

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]

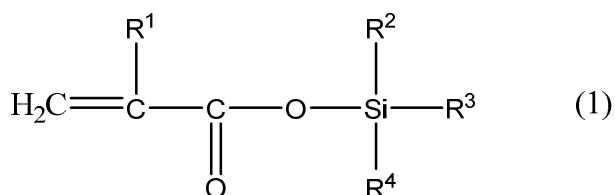
The present invention has been made by taking the afore-mentioned circumstances into consideration. The present invention provides a composition which can form an antifouling coating film which continues to dissolve for a long time even after being exposed to sunlight for a long time and realizes a good 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), R^1 is hydrogen or a methyl group, and R^2 , R^3 and R^4 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); content of the copolymer A is 5 to 45mass% with respect to a total mass of the copolymer A and the copolymer B is provided.

(A1) Content of compound in which R^1 is hydrogen in the monomer (a) is 30 to 80 mass% 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 5 to 30mass% with respect to the total mass of the monomer (a) and the monomer (b).

(B1) Content of compound in which R^1 is a methyl group in the monomer (a) is 30 to 80 mass% 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 15 to 50mass% with respect to a 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 a copolymer A, obtained by copolymerizing a mixture containing a silyl acrylate ester and 2-methoxyethyl acrylate in specific amount each, and a copolymer B, obtained by copolymerizing a mixture containing a silyl methacrylate ester 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) may be the same or different in the copolymer A and the copolymer B. When the compounds contained in monomer (a) are the same in copolymers A and B, its compounding ratio is preferably different. 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 preferably different.

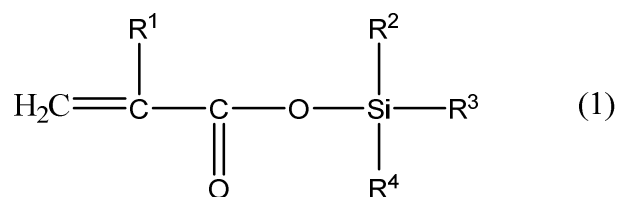
[0012]

<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. 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), (B1) to (B2) and compounding ratio of the copolymer A and the copolymer B >

In the present invention, it is essential that the copolymer A satisfies requirements (A1) to (A2) and that the copolymer B satisfies requirements (B1) to (B2) and that content of the copolymer A is 5 to 45mass% with respect to a total mass of the copolymer A and the copolymer B.

[0018]

(A1) Content of compound in which R¹ is hydrogen in the monomer (a) (hereinafter, "(silyl acrylate ester)") is 30 to 80 mass% 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 5 to 30mass% with respect to the total mass of the monomer (a) and the monomer (b).

(B1) Content of compound in which R¹ is a methyl group in the monomer (a) (hereinafter, "(silyl methacrylate ester)") is 30 to 80 mass% 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 15 to 50mass% with respect to a total mass of the monomer (a) and the monomer (b).

[0019]

The following points should be noted.

(1) In the copolymer A, the monomer (a) contains silyl acrylate ester, and in the copolymer B, the monomer (b) contains silyl methacrylate ester.

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

(3) The content of the copolymer A is 5 to 45mass% with respect to a total mass of the copolymer A and the copolymer B

[0020]

Thus, the present invention is characterized that the copolymer A, which is obtained by copolymerizing a mixture containing silyl acrylate ester and 2-methoxyethyl acrylate in specific amount each, and the copolymer B, obtained by copolymerizing a mixture containing silyl methacrylate ester and 2-methoxyethyl methacrylate in specific amount each, are contained in a specific ratio. 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 silyl acrylate ester may be, for example, 30, 35 40 45 50 55 60 65 70 75 80mass% 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 (a) of the copolymer A may contain silyl methacrylate ester, but the content of silyl methacrylate ester in the monomer (a) of the copolymer A is preferably less than the content of silyl methacrylate ester in the

monomer (a) of the copolymer B and is preferably 1/2 or less of the content of silyl methacrylate ester in the monomer (a) of the copolymer B. The monomer (a) of the copolymer A preferably does not contain silyl methacrylate ester.

[0022]

In the requirement (A2), the content of 2-methoxyethyl acrylate may be, for example, 5, 10, 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 silyl methacrylate ester is, for example, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80mass% 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 (a) of the copolymer B may contain silyl acrylate ester, but the content of silyl acrylate ester in the monomer (a) of the copolymer B is preferably less than the content of silyl acrylate ester in the monomer (a) of the copolymer A and is preferably 1/2 or less of the content of silyl acrylate ester in the monomer (a) of the copolymer A. The monomer (a) of the copolymer B preferably does not contain silyl acrylate ester.

[0024]

In the requirement (B2), the content of 2-methoxyethyl methacrylate is, for example, 15, 20, 25, 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, in the copolymer A, 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 95mass%, and specifically, for example, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95mass%, and may be in the range between the two values exemplified herein. In the copolymer B, 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 85mass%, and specifically, for example, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85mass%, 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 5 to 45mass% 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, 5, 10, 15, 20, 25, 30, 35, 40, 45mass%, 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 include, 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 (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, 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 86-90°C under nitrogen atmosphere. With agitation, a mixture of 150 g of triisopropyl silyl acrylate, 100 g of ethyl acrylate, 225 g of methyl methacrylate, 25 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 hour while keeping the temperature at 86-90°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 86-90°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 49.6% and the weight average molecular weight was 51,000.

[0041]

<Production Example 2-12, Comparative Production Example1-2>

The organic solvents, monomer, and polymerization initiator shown in Table 1 were used, and polymerization was performed by processes similar to those of Production Example 1, thereby obtaining copolymer solutions SA-2 to SA-6 of copolymer A, copolymer solution SB-1 to SB-6 of copolymer B, and copolymer solution T-1 to T-2 of other copolymers. The non-volatile content and weight average molecular weight of each copolymer solution obtained were measured.

The results are shown in Table 1.

[0042]

[Table 1]

Table 1

component	Production Example												Comparative Production Example
	1	2	3	4	5	6	7	8	9	10	11	12	
	copolymer A						copolymer B						other copolymer
monomer (a)	400	400	400	350	350	350	400	400	400	350	350	350	400
	150	150	400	180	180	480							200
monomer (b)	100			120			150	150	400	180	180	480	150
	ethyl acrylate												
	methyl methacrylate	225	200	270	240	90	175	75	5	210	90	6	300
	n-butyl acrylate						100	25	20	120	30	24	100
	2-methoxyethyl acrylate	25	150	25	30	30							
	2-methoxyethyl methacrylate						75	250	75	90	300	90	
ratio of silyl acrylate ester (mass%)	30%	30%	80%	30%	30%	80%							40%
ratio of silyl methacrylate ester (mass%)							30%	30%	80%	30%	30%	80%	30%
ratio of 2-methoxyethyl acrylate (mass%)	5%	30%	5%	5%	30%	5%							
ratio of 2-methoxyethyl methacrylate (mass%)							15%	50%	15%	15%	50%	15%	
polymerization initiator	5	5	5	7	7	7	5	5	5	7	7	7	5
	0.5	0.5	0.5	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	50	50	50	100	100	100	50	50	50	100
reaction temperature [°C] (within ±2°C)	88	88	88	88	88	88	85	85	85	85	85	85	85
copolymer physical property	49.6	49.9	50.1	60.5	60.2	60.3	49.8	49.8	49.8	60.3	60.1	60.4	49.8
	weight average												
	molecular weight [Mw]	51000	50000	22000	27000	26000	52000	48000	49000	25000	22000	21000	49000
	viscosity [mPa·s] (25°C)	480	200	320	530	220	400	660	510	440	700	710	890
copolymer solution	SA-1	SA-2	SA-3	SA-4	SA-5	SA-6	SB-1	SB-2	SB-3	SB-4	SB-5	SB-6	T-1
													T-2

[0043]

<Production Example 13 (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%.

[0044]

<Production Example 14(Production of hydrogenated rosin metal salt solution)>

To a flask equipped with a thermometer, a reflux condenser, and a stirrer, 240 g of HYPALE 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%.

[0045]

<Example 1-41, Comparison Examples 1-26>

Copolymer solutions SA-1 to SA-6, SB-1 to SB-6, T-1 to T-2 were used, and the antifouling coating compositions were formulated by the content ratio shown in Tables 2 to 9.

[0046]

(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.

[0047]

[Table 2]

Table 2

component		Example								
		1	2	3	4	5	6	7	8	9
copolymer A	SA-1	1.25	1.25	1.25						
	SA-2				1.25	1.25	1.25			
	SA-3							1.25	1.25	1.25
copolymer B	SB-1	23.75			23.75			23.75		
	SB-2		23.75			23.75			23.75	
	SB-3			23.75			23.75			23.75
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 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%)		5%	5%	5%	5%	5%	5%	5%	5%	5%
test result	condition of coating film after 3 months	○	○	○	○	○	○	○	○	○
	condition of coating film after 6 months	○	○	○	○	○	○	○	○	○

[0048]

[Table 3]

Table 3

component		Example																
		10	11	12	13	14	15	16	17	18								
copolymer A	SA-4	1.25	1.25	1.25														
	SA-5				1.25	1.25	1.25											
	SA-6											1.25	1.25	1.25	1.25	1.25		
copolymer B	SB-4	23.75			23.75			23.75				23.75						
	SB-5		23.75						23.75					23.75				
	SB-6			23.75						23.75							23.75	
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 thixotropic agent	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	
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%)		5%	5%	5%	5%	5%	5%	5%	5%	5%	5%	5%	5%	5%	5%	5%	5%	
test result	condition of coating film after 3 months	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	
	condition of coating film after 6 months	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	

[0049]

[Table 4]

Table 4

component		Example									
		19	20	21	22	23	24	25	26	27	
copolymer A	SA-1	11.25	11.25	11.25							
	SA-2				11.25	11.25	11.25				
	SA-3							11.25	11.25	11.25	
copolymer B	SB-1	13.75			13.75			13.75			
	SB-2		13.75			13.75			13.75		
	SB-3			13.75			13.75			13.75	
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%)		45%	45%	45%	45%	45%	45%	45%	45%	45%	
test result	condition of coating film after 3 months	○	○	○	○	○	○	○	○	○	
	condition of coating film after 6 months	○	○	○	○	○	○	○	○	○	

[0050]

[Table 5]

Table 5

component		Example													
		28	29	30	31	32	33	34	35	36					
copolymer A	SA-4	11.25	11.25	11.25											
	SA-5				11.25	11.25	11.25								
	SA-6							11.25	11.25	11.25					
copolymer B	SB-4	13.75			13.75			13.75							
	SB-5		13.75			13.75			13.75						
	SB-6			13.75			13.75			13.75					
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
	talc	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
	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 thixotropic agent	3	3	3	3	3	3	3	3	3	3	3	3	3	3
solvent	xylene	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
ratio of copolymer A (mass%)		45%	45%	45%	45%	45%	45%	45%	45%	45%	45%	45%	45%	45%	45%
test result	condition of coating film after 3 months	○	○	○	○	○	○	○	○	○	○	○	○	○	○
	condition of coating film after 6 months	○	○	○	○	○	○	○	○	○	○	○	○	○	○

[0051]

[Table 6]

Table 6

component		Example				
		37	38	39	40	41
copolymer A	SA-1	11.25	11.25	11.25	11.25	11.25
copolymer B	SB-1	13.25	13.25	13.25	13.25	13.25
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	5
	talc	2	2	5	5	3
other additives	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%)		45%	45%	45%	45%	45%
test result	condition of coating film after 3 months	○	○	○	○	○
	condition of coating film after 6 months	○	○	○	○	○

Table 7

component		Comparative Example					
		1	2	3	4	5	6
copolymer A	SA-1	25.00					
	SA-2		25.00				
	SA-3			25.00			
copolymer B	SB-1				25.00		
	SB-2					25.00	
	SB-3						25.00
elution regulator	rosin metal salt solution	3	3	3	3	3	3
	gum rosin solution	3	3	3	3	3	3
plasticizer	chlorinated paraffin	1	1	1	1	1	1
	epoxidized soybean oil	1	1	1	1	1	1
antifouling agent	cuprous oxide	40	40	40	40	40	40
	copper pyrithione	3	3	3	3	3	3
	talc	2	2	2	2	2	2
other additives	zinc oxide	5	5	5	5	5	5
	red oxide	3	3	3	3	3	3
	titanium oxide	1	1	1	1	1	1
	tetraethoxysilane	1	1	1	1	1	1
	aliphatic amide thixotropic agent	3	3	3	3	3	3
	xylene	9	9	9	9	9	9
solvent	sum	100	100	100	100	100	100
ratio of copolymer A (mass%)		100%	100%	100%	0%	0%	0%
test result	condition of coating film after 3 months	×	×	×	×	×	×
	condition of coating film after 6 months	×	×	×	×	×	×

[0053]

[Table 8]

Table 8

component		Comparative Example													
		7	8	9	10	11	12	13	14	15					
copolymer A	SA-1	12.50	12.50	12.50											
	SA-2				12.50	12.50	12.50								
	SA-3							12.50	12.50	12.50					
copolymer B	SB-1	12.50			12.50										
	SB-2		12.50			12.50			12.50						
	SB-3			12.50			12.50			12.50					
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 pyrithione	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%)		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	×	×	×	×	×	×	×	×	×					

[0054]

[Table 9]

Table 9

component		Comparative Example													
		16	17	18	19	20	21	22	23	24	25	26			
copolymer A	SA-1	23.75	23.75	23.75											
	SA-2				23.75	23.75	23.75				12.50				
	SA-3							23.75	23.75	23.75					
copolymer B	SB-1	1.25			1.25			1.25							
	SB-2		1.25			1.25			1.25			12.50			
	SB-3			1.25			1.25			1.25					
other copolymer	T-1											12.50			
	T-2										12.50				
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
	talc	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
	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 thixotropic agent	3	3	3	3	3	3	3	3	3	3	3	3	3	3
solvent	xylene	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
ratio of copolymer A (mass%)		95%	95%	95%	95%	95%	95%	95%	95%	95%	95%	95%	95%	95%	95%
test result	condition of coating film after 3 months	×	×	×	×	×	×	×	×	×	×	×	×	×	×
	condition of coating film after 6 months	×	×	×	×	×	×	×	×	×	×	×	×	×	×

[0055]

The details of the elution regulators, plasticizers, antifouling agents, and other additives in Tables 2 to 9 are as follows.

[0056]

<Elution regulator>

rosin metal salt solution: The one produced in Production Example 13 was used.

hydrogenated rosin metal salt solution: The one produced in Production Example 14 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.)

[0057]

<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)

[0058]

<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 "Econea 028" (2-(p-chlorophenyl)3-cyano-4-bromo-5-trifluoromethyl pyrrole, available from JANSSEN PMP)

[0059]

<Other additives>

talco: 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.)

[0060]

Tables 2 to 9 show that the coating films formed with the coating compositions of the present invention (Examples 1-41) have better adhesiveness to a glass surface than those formed with the coating compositions of comparative examples 1-26 and do not peel off even after a wet and dry cycle test (after 6 months). On the other hand, the coating films formed with the coating compositions of comparative examples 1-26 have poor adhesion to the glass surface and peel off after the wet and dry cycle test (after 3 months).

CLAIMS

1 A method of forming an antifouling coating film on a ship by use of an antifouling coating composition, comprising:

a copolymer A;

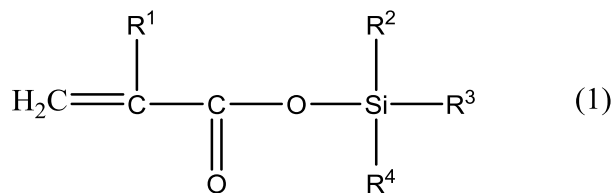
a copolymer B; and

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); and

content of the copolymer A is 5 to 45mass% with respect to a total mass of the copolymer A and the copolymer B.

(A1) Content of compound in which R¹ is hydrogen in the monomer (a) is 30 to 80 mass% 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 5 to 30mass% with respect to the total mass of the monomer (a) and the monomer (b).

(B1) Content of compound in which R¹ is a methyl group in the monomer (a) is 30 to 80 mass% 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 15 to 50mass% with respect to a total mass of the monomer (a) and the monomer (b).