

DESCRIPTION**ANTIFOULING COATING COMPOSITION****TECHNICAL FIELD**

[0001]

The present invention relates to an antifouling coating composition.

BACKGROUND

[0002]

Aquatic fouling organisms such as barnacles, tubeworms, common mussels, *Bugula neritina*, sea squirts, green laver, sea lettuce, and slimes adhere to 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 and the like.

In order to prevent such problems, a technique which forms an antifouling coating film by coating an antifouling coating composition on a ship and the like, and allows controlled release of an antifouling agent to realize an antifouling performance for a long period of time has been known (Patent Literature 1).

CITATION LIST**PATENT LITERATURE**

[0003]

[Patent Literature 1] JP-A-2000-17203

SUMMARY OF INVENTION

TECHNICAL PROBLEM

[0004]

Antifouling coating film made from the antifouling coating composition had room for improvement in terms of insufficient elution speed during initial stage after immersion in seawater. In addition, when hydrophilic component is added to improve the elution speed during relatively initial stage after immersion in seawater, physical property of the coating film can be deteriorated.

[0005]

The present invention has been made by taking the aforementioned circumstances into consideration. The present invention provides an antifouling coating composition which can form a coating film having superior coating film property and superior elution speed during initial stage after immersion in seawater.

SOLUTION TO PROBLEM

[0006]

According to the present invention, an antifouling coating composition comprising copolymer A and antifouling agent B; wherein: the copolymer A is a copolymer of monomer (a), monomer (b), and ethylenically unsaturated monomer (c) other than the monomers (a) and (b); the monomer (a) is represented by general formula (1); the monomer (b) has an oxygen atom at a position other than a (meth)acrylic group; the monomer (a) is contained by 10 to 40 mass% with respect to total mass of the monomers (a) to (c); mass ratio of content of the monomer (a) and content of the monomer (b) ((a)/(b)) is 0.40 to 2.00; and the antifouling agent B is at least one of 2-(p-chlorophenyl)-3-cyano-4-bromo-5-trifluoromethyl pyrrole and 4,5-dichloro-2-n-octyl-3-isothiazolone, is provided.

[0007]

The present inventors have conducted intensive studies to solve the afore-mentioned problems, and have found that a composition

comprising copolymer A and antifouling agent B can solve the aforementioned problem, thereby leading to completion of the present invention.

MODE FOR CARRYING OUT THE INVENTION

[0008]

Hereinafter, the present invention will be described in detail.

1. antifouling coating composition

The antifouling coating composition according to the present invention comprises copolymer A and antifouling agent B.

[0009]

1-1. copolymer A

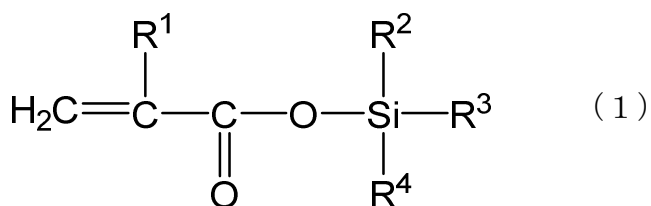
Copolymer A is a copolymer of monomer (a), oxygen atom containing monomer (b), and ethylenically unsaturated monomer (c) other than monomers (a) and (b). Copolymer A includes monomer unit derived from monomers (a), (b), and (c).

[0010]

<monomer (a)>

Monomer (a) is triorganosilyl methacrylate monomer, and is represented by general formula (1).

[Chemical formula 1]



(wherein, R¹ represents methyl group, R² to R⁴ are the same or different from each other, and each represents branched alkyl group having 3 to 8 carbon atoms or phenyl group)

[0011]

As the branched alkyl group having 3 to 8 carbon atoms represented by R² to R⁴, isopropyl group, isobutyl group, s-butyl group, t-butyl group, 1-ethylpropyl group, 1-methylbutyl group, 1-methylpentyl group, 1,1-dimethylpropyl group, 1,1-dimethylbutyl

group, texyl group, cyclohexyl group, 1,1-dimethylpentyl group, 1-methylhexyl group, 1,1-dimethylhexyl group, 1-methylheptyl group, 2-methylbutyl group, 2-ethylbutyl group, 2,2-dimethylpropyl group, cyclohexylmethyl group, 2-ethylhexyl group, 2-propylpentyl group, 3-methylpentyl group and the like can be mentioned for example. Isopropyl group, s-butyl group, t-butyl group, phenyl group, and 2-ethylhexyl group are preferable as R² to R⁴. Isopropyl group and 2-ethylhexyl group are especially preferable as R² to R⁴.

[0012]

As the monomer (a), tri-isopropyl silyl methacrylate, tri-isobutyl silyl methacrylate, tri-s-butyl silyl methacrylate, tri-isopentyl silyl methacrylate, tri-phenyl silyl methacrylate, di-isopropyl phenyl silyl methacrylate, di-isopropyl isobutyl silyl methacrylate, di-isopropyl s-butyl silyl methacrylate, di-isopropyl isopentyl silyl methacrylate, isopropyl di-isobutyl silyl methacrylate, isopropyl di-s-butyl silyl methacrylate, t-butyl di-isobutyl silyl methacrylate, t-butyl di-isopentyl silyl methacrylate, t-butyl diphenyl silyl methacrylate, di-isopropyl texyl silyl methacrylate, di-isopropyl cyclohexyl silyl methacrylate, tri-cyclohexyl silyl methacrylate, tri-1,1-dimethyl pentyl silyl methacrylate, tri-2,2-dimethyl propyl silyl methacrylate, tri-cyclohexyl methyl silyl methacrylate, di-isopropyl cyclohexyl methyl silyl methacrylate, tri-2-ethylhexyl silyl methacrylate, tri-2-propylpentyl silyl methacrylate and the like can be mentioned. Preferably, tri-isopropyl silyl methacrylate, tri-s-butyl silyl methacrylate, t-butyl diphenyl silyl methacrylate, tri-2-ethylhexyl silyl methacrylate and the like can be mentioned. These monomers (a) can be used alone or two or more of these can be used in combination.

[0013]

<oxygen atom containing monomer (b)>

Monomer (b) is oxygen atom containing monomer having an oxygen atom at a position other than a (meth)acrylic group, and is a monomer having an oxygen atom containing group other than the (meth)acrylic

group. As the oxygen atom containing group, alkoxy group, hydroxy group, ether group and the like can be mentioned.

[0014]

As the monomer (b), oxygen atom containing ethylenically unsaturated monomer such as 2-methoxyethyl (meth)acrylate, 2-methoxypropyl (meth)acrylate, 4-methoxybutyl (meth)acrylate, 2-ethoxyethyl (meth)acrylate, propylene glycol monomethyl (meth)acrylate, 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate and the like can be mentioned.

[0015]

<monomer (c)>

Monomer (c) is ethylenically unsaturated monomer other than monomers (a) and (b). For example, acrylic acid silyl ester, (meth)acrylic acid ester, vinyl compound, aromatic compound, dialkyl ester compound of dibasic acid and the like can be mentioned. Here, in the present specification, (meth)acrylic acid ester means acrylic acid ester or methacrylic acid ester.

[0016]

As the (meth)acrylic acid ester, for example, acrylic acid ester and the like such as methyl (meth)acrylate, ethyl (meth)acrylate, butyl (meth)acrylate, isobutyl (meth)acrylate, t-butyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, lauryl (meth)acrylate, benzyl (meth)acrylate, phenyl (meth)acrylate, dimethyl aminoethyl (meth)acrylate, diethyl aminoethyl (meth)acrylate and the like can be mentioned.

[0017]

As the vinyl compound, for example, vinyl compounds having functional group such as vinyl chloride, vinylidene chloride, acrylonitrile, methacrylonitrile, vinyl acetate and the like can be mentioned.

[0018]

As the aromatic compound, for example, styrene, vinyl toluene, α -methyl styrene and the like can be mentioned.

[0019]

As the dialkyl ester compound of dibasic acid, dimethyl maleate, dibutyl maleate, dimethyl fumarate and the like can be mentioned.

[0020]

In the present invention, these monomers (c) can be used alone or two or more of these can be used in combination. Especially, in terms of coating film property, (meth)acrylic acid ester is preferable as the monomer (c). Especially, in terms of crack resistance, methyl methacrylate, butyl (meth)acrylate, isobutyl (meth)acrylate, t-butyl (meth)acrylate, 2-ethylhexyl (meth)acrylate and the like are preferable as the monomer (c).

[0021]

Monomer (a) contained in copolymer A is 10 to 40 mass%, preferably 15 to 40 mass%, and more preferably 20 to 40 mass%.

[0022]

Content of monomer (a) is, particularly for example, 10, 15, 20, 25, 30, 35, or 40 mass%, and can be in the range between the two values exemplified herein.

[0023]

Mass ratio of monomer (a) and monomer (b) contained in copolymer A ((a)/(b)) is 0.40 to 2.00, preferably 0.45 to 2.00, and further preferably 0.50 to 1.60. This mass ratio is, particularly for example, 0.40, 0.45, 0.50, 0.55, 0.60, 0.65, 0.70, 0.75, 0.80, 0.85, 0.90, 0.95, 1.00, 1.05, 1.10, 1.15, 1.20, 1.25, 1.30, 1.35, 1.40, 1.45, 1.50, 1.55, 1.60, 1.65, 1.70, 1.75, 1.80, 1.85, 1.90, 1.95, or 2.00, and can be in the range between the two values exemplified herein.

[0024]

When the copolymer A satisfying the afore-mentioned range is used as the coating composition of the present invention, film dissolution property particularly becomes superior.

[0025]

The weight average molecular weight (M_w) of copolymer A is preferably 5,000 to 300,000. When the molecular weight is lower than 5,000, the coating film of the antifouling coating would become

weak, thereby becoming prone to peeling off and occurrence of cracks. When the molecular weight exceeds 300,000, viscosity of polymer solution rises, and thus handling becomes difficult. Mw is, particularly for example, 5,000, 10,000, 20,000, 30,000, 40,000, 50,000, 60,000, 70,000, 80,000, 90,000, 100,000, 200,000, or 300,000, and can be in the range between the two values exemplified herein.

[0026]

As the method for measuring Mw, gel permeation chromatography (GPC) can be mentioned for example.

[0027]

Copolymer A can be a random copolymer, an alternating copolymer, a periodic copolymer, or a block copolymer of monomer (a), monomer (b), and monomer (c).

[0028]

Copolymer A can be, for example, obtained by polymerizing monomer (a), monomer (b), and monomer (c) in the presence of a polymerization initiator.

[0029]

As the polymerization initiator, for example, azo compounds such as 2,2'-azobisisobutyronitrile, 2,2'-azobis(2-methylbutyronitrile), 2,2'-azobis(2,4-dimethylvaleronitrile), dimethyl-2,2'-azobisisobutyrate, 2,2'-azobis(N-butyl-2-methylpropionamide); peroxides such as benzoyl peroxide, di-tert-butyl peroxide, tert-butyl peroxy benzoate, tert-butyl peroxy isopropyl carbonate, t-butyl peroxy-2-ethyl hexanoate, t-hexyl peroxy-2-ethyl hexanoate, di-t-hexyl peroxide, t-butyl peroxy-2-ethyl hexyl monocarbonate, di-t-butyl peroxide, 1,1,3,3-tetramethylbutyl peroxy neodecanoate, t-amyl peroxy neodecanoate, t-hexyl peroxy pivalate, t-amyl peroxy pivalate, 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 of these can be used in combination. As the polymerization initiator, 2,2'-azobisisobutyronitrile, 2,2'-azobis(2-methylbutyronitrile), 2,2'-azobis(2,4-

dimethylvaleronitrile), dimethyl 2,2'-azobisisobutyrate, and 1,1,3,3-tetramethylbutyl peroxy-2-ethylhexanoate are preferable. By controlling the amount of polymerization initiator being used, molecular weight of the copolymer A can be adjusted.

[0030]

As the method of polymerization, solution polymerization, bulk polymerization, emulsion polymerization, suspension polymerization, non-aqueous dispersion polymerization and the like can be mentioned. Among these, in view of the capability of obtaining the copolymer A simply with accuracy, solution polymerization or non-aqueous dispersion polymerization is preferable.

[0031]

In the polymerization reaction, organic solvent can be used if necessary. As the organic solvent, there is no particular limitation, and for example, aromatic hydrocarbon solvents such as xylene and toluene; aliphatic hydrocarbon solvents; ester solvents such as ethyl acetate, butyl acetate, isobutyl acetate, and methoxypropyl acetate; alcohol solvents such as isopropyl alcohol, butyl alcohol, and propylene glycol monomethyl ether; ether solvents such as dioxane, diethyl ether, and dibutyl ether; and ketone solvents such as methyl ethyl ketone, and methyl isobutyl ketone; can be mentioned.

Among these, butyl acetate, isobutyl acetate, butyl alcohol, propylene glycol monomethyl ether, propylene glycol 1-monomethyl ether 2-acetate, toluene, and xylene are preferable. These solvents can be used alone, or two or more of these can be used in combination.

[0032]

The reaction temperature in the polymerization reaction shall be suitably controlled depending on the type of the polymerization initiator used and the like. The reaction temperature is usually 50 to 160°C, preferably 60 to 150°C.

[0033]

The polymerization reaction is preferably performed under inert gas atmosphere such as nitrogen gas and argon gas.

[0034]

1-2. antifouling agent B

The antifouling agent B is at least one of 2-(p-chlorophenyl)-3-cyano-4-bromo-5-trifluoromethyl pyrrole and 4,5-dichloro-2-n-octyl-3-isothiazolone.

As commercially available 2-(p-chlorophenyl)-3-cyano-4-bromo-5-trifluoromethyl pyrrole, Econeal 028 (available from JANSSEN PMP) can be mentioned.

As commercially available 4,5-dichloro-2-n-octyl-3-isothiazolone, SEA-NINE 211N (available from The Dow Chemical Company) can be mentioned.

The content of antifouling agent B in the composition of the present invention is not particularly limited, and is usually, by conversion as solid content, 0.1 to 10.0 mass%, preferably 0.5 to 7.0 mass%, especially preferably 4.0 to 6.0 mass%. The content of the antifouling agent B is, particularly for example, 0.1, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, 5.0, 5.5, 6.0, 6.5, 7.0, 7.5, 8.0, 8.5, 9.0, 9.5, or 10.0 mass%, and can be in the range between the two values exemplified herein.

[0035]

1-3. other additives

The resin for antifouling coating of the present invention can contain resin component other than the copolymer A, release modifier, plasticizer, antifouling agent other than the antifouling agent B, pigment, dye, defoaming agent, dehydrating agent, shaking agent, organic solvent and the like if necessary to prepare an antifouling coating.

[0036]

As the other resin component, polymer P can be mentioned for example.

Polymer P is a polymer obtained by polymerizing monomer (d). Monomer (d) is ethylenically unsaturated monomer other than monomer (a) (that is, monomer (b) or monomer (c)). Monomer (d) used for polymerization of polymer P can be the same composition or can be a different composition of monomer (b) or monomer (c) used for

polymerizing copolymer A.

In the present invention, such monomer (d) can be used alone, or two or more of monomer (d) can be used in combination. In particular, in view of compatibility with copolymer A, methyl (meth)acrylate, ethyl (meth)acrylate, butyl (meth)acrylate, isobutyl (meth)acrylate, t-butyl (meth)acrylate, 2-ethyl hexyl (meth)acrylate, 2-methoxy ethyl (meth)acrylate, 2-ethoxy ethyl (meth)acrylate, furfuryl (meth)acrylate, tetrahydrofurfuryl (meth)acrylate, benzyl (meth)acrylate are preferable.

As the polymerization method, initiator, solvent, temperature, and other conditions, measurement method of Mw and the like, those described for copolymer A can be applied.

The content of polymer P in the composition of the present invention is not particularly limited. Here, content ratio with respect to copolymer A by mass (polymer P/copolymer A) is, by conversion as solid content, usually 0.1 to 9.0, preferably 0.1 to 4.0.

[0037]

As the release modifier, for example, rosin, rosin derivative, monocarboxylic acid and salts thereof such as naphthenic acid, cycloalkenyl carboxylic acid, bicycloalkenyl carboxylic acid, versatic acid, trimethyl isobutenyl cyclohexene carboxylic acid, and metal salts thereof, or alicyclic hydrocarbon resin can be mentioned. These can be used alone, or two or more of these can be used in combination.

As the rosin derivative, hydrogenated rosin, disproportionated rosin, maleic acid modified rosin, formylated rosin, polymerized rosin and the like can be exemplified.

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

Among these, rosin, rosin derivative, naphthenic acid, versatic acid, trimethyl isobutenyl cyclohexene carboxylic acid or

metal salts thereof are preferable, and rosin and rosin derivative are further preferable.

By using rosin and rosin derivative, anti-peeling property of the coating film of the antifouling coating composition containing the afore-mentioned components (A) and (B) can be improved prominently, and film dissolution property (especially in the initial stage) can be improved prominently.

[0038]

As the plasticizer, for example, phosphate ester, phthalic acid ester, adipic acid ester, sebacic acid ester, epoxidized soybean oil, alkyl vinyl ether polymer, polyalkylene glycol, t-nonyl pentasulfide, petrolatum, polybutene, trimellitic acid tris (2-ethylhexyl), silicone oil, 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.

[0039]

As the antifouling agent for example, inorganic agent and organic agent can be mentioned.

As the inorganic agent, for example, cuprous oxide, cuprous thiocyanate (generic name: copper rhodanide), copper powder and the like can be mentioned. Among these, cuprous oxide and copper rhodanide are preferable. With respect to cuprous oxide, the one having its surface treated with glycerin, sucrose, stearic acid, lauric acid, lysine, mineral oil and the like are preferable in terms of long term stability during storage.

As the organic agent, for example, copper 2-mercaptopyridine-N-oxide (generic name: copper pyrithione), zinc 2-mercaptopyridine-N-oxide (generic name: zinc pyrithione) zinc ethylenebis dithiocarbamate (generic name: Zineb), 3,4-dichlorophenyl-N,N-dimethylurea (generic name: Diuron), 2-methylthio-4-t-butylamino-6-cyclopropylamino-s-triazine (generic name: Irgarol 1051), 4-[1-(2,3-dimethylphenyl)ethyl]-1H-imidazole (generic name: Medetomidine) and the like can be mentioned. These antifouling agent can be used alone, or two or more of these can be used in combination.

[0040]

As the dehydrating agent, for example, calcium sulfate, sodium sulfate, magnesium sulfate, synthetic zeolite adsorbent, orthoester, silicate such as tetramethoxysilane and tetraethoxysilane, isocyanate, carbodiimide, carbodiimidazole and the like can be mentioned. These can be used alone, or two or more of these can be used in combination.

[0041]

2. manufacturing method of antifouling coating composition

The antifouling coating composition of the present invention can be manufactured by mixing and dispersing a mixture solution containing the copolymer A, antifouling agent B, and other additives using a disperser.

As the mixture solution, the one prepared by dissolving or dispersing various materials such as copolymer A and antifouling agent B in a solvent is preferable.

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, disper 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.

[0042]

3. 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 continuously renewed.

Examples of objects on which a coating film can be formed

include ships (in particular, ship bottoms), fishing tools, and structures submerged in seawater.

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, navigation speed of a ship, 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 700 μm , and preferably 100 to 600 μm .

EXAMPLE

[0043]

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 the Production Examples, Examples, and Comparative Examples, "%" denotes "mass%".

The weight-average molecular weight (M_w) was determined by gel permeation chromatography (GPC) (using a polystyrene standard). GPC was performed under the following conditions.

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

Column: TSK-gel Super HZM-M, two columns used

Flow rate: 0.35 mL/min

Detector: RI

Column thermostat temperature: 40°C

Developing solvent: THF

The non-volatile content is a value determined in accordance with JIS K 5601-1-2:1999 (ISO 3251:1993) "Testing methods for paint components- Determination of non-volatile matter content".

[0044]

<production example 1 (production of copolymer solution A-1)>

To a four-necked flask equipped with a thermometer, condenser, stirrer, and dropping funnel, 230 g of xylene (initial solvent) was charged, nitrogen gas was introduced, and then the temperature was

kept at 100°C under agitation. A mixture of 200g of tri-isopropyl silyl methacrylate, 125g of 2-methoxyethyl methacrylate, 25g of 2-methoxyethyl acrylate, 100g of methyl methacrylate, 25g of ethyl acrylate, 25g of n-butyl acrylate, 5.0g of t-butyl peroxy-2-ethyl hexanoate (initial addition) was added dropwise over 3 hours while maintaining the temperature at 100°C. Thereafter, the reaction mixture was agitated for 1 hour at 100°C, and then 1.0g of t-butyl peroxy-2-ethyl hexanoate (later addition) was added three times every one hour. The reaction mixture was agitated further for 2 hours at the same temperature. Subsequently, 270g of xylene (diluting solvent) was added, and the reaction mixture was cooled to room temperature, thereby obtaining copolymer solution A-1 including copolymer containing tri-isopropyl silyl methacrylate. Viscosity, non-volatile content, Mw, and glass transition temperature of A-1 are shown in Table 1.

[0045]

<production example 2 (production of copolymer solution A-2)>

Monomer, polymerization initiator and organic solvent shown in Table 1 were used, and polymerization was performed by processes similar to those of production example 1 under each reaction temperature conditions, thereby obtaining copolymer solution A-2 including copolymer containing tri-isopropyl silyl methacrylate. Viscosity, non-volatile content, Mw, and glass transition temperature of A-2 are shown in Table 1. Unless specified otherwise, the unit of formulation values in Table 1 is g.

[0046]

<production example 3 (production of copolymer solution P-1)>

Monomer, polymerization initiator and organic solvent shown in Table 1 were used, and polymerization was performed by processes similar to those of production example 1 under each reaction temperature conditions, thereby obtaining copolymer solution P-1 including copolymer containing ethylenically unsaturated monomer. Viscosity, non-volatile content, Mw, and glass transition temperature of P-1 are shown in Table 1.

[0047]

<comparative production examples 1 to 3 (production of copolymer solutions H-1, H-2, and H-3)>

Monomer, polymerization initiator and organic solvent shown in Table 1 were used, and polymerization was performed by processes similar to those of production example 1 under each reaction temperature conditions, thereby obtaining copolymer solution H-1 including copolymer containing tri-isopropyl silyl acrylate, copolymer solution H-2 including copolymer containing tri-isopropyl silyl methacrylate, and copolymer solution H-3 including copolymer containing tri-isopropyl silyl methacrylate. Viscosity, non-volatile content, Mw, and glass transition temperature of H-1, H-2, and H-3 are shown in Table 1.

[0048]

[Table 1]

Table 1

category of component	name of component	production example			comparative production example		
		1	2	3	1	2	3
initial solvent in flask	name of copolymer solution	A-1	A-2	P-1	H-1	H-2	H-3
	xylene	230	280	450	230	230	230
monomer (a)	tri-isopropyl silyl methacrylate	200	100			275	75
monomer (b)	2-methoxyethyl methacrylate	125	150		125	100	150
	2-methoxyethyl acrylate	25	50	120	25	30	75
monomer (c)	tri-isopropyl silyl acrylate				200		
	methyl methacrylate	100	150		125	50	150
	ethyl acrylate	25				20	25
	n-butyl methacrylate		25		25		
	n-butyl acrylate	25	25	180		25	
	i-butyl methacrylate			200			25
total of monomers		500	500	500	500	500	500
mass ratio (monomer (a)/monomer (b))		1.33	0.50	0.00	0.00	2.12	0.33
polymerization initiator/initial addition	t-butyl peroxy-2-ethyl hexanoate	5	5	14	5	4	5
polymerization initiator/after addition	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
diluting solvent after polymerization reaction	xylene	270	220	50	270	260	270
reaction temperature (°C)		100 ± 2	100 ± 2	100 ± 2	100 ± 2	100 ± 2	100 ± 2
physical property of copolymer	viscosity (mPa s / 25°C)	400	1050	80	370	320	1200
	non-volatile content (% / 110°C, 3 h)	49.8	49.4	50.1	49.7	49.9	49.5
	weight average molecular weight (M _w)	48,000	50,000	25,000	49,000	46,000	52,000
	glass transition temperature (°C / T _g)	43	36	-21	37	45	32

<production example 4 (production of rosin zinc salt solution)>

To a flask equipped with a thermometer, reflux condenser, and a stirrer, 240 g of gum rosin available from China (WW) and 360 g of xylene were charged, and 120 g of zinc oxide was added so that all of the resin acid in the rosin would form zinc salt. The reaction mixture was dehydrated under reflux under reduced pressure for 3 hours at 70 to 80°C. Then, the reaction mixture was cooled and filtered to give a xylene solution of rosin zinc salt (dark brown transparent liquid, 50% solids). The non-volatile content of the solution obtained was 50.2%.

[0050]

<production example 5 (production of hydrogenated rosin zinc salt solution)>

To a flask equipped with a thermometer, reflux condenser, and a stirrer, 240 g of HYPAL CH (hydrogenated rosin) and 360 g of xylene were charged, and 120 g of zinc oxide was added so that all of the resin acid in the rosin would form zinc salt. The reaction mixture was dehydrated under reflux under reduced pressure for 3 hours at 70 to 80°C. Then, the reaction mixture was condensed, cooled and filtered to give a xylene solution of hydrogenated rosin zinc salt (dark brown liquid, 50% solids). The non-volatile content of the solution obtained was 50.3%.

[0051]

<Examples and Comparative Examples (production of coating composition)>

The components shown in Table 2 to Table 3 were formulated by the ratio (mass%) shown in the Tables, and were mixed and dispersed with a glass beads having a diameter of 1.5 to 2.5 mm, thereby producing the coating composition.

[0052]

[Table 2]

Table 2			Example											
			1	2	3	4	5	6	7	8	9	10	11	12
composition	copolymer A	copolymer solution A-1	23.0		36.8		23.0		23.0		11.5			
		copolymer solution A-2		23.0		36.8		23.0		23.0		11.5	23.0	23.0
	antifouling agent B	Econea 028	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0
		SEA-NINE 211N	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
	other polymer	copolymer solution P-1									11.5	11.5		
		copolymer solution H-1												
		copolymer solution H-2												
		copolymer solution H-3												
	other antifouling agent	cuprous oxide												
		copper pyrrithione					7.0	7.0						
		zinc pyrrithione	7.0	7.0	7.0	7.0			7.0	7.0	7.0	7.0	7.0	3.5
		Zineb												3.5
		Medetomidine											0.1	
	other additive	gum rosin solution	11.5	11.5	4.6	4.6	11.5	11.5			11.5	11.5	11.5	11.5
		rosin zinc salt solution							11.5	11.5				
		hydrogenated rosin solution	11.5	11.5	4.6	4.6	11.5	11.5			11.5	11.5	11.5	11.5
		hydronated rosin zinc salt solution							11.5	11.5				
		chlorinated paraffin	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
		epoxidized soybean oil	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
		bis(2-ethylhexyl)phthalate	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
		talc	7.0	7.0	7.0	7.0	7.0	7.0	7.0	7.0	7.0	7.0	7.0	7.0
		zinc oxide	18.0	18.0	18.0	18.0	18.0	18.0	18.0	18.0	18.0	18.0	18.0	18.0
		red oxide	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0
		titanium oxide	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
		tetraethoxysilane	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
		aliphatic amide thixotropic agent	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0
	solvent	xylene	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	2.9	3.0
	total		100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
wet & dry cycle test condition of coating film		after 3 months	○	○	○	○	○	○	○	○	○	○	○	○
		after 6 months	○	○	○	○	○	○	○	○	○	○	○	○
rotary test average dissolved amount of coating film (μm/month)		after initial to 6 months	3.0	2.5	3.5	3.0	3.1	2.4	2.8	2.2	4.0	3.7	2.5	2.8
		after 6 to 12 months	2.8	2.8	3.6	3.1	3.0	2.9	2.6	2.5	4.1	3.5	2.9	2.5
		after 12 to 18 months	2.9	3.0	4.2	2.8	3.1	2.9	2.9	2.1	4.4	3.7	2.8	2.4
		after 18 to 24 months	3.2	2.7	4.6	3.3	3.2	2.8	3.0	2.3	4.9	3.7	2.9	2.7

[0053]

[Table 3]

Table 3			Example							Comparative Example			
			13	14	15	16	17	18	19	1	2	3	4
composition	copolymer A	copolymer solution A-1	15.6	24.8	17.2	15.6	23.0	23.0	23.0				23.0
		copolymer solution A-2											
	antifouling agent B	Ecinea 028	2.0	2.0	2.0	2.0	4.0		4.0	4.0	4.0	4.0	
		SEA-NINE 211N	2.0	2.0	2.0	2.0		2.0	4.0	2.0	2.0	2.0	
	other polymer	copolymer solution P-1											
		copolymer solution H-1								23.0			
		copolymer solution H-2									23.0		
		copolymer solution H-3										23.0	
	other antifouling agent	cuprous oxide	30.0	30.0	15.0	30.0							
		copper pyrithione	1.0	1.0	1.0	1.0							
		zinc pyrithione					9.0	11.0		7.0	7.0	7.0	13.0
		Zineb											
		Medetomidine				0.1							
	other additive	gum rosin solution	7.8	3.1	8.6	7.8	11.5	11.5	11.5	11.5	11.5	11.5	11.5
		rosin zinc salt solution											
		hydrogenated rosin solution	7.8	3.1	8.6	7.8	11.5	11.5	11.5	11.5	11.5	11.5	11.5
		hydronated rosin zinc salt solution											
		chlorinated paraffin	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
		epoxidized soybean oil	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
		bis(2-ethylhexyl)phthalate	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
		talc	7.0	7.0	10.0	7.0	7.0	7.0	9.0	7.0	7.0	7.0	7.0
		zinc oxide	14.0	14.0	20.0	14.0	18.0	18.0	20.0	18.0	18.0	18.0	18.0
		red oxide	2.0	2.0	4.0	2.0	4.0	4.0	5.0	4.0	4.0	4.0	4.0
		titanium oxide	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
		tetraethoxysilane	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
		aliphatic amide thixotropic agent	3.0	3.0	3.0	3.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0
	solvent	xylene	2.8	3.0	3.6	2.7	3.0	3.0	3.0	3.0	3.0	3.0	3.0
	total		100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
wet & dry cycle test condition of coating film		after 3 months	○	○	○	○	○	○	○	×	×	○	○
		after 6 months	○	○	○	○	○	○	○	×	×	×	×
rotary test average dissolved amount of coating film (μm/month)		after initial to 6 months	3.3	3.0	3.7	3.5	2.9	3.0	3.5	5.6	3.9	1.0	1.9
		after 6 to 12 months	3.8	3.9	4.0	3.8	3.2	3.1	3.6	18.9	12.0	0.8	2.4
		after 12 to 18 months	3.9	4.3	4.5	4.0	3.3	3.2	3.7	38.0	21.1	1.1	2.1
		after 18 to 24 months	4.2	4.7	4.5	4.1	3.4	3.1	3.5	△	△	0.5	2.3

[0054]

Details of antifouling agent B, other antifouling agent, and other additive in the Table are as follows.

<antifouling agent B>

Ecinea 028: 2-(p-chlorophenyl)-3-cyano-4-bromo-5-trifluoromethyl pyrrole, product name "Ecinea 028", (available from JANSSEN PMP)

SEA-NINE 211N: 4,5-dichloro-2-n-octyl-3-isothiazolone, product name "SEA-NINE 211N", active ingredient 30% xylene solution (available from The Dow Chemical Company)

[0055]

<other antifouling agent>

cuprous oxide: product name "NC-301", average particle size 3 μm (available from NISSIN CHEMCO)

copper pyrithione : product name "copper Omadine" (available from Lonza Group Ltd.)

zinc pyrithione: product name "zinc Omadine" (available from Lonza Group Inc.)

Zineb: (available from FUJIFILM Wako Pure Chemical Corporation)

Medetomidine: product name "Selektope" (available from I-Tech AB)

[0056]

<other additive>

gum rosin solution: xylene solution (50% solids) of Chinese gum rosin (WW)

rosin zinc salt solution: The one produced in production example 4 was used.

hydrogenated rosin solution: xylene solution (50% solids) of product name "HYPALE CH" (available from ARAKAWA CHEMICAL INDUSTRIES, LTD.)

hydronated rosin zinc salt solution: The one produced in production example 5 was used.

chlorinated paraffin: product name "TOYOPARAX A40S" (manufactured by Tosoh Corporation).

epoxidized soybean oil: product name "Sansocizer E-2000H" (manufactured by New Japan Chemical Co., Ltd.).

bis(2-ethylhexyl)phthalate: reagent (available from FUJIFILM Wako Pure Chemical Corporation)

talc: product name "Talc MS" (available from NIPPON TALC Co., Ltd.)

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

red oxide: product name "Bengaragyoku" (available from MORISHITA BENGARA KOGYO CO., LTD.)

titanium oxide: product name "FR-41" (available from FURUKAWA

CO., LTD.)

tetraethoxysilane: special grade reagent (available from KISHIDA CHEMICAL Co., Ltd.)

aliphatic amide thixotropic agent: product name "Disparlon A603-20X" active ingredient 20% xylene paste (available from Kusumoto Chemicals, Ltd.)

[0057]

Following tests were performed with the coating compositions of Examples and Comparative Examples.

<test example 1 (wet & dry cycle test)>

Antifouling coating composition was applied onto a glass plate by using a 400 μm applicator to obtain a test plate. The test plate was subjected to the test in which immersion in fresh water at 40°C for 12 hours and exposure in air for 12 hours were repeated for 6 months, and then the physical properties of the test plate were visually evaluated. Those without peeling were marked with O, and those with peeling were marked with X.

[0058]

<test example 2 (rotary test)>

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

Test plates were prepared in accordance with the following method.

First, an anti-corrosive coating film was formed by applying an anti-corrosive coating (epoxy vinyl-based A/C) onto a titanium plate (71 x 100 x 0.5 mm) such that the thickness after drying would be about 100 μm , followed by drying. Each of the coating compositions obtained in Examples and Comparative Examples was applied onto the anti-corrosive coating film so that the thickness after drying would be about 400 μm . The applied coating was dried

for 3 days at 40°C, and the test plate having a dried coating film of about 400 μm thickness was prepared.

The thus-prepared test plates were secured to the rotating drum of the rotary apparatus of the above-mentioned equipment and was made 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 10 to 15°C and the pH at 8.0 to 8.2; and the seawater was replaced once every week.

The initial thickness of the coating film and the remaining thickness of the coating film was measured every 6 months by using a laser focus displacement meter for each test plate. The thickness of the dissolved coating film was calculated from the difference therebetween to obtain the dissolved amount of the coating film. The dissolved amount of the coating film is expressed as the dissolved amount per month ($\mu\text{m}/\text{month}$).

[0059]

<result of test>

From the results of test example 1 and test example 2, it became apparent that the coating film formed by using the composition containing copolymer A and antifouling agent B can achieve superior coating film property, and superior elution speed during initial stage after immersion in seawater.

CLAIMS

Claim 1 An antifouling coating composition comprising copolymer A and antifouling agent B; wherein:

the copolymer A is a copolymer of monomer (a), monomer (b), and ethylenically unsaturated monomer (c) other than the monomers (a) and (b);

the monomer (a) is represented by general formula (1);

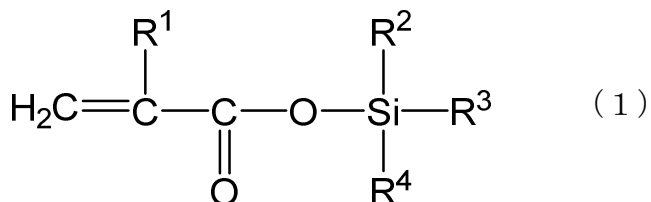
the monomer (b) has an oxygen atom at a position other than a (meth)acrylic group;

the monomer (a) is contained by 10 to 40 mass% with respect to total mass of the monomers (a) to (c);

mass ratio of content of the monomer (a) and content of the monomer (b) ((a)/(b)) is 0.40 to 2.00; and

the antifouling agent B is at least one of 2-(p-chlorophenyl)-3-cyano-4-bromo-5-trifluoromethyl pyrrole and 4,5-dichloro-2-n-octyl-3-isothiazolone.

[chemical formula 1]



(wherein, R¹ represents methyl group, R² to R⁴ are the same or different from each other, and each represent branched alkyl group having 3 to 8 carbon atoms or phenyl group)