DESCRIPTION

COPOLYMER FOR STAIN-PROOF COATING COMPOSITIONS, AND STAIN-PROOF COATING COMPOSITION CONTAINING SAID COPOLYMER

Technical Field

[0001]

The present invention relates to a copolymer for an antifouling coating composition and an antifouling coating composition containing the copolymer.

Background Art

[0002]

Aquatic fouling organisms such as barnacles, tubeworms, common mussels, Bugula neritina, sea squirts, green laver, sea lettuce, and slimes adhere to surfaces 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, the structures and the like. Particularly in the case of the ships, an increase in resistance causes a decrease in speed and an increase in fuel consumption, thereby resulting in great damage.

[0003]

Therefore, in order to prevent such damage, an antifouling coating, which includes a copolymer containing a triorganosilyl group as a vehicle, is now widely used and applied to form an antifouling coating film on surfaces 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.

[0004]

The copolymer containing a triorganosilyl group realizes an antifouling performance when the triorganosilyl ester part of the copolymer is hydrolyzed in seawater and the copolymer gradually dissolves in seawater and the coating surface is renewed.

[0005]

As the copolymers containing a triorganosilyl group, copolymers containing a triorganosilyl group, which is obtained by copolymerizing a monomer containing triorganosilyl ester comprising a branched alkyl group or aryl group, such as triisopropylsilyl ester or t-butyldiphenylsilyl ester, and alkoxyalkyl (meth)acrylate ester such as 2-methoxyethyl (meth)acrylate have been proposed (Patent Literatures 1 to 4).

[0006]

Since the antifouling coating using these copolymer containing a triorganosilyl group as a vehicle has poor storage stability, it has been proposed to use a dehydrating agent such as ethyl silicate or anhydrous gypsum anhydrite in the coating (Patent Literatures 5 to 6). However, its storage stability was not sufficient, and there is a problem that storage stability deteriorated when the coating is manufactured under high humidity.

[0007]

Further, these copolymers containing the triorganosilyl group has problems that the initial coating film dissolution is not sufficient, the coating film whitens, and fouling organisms adhere during the outfitting period or during the initial berthing period.

Citation List

Patent Literature

[0008]

[Patent Literature 1] JP-A-Hei-7-102193

[Patent Literature 2] JP-A-2001-226440

[Patent Literature 3] JP-A-2005-82725

[Patent Literature 4] JP-A-2016-062432

[Patent Literature 5] JP-A-Hei-7-18216

[Patent Literature 6] JP-A-Hei-9-48948

Summary of Invention

Technical Problem

[0009]

An object of the present invention is to provide an antifouling coating composition which has good storage stability as a coating and can form antifouling coating film preventing coating film defects (whitening, peeling, cracks, and the like) in seawater for a long time, and maintaining stable dissolution and the antifouling performance.

Solution to Problem

[0010]

According to the present invention, a copolymer for an antifouling coating composition, which is obtained by copolymerizing a mixture of a monomer (a) and a polymerizable unsaturated monomer (b) other than the monomer (a), wherein:

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

the monomer (b) contains 2-methoxyethyl methacrylate;

content of the monomer (a) is 5 to 45mass% with respect to the total mass of the monomer (a) and the monomer (b);

content of the 2-methoxyethyl methacrylate is 55 to 95mass% with respect to the total mass of the monomer (a) and the monomer (b); is provided.

[0011]

The present inventors have conducted intensive studies and have found that when a copolymer (A) obtained by copolymerizing a monomer (a) having a specific structure and a monomer (b) containing a specific amount of 2-methoxyethyl methacrylate is used as the vehicle, the obtained antifouling coating composition has remarkably improved storage stability even when it is manufactured in a high humidity condition, and in the coating film, no defects such as whitening, peeling, cracks, occur in the seawater for a long time, and the coating film can maintain stable dissolution and the antifouling performance for a long time, thereby completing the present invention.

Description of Embodiments

[0012]

Hereinafter, the present invention will be described in detail.

1. Antifouling coating composition

The antifouling coating composition of the present invention includes a copolymer (A) for an antifouling coating composition and an antifouling agent (B).

[0013]

1-1. Copolymer (A) for antifouling coating composition

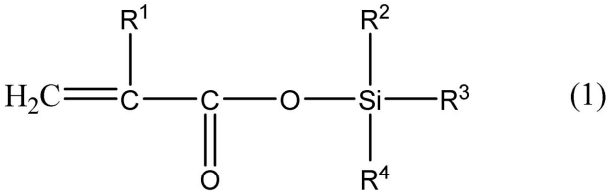
The copolymer (A) for the antifouling coating composition is a copolymer containing a triorganosilyl group and is obtained by copolymerizing a mixture of a monomer (a) and a monomer (b). The copolymer (A) includes monomeric units derived from the monomers (a) and (b).

[0014]

<Monomer (a)>

The monomer (a) is a triorganosilyl methacrylate ester monomer and is represented by general formula (1).

[Chem. 1]



(1)

In the general formula (1), R^1 is a methyl group, R^2, R^3, and R^4 are selected from a C3 to C8 branched alkyl group and a phenyl group and may be the same or different.

[0015]

In the present invention, examples of the monomer (a) represented by the general formula (1) include triisopropylsilyl methacrylate, triisobutylsilyl methacrylate, tri-s-butylsilyl methacrylate, triisoamylsilyl methacrylate, tris(2-ethylhexyl)silyl methacrylate, triphenylsilyl methacrylate, diisopropylisobutylsilyl methacrylate, diisopropylisoamylsilyl methacrylate, diisopropyl(2-ethylhexyl)methacrylate, diisopropylphenylsilyl methacrylate, diisopropylcyclohexylsilyl methacrylate, t-butyldiisopropylsilyl methacrylate, t-butyldiisobutylsilyl methacrylate, t-butyldiisoamylsilyl methacrylate, t-butyldiphenylsilyl methacrylate. T-butyldiphenylsilyl methacrylate and triisopropylsily are preferable, and triisopropylsilyl methacrylate is particularly preferable. These monomers can be used alone or two or more of these can be used in combination.

[0016]

<Monomer (b)>

The monomer (b) is a polymerizable unsaturated monomer other than the monomer (a) and is copolymerizable with the monomer (a). In the present invention, it is essential that the monomer (b) contains 2-methoxyethyl methacrylate, and when the monomer (b) contains 2-methoxyethyl methacrylate in a specific amount, the obtained coating composition has remarkably improved storage stability, and in the obtained coating film, no defects, such as whitening, peeling, cracks, occur for a long time, and the coating film can maintain stable dissolution and the antifouling performance for a long time, thereby achieving the technical effect.

[0017]

The monomer (b) may contain only 2-methoxyethyl methacrylate or may contain a monomer other than 2-methoxyethyl methacrylate. Examples of the monomer other than 2-methoxyethyl methacrylate include the following.

[0018]

Triorganosilyl acrylate esters such as triisopropylsilyl acrylate, triisobutylsilyl acrylate, tr-s-butylsilyl acrylate, triisoamylsilyl acrylate, tris(2-ethylhexyl)silyl acrylate, triphenylsilyl acrylate, diisopropylisobutylsilyl acrylate, diisopropylisoamylsilyl acrylate,

diisopropyl(2-ethylhexyl)silyl acrylate, diisopropylphenylsilyl acrylate, diisopropylcyclohexylsilyl acrylate, t-butyldiisopropylsilyl acrylate, t-butyldiisobutylsilyl acrylate, t-butyldiisoamylsilyl acrylate, t-butyldiphenylsilyl acrylate.

[0019]

(Meth)acrylate esters such as methyl (meth)acrylate, 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 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.

[0020]

Metal pendant (meth)acrylate 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, and copper stearate (meth)acrylate; metal (meth)acrylate such as zinc (meth)acrylate, and copper (meth)acrylate.

[0021]

Vinyl compounds having a functional group such as vinyl chloride, vinylidene chloride, acrylonitrile, methacrylonitrile, vinyl acetate, vinyl benzoate, vinyl butyrate, butyl vinyl ether, lauryl vinyl ether, and N-vinylpyrrolidone.

[0022]

Aromatic compounds such as styrene, vinyltoluene, and α-methylstyrene.

[0023]

Dialkyl ester compounds of unsaturated dibasic acid such as dimethylmalate, dibutylmalate, and dimethylfumarate.

[0024]

The polymerizable monomer other than 2-methoxyethyl methacrylate can be used alone or two or more of these can be used in combination. (Meth)acrylate esters are preferable, and methyl methacrylate is particularly preferable.

[0025]

The mass ratio of the content of 2-methoxyethyl methacrylate in the monomer (b) is preferably 0.75 to 0.95, more preferably 0.8 to 0.95, and for example, 0.75, 0.8, 0.85, 0.9, 0.95, and may be within the range between the two of the numerical values exemplified here.

[0026]

<Synthesis of copolymer (A)>

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

[0027]

The content of the monomer (a) in the mixture is 5 to 45mass%, preferably 10 to 40mass%, more preferably 15 to 35mass%. When the content of a monomer (a) is 5 to 45mass%, the obtained antifouling coating composition has remarkably improved storage stability, and in the coating film, no defects such as whitening, peeling, cracks, occur in the seawater for a long time, and the coating

film can maintain stable dissolution and good antifouling performance from the initial stage. This content is, specifically, for example, 5, 10, 15, 20, 25, 30, 35, 40, 45mass%, and may be in the range between the two values exemplified herein.

[0028]

The content of 2-methoxyethyl methacrylate in the mixture is 55 to 95mass%, preferably 60 to 90mass%, more preferably 60 to 85mass%. When the content of 2-methoxyethyl methacrylate is 55 to 95mass%, the coating film formed by using the obtained antifouling coating composition can sufficiently dissolve and have good antifouling performance in seawater from the initial stage and can maintain stable dissolution and good antifouling performance for a long time without causing coating film defects such as whitening, peeling, cracks. This content is specifically, for example, 55, 60, 65, 70, 75, 80, 85, 90, 95mass%, and may be in the range between the two values exemplified herein.

[0029]

The total content of the monomer (a) and 2-methoxyethyl methacrylate is 60mass% or more, preferably 70mass% or more, and more preferably 80mass% or more with respect to the total mass of the monomer (a) and the monomer (b). When the total content of the monomer (a) and 2-methoxyethyl methacrylate is within the above range, in the coating film, no defects such as whitening, peeling, cracks, occur, and the coating film can maintain stable dissolution for a long time and realize an excellent antifouling performance. This content is specifically, for example, 60, 65, 70, 75, 80, 85, 90, 95, 100mass%, and may be in the range between the two values exemplified herein.

[0030]

The weight average molecular weight of the copolymer of the present invention is preferably 5,000 to 300,000. When the molecular weight is less than 5,000, the coating film of the antifouling coating becomes fragile and easily peels off or cracks, and when it exceeds 300,000, the viscosity of the copolymer solution increases and the handling becomes difficult. This Mw is specifically, for example, 5000, 10000, 20000, 30,000, 40,000, 50,000, 60,000, 70,000, 80,000, 90,000, 100,000, 200,000, 300,000, and may be in the range between the two values exemplified herein.

[0031]

Examples of the polymerization initiator include azo compounds such as 2,2'-azobisisobutyronitrile (AIBN), 2,2'-azobis(2-methylbutyronitrile), and dimethyl-2,2'-azobisisobutylate; and peroxides such as benzoyl peroxide, di-tert-butylperoxide, tert-butyl peroxybenzoate, tert-butyl peroxyisopropyl carbonate, t-butyl peroxy 2-ethylhexanoate, and 1,1,3,3-tetramethylbutylperoxy-2-ethylhexanoate. 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 and 1,1,3,3-tetramethylbutylperoxy-2-ethylhexanoate are especially preferable.

[0032]

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

[0033]

As the method of polymerization, solution polymerization, bulk polymerization, emulsion polymerization, suspension polymerization and the like can be mentioned. Among these, in view

of the capability of obtaining the copolymer (A) simply with accuracy, solution polymerization is preferable.

[0034]

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

[0035]

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

[0036]

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

[0037]

1-2. Antifouling agent (B)

As the antifouling agent (B), for example, an inorganic chemical and an organic chemical can be mentioned.

As the inorganic chemical, 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 particularly preferable. From the viewpoint of long-term storage stability, the cuprous oxide surface-treated with glycerin, sucrose, stearic acid, lauric acid, lecithin, mineral oil, and the like is more preferable.

[0038]

As the organic chemical, 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), 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-(p-chlorophenyl)-3-cyano-4-bromo-5-trifluoromethyl pyrrole (generic name: ECONEA 28), (±)-4-[1-(2,3-dimethylphenyl)ethyl]-1H-imidazole (generic name: Medetomidine) can be mentioned.

These antifouling agents can be used alone, or two or more of these can be used in combination.

The content of the antifouling agent in the composition of the present invention is not particularly limited, but is usually 0.1 to 75mass%, preferably 1 to 60mass% in the solid content of the composition of the present invention. When the content of the antifouling agent is less than 0.1mass%, sufficient antifouling performance may not be obtained. When the content of the antifouling agent is more than 75mass%, the coating film formed is fragile, and further, can not

sufficiently adhere to the object to be coated and can not work sufficiently as an antifouling coating film.

[0039]

1-3. Other additives

Further, if necessary, the resin for antifouling coating of the present invention may be added with an elution regulator, a plasticizer, a pigment, a dye, an antifoaming agent, a dehydrating agent, a thixotropic agent, an organic solvent, and the like to obtain the antifouling coating.

As the elution regulator, monocarboxylic acids and salts thereof, such as rosin, rosin derivatives, naphthenic acid, cycloalkenyl carboxylic acid, bicycloalkenyl carboxylic acid, versatic acid, trimethyl isobutenylcyclohexene carboxylic acid, and their metal salts, or the alicyclic hydrocarbon resins as mentioned above can be exemplified. 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 resins, 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.

As the plasticizer, for example, phosphoric acid esters, phthalic acid esters, adipic acid esters, sebacic acid esters, epoxidized soybean oil, alkyl vinyl ether polymer, polyalkylene glycols, t-nonyl pentasulfide, vaseline, polybutene, tris(2-ethylhexyl) trimellitate, silicone oil, liquid paraffin, chlorinated paraffin and the like can be mentioned. These can be used alone, or two or more of these can be used in combination.

As the dehydrating agent, for example, synthetic zeolite adsorbents, orthoesters, silicates such as tetramethoxysilane and tetraethoxysilane, isocyanates, carbodiimides, carbodiimidazoles, and the like can be mentioned. These can be used alone, or two or more of these can be used in combination.

[0040]

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 including the copolymer, the antifouling agent, and other additives using a disperser.

Regarding the mixture solution, the ingredients such as the copolymers, the antifouling agent, and the like are preferably dissolved or dispersed in the solvent.

As the disperser, for example, the one which can be used as a micro-pulverizer can be suitably used. For example, a commercially available dissolver, 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.

[0041]

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 continually

renewed.

Examples of objects on which the coating film can be formed include ships (in particular, ship bottoms), fishing tools, structures submerged in seawater, and the like.

The thickness of the antifouling coating film can be suitably selected depending on the type of the 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 700 μm, and preferably 100 to 600 μm.

EXAMPLES

[0042]

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".

The non-volatile content is a value obtained by heating at 125°C for 1 hour in accordance with JIS K 5601-1-2 (ISO 3251).

[0043]

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 (available from Tosoh Corporation)

Column: TSK-gel 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

[0044]

The formulation among of each component shown in Tables is represented in grams.

[0045]

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

To a 2000 ml flask equipped with a thermometer, reflux condenser, stirrer, and dropping funnel, 400 g of xylene was charged and heated to 85±2°C with agitation under nitrogen atmosphere, and a mixed solution of 175 g of triisopropylsilyl methacrylate, 300 g of 2-methoxyethyl methacrylate, 25 g of methyl methacrylate, 5 g of 1,1,3,3-tetramethyl butylperoxy-2-ethylhexanoate (Perocta O available from NOF CORPORATION) was added dropwise over 1 hour while keeping the temperature at 85±2°C. After dropping, 0.5 g of 1,1,3,3-tetramethylbutylperoxy-2-ethylhexanoate was added 3 times every hour while keeping the temperature at 85±2°C to complete the polymerization reaction. Then the resulting solution was heated to 110°C, held for 30 minutes, and cooled. Then, 100 g of xylene was added and dissolved at 90°C or lower to obtain a copolymer solution P-1. The non-volatile content of P-1 was 49.7%, and the weight average molecular weight was 52,000.

[0046]

<Production Examples 2 to 8, Reference Examples1 to 12>

The organic solvents, monomers, and polymerization initiators shown in Tables 1 to 2 were

used, and polymerization was performed by processes similar to those of Production Example 1, thereby obtaining copolymer solutions P-2 to P-8 and comparative copolymer solution H-1 to H-12. The non-volatile content and weight average molecular weight of each copolymer solution obtained were measured.

The results are shown in Tables 1 to 2.

[0047]

[Table 1]

Table 1

kind of component	component	Production Example							
		1	2	3	4	5	6	7	8
initial solvent	xylene	400	400	400	400	400	400	400	400
monomer (a)	triisopropylsilyl methacrylate	175	150	150	125	125	100	100	75
monomer (b)	2-methoxyethyl methacrylate	300	300	325	300	325	325	350	400
	methyl methacrylate	25	50	25	50	50	50	50	25
	ethyl acrylate				25		25		
	n-butyl acrylate								
	2-methoxyethyl acrylate								
	triisopropylsilyl acrylate								
monomer (a) ／ (sum of monomer (a) and monomer (b))		0.35	0.30	0.30	0.25	0.25	0.20	0.20	0.15
(2-methoxyethyl methacrylate)／ (sum of monomer (a) and monomer (b))		0.60	0.60	0.65	0.60	0.65	0.65	0.70	0.80
(sum of monomer (a) and 2-methoxyethyl methacrylate)／ (sum of monomer (a) and monomer (b))		0.95	0.90	0.95	0.85	0.90	0.85	0.90	0.95
polymerization initiator	initial addition	5	5	5	6	5	6	5	5
	post addition 3 times	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
diluting solvent	xylene	100	100	100	100	100	100	100	100
reaction temperature [℃] (within ±2℃)		85	85	85	85	85	85	85	85
non-volatile content (%、125℃,1hr)		49.7	49.9	49.9	49.8	49.7	49.9	49.8	49.9
weight average molecular weight (Mw)		52,000	53,000	53,000	54,000	52,000	53,000	52,000	53,000
copolymer solution		P－1	P－2	P－3	P－4	P－5	P－6	P－7	P－8

[0048]

[Table 2]

Table 2-1

kind of component	component	Reference Example					
		1	2	3	4	5	6
initial solvent	xylene	400	400	400	400	400	400
monomer (a)	triisopropylsilyl methacrylate	300	300	250	225	200	175
monomer (b)	2-methoxyethyl methacrylate	125		175	100	200	125
	methyl methacrylate	50	150	25	75	50	100
	ethyl acrylate				50		
	n-butyl acrylate	25		50	50	50	100
	2-methoxyethyl acrylate		100				
	triisopropylsilyl acrylate						
monomer (a) ／ (sum of monomer (a) and monomer (b))		0.60	0.55	0.50	0.45	0.40	0.35
(2-methoxyethyl methacrylate)／ (sum of monomer (a) and monomer (b))		0.25	0.00	0.35	0.20	0.40	0.25
(sum of monomer (a) and 2-methoxyethyl methacrylate)／ (sum of monomer (a) and monomer (b))		0.85	0.55	0.85	0.65	0.80	0.60
polymerization initiator	initial addition	5	5	5	5	5	5
	post addition 3 times	0.5	0.5	0.5	0.5	0.5	0.5
diluting solvent	xylene	100	100	100	100	100	100
reaction temperature [℃] (within ±2℃)		85	85	85	85	85	85
non-volatile content (%、125℃,1hr)		49.8	49.7	49.9	49.8	49.9	49.8
weight average molecular weight (Mw)		51,000	50,000	53,000	52,000	50,000	54,000
copolymer solution		H-1	H-2	H-3	H-4	H-5	H-6

Table 2-2

kind of component	component	Reference Example					
		7	8	9	10	11	12
initial solvent	xylene	400	400	400	400	400	400
monomer (a)	triisopropylsilyl methacrylate	150	150	150	150		
monomer (b)	2-methoxyethyl methacrylate					150	300
	methyl methacrylate	300	50	50	50	25	25
	ethyl acrylate		300			25	
	n-butyl acrylate	50		300			
	2-methoxyethyl acrylate				300		
	triisopropylsilyl acrylate					300	175
monomer (a) ／ (sum of monomer (a) and monomer (b))		0.30	0.30	0.30	0.30	0.00	0.00
(2-methoxyethyl methacrylate)／ (sum of monomer (a) and monomer (b))		0.00	0.00	0.00	0.00	0.30	0.60
(sum of monomer (a) and 2-methoxyethyl methacrylate)／ (sum of monomer (a) and monomer (b))		0.30	0.30	0.30	0.30	0.30	0.60
polymerization initiator	initial addition	5	5	5	5	5	5
	post addition 3 times	0.5	0.5	0.5	0.5	0.5	0.5
diluting solvent	xylene	100	100	100	100	100	100
reaction temperature [℃] (within ±2℃)		85	85	85	85	85	85
non-volatile content (%、125℃,1hr)		49.9	49.9	50.0	49.9	49.6	49.7
weight average molecular weight (Mw)		52,000	55,000	51,000	52,000	51,000	52,000
copolymer solution		H-7	H-8	H-9	H-10	H-11	H-12

[0049]

<Examples 1 to 12, Comparison Examples 1 to 12>

Copolymer solutions P-1 to P-8 and comparative copolymer solutions H-1 to H-12 obtained in Production Examples 1 to 8 and Reference Examples 1 to 12 were used, and antifouling coating compositions were formulated by the content ratio shown in Tables 3 to 4.

[0050]

(Preparation method of coating composition)

The antifouling coating compositions of Examples 1 to 12 and Comparative Examples 1 to 12 were prepared by mixing and dispersing for 1 hour using a small tabletop sand mill for experiments (using glass beads having a diameter of 1.5 to 2.5 mm) in a draft with two humidifiers operating to keep humidity at 90% or more. Then, the product was divided into two 100 ml tin cans. The coating in one tin was used for various coating tests, and the coating in the other tin can was used for storage stability evaluation.

[0051]

(Evaluation of storage stability of coating)

After measuring the viscosity of the coating in one tin can, it was sealed and stored in a thermostat at 45°C for 3 months, then the viscosity of the coating was measured with a Brookfield viscometer.

The storage stability of the coating was evaluated by the following method.

AA: Change in viscosity of the coating was less than 500 mPa·s/25°C (viscosity hardly increased)

A: Change in viscosity of the coating was 500 to 5000 mPa·s/25°C (viscosity slightly increased)

B: Change in viscosity of the coating was 5000 mPa·s/25°C or more (viscosity significantly increased)

C: Viscosity of the coating changed so much that the viscosity could not be measured. (the coating became gel or solidified)

The results are shown in Tables 3 to 4.

[0052]

(Measurement of hardness of coating film)

The coating film hardness of each coating was measured with a pendulum hardness tester.

Each coating sample was applied on a glass plate (100 x 200 x 2 mm) and dried at 40°C for 1 day so that the thickness after drying was about 100 μm, and the coating film hardness was measured with a pendulum hardness tester at 25°C indoors. The value is a count number.

The results are shown in Tables 3 to 4.

[0053]

(Rotary test)

A rotating drum with a diameter of 515 mm and a height of 440 mm was attached to the center of the water tank so that it could be rotated by a motor. Further, a cooling device for keeping the temperature of seawater constant and a pH automatic controller for keeping the pH of seawater constant were attached.

A test plate for the rotary test was prepared according to the following method.

First, a rust preventive coating (epoxy vinyl A/C) was applied on a titanium plate (71×100×0.5 mm) and dried to form a rust preventive coating film so that the thickness of the film

after drying was about 100 μm. Then, each of the coating compositions obtained in Examples 1 to 12 and Comparative Examples 1 to 12 was applied on the rust preventive coating film so that the thickness after drying was about 300 μm. The obtained coated product was dried at 40°C for 3 days to prepare a test plate having a dry coating film with a thickness of about 300 μm.

The prepared test plates were fixed to the rotating drum of the rotating device of the above device so that it came into contact with seawater, and the rotating drum was rotated at a speed of 20 knots. During rotating, the temperature of seawater was kept at 25°C, the pH was kept at 8.0 to 8.2, and the seawater was replaced every week.

[0054]

・Measurement of amount of coating film dissolved

The initial film thickness and the remaining film thickness every month after the start of the test were measured with a shape measurement laser microscope VK-X100 manufactured by Keyence Corporation, and the amount of coating film dissolved per month (μm/month) was obtained by calculating the thickness of the coating film dissolved from the difference of the thicknesses

The results are shown in Tables 3 and 4.

[0055]

・Observation of surface condition of coating film

When the remaining film thickness was measured after 6 months of the rotary test, the surface condition of each coating film was evaluated by observing the surface of each coating film with the naked eye and a microscope.

The surface condition of the coating film was evaluated according to the following criteria.

AA: No defects were observed.

A: Hairline cracks were slightly observed.

B: Hairline cracks were observed on the entire surface of the coating film.

C: Defects such as cracks, blisters, peelings were observed on the coating film.

The results are shown in Tables 3 and 4.

[0056]

・Observation of coating film whitening

When the remaining film thickness was measured after 6 months of the rotary test, the surface of each coating film was visually observed to evaluate the presence or absence of whitening.

The following criteria were used to visually evaluate the presence or absence of whitening on the surface of the coating film.

A: The color of the coating film surface hardly changed.

B: The color of the coating film surface slightly whitened.

C: The color of the entire surface of the coating film obviously whitened.

The results are shown in Tables 3 and 4.

[0057]

・L value measurement of coating film

The L value (brightness) of the coating film before the rotary test and the remaining coating film after 6 months of the rotary test were measured using a colorimeter. As the colorimeter, Color Meter ZE6000 manufactured by NIPPON DENSHOKU INDUSTRIES CO.、LTD. was used. As the L value (brightness), the value specified in JIS Z 8781-4 (calculation formula of CIE method) was used. The L value (brightness) is 100 for white and 0 for black, and when the coating surface whitens, the coating film becomes brighter and the L value increases.

[0058]

(Antifouling test (stationary immersion test))

Each of the antifouling coating compositions obtained in Examples 1 to 12 and Comparative Examples 1 to 12 was applied to both sides of a hard vinyl chloride board (100×200×2 mm) and dried so that the thickness of the coating film after drying was about 200μm. This test plate was immersed in 1.5 m below the sea level in Owase City, Mie Prefecture, and fouling on the test plate due to adhesion of organisms was observed for 12 months and evaluated.

The evaluation was carried out by visually observing the condition of the coating film surface and determined according to the following criteria.

AA: Fouling organisms such as shellfish and algae do not adhere, and slime hardly adheres.

A: Level where fouling organisms such as shellfish and algae do not adhere, slime thinly adheres (the coating surface can be seen) and can be wiped lightly with a brush.

B: Level where fouling organisms such as shellfish and algae do not adhere, slime adheres so thickly that the coating film surface cannot be seen and cannot be removed even by wiping strongly with a brush.

C: Level where fouling organisms such as shellfish and algae adhere.

The results are shown in Tables 3 and 4.

[0059]

[Table 3]

Table 3-1

component		Example					
		1	2	3	4	5	6
copolymer solution	P－1	30					
	P－2		30				
	P－3			30			
	P－4				30		
	P－5					30	
	P－6						30
	P－7						
	P－8						
antifouling agent	cuprous oxide	45	45	45	45	45	45
	copper pyrithione	3	3	3	3	3	3
pigment	red 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
other additives	tetraethoxysilane	0.5	0.5	0.5	0.5	0.5	0.5
	rosin zinc salt						
	chlorinated paraffin						
	Disparlon A603-20x	3	3	3	3	3	3
solvent	xylene	9.5	9.5	9.5	9.5	9.5	9.5
sum		100	100	100	100	100	100
storage stability of coating		AA	AA	AA	AA	AA	AA
hardness of coating film		34	33	33	30	31	29
amount of coating film dissolved μm/month	0-1 months	14.3	14.0	15.2	15.7	15.2	14.8
	1-2 months	14.5	14.1	15.3	15.7	15.5	15.0
	2-3 months	14.5	14.3	15.5	15.9	15.6	15.1
	3-4 months	14.8	14.4	15.5	15.8	15.4	15.2
	4-5 months	14.7	14.2	15.6	15.8	15.5	15.0
	5-6 months	14.7	14.3	15.4	15.9	15.4	15.1
observation of surface condition of coating film (6 months later)		AA	AA	AA	AA	AA	AA
observation of coating film whitening (6 months later)		A	A	A	A	A	A
L value of coating film (initial)		36.3	36.4	36.3	36.5	36.4	36.4
L value of coating film (6 months later)		39.6	40.3	40.1	39.5	40.7	39.4
antifouling test	2 months later	AA	AA	AA	AA	AA	AA
	4 months later	AA	AA	AA	AA	AA	AA
	6 months later	AA	AA	AA	AA	AA	AA
	8 months later	AA	AA	AA	AA	AA	AA
	10 months later	AA	AA	AA	AA	AA	AA
	12 months later	AA	AA	AA	AA	AA	AA

Table 3-2

component		Example					
		7	8	9	10	11	12
copolymer solution	P－1			25			
	P－2				25		
	P－3					25	
	P－4						25
	P－5						
	P－6						
	P－7	30					
	P－8		30				
antifouling agent	cuprous oxide	45	45	45	45	45	45
	copper pyrithione	3	3	3	3	3	3
pigment	red 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
other additives	tetraethoxysilane	0.5	0.5	1	1	1	1
	rosin zinc salt			5	5	5	5
	chlorinated paraffin			1	1	1	1
	Disparlon A603-20x	3	3	3	3	3	3
solvent	xylene	9.5	9.5	8	8	8	8
sum		100	100	100	100	100	100
storage stability of coating		AA	AA	AA	AA	AA	AA
hardness of coating film		28	27	43	44	42	40
amount of coating film dissolved μm/month	0-1 months	15.7	12.1	8.1	7.5	7.8	8.0
	1-2 months	15.6	12.0	8.2	7.7	7.7	8.5
	2-3 months	15.4	12.2	8.3	7.8	7.7	8.5
	3-4 months	15.7	12.2	8.2	7.5	7.9	8.2
	4-5 months	15.8	12.0	8.4	7.7	7.9	8.4
	5-6 months	15.9	12.2	8.3	7.8	8.1	8.3
observation of surface condition of coating film (6 months later)		AA	AA	AA	AA	AA	AA
observation of coating film whitening (6 months later)		A	A	A	A	A	A
L value of coating film (initial)		36.4	36.4	33.4	33.3	33.5	33.4
L value of coating film (6 months later)		39.2	40.8	39.5	39.2	39.8	39.9
antifouling test	2 months later	AA	AA	AA	AA	AA	AA
	4 months later	AA	AA	AA	AA	AA	AA
	6 months later	AA	AA	AA	AA	AA	AA
	8 months later	AA	AA	AA	AA	AA	AA
	10 months later	AA	AA	AA	AA	AA	AA
	12 months later	AA	AA	AA	AA	AA	AA

[0060]

[Table 4]

Table 4-1

component		Comparative Example					
		1	2	3	4	5	6
copolymer solution	H－1	30					
	H－2		30				
	H－3			30			
	H－4				30		
	H－5					30	
	H－6						30
	H－7						
	H－8						
	H－9						
	H－10						
	H－11						
	H－12						
antifouling agent	cuprous oxide	45	45	45	45	45	45
	copper pyrithione	3	3	3	3	3	3
pigment	red 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
other additives	tetraethoxysilane	0.5	0.5	0.5	0.5	0.5	0.5
	rosin zinc salt						
	chlorinated paraffin						
	Disparlon A603-20x	3	3	3	3	3	3
solvent	xylene	9.5	9.5	9.5	9.5	9.5	9.5
sum		100	100	100	100	100	100
storage stability of coating		B	B	B	A	A	A
hardness of coating film		55	27	41	32	30	26
amount of coating film dissolved μm/month	0-1 months	1.2	1.0	2.1	1.7	2.3	1.5
	1-2 months	1.9	1.5	2.4	2.0	2.7	1.7
	2-3 months	2.9	2.7	3.3	2.5	3.5	2.1
	3-4 months	3.8	3.5	4.0	3.1	4.2	2.5
	4-5 months	4.7	4.6	4.8	3.6	5.1	2.7
	5-6 months	5.5	5.8	5.1	4.2	5.6	3.2
observation of surface condition of coating film (6 months later)		AA	AA	AA	AA	AA	AA
observation of coating film whitening (6 months later)		C	C	C	C	C	C
L value of coating film (initial)		36.4	36.4	36.3	36.5	36.4	36.4
L value of coating film (6 months later)		58.5	61.4	60.2	59.1	62.3	61.7
antifouling test	2 months later	AA	AA	AA	AA	AA	AA
	4 months later	AA	AA	AA	AA	AA	AA
	6 months later	AA	AA	AA	AA	AA	AA
	8 months later	AA	AA	AA	AA	AA	AA
	10 months later	AA	AA	AA	AA	AA	AA
	12 months later	AA	AA	AA	AA	AA	A

Table 4-2

component		Comparative Example					
		7	8	9	10	11	12
copolymer solution	H－1						
	H－2						
	H－3						
	H－4						
	H－5						
	H－6						
	H－7	30					
	H－8		30				
	H－9			30			
	H－10				30		
	H－11					30	
	H－12						30
antifouling agent	cuprous oxide	45	45	45	45	45	45
	copper pyrithione	3	3	3	3	3	3
pigment	red 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
other additives	tetraethoxysilane	0.5	0.5	0.5	0.5	0.5	0.5
	rosin zinc salt						
	chlorinated paraffin						
	Disparlon A603-20x	3	3	3	3	3	3
solvent	xylene	9.5	9.5	9.5	9.5	9.5	9.5
sum		100	100	100	100	100	100
storage stability of coating		AA	AA	AA	B	C	B
hardness of coating film		63	1	1	1	15	13
amount of coating film dissolved μm/month	0-1 months	1.0	0.5	0.2	8.5	1.1	16.1
	1-2 months	1.2	1.0	0.5	11.2	2.0	18.5
	2-3 months	2.0	1.2	0.7	13.0	2.8	20.8
	3-4 months	2.2	1.5	0.5	15.6	3.5	24.7
	4-5 months	2.5	1.5	0.8	17.5	4.6	30.4
	5-6 months	2.9	1.8	0.8	19.1	5.9	39.6
observation of surface condition of coating film (6 months later)		AA	A	A	A	AA	A
observation of coating film whitening (6 months later)		A	A	A	C	C	B
L value of coating film (initial)		36.5	36.4	36.4	36.3	36.5	36.4
L value of coating film (6 months later)		40.2	40.4	39.5	55.3	63.5	45.8
antifouling test	2 months later	AA	AA	AA	AA	AA	AA
	4 months later	A	AA	AA	AA	AA	AA
	6 months later	A	AA	A	AA	AA	AA
	8 months later	B	A	A	AA	AA	AA
	10 months later	B	A	B	AA	AA	AA
	12 months later	C	C	C	AA	AA	AA

[0061]

The details of the antifouling agents, pigments, and other additives in Tables 3 to 4 are as follows.

<Antifouling agent>

cuprous oxide (product name “NC-301” available from NISSIN CHEMCO LTD., average particle size 3μm)

copper pyrithione (product name “copper Omadine” available from Arch Chemical, Inc.)

<pigment>

red oxide (product name “TODA COLOR EP-13D” available from Toda Pigment Corp.)

talc (product name “CROWN TALC 3S” available from matsumura sangyo Co., Ltd.)

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

titanium oxide (product name “FR-41” available from FURUKAWA CO., LTD.)

<other additives>

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

rosin zinc salt (50% xylene solution)

chlorinated paraffin (product name “EMPARA A-40S” available from Tosoh Corporation)

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

[0062]

From Tables 3 and 4, the coatings produced using the coating compositions of the present invention (Examples 1 to 12) have excellent storage stability, and the formed coating films can maintain a high dissolution amount in seawater. Also, in the antifouling test, fouling organisms such as shellfish and algae do not adhere, and slime hardly adheres. Further, it can be seen that the condition of the dried coating film after 6 months of the rotary test is also good without any defects such as whitening, cracks, and peelings.

On the other hand, the coatings produced by using the coating compositions of Comparative Examples 1 to 6 or 10 to 12 had poorer storage stability than the coatings of Examples, and the coating films formed using these coating easily whitened.

The coatings produced using the coating compositions of Comparative Examples 7 to 9 had a low amount of dissolution in seawater and could not sufficiently prevent the adhesion of fouling organisms.