

DESCRIPTION

ANTIFOULING COATING COMPOSITION

Technical Field

[0001]

The present invention relates to an antifouling coating composition.

Background Art

[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.

[0003]

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 time has been known (Patent Literature 1).

Citation List

Patent Literature

[0004]

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

Summary of Invention

Technical Problem

[0005]

However, even when the technique of Patent Literature 1 is used, there is a problem that the antifouling performance is not sufficiently realized in a draft section, which is waterline reached by water, while in a coating film section, which is constantly submerged in seawater, its antifouling performance is maintained for a long time. This is because the coating film in the draft section is subjected to repeated dry and wet and is more affected by various factors such as sunlight.

[0006]

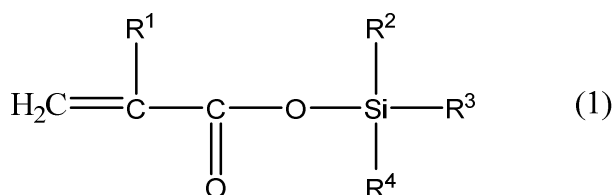
The present invention has been made by taking the afore-mentioned circumstances into consideration. The present invention provides a composition which can form an antifouling coating film which continues to dissolve for a long time even after being exposed to sunlight for a long time and realizes a good antifouling performance even in the draft section, where adhesion of aquatic fouling organisms is easy to occur, and high environmental safety.

Solution to Problem

[0007]

According to the present invention, an antifouling coating composition, comprising: a copolymer A; a copolymer B; and an antifouling agent; wherein: the copolymer A and the copolymer B are each obtained by copolymerizing a mixture of a monomer (a) and a polymerizable unsaturated monomer (b) other than the monomer (a); the monomer (a) is represented by general formula (1);

[chemical formula 1]



in the general formula (1), R¹ is hydrogen or a methyl group, and R², R³ and R⁴ are selected from a C3-C8 branched alkyl group and a phenyl group and may be the same or different; the copolymer A satisfies following requirements (A1) to (A2); the copolymer B satisfies following requirements (B1) to (B2) is provided.

(A1) Content of the monomer (a) is 30 to 50mass% with respect to the total mass of the monomer (a) and the monomer (b).

(A2) Content of 2-methoxyethyl acrylate in the monomer (b) is 15 to 30mass% with respect to the total mass of the monomer (a) and the monomer (b).

(B1) Content of the monomer (a) is 30 to 40mass% with respect to the total mass of the monomer (a) and the monomer (b).

(B2) Content of 2-methoxyethyl methacrylate in the monomer (b) is 30 to 50mass% with respect to the total mass of the monomer (a) and the monomer (b)

[0008]

The present inventors have conducted intensive studies, and have found that when an antifouling coating film was formed using a composition comprising copolymer A, obtained by copolymerizing a mixture containing a silyl ester monomer and 2-methoxyethyl acrylate in specific amount each, and a copolymer B, obtained by copolymerizing a mixture containing a silyl ester monomer and 2-methoxyethyl methacrylate in a specific amount each, good antifouling performance can be realized even in the draft section, thereby completing the present invention.

Description of Embodiments

[0009]

Hereinafter, the present invention will be described in detail.

[0010]

1. Antifouling coating composition

An antifouling coating composition of the present invention includes a copolymer A, a copolymer B, and an antifouling agent.

[0011]

1-1. Copolymer A and a copolymer B

A copolymer A and a copolymer B are each a tri-organosilyl (meth)acrylate ester copolymer, which is obtained by copolymerizing a mixture of a monomer (a) and a polymerizable unsaturated monomer (b) other than said monomer (a). Thus, each of the copolymer A and the copolymer B includes monomeric units derived from the monomer (a) and the monomer (b). The compounds contained in the monomer (a) and its compounding ratio may be the same or different in the copolymer A and the copolymer B. The compounds in the monomer (b) may be the same or different in the copolymers A and the copolymer B. When the compounds contained in monomer (b) are the same in copolymers A and B, its compounding ratio is different.

[0012]

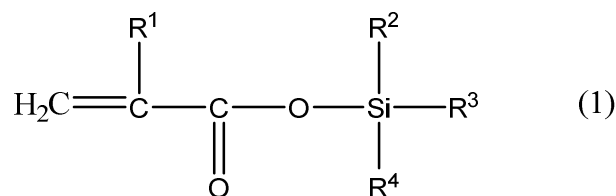
<Monomer(a)>

The monomer (a) is a tri-organosilyl (meth)acrylate ester monomer, which is represented by

general formula (1).

[0013]

[chemical formula 1]



In the general formula (1), R¹ is hydrogen or a methyl group, and R², R³ and R⁴ are selected from a C3-C8 branched alkyl group and a phenyl group and may be the same or different.

[0014]

In the present invention, the monomer (a) represented by the general formula (1) includes, for example, triisopropylsilyl (meth)acrylate, triisobutylsilyl (meth)acrylate, tri-s-butylsilyl (meth)acrylate, triisoamylsilyl (meth)acrylate, tris(2-ethylhexyl)silyl (meth)acrylate, triphenylsilyl (meth)acrylate, diisopropylisobutylsilyl (meth)acrylate, diisopropylisoamylsilyl (meth)acrylate, diisopropyl(2-ethylhexyl)silyl (meth)acrylate, diisopropylphenylsilyl (meth)acrylate, diisopropylcyclohexylsilyl (meth)acrylate, t-butyl diisopropylsilyl (meth)acrylate, t-butyl diisobutylsilyl (meth)acrylate, t-butyl diisoamylsilyl (meth)acrylate, t-butyl diphenylsilyl (meth)acrylate, and the like. Triisopropylsilyl(meth)acrylate is preferable and triisopropylsilyl methacrylate particularly preferable. 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 copolymerizable with the monomer (a), and examples thereof include the following.

(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 (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.

Metal pendant (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.

Metal (meth)acrylates such as zinc (meth)acrylate and copper (meth)acrylate.

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.

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

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

[0016]

The monomer (b) can be used alone or two or more of these can be used in combination, and preferably (meth) acrylate ester.

[0017]

<Requirements (A1) to (A2) and (B1) to (B2)>

In the present invention, it is essential that a copolymer A satisfies requirements (A1) to (A2) and that a copolymer B satisfies requirements (B1) to (B2).

[0018]

(A1) Content of the monomer (a) is 30 to 50mass% with respect to the total mass of the monomer (a) and the monomer (b).

(A2) Content of 2-methoxyethyl acrylate in the monomer (b) is 15 to 30mass% with respect to the total mass of the monomer (a) and the monomer (b).

(B1) Content of the monomer (a) is 30 to 40mass% with respect to the total mass of the monomer (a) and the monomer (b).

(B2) Content of 2-methoxyethyl methacrylate in the monomer (b) is 30 to 50mass% with respect to the total mass of the monomer (a) and the monomer (b).

[0019]

The following points should be noted.

(1) The content of the monomer (a) is 30 to 50mass% in the copolymer A and 30 to 40% in the copolymer B, both of which are relatively small amounts.

(2) In the copolymer A, the monomer (b) contains 2-methoxyethyl acrylate, and in the copolymer B, the monomer (b) contains 2-methoxyethyl methacrylate.

[0020]

Thus, the present invention is characterized that it uses two types of copolymers having a relatively small ratio of silyl ester monomeric units, one of which contains 2-methoxyethyl acrylate units and the other of which contains 2-methoxyethyl methacrylate units. And, as shown in the Examples described below, by having these characteristics, the technical effects of improving the hydrophilicity of the coating film, improving the adhesiveness of the coating film to a highly polar surface such as glass, and improving resistance in wet and dry cycle tests can be achieved. This is equivalent to the technical effect of improving the adhesiveness when the coating is overcoated on the surface of the existing coating film.

[0021]

In the requirement (A1), the content of the monomer (a) may be, for example, 30, 35, 40, 45, 50mass% with respect to the total mass of the monomer (a) and the monomer (b), and may be in the range between the two values exemplified herein.

[0022]

In the requirement (A2), the content of 2-methoxyethyl acrylate may be, for example, 15, 20, 25, 30mass% with respect to the total mass of the monomer (a) and the monomer (b), and may be in the range between the two values exemplified herein. The monomer (b) of the copolymer A may contain 2-methoxyethyl methacrylate, but the content of 2-methoxyethyl methacrylate in the monomer (b) of the copolymer A is preferably less than the content of 2-methoxyethyl methacrylate in the monomer (b) of the copolymer B and is preferably 1/2 or less of the content of 2-methoxyethyl methacrylate in the monomer (b) of the copolymer B. The monomer (b) of the copolymer A preferably does not contain 2-methoxyethyl methacrylate.

[0023]

In the requirement (B1), the content of the monomer (a) is, for example, 30, 35, 40mass% with respect to the total mass of the monomer (a) and the monomer (b), and may be in the range between the two values exemplified herein.

[0024]

In the requirement (B2), the content of 2-methoxyethyl methacrylate is, for example, 30, 35, 40, 45, 50mass% with respect to the total mass of the monomer (a) and the monomer (b), and may be in the range between the two values exemplified herein. The monomer (b) of the copolymer B may contain 2-methoxyethyl acrylate, but the content of 2-methoxyethyl acrylate in the monomer (b) of the copolymer B is preferably less than the content of 2-methoxyethyl acrylate in the monomer (b) of the copolymer A and is preferably 1/2 or less of the content of 2-methoxyethyl acrylate in the monomer (b) of the copolymer A. The monomer (b) of the copolymer B preferably does not contain 2-methoxyethyl acrylate.

[0025]

In the copolymer A and the copolymer B, the monomer (b) may contain a silyl ester other than the monomer (a). In that case, the content of the total silyl ester with respect to the total mass of the monomer (a) and the monomer (b) is, for example, 30 to 60mass%, and specifically, for example, 30, 35, 40, 45, 50, 55, 60mass%, and may be in the range between the two values exemplified herein. The content of the silyl ester other than the monomer (a) is preferably less than the content of the monomer (a), preferably 1/2 or less of the content of the monomer (a) and more preferably 1/5 or less.

[0026]

The content of the copolymer A is preferably 25 to 75mass% with respect to the total mass of the copolymer A and the copolymer B. In this case, the effect of improving the resistance in the wet and dry cycle tests is remarkable. Specifically, the content of the copolymer A is, for example, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75mass%, and may be in the range between the two values exemplified herein.

[0027]

<Synthesis of the copolymer A and the copolymer B>

The copolymer A and the copolymer B 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.

[0028]

The weight average molecular weight of the copolymer A and the copolymer B 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 weight average molecular weight may be, 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.

[0029]

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, tert-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.

[0030]

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

[0031]

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 resin component simply with accuracy, solution polymerization is preferable.

[0032]

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.

[0033]

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.

[0034]

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

[0035]

1-2. Antifouling agent

As the antifouling agent, 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 shelf stability, the cuprous oxide surface-treated with glycerin, sucrose, stearic acid, lauric acid, lecithin, mineral oil and the like is more preferable.

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.

[0036]

1-3. Other additives

Further, if necessary, the resin for antifouling coating of the present invention is 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 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.

[0037]

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 A, the copolymer B, 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 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.

[0038]

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

[0039]

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, Comparative Production Examples, Examples, and Comparative Examples, "%" denotes "% by mass". The viscosity was measured at 25°C using a Brookfield viscometer. 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".

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

[0040]

<Production Example 1 (Production of copolymer solution SA-1)>

To a 2000 ml flask equipped with a thermometer, reflux condenser, stirrer, and dropping funnel, 400 g of xylene was charge and heated to 83-87°C under nitrogen atmosphere. With agitation, a mixture of 150 g of triisopropyl silyl methacrylate, 37 g of ethyl acrylate, 238 g of methyl methacrylate, 75 g of 2-methoxyethyl acrylate and 5 g of 1,1,3,3-tetramethylbutylperoxy-2-ethylhexanoate (Perocta O available from NOF CORPORATION) was added dropwise over 1 hours while keeping the temperature at 83-87°C. After dropping, 0.5 g of 1,1,3,3-tetramethylbutyl peroxy 2-ethylhexanoate was added three times every hour, while keeping the temperature at 83-87°C, and the polymerization reaction was completed. Then, 100 g of xylene was added so that the product was dissolved, and the copolymer solution SA-1 was obtained. The non-volatile content of copolymer solution SA-1 was 49.8% and the weight average molecular weight was 52,000.

[0041]

<Production Example 2-20, Comparative Production Example1-4>

The organic solvents, monomer, and polymerization initiator shown in Tables 1 to 3 were used, and polymerization was performed by processes similar to those of Production Example 1, thereby obtaining copolymer solutions SA-2 to SA-10 of copolymer A, copolymer solution SB-1 to SB-10 of copolymer B, and copolymer solution T-1 to T-4 of other copolymers. The non-volatile content and weight average molecular weight of each copolymer solution obtained were measured.

The results are shown in Tables 1 to 3.

[0042]

[Table 1]

Table 1		Production Example									
		1	2	3	4	5	6	7	8	9	10
		copolymer A									
monomer (a)	xylene	400	400	400	400	400	350	350	350	350	350
	triisopropylsilyl acrylate										
monomer (b)	triisopropylsilyl methacrylate	150	150	250		250	180	180	300	180	300
	ethyl acrylate	37		75			44		90		
	methyl methacrylate	238	200	100	200	175	286	240	120	240	210
	n-butyl acrylate										
	2-methoxyethyl acrylate	75	150	75	150	75	90	180	90	180	90
	2-methoxyethyl methacrylate										
ratio of monomer(a) (mass%)		30%	30%	50%	30%	50%	30%	30%	50%	30%	50%
ratio of 2-methoxyethyl acrylate (mass%)		15%	30%	15%	30%	15%	15%	30%	15%	30%	15%
ratio of 2-methoxyethyl methacrylate (mass%)											
polymerization initiator	first added	5	5	5	5	5	7	7	7	7	7
	later added 3 times	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
amount of xylene added after completing the reaction		100	100	100	100	100	50	50	50	50	50
reaction temperature[°C](within ±2°C)		85	85	85	88	88	85	85	85	85	85
copolymer physical property	Solid content [%]	49.8	49.6	49.7	49.6	50.1	60.3	60.5	60	60.3	60.4
	weight average molecular weight [Mw]	52000	49000	51000	48000	48000	23000	26000	21000	25000	24000
	viscosity [mPa·s](25°C)	820	700	410	820	700	810	730	430	860	720
copolymer solution		SA-1	SA-2	SA-3	SA-4	SA-5	SA-6	SA-7	SA-8	SA-9	SA-10

[0043]

[Table 2]

Table 2		Production Example									
		11	12	13	14	15	16	17	18	19	20
		copolymer B									
monomer (a)	xylene	400	400	400	400	400	350	350	350	350	350
	triisopropylsilyl acrylate				150	200				180	240
monomer (b)	triisopropylsilyl methacrylate	150	150	200			180	180	240		
	ethyl acrylate										
	methyl methacrylate	140	70	90	85	135	168	84	108	102	162
	n-butyl acrylate	60	30	60	15	15	72	36	72	18	18
	2-methoxyethyl acrylate										
	2-methoxyethyl methacrylate	150	250	150	250	150	180	300	180	300	180
ratio of monomer(a) (mass%)		30%	30%	40%	30%	40%	30%	30%	40%	30%	40%
ratio of 2-methoxyethyl acrylate (mass%)											
ratio of 2-methoxyethyl methacrylate (mass%)		30%	50%	30%	50%	30%	30%	50%	30%	50%	30%
polymerization initiator	first added	5	5	5	5	5	7	7	7	7	7
	later added 3 times	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
amount of xylene added after completing the reaction		100	100	100	100	100	50	50	50	50	50
reaction temperature[°C](within ±2°C)		85	85	85	88	88	88	88	88	88	88
copolymer physical property	Solid content [%]	49.9	49.8	49.8	50.1	49.9	60.2	60.5	60.1	60.1	60.5
	weight average molecular weight [Mw]	51000	49000	49000	48000	50000	27000	25000	26000	22000	20000
	viscosity [mPa·s](25°C)	410	250	340	200	310	440	320	390	240	340
	copolymer solution	SB-1	SB-2	SB-3	SB-4	SB-5	SB-6	SB-7	SB-8	SB-9	SB-10

Table 3		Comparative			
		Production Example			
		1	2	3	4
		other copolymer			
xylene		400	400	400	400
monomer (a)	triisopropylsilyl acrylate			250	250
	triisopropylsilyl methacrylate	250	250		
monomer (b)	ethyl acrylate				
	methyl methacrylate	250	200	250	200
	n-butyl acrylate		50		50
	2-methoxyethyl acrylate				
	2-methoxyethyl methacrylate				
ratio of monomer(a) (mass%)		50%	50%	50%	50%
ratio of 2-methoxyethyl acrylate (mass%)					
ratio of 2-methoxyethyl methacrylate (mass%)					
polymerization initiator	first added	5	5	5	5
	later added 3 times	0.5	0.5	0.5	0.5
amount of xylene added after completing the reaction		100	100	100	100
reaction temperature[°C](within ±2°C)		85	85	85	88
copolymer physical property	Solid content [%]	49.7	49.9	49.6	49.7
	weight average molecular weight [Mw]	52000	49000	51000	48000
	viscosity [mPa·s](25°C)	980	870	700	660
copolymer solution		T-1	T-2	T-3	T-4

[0045]

<Production Example 21 (Production of rosin metal salt solution)>

To a flask equipped with a thermometer, a reflux condenser, and a stirrer, 240 g of Chinese gum rosin (WW) and 360 g of xylene were charged, and furthermore, 120 g of zinc oxide was added so that all the resin acids in the said rosin formed zinc salts, and the mixture was refluxed and dehydrated under reduced pressure at 70-80°C for 3 hours. The mixture was then cooled and filtered to obtain a xylene solution of rosin zinc salts (dark brown transparent liquid, 50% solids). The non-volatile content of the solution obtained was 50.4%.

[0046]

<Production Example 22(Production of hydrogenated rosin metal salt solution)>

To a flask equipped with a thermometer, a reflux condenser, and a stirrer, 240 g of Hyper CH and 360 g of xylene were charged, and furthermore, 120 g of zinc oxide was added so that all the resin acids in the said rosin formed zinc salts, and the mixture was refluxed and dehydrated under reduced pressure at 70-80°C for 3 hours. The mixture was then cooled and filtered to obtain a xylene solution of rosin zinc salts (dark brown transparent liquid, 50% solids). The non-volatile content of the solution obtained was 50.3%.

[0047]

<Example 1-83, Comparison Examples 1-14>

Copolymer solutions SA-1 to SA-10, SB-1 to SB-10, T-1 to T-4 were used, and the antifouling coating compositions were formulated by the content ratio shown in Table 4 to 14.

[0048]

(Wet and dry cycle test of the coating)

Each of the 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.

[0049]

[Table 4]

Table 4

component		Example								
		1	2	3	4	5	6	7	8	9
copolymer A	SA-1	12.5	12.5	12.5						
	SA-2				12.5	12.5	12.5			
	SA-3							12.5	12.5	12.5
copolymer B	SB-1	12.5			12.5			12.5		
	SB-2		12.5			12.5			12.5	
	SB-3			12.5			12.5			12.5
elution regulator	rosin metal salt solution	3	3	3	3	3	3	3	3	3
	gum rosin solution	3	3	3	3	3	3	3	3	3
plasticizer	chlorinated paraffin	1	1	1	1	1	1	1	1	1
	epoxidized soybean oil	1	1	1	1	1	1	1	1	1
antifouling agent	cuprous oxide	40	40	40	40	40	40	40	40	40
	copper pyrrhione	3	3	3	3	3	3	3	3	3
	talc	2	2	2	2	2	2	2	2	2
other additives	zinc oxide	5	5	5	5	5	5	5	5	5
	red oxide	3	3	3	3	3	3	3	3	3
	titanium oxide	1	1	1	1	1	1	1	1	1
	tetraethoxysilane	1	1	1	1	1	1	1	1	1
	aliphatic amide	3	3	3	3	3	3	3	3	3
	thixotropic agent									
solvent	xylene	9	9	9	9	9	9	9	9	9
	sum	100	100	100	100	100	100	100	100	100
ratio of copolymer A (mass%)		50%	50%	50%	50%	50%	50%	50%	50%	50%
test result	condition of coating film after 3 months	○	○	○	○	○	○	○	○	○
	condition of coating film after 6 months	○	○	○	○	○	○	○	○	○

[0050]

[Table 5]

Table 5

component		Example																
		10	11	12	13	14	15	16	17	18								
copolymer A	SA-6	12.5	12.5	12.5														
	SA-7				12.5	12.5	12.5											
	SA-8											12.5	12.5	12.5	12.5	12.5		
copolymer B	SB-6	12.5			12.5							12.5						
	SB-7		12.5			12.5							12.5			12.5		
	SB-8			12.5			12.5				12.5						12.5	
elution regulator	rosin metal salt solution	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	
	gum rosin solution	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	
plasticizer	chlorinated paraffin	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	
	epoxidized soybean oil	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	
antifouling agent	cuprous oxide	40	40	40	40	40	40	40	40	40	40	40	40	40	40	40	40	
	copper pyrithione	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	
	talc	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	
other additives	zinc oxide	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	
	red oxide	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	
	titanium oxide	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	
	tetraethoxysilane	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	
	aliphatic amide	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	
	thixotropic agent																	
solvent	xylene	9	9	9	9	9	9	9	9	9	9	9	9	9	9	9	9	
sum		100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	
ratio of copolymer A (mass%)		50%	50%	50%	50%	50%	50%	50%	50%	50%	50%	50%	50%	50%	50%	50%	50%	
test result	condition of coating film after 3 months	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	
	condition of coating film after 6 months	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	

[0051]

[Table 6]

Table 6

component		Example									
		19	20	21	22	23	24	25	26	27	
copolymer A	SA-1	18.8	18.8	18.8							
	SA-2				18.8	18.8	18.8				
	SA-3							18.8	18.8	18.8	
copolymer B	SB-1	6.3			6.3			6.3			
	SB-2		6.3			6.3			6.3		
	SB-3			6.3			6.3			6.3	
elution regulator	rosin metal salt solution	3	3	3	3	3	3	3	3	3	3
	gum rosin solution	3	3	3	3	3	3	3	3	3	3
plasticizer	chlorinated paraffin	1	1	1	1	1	1	1	1	1	1
	epoxidized soybean oil	1	1	1	1	1	1	1	1	1	1
antifouling agent	cuprous oxide	40	40	40	40	40	40	40	40	40	40
	copper pyrrhione	3	3	3	3	3	3	3	3	3	3
	talc	2	2	2	2	2	2	2	2	2	2
other additives	zinc oxide	5	5	5	5	5	5	5	5	5	5
	red oxide	3	3	3	3	3	3	3	3	3	3
	titanium oxide	1	1	1	1	1	1	1	1	1	1
	tetraethoxysilane	1	1	1	1	1	1	1	1	1	1
	aliphatic amide										
	thixotropic agent	3	3	3	3	3	3	3	3	3	3
solvent	xylene	9	9	9	9	9	9	9	9	9	9
	sum	100	100	100	100	100	100	100	100	100	100
ratio of copolymer A (mass%)		75%	75%	75%	75%	75%	75%	75%	75%	75%	75%
test result	condition of coating film after 3 months	○	○	○	○	○	○	○	○	○	○
	condition of coating film after 6 months	○	○	○	○	○	○	○	○	○	○

[0052]

[Table 7]

Table 7

component		Example													
		28	29	30	31	32	33	34	35	36					
copolymer A	SA-6	18.75	18.75	18.75											
	SA-7				18.75	18.75	18.75								
	SA-8							18.75	18.75	18.75					
copolymer B	SB-6	6.25			6.25			6.25							
	SB-7		6.25			6.25			6.25						
	SB-8			6.25			6.25			6.25					
elution regulator	rosin metal salt solution	3	3	3	3	3	3	3	3	3					
	gum rosin solution	3	3	3	3	3	3	3	3	3					
plasticizer	chlorinated paraffin	1	1	1	1	1	1	1	1	1					
	epoxidized soybean oil	1	1	1	1	1	1	1	1	1					
antifouling agent	cuprous oxide	40	40	40	40	40	40	40	40	40					
	copper pyrrithione	3	3	3	3	3	3	3	3	3					
	talc	2	2	2	2	2	2	2	2	2					
other additives	zinc oxide	5	5	5	5	5	5	5	5	5					
	red oxide	3	3	3	3	3	3	3	3	3					
	titanium oxide	1	1	1	1	1	1	1	1	1					
	tetraethoxysilane	1	1	1	1	1	1	1	1	1					
	aliphatic amide	3	3	3	3	3	3	3	3	3					
	thixotropic agent														
solvent	xylene	9	9	9	9	9	9	9	9	9					
sum		100	100	100	100	100	100	100	100	100					
ratio of copolymer A (mass%)		75%	75%	75%	75%	75%	75%	75%	75%	75%					
test result	condition of coating film after 3 months	○	○	○	○	○	○	○	○	○					
	condition of coating film after 6 months	○	○	○	○	○	○	○	○	○					

[0053]

[Table 8]

Table 8

component		Example												
		37	38	39	40	41	42	43	44	45				
copolymer A	SA-1	6.3	6.3	6.3										
	SA-2				6.3	6.3	6.3							
	SA-3							6.3	6.3	6.3				
copolymer B	SB-1	18.8			18.8			18.8						
	SB-2		18.8			18.8			18.8					
	SB-3			18.8			18.8			18.8				
elution regulator	rosin metal salt solution	3	3	3	3	3	3	3	3	3				
	gum rosin solution	3	3	3	3	3	3	3	3	3				
plasticizer	chlorinated paraffin	1	1	1	1	1	1	1	1	1				
	epoxidized soybean oil	1	1	1	1	1	1	1	1	1				
antifouling agent	cuprous oxide	40	40	40	40	40	40	40	40	40				
	copper pyrrhione	3	3	3	3	3	3	3	3	3				
other additives	talc	2	2	2	2	2	2	2	2	2				
	zinc oxide	5	5	5	5	5	5	5	5	5				
	red oxide	3	3	3	3	3	3	3	3	3				
	titanium oxide	1	1	1	1	1	1	1	1	1				
	tetraethoxysilane	1	1	1	1	1	1	1	1	1				
	aliphatic amide													
	thixotropic agent	3	3	3	3	3	3	3	3	3				
solvent	xylene	9	9	9	9	9	9	9	9	9				
sum		100	100	100	100	100	100	100	100	100				
ratio of copolymer A (mass%)		25%	25%	25%	25%	25%	25%	25%	25%	25%				
test result	condition of coating film after 3 months	○	○	○	○	○	○	○	○	○				
	condition of coating film after 6 months	○	○	○	○	○	○	○	○	○				

[0055]

[Table 9]

Table 9

component		Example										
		46	47	48	49	50	51	52	53	54		
copolymer A	SA-6	6.25	6.25	6.25								
	SA-7				6.25	6.25	6.25					
	SA-8							6.25	6.25	6.25		
copolymer B	SB-6	18.75			18.75			18.75				
	SB-7		18.75			18.75			18.75			
	SB-8			18.75			18.75			18.75		
elution regulator	rosin metal salt solution	3	3	3	3	3	3	3	3	3	3	3
	gum rosin solution	3	3	3	3	3	3	3	3	3	3	3
plasticizer	chlorinated paraffin	1	1	1	1	1	1	1	1	1	1	1
	epoxidized soybean oil	1	1	1	1	1	1	1	1	1	1	1
antifouling agent	cuprous oxide	40	40	40	40	40	40	40	40	40	40	40
	copper pyrrithione	3	3	3	3	3	3	3	3	3	3	3
other additives	talc	2	2	2	2	2	2	2	2	2	2	2
	zinc oxide	5	5	5	5	5	5	5	5	5	5	5
	red oxide	3	3	3	3	3	3	3	3	3	3	3
	titanium oxide	1	1	1	1	1	1	1	1	1	1	1
	tetraethoxysilane	1	1	1	1	1	1	1	1	1	1	1
	aliphatic amide thixotropic agent	3	3	3	3	3	3	3	3	3	3	3
solvent	xylene	9	9	9	9	9	9	9	9	9	9	9
	sum	100	100	100	100	100	100	100	100	100	100	100
ratio of copolymer A (mass%)		25%	25%	25%	25%	25%	25%	25%	25%	25%	25%	25%
test result	condition of coating film after 3 months	○	○	○	○	○	○	○	○	○	○	○
	condition of coating film after 6 months	○	○	○	○	○	○	○	○	○	○	○

[0056]

[Table 10]

Table 10

component		Example													
		55	56	57	58	59	60	61	62	63	64	65	66		
copolymer A	SA-4	12.5	12.5			18.75	18.75			6.25	6.25				
	SA-5			12.5	12.5			18.75	18.75			6.25	6.25		
copolymer B	SB-4	12.5		12.5		6.25		6.25		18.75		18.75			
	SB-5		12.5		12.5		6.25		6.25		18.75		18.75		
elution regulator	rosin metal salt solution	3	3	3	3	3	3	3	3	3	3	3	3	3	3
	gum rosin solution	3	3	3	3	3	3	3	3	3	3	3	3	3	3
plasticizer	chlorinated paraffin	1	1	1	1	1	1	1	1	1	1	1	1	1	1
	epoxidized soybean oil	1	1	1	1	1	1	1	1	1	1	1	1	1	1
antifouling agent	cuprous oxide	40	40	40	40	40	40	40	40	40	40	40	40	40	40
	copper pyrithione	3	3	3	3	3	3	3	3	3	3	3	3	3	3
other additives	talc	2	2	2	2	2	2	2	2	2	2	2	2	2	2
	zinc oxide	5	5	5	5	5	5	5	5	5	5	5	5	5	5
	red oxide	3	3	3	3	3	3	3	3	3	3	3	3	3	3
	titanium oxide	1	1	1	1	1	1	1	1	1	1	1	1	1	1
	tetraethoxysilane	1	1	1	1	1	1	1	1	1	1	1	1	1	1
	aliphatic amide	3	3	3	3	3	3	3	3	3	3	3	3	3	3
solvent	thixotropic agent														
	xylene	9	9	9	9	9	9	9	9	9	9	9	9	9	9
ratio of copolymer A (mass%)	sum	100	100	100	100	100	100	100	100	100	100	100	100	100	100
		50%	50%	50%	50%	75%	75%	75%	75%	25%	25%	25%	25%	25%	25%
test result	condition of coating film after 3 months	○	○	○	○	○	○	○	○	○	○	○	○	○	○
	condition of coating film after 6 months	×	×	×	×	×	×	×	×	×	×	×	×	×	×

[0057]

[Table 11]

Table 11

component		Example															
		67	68	69	70	71	72	73	74	75	76	77	78				
copolymer A	SA-9	12.5	12.5			18.75	18.75			6.25	6.25						
	SA-10			12.5	12.5			18.75	18.75			6.25	6.25				
copolymer B	SB-9	12.5		12.5		6.25		6.25		18.75							
	SB-10		12.5		12.5		6.25		6.25		18.75		18.75				
elution regulator	rosin metal salt solution	3	3	3	3	3	3	3	3	3	3	3	3				
	gum rosin solution	3	3	3	3	3	3	3	3	3	3	3	3				
plasticizer	chlorinated paraffin	1	1	1	1	1	1	1	1	1	1	1	1				
	epoxidized soybean oil	1	1	1	1	1	1	1	1	1	1	1	1				
antifouling agent	cuprous oxide	40	40	40	40	40	40	40	40	40	40	40	40				
	copper pyrithione	3	3	3	3	3	3	3	3	3	3	3	3				
other additives	talc	2	2	2	2	2	2	2	2	2	2	2	2				
	zinc oxide	5	5	5	5	5	5	5	5	5	5	5	5				
	red oxide	3	3	3	3	3	3	3	3	3	3	3	3				
	titanium oxide	1	1	1	1	1	1	1	1	1	1	1	1				
	tetraethoxysilane	1	1	1	1	1	1	1	1	1	1	1	1				
	aliphatic amide																
solvent	thixotropic agent	3	3	3	3	3	3	3	3	3	3	3	3				
	xylene	9	9	9	9	9	9	9	9	9	9	9	9				
sum		100	100	100	100	100	100	100	100	100	100	100	100				
ratio of copolymer A (mass%)		50%	50%	50%	50%	75%	75%	75%	75%	25%	25%	25%	25%				
test result	condition of coating film after 3 months	○	○	○	○	○	○	○	○	○	○	○	○				
	condition of coating film after 6 months	×	×	×	×	×	×	×	×	×	×	×	×				

[0058]

[Table 12]

Table 12

component		Example				
		79	80	81	82	83
copolymer A	SA-1	12.5	12.5	12.5	12.5	12.5
copolymer B	SB-1	12.5	12.5	12.5	12.5	12.5
elution regulator	rosin metal salt solution		4	10	10	2
	hydrogenated rosin metal salt solution	3				2
	gum rosin solution		4	10	10	2
	hydrogenated gum rosin solution	3				2
plasticizer	chlorinated paraffin	1	1	1	1	1
	epoxidized soybean oil	1	1	1	1	1
	tris(2-ethylhexyl) trimellitate					1
	Hexamoll DINCH					1
antifouling agent	cuprous oxide	40	40			35
	copper pyrithione	3				3
	zinc pyrithione			2.5	2	2
	Zineb				0.5	0.5
	SeaNine			1	1	1
	medetomidine		0.5	0.5	0.5	0.5
	Econea			7	7	6
other additives	talc	2	2	5	5	2
	zinc oxide	5	5	15	15	3
	red oxide	3	3	2	2	3
	titanium oxide	1	1	1	1	1
	tetraethoxysilane	1	1	1	1	1
	aliphatic amide thixotropic agent	3	3	3	3	2
solvent	xylene	9	9.5	15	15	3
sum		100	100	100	100	100
ratio of copolymer A (mass%)		50%	50%	50%	50%	50%
test result	condition of coating film after 3 months	○	○	○	○	○
	condition of coating film after 6 months	○	○	○	○	○

Table 13

component		Comparative Example									
		1	2	3	4	5	6	7	8	9	10
copolymer A	SA-1	25									
	SA-2		25								
	SA-3			25							
	SA-4				25						
	SA-5					25					
copolymer B	SB-1						25				
	SB-2							25			
	SB-3								25		
	SB-4									25	
	SB-5										25
elution regulator	rosin metal salt solution	3	3	3	3	3	3	3	3	3	3
	gum rosin solution	3	3	3	3	3	3	3	3	3	3
plasticizer	chlorinated paraffin	1	1	1	1	1	1	1	1	1	1
	epoxidized soybean oil	1	1	1	1	1	1	1	1	1	1
antifouling agent	cuprous oxide	40	40	40	40	40	40	40	40	40	40
	copper pyrithione	3	3	3	3	3	3	3	3	3	3
	talc	2	2	2	2	2	2	2	2	2	2
other additives	zinc oxide	5	5	5	5	5	5	5	5	5	5
	red oxide	3	3	3	3	3	3	3	3	3	3
	titanium oxide	1	1	1	1	1	1	1	1	1	1
	tetraethoxysilane	1	1	1	1	1	1	1	1	1	1
	aliphatic amide thioxotropic agent	3	3	3	3	3	3	3	3	3	3
solvent	xylene	9	9	9	9	9	9	9	9	9	9
	sum	100	100	100	100	100	100	100	100	100	100
test result	condition of coating film after 3 months	x	x	x	x	x	x	x	x	x	x
	condition of coating film after 6 months	x	x	x	x	x	x	x	x	x	x

[0060]

[Table 14]

Table 14

component		Comparative Example			
		11	12	13	14
copolymer A	SA-2	12.5			
	SA-4		12.5		
copolymer B	SB-2			12.5	
	SB-4				12.5
other copolymer	T-1	12.5			
	T-2			12.5	
	T-3		12.5		
	T-4				12.5
elution regulator	rosin metal salt solution	3	3	3	3
	gum rosin solution	3	3	3	3
plasticizer	chlorinated paraffin	1	1	1	1
	epoxidized soybean oil	1	1	1	1
antifouling agent	cuprous oxide	40	40	40	40
	copper pyrithione	3	3	3	3
other additives	talc	2	2	2	2
	zinc oxide	5	5	5	5
	red oxide	3	3	3	3
	titanium oxide	1	1	1	1
	tetraethoxysilane	1	1	1	1
	aliphatic amide thixotropic agent	3	3	3	3
solvent	xylene	9	9	9	9
sum		100	100	100	100
test result	condition of coating film after 3 months	×	×	×	×
	condition of coating film after 6 months	×	×	×	×

[0061]

The details of the elution regulators, plasticizers, antifouling agents, and other additives in Tables 4 to 14 are as follows.

[0062]

<Elution regulator>

rosin metal salt solution: The one produced in Production Example 21 was used.

hydrogenated rosin metal salt solution: The one produced in Production Example 22 was used.

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

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

[0063]

<Plasticizer>

chlorinated paraffin: product name "Paraffin Chlorinated" (Cl: 40%) (available from available from Wako Pure Chemical Industries, Ltd.)

E-2000H: epoxidized soybean oil: product name "Sansozizer E-2000H" (available from New Japan Chemical Co., Ltd.)

Tris (2-ethylhexyl trimellitic acid): product name " Tris (2-ethylhexyl trimellitic acid)" (available from TOKYO CHEMICAL INDUSTRY CO., LTD.)

Hexamoll (registered trademark) DINCH (registered trademark): non-phthalate plasticizer (available from BASF)

[0064]

<Antifouling agent>

cuprous oxide : product name "NC-301" (available from NISSIN CHEMCO LTD.)

copper pyrithione : product name "copper Omadine" (available from Arch Chemical, Inc.)

zinc pyrithione: product name "zinc Omadine" (available from Arch Chemical, Inc.)

Zineb: product name "Zineb" (available from Sigma-Aldrich, Inc.)

Sea Nine: product name "Sea Nine 211", 4,5-dichloro-2-n-octyl-3-isothiazoline (30% solids xylene solution, available from Rohm & Haas, Inc.)

medetomidine: product name "4-(1-(2,3-Dimethylphenyl) ethyl)-1H-imidazole" (available from Wako Pure Chemical Industries, Ltd.)

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

[0065]

<Other additives>

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.)

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

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

tetraethoxysilane: product name "Tetraethyl Orthosilicate" (available from TOKYO CHEMICAL INDUSTRY CO., LTD.)

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

[0066]

<Discussion>

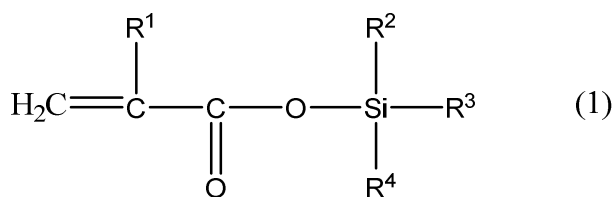
Tables 4 to 14 show that the coating films formed with the coating compositions of the present invention (Examples 1-83) have better adhesiveness to a glass surface than those formed with the coating compositions of comparative examples 1-14 and do not peel off even after a wet and dry cycle test (after 6 months).

[0067]

On the other hand, the coating films formed with the coating compositions of comparative examples 1-14 have poor adhesion to the glass surface and peel off after the wet and dry cycle test (after 3 months).

CLAIMS

1. An antifouling coating composition, comprising:
a copolymer A;
a copolymer B; and
an antifouling agent; wherein:
the copolymer A and the copolymer B are each obtained by copolymerizing a mixture of a monomer (a) and a polymerizable unsaturated monomer (b) other than the monomer (a);
the monomer (a) is represented by general formula (1);
[chemical formula 1]



in the general formula (1), R¹ is hydrogen or a methyl group, and R², R³ and R⁴ are selected from a C3-C8 branched alkyl group and a phenyl group and may be the same or different;

the copolymer A satisfies following requirements (A1) to (A2);

the copolymer B satisfies following requirements (B1) to (B2).

(A1) Content of the monomer (a) is 30 to 50mass% with respect to a total mass of the monomer (a) and the monomer (b).

(A2) Content of 2-methoxyethyl acrylate in the monomer (b) is 15 to 30mass% with respect to the total mass of the monomer (a) and the monomer (b).

(B1) Content of the monomer (a) is 30 to 40mass% with respect to the total mass of the monomer (a) and the monomer (b).

(B2) Content of 2-methoxyethyl methacrylate in the monomer (b) is 30 to 50mass% with respect to the total mass of the monomer (a) and the monomer (b).