

DESCRIPTION

COPOLYMER FOR ANTIFOULING COATING COMPOSITION, ANTIFOULING COATING COMPOSITION, ANTIFOULING COATING FILM FORMED FROM SAID COMPOSITION, COATED OBJECT HAVING SAID COATING FILM IN SURFACE, AND ANTIFOULING TREATMENT METHOD FOR FORMING SAID COATING FILM

TECHNICAL FIELD

[0001]

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

BACKGROUND

[0002]

Aquatic fouling organisms such as barnacles, tubeworms, common mussels, *Bugula neritina*, sea squirts, green laver, sea lettuce, and slimes attach to surface of ships (especially 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 appearance, and other problems of the ships, structures submerged in seawater and so on. Especially regarding ships, resistance would increase, leading to reduced speed and increased fuel consumption, thereby resulting in greater damage.

[0003]

Accordingly, in recent days, antifouling coating is coated on the surface of ships (especially ship bottoms), fishing tools such as fishing nets and fishing net accessories, and structures submerged in seawater such as power plant aqueducts, thereby forming an antifouling coating film to prevent such damages. Usage of organotin-containing copolymers which were conventionally used in the antifouling coating has been banned, and thus triorganosilyl group-containing copolymer having lower toxicity and lower environmental impact has been developed in place of the organotin-containing copolymer.

[0004]

Regarding the triorganosilyl group-containing copolymer,

the triorganosilyl ester moiety is hydrolyzed in seawater, allowing the copolymer to gradually dissolve in the seawater, and thus exhibiting an antifouling effect by renewing the coating surface. Here, when a copolymer comprising a monomer comprising a triorganosilyl ester having at least one linear alkyl group within its molecule, such as tri-n-butylsilyl ester and tri-n-hexylsilyl ester (Patent Literature 1), dimethyl n-octylsilyl ester (Patent Literatures 2 and 3), dimethyl n-decylsilyl ester (Patent Literature 4), dimethyl (n-octadecyl)silyl ester (Patent Literature 5), diisopropyl (n-dodecyl)silyl ester (Patent Literature 6) and the like is used, shelf stability of the coating was inferior, the hydrolysis rate of the coating film was extremely high, and water resistance was also inferior. Accordingly, it was difficult to control the dissolving rate of the coating film. Therefore, it was difficult to utilize it as a coating composition for ship bottom.

[0005]

Further, when a copolymer containing a triorganosilyl ester comprising a branched alkyl group or aryl group such as triisopropylsilyl ester, t-butylsilyl ester and the like is used, the hydrolysis rate is low and thus it takes time for the coating film to start to dissolve. Accordingly, the antifouling effect cannot be exhibited sufficiently, and utilization was difficult.

[0006]

Accordingly, copolymer obtained by copolymerization of triorganosilyl group-containing monomer with (meth)acrylic acid alkoxyalkyl ester such as (meth)acrylic acid 2-methoxyethyl ester (Patent Literatures 8, 9, and 10), copolymer obtained by copolymerization of triorganosilyl group-containing monomer with (meth)acrylic acid hydroxyalkyl ester such as (meth)acrylic acid 2-hydroxyethyl ester (Patent Literature 11), and copolymer obtained by copolymerization of triorganosilyl group-containing monomer with meth(acrylic) acid ester having various functional groups such as (meth)acrylic acid dimethylaminoethyl ester (Patent Literature 12) have been proposed.

[0007]

However, although these triorganosilyl group-containing copolymers showed higher dissolving rate of the coating film and thus utilization became possible, the initial dissolution characteristics of the coating film was still low. Therefore, there was a problem in that fouling organisms would adhere during the rigging period and the initial anchorage period.

Further, when the formulation ratio of the monomer was altered to increase the initial dissolution characteristics of the coating film, the dissolution characteristics of the coating film becomes extremely high upon time, thereby bringing rise to problems such as occurrence of defects such as cracks and blisters in the coating film after a short period of time, and complete dissolution of the coating film after a short period of time resulting in no coating film left.

CITATION LIST

PATENT LITERATURE

[0008]

- [Patent Literature 1] US 4,593,055B
- [Patent Literature 2] JP-A-Hei 11-43642
- [Patent Literature 3] JP-A-Sho 63-118381
- [Patent Literature 4] JP-A-Hei 9-286933
- [Patent Literature 5] JP-A-Hei 3-31372
- [Patent Literature 6] JP-A-Hei 7-18216
- [Patent Literature 7] JP-A-2005-82725
- [Patent Literature 8] JP-A-Hei 7-102193
- [Patent Literature 9] JP-A-Hei 8-199095
- [Patent Literature 10] JP-A-2001-226440
- [Patent Literature 11] JP-A-2000-17203
- [Patent Literature 12] JP-A-Hei 8-269389

SUMMARY OF INVENTION

TECHNICAL PROBLEM

[0009]

It is an object of the present invention to provide an antifouling coating composition which can achieve superior initial dissolution characteristics of the coating film and antifouling effect in seawater, maintain stable dissolution characteristics of the coating film and antifouling effect for a long period of time, and can achieve superior physical properties with no peeling and cracks in the coating film in seawater for a long period of time.

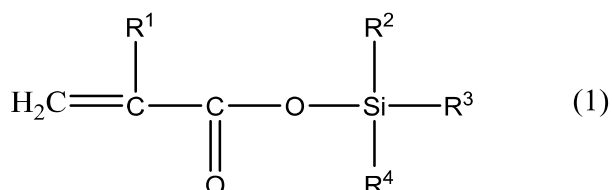
SOLUTION TO PROBLEM

[0010]

According to the present invention, provided is a copolymer for antifouling coating composition obtained by copolymerizing a mixture of methacrylic acid triorganosilyl

ester monomer (a) represented by the following general formula (1):

[Chemical Formula 1]



(wherein, R^1 represents a methyl group, R^2 , R^3 , and R^4 are the same or different from each other, and each is selected from a branched alkyl group having 3 to 8 carbon atoms and a phenyl group); and polymerizable unsaturated monomer (b) other than the monomer (a); wherein the monomer (b) comprises methyl acrylate; content of the monomer (a) is 25 to 65 mass% of total mass of the monomer (a) and the monomer (b); and content of methyl acrylate is 25 to 75 mass% of total mass of the monomer (a) and the monomer (b).

[0011]

The inventors of the present invention have conducted extensive study, and found that when copolymer (A) obtained by allowing monomer (b) to include a certain amount of methyl acrylate, which is copolymerized with methacrylic acid triorganosilyl ester monomer (a) having a particular structure is used as a vehicle, an antifouling coating composition which can achieve superior initial dissolution characteristics of the coating film and antifouling effect in seawater, achieve superior physical properties with no peeling and cracks in the coating film in seawater for a long period of time, and can maintain stable dissolution characteristics of the coating film and antifouling effect for a long period of time can be obtained, thereby leading to completion of the present invention.

MODE FOR CARRYING OUT THE INVENTION

[0012]

Hereinafter, the present invention will be explained in detail.

The antifouling coating composition of the present invention comprises a triorganosilyl group-containing copolymer (A) and an antifouling agent (B).

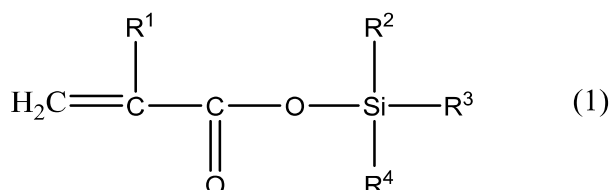
[0013]

<Triorganosilyl Group-Containing Copolymer (A)>

The triorganosilyl group-containing copolymer (A) is obtained by copolymerizing a mixture of methacrylic acid

triorganosilyl ester monomer (a) represented by the general formula (1):

[Chemical Formula 1]



(wherein, R¹ represents a methyl group; R², R³, and R⁴ are the same or different from each other, and each is selected from a branched alkyl group having 3 to 8 carbon atoms and a phenyl group.) and a polymerizable unsaturated monomer (b) other than the monomer (a).

[0014]

<Monomer (a)>

In the present invention, the monomer (a) represented by the general formula (1) is, for example, triisopropylsilyl methacrylate, triisobutylsilyl methacrylate, tri-s-butylsilyl methacrylate, triisoamylsilyl methacrylate, tris(2-ethylhexyl)silyl methacrylate, triphenylsilyl methacrylate, diisopropyl isobutylsilyl methacrylate, diisopropyl isoamylsilyl methacrylate, diisopropyl (2-ethylhexyl)silyl methacrylate, diisopropyl phenylsilyl methacrylate, diisopropyl cyclohexylsilyl methacrylate, t-butyl diisopropylsilyl methacrylate, t-butyl diisobutylsilyl methacrylate, t-butyl diisoamylsilyl methacrylate, t-butyl diphenylsilyl methacrylate, and the like. Preferably, the monomer (a) is triisopropylsilyl methacrylate, and especially preferably triisopropylsilyl methacrylate. These monomers can be used alone or two or more of these can be used in combination.

[0015]

<Monomer (b)>

The monomer (b) is a monomer which is co-polymerizable with the monomer (a). In the present invention, it is an essential requirement for the monomer (b) to comprise methyl acrylate. The technical effect of maintaining dissolution characteristics of the coating film and antifouling effect stably for a long period of time can be achieved by allowing the monomer (b) to comprise methyl acrylate.

[0016]

The monomer (b) can comprise only methyl acrylate, or can comprise monomers other than the methyl acrylate. As the monomer other than the methyl acrylate, the followings can be

mentioned for example.

Acrylic acid triorganosilyl esters such as triisopropylsilyl acrylate, triisobutylsilyl acrylate, tri n-butylsilyl acrylate, triisoamylsilyl acrylate, tris (2-ethylhexyl)silyl acrylate, triphenylsilyl acrylate, diisopropyl isobutylsilyl acrylate, diisopropyl isoamylsilyl acrylate, diisopropyl (2-ethylhexyl)silyl acrylate, diisopropyl phenylsilyl acrylate, diisopropyl cyclohexylsilyl acrylate, t-butyl diisopropylsilyl acrylate, t-butyl diisobutylsilyl acrylate, t-butyl diisoamylsilyl acrylate, t-butyl diphenylsilyl acrylate and the like.

(Meth)acrylic acid esters such as methyl methacrylate, ethyl (meth)acrylate, n-butyl (meth)acrylate, i-butyl (meth)acrylate, t-butyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, phenyl (meth)acrylate, cyclohexyl (meth)acrylate, benzyl (meth)acrylate, 2-hydroxyethyl (meth)acrylate, 4-hydroxybutyl (meth)acrylate, 2-methoxyethyl (meth)acrylate, 2-methoxypropyl (meth)acrylate, 4-methoxybutyl (meth)acrylate, 2-ethoxyethyl (meth)acrylate, polyethylene glycol methyl ether (meth)acrylate, dimethylaminoethyl (meth)acrylate, diethylaminoethyl (meth)acrylate and the like.

Metal (meth)acrylates such as zinc versatate (meth)acrylate, magnesium versatate (meth)acrylate, copper versatate (meth)acrylate, zinc octylate (meth)acrylate, magnesium octylate (meth)acrylate, copper octylate (meth)acrylate, zinc laurate (meth)acrylate, magnesium laurate (meth)acrylate, copper laurate (meth)acrylate, zinc stearate (meth)acrylate, magnesium stearate (meth)acrylate, copper stearate (meth)acrylate and the like; metal (meth)acrylates such as zinc (meth)acrylate, copper (meth)acrylate and the like.

Vinyl compounds having functional groups such as vinyl chloride, vinylidene chloride, acrylonitrile, methacrylonitrile, vinyl acetate, vinyl benzoate, vinyl butyrate, butyl vinyl ether, lauryl vinyl ether, N-vinyl pyrrolidone and the like.

Aromatic compounds such as styrene, vinyl toluene, α -methyl styrene and the like.

Dialkyl ester compounds of unsaturated dibasic acid such as dimethyl malate, dibutyl malate, dimethyl fumarate and the like.

[0017]

The other co-polymerizable monomers other than the methyl acrylate are each used alone or in combination of two

or more. Preferably, the other co-polymerizable monomer is (meth)acrylate esters, and especially preferably methyl methacrylate, 2-methoxyethyl methacrylate, and 2-methoxyethyl acrylate.

[0018]

The mass ratio of the methyl acrylate in the monomer (b) is 0.33 to 1 for example, preferably 0.5 to 1, particularly for example, 0.33, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, and 1, and can be in the range between the two values exemplified herein. The mass ratio of triorganosilyl acrylate esters, (meth)acrylate esters, metal (meth)acrylates, vinyl compounds, aromatic compounds, dialkyl ester compounds other than the methyl acrylate in the monomer (b) are each for example, 0 to 0.5, particularly for example, 0, 0.1, 0.2, 0.3, 0.4, and 0.5, and can be in the range between the two values exemplified herein. In addition, the mass ratio of the monomer having a hydroxy group or an alkoxy group in the monomer (b) is for example, 0 to 0.5, particularly for example, 0, 0.1, 0.2, 0.3, 0.4, and 0.5, and can be in the range between the two values exemplified herein.

[0019]

<Synthesis of Copolymer (A)>

The copolymer (A) used in the antifouling coating of the present invention can be obtained by copolymerizing a mixture of monomer (a) and monomer (b). The copolymerization is performed, for example, under existence of a polymerization initiator.

[0020]

The content of the monomer (a) in the mixture is 25 to 65 mass%, preferably 25 to 60 mass%, and more preferably 25 to 50 mass%. When the content of the monomer (a) is 25 to 65 mass%, the coating film formed by using the obtained antifouling coating composition would not show defects such as cracks in the coating film in the seawater for a long period of time from the initial timing, and can maintain stable dissolution characteristics of the coating film and antifouling performance.

[0021]

The content of methyl acrylate in the mixture is 25 to 75 mass%, preferably 30 to 75 mass%, and more preferably 35 to 75 mass%. When the content of the methyl acrylate is 25 to 75 mass%, the coating film formed by using the obtained antifouling coating composition can achieve superior dissolution characteristics of the coating film and antifouling effect in seawater from the initial timing, avoid

coating film defects such as peeling and cracks for a long period of time, and can maintain stable dissolution characteristics of the coating film and antifouling effect for a long period of time.

[0022]

The total content of the monomer (a) and methyl acrylate is 70 mass% or more of the total mass of the monomer (a) and the monomer (b), preferably 80 mass% or more, and more preferably 90 mass% or more. When the content is in the afore-mentioned range, the dissolution characteristics of the coating film can be maintained stable for a long period of time and thus especially superior antifouling effect can be achieved.

[0023]

The weight average molecular weight of the copolymer of the present invention is preferably 5000 to 300000. When the molecular weight is lower than 5000, the antifouling coating film would become brittle, prone to peeling and cracks. On the other hand, when the molecular weight exceeds 300000, viscosity of the copolymer solution would increase, thereby causing difficulty in handling.

[0024]

As the polymerization initiator, for example, azo compounds such as 2,2'-azobisisobutyronitrile (AIBN), 2,2'-azobis-2-methylbutyronitrile, dimethyl-2,2'-azobisisobutyrate and the like; and peroxides such as benzoyl peroxide, di-tert-butyl peroxide, tert-butyl peroxybenzoate, tert-butyl peroxyisopropylcarbonate, t-butyl peroxy-2-ethylhexanoate, 1,1,3,3-tetramethylbutyl peroxy-2-ethylhexanoate and the like can be mentioned. These polymerization initiators can be used alone, or two or more can be used in combination. As the polymerization initiator, 2,2'-azobisisobutyronitrile and 1,1,3,3-tetramethylbutyl peroxy-2-ethylhexanoate are especially preferable.

[0025]

By suitably selecting the amount of the polymerization initiator being used, the molecular weight of the triorganosilyl ester-containing copolymer can be adjusted.

[0026]

As the polymerization method, liquid polymerization, bulk polymerization, emulsion polymerization, suspension polymerization and the like can be mentioned. Among these, liquid polymerization is especially preferable since it can synthesize the copolymer (A) simply with high accuracy.

[0027]

In the polymerization reaction, organic solvent can be used as necessary. As the organic solvent, for example, aromatic hydrocarbon solvents such as xylene, ethyl benzene, toluene and the like; aliphatic hydrocarbon solvents such as hexane, heptane and the like; ester solvents such as ethyl acetate, butyl acetate, isobutyl acetate, methoxy propyl acetate and the like; alcohol solvents such as isopropyl alcohol, butyl alcohol and the like; ether solvents such as dioxane, diethyl ether, dibutyl ether and the like; ketone solvents such as methyl ethyl ketone, methyl isobutyl ketone and the like; can be mentioned. Among these, aromatic hydrocarbon solvents are preferable, and xylene is more preferable. These solvents can be used alone, or two or more of these can be used in combination.

[0028]

The reaction temperature during polymerization reaction can be suitably selected depending on the type of the polymerization initiator and the like, and is usually approximately 70 to 120 °C, preferably approximately 70 to 100°C. The reaction time during polymerization reaction can be suitably selected depending on the reaction temperature and the like, and is usually approximately 4 to 8 hours.

[0029]

Polymerization reaction is carried out preferably under inert gas atmosphere, such as nitrogen gas, argon gas and the like.

[0030]

<Antifouling Agent (B)>

By adding the antifouling agent (B) to the copolymer (A) of the present invention, an antifouling coating which can maintain antifouling effect for a long period of time can be obtained.

[0031]

As the antifouling agent, there is no particular limitation so long as it is a substance having a killing or repellent effect to marine fouling organisms. For example, an inorganic chemical and an organic chemical can be mentioned.

[0032]

As the inorganic chemical for example, cuprous oxide, cuprous thiocyanate (generic name: copper rhodanide), cupronickel, copper powder and the like can be mentioned. Among these, cuprous oxide and copper rhodanide are particularly preferable.

[0033]

As the organic chemical for example, organic copper compounds such as copper 2-mercaptopyridine-N-oxide (generic name: copper pyrithione) and the like; organic zinc compounds such as zinc 2-mercaptopyridine-N-oxide (generic name: zinc pyrithione), zinc ethylenebis(dithiocarbamate) (generic name: zineb), zinc bis(dimethyldithiocarbamate) (generic name: ziram), bis(dimethyldithiocarbamate) ethylenebis(dithiocarbamate)dizinc (generic name: polycarbamate) and the like; organic boron compounds such as pyridine-triphenylborane, 4-isopropylpyridine-diphenylmethylborane, 4-phenylpyridine-diphenylborane, triphenylboron-n-octadecylamine, triphenyl[3-(2-ethylhexyloxy)propylamine]boron and the like; maleimide compounds such as 2,4,6-trichloromaleimide, N-(2,6-diethylphenyl) 2,3-dichloromaleimide and the like; and other compounds such as 4,5-dichloro-2-n-octyl-3-isothiazolone (generic name: Sea-nine 211), 3,4-dichlorophenyl-N-N-dimethylurea (generic name: Diuron), 2-methylthio-4-t-butylamino-6-cyclopropylamino-s-triazine (generic name: Irgarol 1051), 2,4,5,6-tetrachloroisophthalonitrile (generic name: Chlorothalonil), N-dichlorofluoromethylthio-N',N'-dimethyl-N-p-tolylsulfamide (generic name: Tolyfluanid), N-dichloromethylthio-N',N'-dimethyl-N-phenylsulfamide (generic name: Dichlofluanid), 2-(4-thiazolyl)benzimidazole (generic name: Thiabendazole), 3-(benzo[b]thien-2-yl)-5,6-dihydro-1,4,2-oxathiazine-4-oxide (generic name: Bethoxazin), 2-(p-chlorophenyl)-3-cyano-4-bromo-5-trifluoromethyl pyrrole (generic name: ECONEA 028) and the like can be mentioned. Among these, zinc pyrithione, copper pyrithione, Zineb, Diuron, Sea-nine 211, Irgarol 1051, Tolyfluanid, Dichlofluanid, and ECONEA 028 are preferable, and copper pyrithione, zinc pyrithione, Sea-nine 211, and ECONEA 028 are more preferable.

[0034]

These antifouling agents (B) can be used alone, or two or more types can be used in combination. The content of the antifouling agent in the composition of the present invention is not particularly limited, and is usually 0.1 to 75 mass%, preferably 1 to 60 mass% in the solids of the composition of the present invention. When the content of the antifouling agent (B) is less than 0.1 mass%, sufficient antifouling effect can not be obtained. On the other hand, when the content of the antifouling agent (B) exceeds 75 mass%, the coating film formed would become brittle, and the adhesion property with the object onto which the coating film is

formed would become weak, and thus function as the antifouling coating film cannot be fully realized.

[0035]

<Other Additives>

Further, the resin for antifouling coating of the present invention can further contain release modifier, plasticizer, pigment, dye, antifoaming agent, dehydrating agent, thixotropic agent, organic solvent and the like as necessary, thereby obtaining an antifouling coating.

[0036]

As the release modifier for example, rosin, rosin derivative, and metal salts thereof, monocarboxylic acid and salt thereof, or alicyclic hydrocarbon resin and the like can be mentioned. These can be used alone, or two or more of these can be used in combination.

[0037]

As the rosin, tall oil rosin, gum rosin, wood rosin and the like can be exemplified. As the rosin derivative, hydrogenated rosin, disproportionated rosin, maleic acid modified rosin, formylated rosin, polymerized rosin and the like can be exemplified. Reactant of metal compound and rosin can be used as the metal salt of rosin and metal salt of rosin derivative. As the metal salt of rosin for example, gum rosin zinc (or copper) salt, wood rosin zinc (or copper) salt, tall oil rosin zinc (or copper) salt and the like can be mentioned. As the metal salt of rosin derivative, hydrogenated rosin zinc (or copper) salt, disproportionated rosin zinc (or copper) salt, maleic acid modified rosin zinc (or copper) salt, formylated rosin zinc (or copper) salt, polymerized rosin zinc (or copper) salt and the like can be mentioned.

[0038]

As the monocarboxylic acid for example, fatty acid having approximately 5 to 30 carbon atoms, synthetic fatty acid, naphthenic acid and the like can be mentioned. As the salt of monocarboxylic acid, copper salt, zinc salt, magnesium salt, calcium salt and the like can be mentioned.

[0039]

As the alicyclic hydrocarbon resin, Quintone 1500, Quintone 1525L, Quintone 1700 (product name, available from Zeon Corporation) and the like can be mentioned as commercially available product for example.

[0040]

As the plasticizer for example, phosphoric acid ester such as tricresyl phosphate, trioctyl phosphate, triphenyl

phosphate and the like; phthalic acid ester such as dibutyl phthalate, dioctyl phthalate and the like; adipic acid ester such as dibutyl adipate, dioctyl adipate and the like; sebacic acid ester such as dibutyl sebacate, dioctyl sebacate and the like; epoxidized oil such as epoxidized soybean oil, epoxidized linseed oil and the like; alkyl vinyl ether polymer such as methyl vinyl ether polymer, ethyl vinyl ether polymer and the like; polyalkylene glycol such as polyethylene glycol, polypropylene glycol and the like; t-nonylpentasulfide; Vaseline; polybutene; tris(2-ethylhexyl)trimellitate; silicone oil; liquid paraffin; chlorinated paraffin and the like can be mentioned. These plasticizers can be used alone, or two or more of these can be used in combination.

[0041]

As the pigment, red iron oxide, talc, titanium oxide, silica, calcium carbonate, barium sulfate, calcium oxide and the like can be mentioned. These can be used alone, or two or more of these can be used in combination.

[0042]

As the dye, various kinds of organic dyes and the like soluble in an organic solvent can be mentioned.

[0043]

As the antifoaming agent, a silicone resin-based antifoaming agent, an acryl resin-based antifoaming agent and the like can be mentioned.

[0044]

As the dehydrating agent, a synthetic zeolite-based adsorbent, orthoesters, silicates such as tetraethoxysilane, isocyanates and the like can be mentioned. These can be used alone, or two or more of these can be used in combination.

[0045]

As the thixotropic agent, bentonite, fatty acid amide wax, oxidized polyethylene, various amide compounds and the like can be mentioned. These can be used alone, or two or more of these can be used in combination.

[0046]

As the organic solvent, organic solvents which are usually formulated in the antifouling coating such as an aliphatic solvent, an aromatic solvent, a ketone-based solvent, an ester-based solvent, an ether-based solvent and the like can be mentioned. These can be used alone, or two or more of these can be used in combination.

[0047]

<Method for Manufacturing Antifouling Coating Composition>

The antifouling coating composition of the invention can be manufactured for example, by mixing and dispersing a mixed solution containing the copolymer (A), an antifouling agent (B), other additives and the like by use of a disperser.

[0048]

The content of the copolymer, antifouling agent and the like in the mixed solution can be suitably adjusted so that the content of each of the copolymer, antifouling agent and the like in the antifouling coating composition would be satisfied.

[0049]

The mixed solution is preferably obtained by dissolving or dispersing various materials such as the copolymer, an antifouling agent and the like in a solvent. As the solvent, those similar to the afore-mentioned organic solvent can be used.

[0050]

As 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 and the like can be used. Furthermore, the mixed solution can be mixed and dispersed by using a stirrer-equipped container containing glass beads for mixing and dispersing.

[0051]

<Method for Antifouling Treatment, Antifouling Coating Film, and Coated Object>

The method for antifouling treatment of the present invention is characterized in that an antifouling coating film is formed using the above-explained antifouling coating composition on the surface of an object that is subjected to coating. The method for 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 such that the surface of the coating film is continually renewed. After the dissolution of the coating film, the antifouling effect can be continuously exhibited by recoating the composition.

[0052]

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 ropes and floats attached to fishing nets. Examples of the structures submerged in seawater include power plant

aqueducts, bridges, and port facilities.

[0053]

The antifouling coating film can be formed by applying the antifouling coating composition onto the surface (entirely or partially) of an object on which the coating film is to be formed. Examples of the coating method include brush coating, spray coating, dipping, flow coating, and spin coating. These coating methods can be employed singly or in combination. The coating composition is dried after the application. The drying temperature can be room temperature. The drying time can be suitably selected depending on the thickness of the coating film and the like.

[0054]

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

[0055]

The thickness of the antifouling coating film can be suitably selected depending on the type of an object on which the coating film is to be formed, the navigation speed of a ship, the seawater temperature and the like. For example, when the object on which a coating film is formed is a ship bottom, the thickness of the antifouling coating film is usually 50 to 500 μm , and preferably 100 to 400 μm . The antifouling coating film of the present invention has a suitable hardness. Specifically, the antifouling coating film of the present invention has a hardness sufficient enough to cause no coating film defects such as cold flow.

[0056]

The coated object of the present invention has the antifouling coating film on its surface. The coated object of the present invention can have the antifouling coating film on the entire surface thereof or on the partial surface thereof. The coated object of the present invention is provided with a coating film having long-term stable surface renewal and excellent recoating performance since the suitable dissolving rate and properties of the coating film in seawater are improved. Accordingly, the coated object can be preferably applied for the above ships (in particular, ship bottoms), fishing tools, structures submerged in

seawater, etc. 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 aquatic fouling organisms.

[0057]

Further, the antifouling coating film shows a high dissolution characteristics of the coating film from the initial timing of immersion in seawater, and can maintain the dissolution characteristics stably for a long period of time. Accordingly, the ship can maintain the antifouling performance for a long period of time. For example, when the ship is in a static state such as during the anchorage period and during the rigging period, adhesion and accumulation of the aquatic fouling organisms hardly occur, thereby exhibiting antifouling effect for a long period of time. In addition, the surface of the antifouling coating film is basically free from cracks or peeling even after a long period of time. Accordingly, it is unnecessary to completely remove the existing coating film before re-forming a new coating film. Thus, by directly recoating the antifouling coating film composition, the antifouling coating film can be effectively formed. This makes it possible to continuously maintain the antifouling performance in a simple and inexpensive manner.

EXAMPLES

[0058]

Examples and the like are provided hereinafter, and further clarifies characteristics of the present invention. The present invention, however, is not limited to these Examples.

In each of Production Examples, Reference Examples, Examples, and Comparative Examples, "%" denotes "% by mass".

[0059]

The non-volatile content was determined in accordance with JIS K 5601-1-2 (ISO 3251), by heating for 1 hour at 125°C.

[0060]

The weight-average molecular weight (Mw) was determined by GPC (using a polystyrene standard).

GPC was performed under the following conditions.

Equipment: HLC-8220GPC (available from Tosoh Corporation)

Column: TSKgel Super HZM-M (available from Tosoh

Corporation), two columns used

Flow rate: 0.35 mL/min

Detector: RI

Column thermostat temperature: 40°C

Developing solvent: THF

[0061]

The formulation amount of each component shown in the Tables are represented in grams.

[0062]

<Production Example 1 (Production of Copolymer P-1)>

First, 400g of xylene was charged to a 2000mL flask equipped with a thermometer, a reflux condenser, a stirrer, and a dropping funnel. Then, the temperature was raised to 83 to 87°C under nitrogen atmosphere, a mixture of 150 g of triisopropylsilyl methacrylate, 350 g of methyl acrylate, and 5 g of 1,1,3,3-tetramethylbutyl peroxy-2-ethylhexanoate (PEROCTA O, available from NOF CORPORATION) was added in a dropwise manner into the flask over a period of 1 hour, under agitation at 83 to 87°C. After such dropwise addition, the reaction solution was maintained at 83 to 87°C, while 0.5 g of 1,1,3,3-tetramethylbutyl peroxy-2-ethylhexanoate was added three times with 1-hour intervals to complete the polymerization reaction. Subsequently, 100g of xylene was added and dissolved to obtain the copolymer solution P-1. The non-volatile content of P-1 was 49.8%, and weight average molecular weight was 55000.

[0063]

<Production Examples 2 to 8, Reference Examples 1 to 18>

Organic solvents, monomers, and polymerization initiators shown in Table 1 and Table 2 were used under similar conditions as Production Example 1, thereby obtaining copolymer solutions P-2 to P-8 and comparative copolymer solutions H-1 to H-18. The non-volatile content and the weight average molecular weight of each of the obtained copolymer solution were measured.

Results are shown in Table 1 and Table 2.

[0064]

[Table 1]

Table 1

type of component	component name	Production Example							
		1	2	3	4	5	6	7	8
solvent in initial container	xylene	400	400	400	400	400	400	400	400
monomer (a)	triisopropylsilyl methacrylate	150	170	200	200	200	200	220	250
monomer (b)	methyl acrylate	350	300	300	250	225	175	250	250
	methyl methacrylate		20		20	25	40		
	2-methoxyethyl methacrylate		10		30	50	75	20	
	ethyl acrylate								
	n-butyl acrylate								
	2-methoxyethyl acrylate						10	10	
	2-hydroxyethyl acrylate								
	triisopropylsilyl acrylate								
	monomer (a)/ (sum of monomer (a) + monomer (b))	0.3	0.34	0.4	0.4	0.4	0.4	0.44	0.5
	methyl acrylate/ (sum of monomer (a) + monomer (b))	0.7	0.6	0.6	0.5	0.45	0.35	0.5	0.5
	(sum of monomer (a) + methyl acrylate)/ (sum of monomer (a) + monomer (b))	1	0.94	1	0.9	0.85	0.75	0.94	1
polymerization initiator	initial addition	5	5	5	5	5	5	5	5
	post addition, 3 times	0.5 × 3 times	0.5 × 3 times	0.5 × 3 times	0.5 × 3 times	0.5 × 3 times	0.5 × 3 times	0.5 × 3 times	0.5 × 3 times
solvent added after completion of polymerization reaction		100	100	100	100	100	100	100	100
reaction temperature (°C)		83~87	83~87	83~87	83~87	83~87	83~87	83~87	83~87
non-volatile content (%; 125°C, 1hrs)		49.8	50.1	50.1	49.9	49.7	49.8	50.0	50.2
weight average molecular weight (Mw)		55,000	53,000	54,000	54,000	51,000	49,000	51,000	52,000
name of copolymer		P-1	P-2	P-3	P-4	P-5	P-6	P-7	P-8

Table 1 (continued)

type of component	component name	Reference Example					
		1	2	3	4	5	6
solvent in initial container	xylene	400	300	300	300	300	400
monomer (a)	triisopropylsilyl methacrylate	200	200	200	200	200	200
monomer (b)	methyl acrylate						
	methyl methacrylate	300					200
	2-methoxyethyl methacrylate		300				
	ethyl acrylate			300			
	n-butyl acrylate				300		
	2-methoxyethyl acrylate					300	
	2-hydroxyethyl acrylate						100
	triisopropylsilyl acrylate						
	monomer (a)/ (sum of monomer (a) + monomer (b))	0.4	0.4	0.4	0.4	0.4	0.4
	methyl acrylate/ (sum of monomer (a) + monomer (b))	0	0	0	0	0	0
	(sum of monomer (a) + methyl acrylate)/ (sum of monomer (a) + monomer (b))	0.4	0.4	0.4	0.4	0.4	0.4
polymerization initiator	1,1,3,3-tetramethylbutyl peroxy-2-ethylhexanoate	5	5	5	5	5	5
	1,1,3,3-tetramethylbutyl peroxy-2-ethylhexanoate	0.5 x 3 times	0.5 x 3 times	0.5 x 3 times	0.5 x 3 times	0.5 x 3 times	0.5 x 3 times
solvent added after completion of polymerization reaction		100	200	200	200	200	100
reaction temperature (°C)		83~87	83~87	83~87	83~87	83~87	83~87
non-volatile content (%; 125°C, 1hrs)		49.5	49.9	50.1	50.0	50.2	49.3
weight average molecular weight (Mw)		45,000	53,000	52,000	50,000	51,000	46,000
name of copolymer		H-1	H-2	H-3	H-4	H-5	H-6

[Table 2]

Table 2

type of component		component name	Reference Example												
			7	8	9	10	11	12	13	14	15	16	17	18	
solvent in initial container		xylene	400	300	300	300	300	300	400	400	400	400	400	400	400
monomer (a)		triisopropylsilyl methacrylate	200	200	200	200	200	200	200	200	200				
monomer (b)		methyl acrylate	100	100	100	100	100	100	100	340	300	300	280	250	250
		methyl methacrylate	200						100		20		10		
		2-methoxyethyl methacrylate		200							10			20	
		ethyl acrylate			200									10	
		n-butyl acrylate				200							10		
		2-methoxyethyl acrylate					200								
		2-hydroxyethyl acrylate						100							
		triisopropylsilyl acrylate							160	170	200	200	220	250	250
(sum of monomer (a)/ monomer (a) + monomer (b))		0.4	0.4	0.4	0.4	0.4	0.4	0.4	0	0	0	0	0	0	
(sum of monomer (a) + methyl acrylate/ monomer (a) + monomer (b))		0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.68	0.6	0.6	0.56	0.5	0.5	
(sum of monomer (a) + methyl acrylate)/ (sum of monomer (a) + monomer (b))		0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.68	0.6	0.6	0.56	0.5	0.5	
polymerization initiator	initial addition	1,1,3,3-tetramethylbutyl peroxy-2-ethylhexanoate	5	5	5	5	5	5	5	5	5	5	5	5	
	post addition, 3 times	1,1,3,3-tetramethylbutyl peroxy-2-ethylhexanoate	0.5 × 3 times	0.5 × 3 times	0.5 × 3 times	0.5 × 3 times	0.5 × 3 times	0.5 × 3 times	0.5 × 3 times	0.5 × 3 times	0.5 × 3 times	0.5 × 3 times	0.5 × 3 times	0.5 × 3 times	
solvent added after completion of polymerization reaction		xylene	100	200	200	200	200	200	100	100	100	100	100	100	
reaction temperature (°C)			83~87	83~87	83~87	83~87	83~87	83~87	83~87	83~87	83~87	83~87	83~87	83~87	
non-volatile content (%; 125°C, 1hrs)			50.0	49.8	49.9	49.7	49.7	49.8	50.1	50.0	50.0	49.9	49.7	49.9	
weight average molecular weight (Mw)			47,000	50,000	51,000	53,000	52,000	48,000	55,000	52,000	54,000	55,000	51,000	53,000	
name of copolymer			H-7	H-8	H-9	H-10	H-11	H-12	H-13	H-14	H-15	H-16	H-17	H-18	

[0065]

<Examples 1 to 11, Comparative Examples 1 to 18>

Copolymer solutions P-1 to P-8 and comparative copolymer solutions H-1 to H-18 obtained in Production Examples 1 to 8 and Reference Examples 1 to 18 were used to prepare antifouling coating composition by the formulation as shown in Table 3 and Table 4.

[0066]

(Hardness Measurement of Coating Film)

The coating film hardness of the coating was measured using a Pendulum hardness tester.

Measurement of the hardness of the coating film using the Pendulum hardness tester was carried out by coating a glass plate (100 x 200 x 2 mm) with each of the coating samples so that the thickness after drying would be approximately 100 μm , followed by drying at 40°C for one day. The measurement was performed in a room at 25°C. The values are number of counts.

Results are shown in Table 3 and Table 4.

[0067]

(Solubility Test of Coating Film (Rotary Test))

A rotating drum of 515 mm in diameter and 440 mm in height was mounted at the center of a water tank. The drum was made to be rotatable by a motor. Then, a cooling device for maintaining the temperature of seawater constant and a pH automatic controller for maintaining the pH of seawater constant were attached.

The testing plate of the rotary test was prepared in the following manner.

First, an anticorrosion coating film was formed on a titanium plate (71 x 100 x 0.5 mm) by applying an anticorrosion coating (epoxy vinyl based A/C) so that a coating film having a thickness of approximately 100 μm would be obtained after drying. Subsequently, the coating compositions obtained in Examples 1 to 11 and Comparative Examples 1 to 18 were applied onto the afore-mentioned anticorrosion coating film, respectively, so that the thickness after drying would be approximately 300 μm . The obtained coated product was dried at 40°C for 3 days, thereby preparing a testing plate with a dry coating having a thickness of approximately 300 μm .

The testing plate thus prepared was fixed to the rotating drum of the rotating device of the above apparatus and was allowed to come in contact with seawater. The rotating drum was rotated at a speed of 20 knots. Meanwhile,

the temperature of seawater was kept at 25°C, the pH was kept at 8.0 to 8.2, and seawater was replaced weekly.

Initial film thickness and remaining film thickness were measured in a monthly manner for each of the testing plates, using a shape measurement laser microscope VK-X100 (available from KEYENCE CORPORATION). The dissolved coating film thickness was calculated from the difference between the two values, thereby obtaining dissolution amount of the coating film for one month ($\mu\text{m}/\text{month}$).

Further, when measuring the remaining film thickness after 6 months in the rotary test, the surface of each coating films was observed with naked eye and with a microscope to evaluate the surface condition of the coating film.

[0068]

Evaluation was performed under the following criteria.

A : No defect observed.

B : Scarce hair cracks observed.

C : Hair cracks observed on the entire surface of the coating film.

D : Defects such as cracks, blisters, or peeling observed in the coating film.

Results are shown in Table 3 and Table 4.

[0069]

(Antifouling Test (Static Immersion Test))

Each of the antifouling coating obtained in Examples 1 to 11 and Comparative Examples 1 to 18 was applied onto both sides of a hard polyvinyl chloride plate (100 × 200 × 2 mm) so that the thickness of the dried coating film would be approximately 200 microns. This testing plate was immersed at 1.5 m below sea level in Owase City, Mie Prefecture, Japan, and the testing plate fouling due to adhered organisms was examined for 6 months. The results of evaluation are shown in Table 3 and Table 4.

[0070]

The state of the surface of the coating film was visually evaluated in accordance with criteria shown below.

A: Fouling organisms such as shellfish or algae do not adhere, and slime hardly attaches.

B: Fouling organisms such as shellfish or algae do not adhere, and slime thinly attaches (to the extent that the coating film surface is observable) and the slime can be removed when wiped softly with a brush.

C: Fouling organisms such as shellfish or algae do not adhere, but slime thickly adhere (to the extent that the

coating film surface is not observable) and the slime cannot be removed even when wiped strongly with a brush.

D: Fouling organisms such as shellfish or algae do adhere.

[0071]

[Table 3]

Table 3

component name		Example										
		1	2	3	4	5	6	7	8	9	10	11
copolymer solution	P-1	30								25		30
	P-2		30								25	
	P-3			30								
	P-4				30							
	P-5					30						
	P-6						30					
	P-7							30				
	P-8								30			
	H-1											
	H-2											
	H-3											
	H-4											
	H-5											
	H-6											
antifouling agent	cuprous oxide	45	45	45	45	45	45	45	45	45	45	
	copper pyrithione	3	3	3	3	3	3	3	3	3	3	
	zinc pyrithione											5
	Sea-nine 211											6
pigment	red iron oxide	2	2	2	2	2	2	2	2	2	2	2
	talc	2	2	2	2	2	2	2	2	2	2	16
	zinc oxide	4	4	4	4	4	4	4	4	4	4	20
	titanium oxide	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
other additives	tetraethoxysilane	1	1	1	1	1	1	1	1	1	1	1
	rosin zinc salt									5		5
	hydrogenated rosin zinc salt										5	
	chlorinated paraffin									1	1	
	DISPARLON A603-20X	3	3	3	3	3	3	3	3	3	3	3
solvent	xylene	8	8	8	8	8	8	8	8	7	7	10
total		100	100	100	100	100	100	100	100	100	100	100
coating film hardness (number of Pendulum counts)		15	26	24	27	28	29	26	28	31	35	25
dissolution amount of the coating film (μ m/month) (25°C, 20 knots)	0-1 month	12.5	11.2	12.1	11.7	11.5	12.2	14.3	12.6	10.3	10.7	15.5
	1-2 month	13.1	11.0	12.6	11.4	11.3	11.9	15.3	12.7	12.2	10.1	14.0
	2-3 month	13.5	12.1	12.3	11.2	11.1	12.0	14.5	13.1	11.5	11.6	14.9
	3-4 month	12.9	12.5	13.2	11.8	11.2	12.5	15.1	12.3	11.0	11.4	15.8
	4-5 month	13.0	11.7	12.9	12.0	11.4	12.2	15.6	12.7	10.9	12.6	17.3
	5-6 month	13.4	12.0	12.5	11.8	11.7	12.3	14.8	13.5	11.4	12.7	16.9
condition of coating film after 6 months rotary test		A	A	A	A	A	A	A	A	A	A	A
antifouling test	after 1 month	A	A	A	A	A	A	A	A	A	A	A
	after 2 months	A	A	A	A	A	A	A	A	A	A	A
	after 3 months	A	A	A	A	A	A	A	A	A	A	A
	after 4 months	A	A	A	A	A	A	A	A	A	A	A
	after 5 months	A	A	A	A	A	A	A	A	A	A	A
	after 6 months	A	A	A	A	A	A	A	A	A	A	A

Table 3 (continued)

component name		Comparative Example					
		1	2	3	4	5	6
copolymer solution	P-1						
	P-2						
	P-3						
	P-4						
	P-5						
	P-6						
	P-7						
	P-8						
	H-1	30					
	H-2		30				
	H-3			30			
	H-4				30		
antifouling agent	H-5					30	
	H-6						30
	cuprous oxide	45	45	45	45	45	45
	copper pyrithione	3	3	3	3	3	3
pigment	zinc pyrithione						
	Sea-nine 211						
	red iron oxide	2	2	2	2	2	2
	talc	2	2	2	2	2	2
	zinc oxide	4	4	4	4	4	4
other additives	titanium oxide	1	1	1	1	1	1
	organic red pigment	1	1	1	1	1	1
	tetraethoxysilane	1	1	1	1	1	1
	rosin zinc salt						
solvent	hydrogenated rosin zinc salt						
	chlorinated paraffin						
	DISPARLON A603-20X	3	3	3	3	3	3
	xylene	8	8	8	8	8	8
total		100	100	100	100	100	100
coating film hardness (number of Pendulum counts)		75	30	2	1	1	35
dissolution amount of the coating film ($\mu\text{m}/\text{month}$) (25°C, 20 knots)	0-1 month	0.3	14.5	1.6	0.7	30.3	0.4
	1-2 month	0.1	17.1	1.1	0.5	72.0	0.9
	2-3 month	0.2	20.7	1.8	1.0	122.3	1.5
	3-4 month	0.1	30.3	1.9	1.5	*	2.6
	4-5 month	0.0	35.7	1.3	1.2		2.9
	5-6 month	0.0	52.3	1.1	1.3		4.2
condition of coating film after 6 months rotary test		A	D	B	B	D	D
antifouling test	after 1 month	C	A	A	A	A	B
	after 2 months	D	A	B	B	A	C
	after 3 months	D	A	B	C	A	D
	after 4 months	D	A	C	C	A	D
	after 5 months	D	A	C	D	A	D
	after 6 months	D	A	C	D	A	D

* no coating film

[0072]

[Table 4]

Table 4

component name		Comparative Example					
		7	8	9	10	11	12
copolymer solution	H-7	30					
	H-8		30				
	H-9			30			
	H-10				30		
	H-11					30	
	H-12						30
	H-13						
	H-14						
	H-15						
	H-16						
	H-17						
	H-18						
antifouling agent	cuprous oxide	45	45	45	45	45	45
	copper pyrithione	3	3	3	3	3	3
	zinc pyrithione						
	Sea-nine 211						
pigment	red iron oxide	2	2	2	2	2	2
	talc	2	2	2	2	2	2
	zinc oxide	4	4	4	4	4	4
	titanium oxide	1	1	1	1	1	1
	organic red pigment	1	1	1	1	1	1
other additives	tetraethoxysilane	1	1	1	1	1	1
	rosin zinc salt						
	hydrogenated rosin zinc salt						
	chlorinated paraffin						
	DISPARLON A603-20X	3	3	3	3	3	3
solvent	xylene	8	8	8	8	8	8
total		100	100	100	100	100	100
coating film hardness (number of Pendulum counts)		54	30	3	1	1	35
dissolution amount of the coating film ($\mu\text{m}/\text{month}$) (25°C, 20 knots)	0-1 month	0.5	10.2	2.5	1.1	20.1	4.2
	1-2 month	0.2	13.1	3.3	1.3	27.3	3.5
	2-3 month	0.2	15.3	3.0	2.0	38.2	3.1
	3-4 month	0.3	19.9	2.8	2.5	61.5	4.4
	4-5 month	0.1	22.5	3.6	2.2	127.4	5.1
	5-6 month	0.2	26.2	4.1	2.8	202.7	6.5
condition of coating film after 6 months rotary test		A	C	B	B	C	C
antifouling test	after 1 month	C	A	A	A	A	A
	after 2 months	D	A	A	B	A	A
	after 3 months	D	A	B	B	A	B
	after 4 months	D	A	B	C	A	B
	after 5 months	D	A	C	C	A	B
	after 6 months	D	A	C	D	A	B

Table 4 (continued)

component name		Comparative Example					
		13	14	15	16	17	18
copolymer solution	H-7						
	H-8						
	H-9						
	H-10						
	H-11						
	H-12						
	H-13	30					
	H-14		30				
	H-15			30			
	H-16				30		
	H-17					30	
	H-18						30
antifouling agent	cuprous oxide	45	45	45	45	45	45
	copper pyrithione	3	3	3	3	3	3
	zinc pyrithione						
	Sea-nine 211						
pigment	red iron oxide	2	2	2	2	2	2
	talc	2	2	2	2	2	2
	zinc oxide	4	4	4	4	4	4
	titanium oxide	1	1	1	1	1	1
	organic red pigment	1	1	1	1	1	1
other additives	tetraethoxysilane	1	1	1	1	1	1
	rosin zinc salt						
	hydrogenated rosin zinc salt						
	chlorinated paraffin						
	DISPARLON A603-20X	3	3	3	3	3	3
solvent	xylene	8	8	8	8	8	8
total		100	100	100	100	100	100
coating film hardness (number of Pendulum counts)		4	1	5	5	5	6
dissolution amount of the coating film (μ m/month) (25°C、20 knots)	0-1 month	20.5	15.6	15.0	13.5	12.3	7.7
	1-2 month	21.3	15.8	18.5	13.9	13.2	10.6
	2-3 month	23.4	18.2	21.1	16.2	17.1	14.0
	3-4 month	25.7	20.3	23.7	18.4	20.2	18.2
	4-5 month	32.3	27.5	25.1	22.0	28.3	25.1
	5-6 month	40.1	32.1	28.9	25.3	35.1	33.2
condition of coating film after 6 months rotary test		C	C	D	C	D	D
antifouling test	after 1 month	A	A	A	A	A	A
	after 2 months	A	A	A	A	A	A
	after 3 months	A	A	A	A	A	A
	after 4 months	A	A	A	A	A	A
	after 5 months	A	A	A	A	A	A
	after 6 months	A	A	A	A	A	A

The details of the antifouling agent, pigments, and other additives in Table 3 and Table 4 are as provided below.

Antifouling Agent

cuprous oxide (NC-301, available from NISSIN CHEMCO LTD., average particle size of 3 μ m)

copper pyrithione (copper Omadine, available from Arch Chemical, Inc.)

zinc pyrithione (zinc Omadine, available from Arch Chemical, Inc.)

Sea-Nine 211 (available from Rohm & Haas, Inc., xylene solution with 30% active component)

Pigment

Red iron oxide (TODA COLOR EP-13D, available from Toda Pigment Corp.)

Talc (Crown Talc 3S, available from MATSUMURA INDUSTRIES Co., Ltd.)

zinc oxide (zinc oxide II (product name), available from Seido Chemical Industry Co., Ltd.)

titanium oxide (FR-41, available from FURUKAWA CO., LTD.)

organic red pigment (scarlet TR, available from SANYO COLOR WORKS, Ltd.)

Other Additives

tetraethoxy silane (analytical grade reagent, available from KISHIDA CHEMICAL Co., Ltd.)

rosin zinc salt (50% xylene solution)

hydrogenated rosin zinc salt (50% xylene solution)

chlorinated paraffin

DISPARLON A603-20X (available from Kusumoto Chemicals, Ltd., aliphatic acid amide thixotropic agent)

[0074]

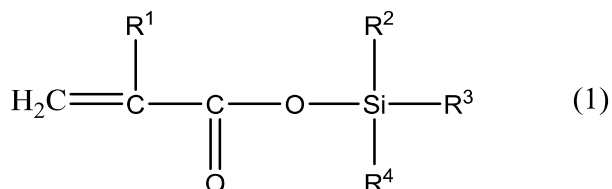
From the results shown in Table 3 and Table 4, it can be understood that the coating films formed by using the coating composition of the present invention (Examples 1 to 11) maintained a higher level of amount of dissolution in seawater when compared with the coating films formed by using the coating composition of Comparative Examples 1, 3, 4, 6 and the like. Further, in the antifouling test, there was no adhesion of fouling organisms such as shellfish or algae, and there was hardly any adhesion of slimes. In addition, the condition of the dried coating film after completion of the rotary test (after 6 months) was superior.

On the other hand, the coating film formed by using the coating composition of Comparative Examples 1 to 18 had a low level of amount of dissolution in seawater. Accordingly,

balance in the performance could not be achieved, being unable to prevent adhesion of fouling organisms, and causing cracks in the coating film.

CLAIMS

1. A copolymer for antifouling coating composition obtained by copolymerizing a mixture of
methacrylic acid triorganosilyl ester monomer (a)
represented by the following general formula (1):
[Chemical Formula 1]



(wherein, R^1 represents a methyl group, R^2 , R^3 , and R^4 are the same or different from each other, and each is selected from a branched alkyl group having 3 to 8 carbon atoms and a phenyl group); and

polymerizable unsaturated monomer (b) other than the monomer (a); wherein

the monomer (b) comprises methyl acrylate;

content of the monomer (a) is 25 to 65 mass% of total mass of the monomer (a) and the monomer (b); and

content of methyl acrylate is 25 to 75 mass% of total mass of the monomer (a) and the monomer (b).

2. The copolymer of Claim 1, wherein total content of the monomer (a) and methyl acrylate is 70 mass% or more of total mass of the monomer (a) and the monomer (b).

3. An antifouling coating composition comprising a copolymer and an antifouling agent; wherein the copolymer is the copolymer for antifouling coating composition of Claim 1.

4. A method for antifouling treatment comprising forming an antifouling coating film by using the antifouling coating composition of Claim 3.

5. An antifouling coating film formed by forming an antifouling coating film on a surface of an object subjected to coating, by using the antifouling coating composition of Claim 3.

6. A coated object having on its surface the antifouling coating film of Claim 5.