetrachloroisophthalonitrile (general name : chlorothalonil),
20 N-dichlorofluoromethylthio-N',N'-dimethyl-N-p-tolylsulfamide (general name : tolylfluorid), N-dichloromethylthio-N',N'-dimethyl-N-phenylsulfamide (general name : dichlofluorid), 2-(4-thiazolyl)benzimidazole (general name : thiabendazole), 3-(benzo[b]thien-2-yl)-5,6-dihydro-1,4,2-oxathiazine-4-oxide (general name : bethoxazine),
25 2-(p-chlorophenyl)-3-cyano-4-bromo-5-trifluoromethyl pyrrole (general name : ECONEA 028), etc. Among them, particularly preferred are zinc pyrithione, copper pyrithione, pyridine-triphenylborane, 4-isopropyl pyridyl-diphenylmethyl borane, bethoxazine, zineb, Sea-Nine 211, and Irgarol 1051. More preferred are copper pyrithione, zinc pyrithione,

pyridine-triphenylborane, and bethoxazine.

[0028]

As the antifoulant B, preferred are cuprous oxide, copper rhodanide, zinc pyrrhithione, copper pyrrhithione, pyridine-triphenylborane, 4-isopropyl
5 pyridyl-diphenylmethyl borane, bethoxazine, zineb, Sea-Nine 211, Irgarol 1051, tolylfluanid, and dichlofluanid. More preferred are cuprous oxide, copper pyrrhithione, zinc pyrrhithione, pyridine-triphenylborane, and bethoxazine.

These antifoulants may be used singly or in combination.

[0029]

10 The amount of the antifoulant B in the composition of the present invention is not particularly limited, but it is usually 0.1 to 75% by mass and preferably 1 to 60% by mass with respect to the solid content of the composition of the present invention. When the amount of the antifoulant B is less than 0.1% by mass, a sufficient antifouling effect might not be obtained. When the amount of
15 the antifoulant B is over 75% by mass, the obtained coating film is fragile, and adherence of the coating film to the coated object is weak, and thus the coating film does not sufficiently exhibit the function as an antifouling coating film.

[0030]

<Release Modifier C>

20 Examples of the release modifier C include rosin, a rosin derivative and a metal salt thereof, monocarboxylic acid and a salt thereof, and an alicyclic hydrocarbon resin.

[0031]

Examples of the rosin include tall oil rosin, gum rosin, and wood rosin.
25 Examples of the rosin derivative include hydrogenated rosin, disproportionated rosin, maleinized rosin, formylated rosin, and polymerized rosin. A reaction product of a metal compound with rosin can be used as a metal salt of the rosin or rosin derivative. Examples of the metal salt of rosin include zinc (or copper) salts of gum rosin, zinc (or copper) salts of wood rosin, and zinc (or copper) salts

of tall oil rosin. Examples of the metal salt of the rosin derivative include hydrogenated rosin zinc (or copper) salts, disproportionated rosin zinc (or copper) salts, maleinized rosin zinc (or copper) salts, formylated rosin zinc (or copper) salts, and polymerized rosin zinc (or copper) salts.

5 [0032]

Examples of the monocarboxylic acid include a fatty acid, a synthetic fatty acid, and naphthenic acid, each of which has a carbon number of about 5 to 30. Examples of the salt of the monocarboxylic acid include copper salts, zinc salts, magnesium salts, and calcium salts.

10 [0033]

Examples of the alicyclic hydrocarbon resin include commercially available Quintone 1500, 1525L, and 1700 (product name; ZEON CORPORATION).

[0034]

In view of giving a composition of the present invention suitable elution
15 facilitation, the composition preferably contains at least one member selected from the group consisting of rosin, a rosin derivative, and a metal salt thereof as the release modifier C. In view of improving crack resistance and water resistance, the composition more preferably contains a copper or zinc salt of rosin or a rosin derivative.

20 [0035]

The amount of the release modifier C in the composition of the present invention is usually 1 to 80 parts by weight, preferably 10 to 50 parts by weight with respect to 100 parts by weight of the copolymer A. When the release modifier C is less than 1 part by weight, the effect of preventing attachment of
25 aquatic fouling organisms, in particular, during rigging cannot be expected. When the amount of the release modifier C is over 80 parts by weight, defects such as cracks and peelings tend to occur, and thus the effect of preventing attachment of aquatic fouling organisms might not be sufficiently exhibited. The amount of the release modifier C is, for example, 1, 5, 10, 15, 20, 25, 30, 35,

40, 45, 50, 55, 60, 65, 70, 75, or 80 parts by weight with respect to 100 parts by weight of the copolymer A. The amount may be between any two of the above-described numbers.

[0036]

5 **<Plasticizer D>**

By adding the plasticizer D to an antifouling coating composition of the present invention, it is possible to improve the plasticity of the composition, and as a result it is possible to suitably form a strong coating film.

[0037]

10 Examples of the plasticizer D include tricresyl phosphate, trioctylphosphate, triphenyl phosphate and like phosphate esters; dibutyl phthalate, dioctyl phthalate and like phthalate esters; dibutyl adipate, dioctyl adipate and like adipate esters; dibutyl sebacate, dioctyl sebacate and like sebacate esters; epoxidized soybean oil, epoxidized linseed oil and like epoxidized oils and fats;
15 methyl vinyl ether polymer, ethyl vinyl ether polymer and like alkyl vinyl ether polymers; polyethylene glycol, polypropylene glycol and like polyalkylene glycols; and, t-nonylpentasulfide, vaseline, polybutene, tris(2-ethyl hexyl) trimellitate, silicone oil, liquid paraffin, and chlorinated paraffin. These plasticizers may be used singly or in combination.

20 [0038]

The amount of the plasticizer D in the composition of the present invention is usually 0.1 to 20 parts by weight, preferably 0.5 to 10 parts by weight with respect to 100 parts by weight of the copolymer A.

[0039]

25 **<Another Resin E>**

Another resin E is added to the antifouling coating composition of the present invention. This makes it possible to reduce cost without impairing an effect of the present invention. Also, a synergetic effect on resin E properties can be obtained.

Examples of another resin E include a metal carboxylate-containing polymer, a trialkylsilyl ester-containing polymer, another (meth)acrylic resin, an alkyd resin, a polyester resin, a chlorinated rubber resin, and a vinyl resin.

[0040]

5 Examples of the metal carboxylate-containing polymer include a polymer containing, in a molecule, a metal carboxylate group represented by the general formula (1):



wherein M is a metal selected from Cu, Zn, Ca, and Mg; and Y is an organic acid
10 residue.

The metal carboxylate-containing polymer is added to the antifouling coating composition of the present invention. This makes it possible to reduce cost without impairing an effect of the present invention. Also, the metal carboxylate-containing polymer can exhibit an excellent initial antifouling effect.

15 More preferably, in the metal carboxylate-containing polymer, the M is Cu or Zn and the Y is an organic acid residue selected from naphthenic acid, rosins (derivatives), and (meth)acrylic acid.

[0041]

Examples of the trialkylsilyl ester-containing polymer include
20 tri-isopropylsilyl (meth)acrylate and tributylsilyl (meth)acrylate.

[0042]

Another resin E can be added to the composition of the present invention in a degree to which a suitable dissolving rate and property of the coating film in seawater are not impaired. Its amount is 1 to 200 parts by weight, preferably 20
25 to 100 parts by weight with respect to 100 parts by weight of the copolymer A.

[0043]

<Other Additives>

Furthermore, the antifouling coating composition of the present invention, if necessary, may include a pigment, a dye, an antifoaming agent, an anti-sagging

agent, a dispersant, an antisetling agent, a dehydrating agent, an organic solvent, and/or the like.

[0044]

5 Examples of the pigment include zinc oxide, red iron oxide, talc, titanium oxide, silica, calcium carbonate, barium sulfate, calcium oxide, and magnesium oxide. These can be used singly or in combination.

[0045]

Examples of the dye include various kinds of organic dyes soluble to an organic solvent.

10 [0046]

Examples of the antifoaming agent include a silicone resin-based antifoaming agent, and an acryl resin-based antifoaming agent.

[0047]

15 Examples of the anti-sagging agent, the dispersant or the antisetling agent include fatty acid amide wax, and oxidized polyethylene.

[0048]

Examples of the dehydrating agent include anhydrous gypsum, a synthetic zeolite-based adsorbent, orthoesters, tetraethoxysilane and like silicates, and isocyanates. These can be used singly or in combination.

20 [0049]

Examples of the organic solvent include an aliphatic solvent, an aromatic solvent, a ketone-based solvent, an ester-based solvent, an ether-based solvent, and like a solvent which is usually used in the antifouling coating material. These can be used singly or in combination.

25 [0050]

Process for Producing Antifouling Coating Composition

An antifouling coating composition of the present invention can be manufactured, for example, by mixing and dispersing a mixed solution containing the copolymer A and the like by use of a disperser.

[0051]

The amounts of the copolymer A and the like in the mixed solution may be suitably adjusted so that the resulting antifouling coating composition contains the copolymer A and the like as described above.

5 [0052]

The mixed solution is preferably obtained by dissolving or dispersing various materials such as the copolymer A in a solvent. As the solvent, those similar to the aforementioned organic solvent may be used.

[0053]

10 For the disperser, for example, the one which can be used as a micro-pulverizer can be suitably used. For example, a commercially available homo mixer, sand mill, bead mill, or the like can be used. Furthermore, the mixed solution can be mixed and dispersed by use of a stirrer-equipped container containing glass beads for mixing and dispersing.

15 [0054]

Method of Antifouling Treatment, Antifouling Coating Film, And Coated Object

A method of antifouling treatment according to an embodiment of the present invention includes using the above antifouling coating composition to
20 produce an antifouling coating film on the surface of an object to be coated. The method of antifouling treatment of the present invention can prevent adhesion of aquatic fouling organisms by the gradual dissolution of the surface of the antifouling coating film, so as to continually renew the surface of the coating film. After the dissolution of the coating film, the antifouling effect can be
25 continuously exhibited by recoating the composition.

[0055]

Examples of objects on which a coating film can be formed include ships (in particular, ship bottoms), fishing tools, and structures submerged in seawater. Examples of the fishing tools include fishing nets for use in aquaculture or in

fixed netting, and fishing net accessories such as floats attached to fishing nets and ropes. Examples of the structures submerged in seawater include power plant aqueducts, bridges, and port facilities.

[0056]

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

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

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

[0057]

15 The antifouling coating film produced using the above antifouling coating composition according to an embodiment of the present invention can exhibit a suitable dissolving rate and property of the coating film in seawater. In addition, a long-term stable surface renewal can remain constant and a desired antifouling effect can be effectively exerted. Also, the coating film can
20 advantageously exert excellent recoating performance.

[0058]

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

[0059]

An antifouling coating film of the present invention has a suitable hardness. Specifically, the antifouling coating film of the present invention has an enough

hardness to cause no coating film defects such as cold flow.

[0060]

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

The coated object of the present invention improves a suitable dissolving rate and property of the coating film in seawater to provide a coating film having long-term stable surface renewal and excellent recoating performance. Accordingly, the coated object can be preferably used as the above ships (in
10 particular, ship bottoms), fishing tools, structures submerged in seawater, etc.

[0061]

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

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

[0062]

The surface of the antifouling coating film is basically free from cracking or peeling even after a long period of time. Accordingly, it is unnecessary to
25 completely remove the existing coating film before a new coating film is re-formed. Therefore, by directly recoating the antifouling coating film composition thereon, the antifouling coating film can be effectively formed. This makes it possible to continuously maintain the antifouling effect in a simple and inexpensive manner.

EXAMPLES

[0063]

The following illustrates Examples, etc., and further clarifies characteristics of the present invention. The present invention, however, is not limited to these Examples.

[0064]

In each of the Production Examples, Comparative Production Examples, Examples, and Comparative Examples, "%" denotes "% by mass". Viscosity was determined at 25°C using a Brookfield viscometer. The weight-average molecular weight (Mw) was determined by gel permeation chromatography (GPC) (using a polystyrene standard). GPC was performed under the following conditions.

Equipment: HLC-8220 GPC; Tosoh Corporation

Column: TSK-gel Super HZM-M (Tosoh Corporation); two

Flow rate: 0.35 mL/min

Detector: RI

Column thermostat temperature: 40°C

Eluent: THF

The non-volatile content was determined after heating for 1 hour at 125°C.

In addition, the amounts of each ingredient shown in Table 1 are represented in grams.

[0065]

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

First, 230 g of xylene was placed in a flask including a thermometer, a reflux condenser, a stirrer, and a dropping funnel. Next, while stirring at $100 \pm 2^\circ\text{C}$ under a nitrogen atmosphere, a mixed solution containing 275 g of t-butyldiphenylsilyl acrylate, 175 g of methyl methacrylate, 50 g of methoxyethyl acrylate, and 4 g of t-butyl peroxy-2-ethyl hexanoate (initially added) was added

dropwise over 1 hour. Then, after stirring the resulting reaction solution at the above temperature for 2 hours, 1 g of t-butyl peroxy-2-ethyl hexanoate (subsequently added) was added three times with 2-hour intervals to complete the polymerization reaction. After that, 270 g of xylene was added and dissolved, thus producing the triorganosilyl ester-containing copolymer solution A-1.

Table 1 shows the viscosity, non-volatile content, and Mw, of A-1.

[0066]

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

An organic solvent, monomer, and polymerization initiator as designated in Table 1 were used, and a polymerization reaction according to the same manner as in Production Example 1 was carried out to yield copolymer solutions A-2 to A-6. Table 1 shows the viscosity, non-volatile content, and Mw of each copolymer solution obtained.

[0067]

[Table 1]

Table 1

Component Classification	Component Name	Production Example						Comparative Production Example			
		1	2	3	4	5	6	1	2	3	4
Initial Solvent in Container	Xylene	230	230	230	200	200	230	230	200	230	200
Triorganosilyl Group-containing Monomer (a)	Tert-butyl/diphenylsilyl Acrylate	275	300	300	350	400	300	270	425		
	Tert-butyl/diphenylsilyl Methacrylate									300	
	Tri-isopropylsilyl Acrylate						25				400
	Methyl Methacrylate	175	175	100	60	20	90	180	10	75	10
Ethylenically Unsaturated Monomer (b)	n-butyl Acrylate				10						10
	2-methoxyethyl Acrylate	50	25	10	10	10		50	10		10
	2-methoxyethyl Methacrylate			90	70	70	85		55	125	70
	t-butyl Peroxy-2-ethyl Hexanoate	4	4	4	4	4	4	4	4	4	4
Polymerization Initiator	t-butyl Peroxy-2-ethyl Hexanoate	1 x 3 Times	1 x 3 Times	1 x 3 Times	1 x 3 Times	1 x 3 Times	1 x 3 Times	1 x 3 Times	1 x 3 Times	1 x 3 Times	1 x 3 Times
Solvent Added After Completion of Polymerization Reaction	Xylene	270	270	270	300	300	270	270	300	270	300
Reaction Temperature (°C)		100±2	100±2	100±2	90±2	90±2	100±2	100±2	90±2	100±2	90±2
Copolymer	Viscosity (mPa·S/25°C)	810	640	380	280	220	320	840	200	730	130
	Non-volatile Content (%; 125°C, 1h)	51.7	52.0	51.5	52.3	52.7	51.6	51.5	53.1	53.0	50.0
	Weight-average Molecular Weight (Mw)	46,000	45,000	43,000	35,000	31,000	45,000	46,000	30,000	40,000	33,000
	Copolymer Name	A-1	A-2	A-3	A-4	A-5	A-6	C-1	C-2	C-3	C-4

[0068]

Production Example 7 (Production of Copolymer Solution A-7)

First, 50 g of propylene glycol methyl ether (PGM) and 130g of xylene were placed in a four-neck flask including a thermometer, a reflux condenser, a stirrer, and a dropping funnel. Next, while stirring at $100 \pm 2^{\circ}\text{C}$ under a nitrogen atmosphere, a mixed solution containing 25 g of PGM, 25 g of xylene, 275 g of t-butyldiphenylsilyl acrylate, 125 g of methyl methacrylate, 75 g of 2-methoxyethyl methacrylate, 25 g of zinc methacrylate, and 4 g of t-butyl peroxy-2-ethyl hexanoate (initially added) was added dropwise over 1 hour. After the dropwise addition, the polymerization reaction was performed for 2 hours at $100 \pm 2^{\circ}\text{C}$. Then, while stirring the resulting reaction solution at $100 \pm 2^{\circ}\text{C}$, 1 g of t-butyl peroxy-2-ethyl hexanoate (subsequently added) was added three times with 2-hour intervals to perform the polymerization reaction. After that, 270 g of xylene was added and dissolved, thus producing a metal carboxylate-containing copolymer solution A-7. The resulting varnish has a non-volatile content of 51.7% and a viscosity of 490 cps/ 25°C .

[0069]

Production Example 8 (Production of Copolymer Solution A-8)

First, 325 g of xylene and 100 g of n-butanol were placed in a four-neck flask including a thermometer, a reflux condenser, a stirrer, and a dropping funnel. Next, the mixture was heated to 100 to 110°C , and a mixed solution containing 275 g of t-butyldiphenylsilyl acrylate, 10 g of acrylic acid, 75 g of ethyl acrylate, 90 g of cyclohexyl methacrylate, and 12 g of azobisisobutyronitrile (initially added) was then added dropwise over 4 hours under a nitrogen atmosphere. During 30 min after completion of the dropwise addition, the mixture was kept at 110°C . Then, a mixed solution containing 50 g of xylene, 25 g of n-butanol, and 2.5 g of azobisisobutyronitrile (subsequently added) was added dropwise over 1 hour, and the resulting mixture was maintained until 2 hours after the dropwise

addition.

After that, the dropping funnel was replaced by a decanter, and 25.2 g of copper acetate, 50 g of naphthenic acid, and 50 g of deionized water were added. Subsequently, the resulting mixture was heated to 100°C, and acetic acid and water generated by the reaction were removed to yield a metal carboxylate-containing copolymer solution A-8. The resulting varnish has a non-volatile content of 51.5% and a viscosity of 330 cps/25°C.

[0070]

Production Example 9

First, 100 g of xylene and 20 g of n-butanol were placed in a flask including a thermometer, a reflux condenser, a stirrer, and a dropping funnel. Next, the mixture was heated to 100 to 110°C, and a mixed solution containing 25.7 g of acrylic acid, 57.8 g of ethyl acrylate, 16.5 g of methyl methacrylate, and 3 g of azobisisobutyronitrile was then added dropwise over 4 hours under a nitrogen atmosphere. During 30 min after completion of the dropwise addition, the mixture was kept at 110°C. Then, a mixed solution containing 20 g of xylene, 10 g of n-butanol, and 0.5 g of azobisisobutyronitrile was added dropwise over 1 hour, and the resulting mixture was maintained until 2 hours after the dropwise addition.

After that, the dropping funnel was replaced by a decanter, and 74.9 g of copper propionate, 91.1 g of naphthenic acid, and 50 g of deionized water were added. Subsequently, the resulting mixture was heated to 100°C, and propionic acid and water generated by the reaction were removed. Meanwhile, the termination point of the reaction was determined by quantifying acetic acid in the distillate solvent. After completion of the reaction, xylene was added to adjust a solid content. Finally, a metal carboxylate-containing copolymer solution B-1 was prepared. The resulting varnish has a non-volatile content of 50.3%, a weight-average molecular weight of 8,000, and a viscosity of 185 cps/25°C.

[0071]

Comparative Production Examples 1 to 4

5 An organic solvent, monomer, and polymerization initiator as designated in Table 1 were used, and a polymerization reaction according to the same manner as in Production Example 1 was carried out to yield copolymer solutions C-1 to C-4. Table 1 shows the viscosity, non-volatile content, and Mw of each copolymer solution obtained.

[0072]

10 **Examples 1 to 19 and Comparative Examples 1 to 4 (Production of Coating Compositions)**

Components as designated in Table 2 were dispensed in a proportion (% by mass) as designated in Table 2, and mixed and dispersed with glass beads with a diameter of 1.5 to 2.5 mm to prepare coating compositions.

[0073]

15 [Table 2]

Table 2 (1)

Component Name		Example												
		1	2	3	4	5	6	7	8	9	10	11	12	13
Copolymer	A-1	23												
	A-2		23							23	26	26	26	23
	A-3			23										
	A-4				23									
	A-5					23								
	A-6						23							
	A-7							23						
	A-8								23					
	B-1													
	C-1													
	C-2													
	C-3													
	C-4													
Modified Rosin Salt Solution, Resin Acid Salt Solution, Rosin Solution	Zn-containing Gum Rosin Solution	8	8	8	8	8	8	8	8					
	Zn-containing Hydrogenated Rosin Solution									8				
	Cu-containing Gum Rosin Solution										5			
	Cu-containing Hydrogenated Rosin Solution											5		
	Gum Rosin Solution												5	
	Quintone 1500													8
Plasti cizer	Epoxidized Linseed Oil	1	1	1	1	1	1	1	1	1	1	1	1	1
	Chlorinated Paraffin	1	1	1	1	1	1	1	1	1	1	1	1	1
Antifoulant	Cuprous Oxide	45	45	45	45	45	45	45	45	45	45	45	45	45
	Copper Pyrithione	3	3	3	3	3	3	3	3	3	3	3	3	3
	Sea-Nine 211													
	Preventol A-5S													
	ECONEA 028													
Pigment	Red Iron Oxide	2	2	2	2	2	2	2	2	2	2	2	2	2
	Talc	2	2	2	2	2	2	2	2	2	2	2	2	2
	Mica	2	2	2	2	2	2	2	2	2	2	2	2	2
	Zinc Oxide	2	2	2	2	2	2	2	2	2	2	2	2	2
	Titanium Oxide	1	1	1	1	1	1	1	1	1	1	1	1	1
	Organic Red Pigment	1	1	1	1	1	1	1	1	1	1	1	1	1
Other Additives	Tetraethoxysilane	1	1	1	1	1	1	1	1	1	1	1	1	1
	DISPARLON A603-20X	3	3	3	3	3	3	3	3	3	3	3	3	3
Sol vent	Xylene	5	5	5	5	5	5	5	5	5	5	5	5	5
Total		100	100	100	100	100	100	100	100	100	100	100	100	100

Table 2 (2)

Component Name		Example						Comparative Example			
		14	15	16	17	18	19	1	2	3	4
Copolymer	A-1										
	A-2	14	23	23	23	15	15				
	A-3										
	A-4										
	A-5										
	A-6										
	A-7										
	A-8										
	B-1					8					
	C-1							23			
	C-2								23		
	C-3									23	
	C-4						8				23
Modified Rosin Salt Solution, Resin Acid Salt Solution, Rosin Solution	Zn-containing Gum Rosin Solution	14	8	8	8	8	8	8	8	8	8
	Zn-containing Hydrogenated Rosin Solution										
	Cu-containing Gum Rosin Solution										
	Cu-containing Hydrogenated Rosin Solution										
	Gum Rosin Solution										
	Quintone 1500										
Plasti cizer	Epoxidized Linseed Oil	3	1	1	1	1	1	1	1	1	1
	Chlorinated Paraffin	1	1	1	1	1	1	1	1	1	1
Antifoulant	Cuprous Oxide	45	45	45	45	45	45	45	45	45	45
	Copper Pyrithione	3	3	3	3	3	3	3	3	3	3
	Sea-Nine 211		2								
	Preventol A-5S			2							
	ECONEA 028				2						
Pigment	Red Iron Oxide	2	2	2	2	2	2	2	2	2	2
	Talc	2	1	1	1	2	2	2	2	2	2
	Mica	2	1	1	1	2	2	2	2	2	2
	Zinc Oxide	2	2	2	2	2	2	2	2	2	2
	Titanium Oxide	1	1	1	1	1	1	1	1	1	1
	Organic Red Pigment	1	1	1	1	1	1	1	1	1	1
Other Additives	Tetraethoxysilane	1	1	1	1	1	1	1	1	1	1
	DISPARLON A603-20X	4	3	3	3	3	3	3	3	3	3
Sol vent	Xylene	5	5	5	5	5	5	5	5	5	5
Total		100	100	100	100	100	100	100	100	100	100

The details of the materials listed in Table 2 are as follows:

Zn-containing Gum Rosin Solution: About 50% of solid content in xylene

solution

Zn-containing Hydrogenated Rosin Solution: About 50% of solid content in xylene solution

5 Cu-containing Gum Rosin Solution: About 50% of solid content in xylene solution

Cu-containing Hydrogenated Rosin Solution: About 50% of solid content in xylene solution

Gum Rosin Solution: About 50% of solid content in xylene solution

10 Quintone 1500: Manufactured by ZEON CORPORATION; 50% xylene solution

Epoxidized Linseed Oil: SANSOCIZER E-9000H, manufactured by New Japan Chemical Co., Ltd.

Chlorinated Paraffin: Manufactured by Wako Pure Chemical Industries, Ltd.

15 Cuprous Oxide: NC-301 with average particle size of 3 μm , manufactured by NISSIN CHEMCO CO., Ltd.

Copper Pyrithione: Copper Omadine, manufactured by Arch Chemical, Inc.

Sea-Nine 211: Manufactured by R&H, Inc., 30% of active component in xylene solution

Preventol A-5S: Manufactured by LANXESS, Inc.

20 ECONEA 028: Manufactured by Janssen Pharmaceutical K.K.

Red Iron Oxide: (TODA COLOR EP-13D, manufactured by TODA PIGMENT CORP.

Talc: Crown Talc 3S, manufactured by Matsumura Sangyo Co., Ltd.

Mica: White Mica, Manufactured by Wakimoto Mica Co., Ltd.

25 Zinc Oxide: Zinc Oxide "2-shu" (Product Name), manufactured by Seido Chemical Industry Co., Ltd.

Titanium Oxide: FR-41, Manufactured by Furukawa Co., Ltd.

Organic Red Pigment: SCARLET TR, manufactured by Sanyo Color Works, LTD.

Tetraethoxysilane: Reagent Grade, manufactured by Kishida Chemical Co., Ltd.

DISPARLON A603-20X: Fatty acid amide-based anti-sagging agent, 30% of active component in xylene paste, manufactured by Kusumoto Chemicals, Ltd.

5 [0074]

Test Example 1 (Stability Test for Coating Compositions)

Each of the coating compositions obtained in Examples 1 to 19 and Comparative Examples 1 to 4 was sealed in a 100-ml wide-mouth tin can and stored in an incubator at 45°C for 3 month. After that, the viscosity of each
10 coating composition was measured using a Brookfield viscometer.

The stability was evaluated as follows.

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

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

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

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

20 Table 3 shows the results.

It can be seen from Table 3 that the coating material formed using the coating composition of the invention (Examples 1 to 19) is excellent in storage stability.

In contrast, the coating material formed using the coating composition of
25 Comparative Example 4 had a significant increase in viscosity after its storage at 45°C for 3 months.

[0075]

[Table 3]

Table 3

		Coating Material Stability	Adhesion Test	Flexibility Test
		45°C After 3 Months		
Example	1	A	A	A
	2	A	A	A
	3	A	A	A
	4	A	A	A
	5	A	A	B
	6	A	A	A
	7	A	A	A
	8	A	A	A
	9	A	A	A
	10	A	A	A
	11	A	A	A
	12	A	A	A
	13	A	A	A
	14	A	A	A
	15	A	A	A
	16	A	A	A
	17	A	A	A
	18	A	A	A
	19	A	A	A
Comparative Example	1	A	A	A
	2	A	C	C
	3	A	D	D
	4	D	B	B

[0076]

Test Example 2 (Adhesion Test for Coating Films)

The adhesion of each coating film was tested in accordance with JIS K-5600-5-6. Specifically, tests were conducted according to the following method. Each of the coating compositions obtained in Examples 1 to 19 and Comparative Examples 1 to 4 was first applied to a blast-finished tin plate (75 x 150 x 2 mm) so that the dry coating film thickness would be about 100 μm . The applied coating was then dried for 1 day at 40°C to prepare a dry coating film with a thickness of about 100 μm . After that, the adhesion test was conducted.

The adhesion was evaluated as follows.

Horizontal eleven lines and vertical eleven lines are formed on the dried

coating film with a cutter so as to reach the base (the tin plate) and to form a crosshatch having 100 squares (each 2 x 2 mm). A cellophane tape (NICHIBAN CO., LTD.; tape width of 24 mm) was affixed to the above-mentioned 100 squares without generating any foam, and one end of the tape was held, and the tape was
5 peeled-off quickly. After that, the adhesion state of the coating film was visually inspected.

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

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

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

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

Table 3 shows the results.

It can be seen from Table 3 that the coating films formed using the coating compositions of the invention (Examples 1 to 19) strongly adhere to the tin plate.
[0077]

15 **Test Example 3 (Flexibility Test for Coating Films)**

Each of the coating compositions obtained in Examples 1 to 19 and Comparative Examples 1 to 4 was applied to a blast-finished tin plate (75 x 150 x 2 mm) so that the dry coating film thickness would be about 100 μm . The applied coating was then dried for 1 day at 40°C to prepare a dry coating film
20 with a thickness of about 100 μm . The tin plate coated with the dry coating film was bent 90 degrees, and the condition of the bent coating film was visually inspected.

The flexibility was evaluated as follows.

A: substantially free of cracks

25 B: contained minute cracks

C: contained large cracks

D: a portion of the coating film was easily peeled-off

Table 3 shows the results.

It can be seen from Table 3 that the coating films formed using the coating

compositions of the invention (Examples 1 to 19) were substantially free of cracks in the flexibility test. Example 5, whose proportion of t-butyldiphenylsilyl acrylate in the copolymer was 80% by mass, had a little less flexibility than the other Examples.

5 [0078]

Test Example 4 (Rotary Test)

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

Two test plates were prepared according to the following method.

First, an anti-corrosive coating film was formed by applying an anti-corrosive coating material (a vinyl-based A/C) to a hard vinyl chloride plate
15 (75 x 150 x 1 mm) so that the thickness after drying would be about 50 μm , followed by drying. Each of the antifouling coating compositions obtained in Examples 1 to 19 and Comparative Examples 1 to 4 was applied to the anti-corrosive coating film so that the thickness after drying would be about 300 μm . The applied coating was dried for 3 days at 40°C, thus preparing a test
20 plate having a dry coating film with a thickness of about 300 μm .

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

The initial coating film thickness and the remaining coating film thickness after every 3 months from the beginning of the test were measured for each test plate, using a laser focus displacement meter, and the thickness of the dissolved coating film was calculated from the difference therebetween to give the

dissolving amount of the coating film per month ($\mu\text{m}/\text{month}$). The measurement was conducted for 24 months, and the coating film dissolving amount was calculated every 12 months.

After the rotary test was completed (after 24 months), the test plate was dried, and the surface of each coating film was visually inspected to evaluate the state of the coating film.

The evaluation was conducted in the following way.

A : No defects are observed

B : Hairline cracks are slightly observed

C : Hairline cracks are observed on the entire surface of the coating film

D : Coating film defects such as large cracks, blisters or peel-offs are observed

[0079]

Table 4 shows the results.

It can be seen from Table 4 that the coating films formed using the coating compositions of the invention (Examples 1 to 19) are dissolved in seawater in amounts of about 3 to 5 μm per month (annual average).

In addition, the coating films formed using the coating compositions of the invention exhibit certain reductions in the dissolving rate, so that they are dissolved stably for an extended period of time. Furthermore, the coating films formed using the coating compositions of the invention are excellent in water resistance, and do not develop cracks or hairline cracks. Accordingly, the antifouling effect can be maintained for a long time. Example 5, whose proportion of t-butyldiphenylsilyl acrylate in the copolymer was 80% by mass, had a little less suitable coating film condition after 24 months than the other Examples.

In contrast, the coating film formed using the coating composition of Comparative Example 3 had a remarkably small dissolving rate, and thus cannot exhibit a sufficient antifouling effect. In addition, because the coating

film is too hard, its water resistance is poor and coating film defects such as cracks and peel-offs occur. Further, the coating film formed using the coating composition of Comparative Example 4 had an increasingly larger dissolving rate over time in seawater, and thus cannot exhibit the antifouling effect for a long time. Furthermore, Comparative Example 1, whose proportion of t-butyldiphenylsilyl acrylate in the copolymer was 54% by mass, had a good coating film condition after 24 months. The average coating film dissolving amount from 12 to 24 months, however, had a larger decrease than that during the first 12 months. This illustrates an unstable coating film dissolving rate. Moreover, Comparative Example 2, whose proportion of t-butyldiphenylsilyl acrylate in the copolymer was 85% by mass, had a poor coating film condition after 24 months. The average coating film dissolving amount from 12 to 24 months had a larger increase than that during the first 12 months. This illustrates an unstable coating film dissolving rate.

[0080]

[Table 4]

Table 4

		Rotary Test: Dissolving Amount and Condition of Coating Film		
		Average Coating Film Dissolving Amount ($\mu\text{m}/\text{month}$) During First 12 Months	Average Coating Film Dissolving Amount ($\mu\text{m}/\text{month}$) from 12 to 24 months	Coating Film Condition after 24 Months
Example	1	3.5	3.0	A
	2	3.4	3.5	A
	3	3.6	3.7	A
	4	3.4	4.3	A
	5	3.8	4.9	B
	6	3.7	4.7	A
	7	4.0	4.1	A
	8	4.2	4.4	A
	9	3.4	3.4	A
	10	3.1	3.2	A
	11	3.3	3.1	A
	12	3.3	3.5	A
	13	4.1	4.4	A
	14	4.3	4.8	A
	15	3.3	3.2	A
	16	4.1	4.4	A
	17	4.2	4.6	A
	18	4.2	4.3	A
	19	4.1	5.0	B
Comparative Example	1	3.3	2.2	A
	2	4.0	6.9	C
	3	0.5	0.3	D
	4	5.9	8.3	C

[0081]

Test Example 5 (Antifouling Test)

Each of the coating compositions obtained in Examples 1 to 19 and Comparative Examples 1 to 4 was applied to both surfaces of a hard vinyl chloride plate (100 x 200 x 2 mm) so that the dry coating film thickness would be about 200 μm . The applied coating was dried for 3 days at room temperature (25°C), thus preparing a test plate having a dry coating film with a thickness of about 200 μm . This test plate was immersed at 1.5 m below sea level in Owase City, Mie Prefecture, Japan, and the test plate fouling due to attached objects was examined for 24 months.

The evaluation was conducted by visual inspection of the state of the surface

of the coating film in accordance with criteria shown below.

A : Fouling organisms such as shellfish or algae are not attached, and slime is little attached.

5 B : Fouling organisms such as shellfish or algae are not attached, and slime is thinly attached (to the extent that the coating film surface is observable) and the slime can be removed when wiped by brush softly.

C : Fouling organisms such as shellfish or algae are not attached, and slime is thickly attached (to the extent that the coating film surface is not observable) and the slime cannot be removed even when wiped by brush strongly.

10 D : Fouling organisms such as shellfish or algae are attached
[0082]

Table 5 shows the results.

It can be seen from Table 5 that the coating films formed using the coating compositions of the invention (Examples 1 to 19) were substantially free of
15 fouling organisms such as shellfish and algae after 36 months of the test. Examples 1 and 5, whose proportion of t-butyldiphenylsilyl acrylate in the copolymer was 55 or 80% by mass, had a little less antifouling performance after 36 months. In contrast, Examples having the proportion of 60 to 70% by mass had no decreased antifouling performance after 36 months. In addition,
20 Examples 7 to 8 and 18 to 19, which included a metal carboxylate-containing copolymer, had a little less antifouling performance after 36 months. In contrast, in Examples without the metal carboxylate-containing copolymer, the antifouling performance did not decrease after 36 months.

Further, the coating film formed using the coating composition of
25 Comparative Example 1, whose proportion of t-butyldiphenylsilyl acrylate in the copolymer was 54% by mass, had thin slime attached at 24 months. After 36 months, however, fouling organisms were attached. Furthermore, in Comparative Example 2, whose proportion of t-butyldiphenylsilyl acrylate in the copolymer was 85% by mass, thin slime was attached at 24 months and thick

slime was attached after 36 months. Moreover, fouling organisms such as shellfish or algae were tightly attached, after 24-month immersion, to the coating film formed using the coating composition of Comparative Example 3 or 4.

[0083]

5 [Table 5]

Table 5

		Evaluation		
		After 12 Months	After 24 Months	After 36 Months
Example	1	A	A	B
	2	A	A	A
	3	A	A	A
	4	A	A	A
	5	A	A	B
	6	A	A	A
	7	A	A	B
	8	A	A	B
	9	A	A	A
	10	A	A	A
	11	A	A	A
	12	A	A	A
	13	A	A	A
	14	A	A	A
	15	A	A	A
	16	A	A	A
	17	A	A	A
	18	A	A	B
	19	A	A	B
Comparative Example	1	A	B	D
	2	A	B	C
	3	B	D	D
	4	A	D	D

CLAIMS

1. An antifouling coating composition, comprising a copolymer A obtainable by
5 copolymerizing (a) 55 to 80% by mass of a t-butyldiphenylsilyl acrylate monomer
and (b) 20 to 45% by mass of an ethylenically unsaturated monomer other than
the monomer (a), wherein the monomer (b) is at least one monomer selected from
the group consisting of methyl methacrylate, butyl (meth)acrylate, and
2-methoxyethyl (meth)acrylate.
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2. The antifouling coating composition according to Claim 1, further
comprising at least one kind selected from the group consisting of rosins, rosin
derivatives, and metal salts thereof.
- 15 3. A copolymer for an antifouling coating composition, wherein the copolymer
is produced by copolymerizing (a) 55 to 80% by mass of a t-butyldiphenylsilyl
acrylate monomer and (b) 20 to 45% by mass of an ethylenically unsaturated
monomer other than the monomer (a); and the monomer (b) is at least one
monomer selected from the group consisting of methyl methacrylate, butyl
20 (meth)acrylate, and 2-methoxyethyl (meth)acrylate.
4. A coated object with a surface having an antifouling coating film formed by
using the antifouling coating composition according to Claim 1.