

DESCRIPTION

Title of the Invention

ANTIFOULING COATING COMPOSITION, COATING FILM, AND
5 COATING-FILM-ATTACHED BASE MATERIAL

Technical Field

[0001]

10 The present invention relates to an antifouling coating composition, a coating film, which is formed using the same, and a substrate with a coating film, which has the coating film on a substrate.

Background Art

[0002]

15 Underwater structures such as ships, harbor facilities, piping materials, bridges and others are exposed to water where living organisms live, and therefore, microorganisms such as bacteria, etc., as well as animals and plants such as barnacles, diatoms and others adhere thereto. When covered with such microorganisms, animals and plants, the surfaces of underwater structures may
20 be corroded, and may cause a problem of bad fuel efficiency of ships owing to increase in the friction resistance against seawater and freshwater.

[0003]

As a method for solving the problem, for example, there may be mentioned a method of forming an antifouling coating film on the surfaces of underwater
25 structures using an antifouling coating composition that contains an antifouling agent such as cuprous oxide (Cu_2O) or the like capable of effectively preventing adhesion of animals such as barnacles and others.

More specifically, PTL 1 proposes an antifouling coating composition containing a copolymer that contains, in 100 parts by weight of the monomer
30 components therein, 55 to 75 parts by weight of a triisopropylsilyl (meth)acrylate (a), 2 to 20 parts by weight of a methoxyethyl acrylate (b), and 43 to 5 parts by mass of any other polymerizable monomer (c), and an antifouling agent such as cuprous oxide or the like.

35 Citation List

Patent Literature

[0004]

PTL 1: JP 2001-226440 A

5 Summary of Invention

Technical Problem

[0005]

10 In the field of an antifouling coating composition, a silyl polymer as in PTL 1 is often used as a binder resin. However, the coating film formed of such an antifouling coating composition has a problem in that the coating film may consume little under the condition in contact with water at an ambient temperature of about 25°C, but under the condition in contact with water at a high temperature of about 30°C, the coating film may consume much and therefore could not be maintained as such for a long period of time.

15 [0006]

The present invention has been made in consideration of the above-mentioned situation, and has an object of providing an antifouling coating composition for forming a coating film which can consume little not only under the condition in contact with water at an ambient temperature of about 25°C but also
20 under the condition in contact with water at a high temperature of about 30°C, and which can maintain the physical properties thereof for a long period of time.

Another object of the present invention is to provide a coating film formed by curing the antifouling coating composition, a substrate with a coating film, including the coating film on a substrate, and a method for producing the same.

25

Solution to Problem

[0007]

As a result of assiduous studies, the present inventor has found that, in an antifouling coating composition containing a silyl polymer, a monobasic acid such
30 as rosin or the like used as an elution aid, and an antifouling agent, for example, cuprous oxide or zinc oxide form a copper salt and a zinc salt, and the ratio of the copper salt to the zinc salt has a significant influence on the waterproofness, the consumption behavior and the like of the coating film of the composition. As a result of further studies, the present inventor has found that the consumption of
35 the coating film under a high-temperature condition increases with the increase

in the ratio of the zinc salt, but on the contrary, with the increase in the ratio of the copper salt, the consumption of the coating film under a high-temperature condition can be reduced to the degree of the consumption thereof under an ambient temperature condition. With that, the present inventor has studied how to control the ratio of the copper salt to the zinc salt, and has found that, when a small amount of a lower alcohol is incorporated in the antifouling coating composition, then the ratio of the copper salt in the antifouling coating composition increases with the result that not only under an ambient temperature condition at about 25°C but also under a high-temperature condition at about 30°C, the consumption of the coating film can be reduced, and have completed the present invention. The gist of the present invention is as follows.

[0008]

The present invention relates to the following [1] to [8].

[1] An antifouling coating composition containing (A) a silylacrylic copolymer having a constituent unit (a1) derived from a triisopropylsilyl (meth)acrylate and a constituent unit (a2) derived from a polymerizable monomer having a polymerizable double bond, (B) a lower alcohol having 1 to 3 carbon atoms, (C) an antifouling agent including a copper component and a zinc component, and (D) a monocarboxylic acid compound, the content of the lower alcohol (B) in the antifouling coating composition being from 0.1 to 3% by mass.

[2] The antifouling coating composition according to the above [1], wherein the ratio by mass of the constituent unit (a1) to the constituent unit (a2) [(a1)/(a2)] is from 40/60 to 95/5.

[3] The antifouling coating composition according to the above [1] or [2], wherein the content of the silylacrylic copolymer (A) in the antifouling coating composition is from 5 to 40% by mass.

[4] The antifouling coating composition according to any of the above [1] to [3], wherein the weight average molecular weight (Mw) of the silylacrylic copolymer (A) is from 5,000 to 100,000.

[5] A coating film formed by curing the antifouling coating composition of any of the above [1] to [4].

[6] A substrate with a coating film, including the coating film of the above [5] on a substrate.

[7] The substrate with a coating film according to the above [6], wherein the substrate is a ship.

[8] A method for producing a substrate with a coating film, including (1) a step of applying the antifouling coating composition of any of the above [1] to [4] on a substrate or impregnating a substrate with the antifouling coating composition of any of the above [1] to [4] to give an applied material or impregnated material, and (2) a step of curing the antifouling coating composition by drying the applied material or impregnated material.

Advantageous Effects of Invention

[0009]

According to the present invention, there can be provided an antifouling coating composition capable of forming a coating film that can reduce the consumption thereof not only under the condition in contact with water at an ambient temperature of about 25°C but also under the condition in contact with water at a high temperature of about 30°C, and can maintain the physical properties thereof for a long period of time.

Also according to the present invention, there can be provided a coating film formed by curing the antifouling coating composition, a substrate with a coating film, including the coating film on a substrate, and a method for producing the same.

Description of Embodiments

[0010]

[Antifouling Coating Composition]

The antifouling coating composition of the present invention is an antifouling coating composition containing (A) a silylacrylic copolymer having a constituent unit (a1) derived from a triisopropylsilyl (meth)acrylate and a constituent unit (a2) derived from a polymerizable monomer having a polymerizable double bond, (B) a lower alcohol having 1 to 3 carbon atoms, (C) an antifouling agent including a copper component and a zinc component, and (D) a monocarboxylic acid compound, wherein the content of the lower alcohol (B) in the antifouling coating composition is 0.1 to 3% by mass.

[0011]

<Silylacrylic Copolymer (A)>

The antifouling coating composition of the present invention contains a silylacrylic copolymer (A) for the purpose of improving the antifouling

performance of coating film, and the silylacrylic copolymer (A) has a constituent unit (a1) derived from a triisopropylsilyl (meth)acrylate and a constituent unit (a2) derived from a polymerizable monomer having a polymerizable double bond.

In the present invention, the "polymerizable monomer having a polymerizable double bond" to constitute the constituent unit (a2) means "a polymerizable monomer having a polymerizable double bond except for the triisopropylsilyl (meth)acrylate to constitute the constituent unit (a1)". Also in the present invention, "(meth)acrylate" means "acrylate or methacrylate", and "(meth)acryl" means "acryl or methacryl", and "(meth)acryloyl" means "acryloyl or methacryloyl".

[0012]

[Constituent Unit (a1) derived from Triisopropylsilyl (meth)acrylate]

The constituent unit (a1) is a constituent unit derived from a triisopropylsilyl (meth)acrylate. In the present invention, the constituent unit (a1) may be a constituent unit derived from any one of triisopropylsilyl acrylate (TIPSA) and triisopropylsilyl methacrylate (TIP SMA), or may be a constituent unit derived from both of triisopropylsilyl acrylate and triisopropylsilyl methacrylate, but from the viewpoint of improving the antifouling performance of coating film, a constituent unit derived from any one of triisopropylsilyl acrylate and triisopropylsilyl methacrylate is preferred.

[0013]

[Constituent Unit (a2) derived from Polymerizable Monomer Having Polymerizable Double Bond]

With no specific limitation, the polymerizable monomer having a polymerizable double bond to constitute the constituent unit (a2) may be any polymerizable monomer having a polymerizable double bond except for triisopropylsilyl (meth)acrylate, and examples thereof include alkyl (meth)acrylates, aryl (meth)acrylates or aralkyl (meth)acrylates such as methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, isopropyl (meth)acrylate, butyl (meth)acrylate, isobutyl (meth)acrylate, tert-butyl (meth)acrylate, pentyl (meth)acrylate, hexyl (meth)acrylate, cyclohexyl (meth)acrylate, octyl (meth)acrylate, isooctyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, 3,5,5-trimethylhexyl (meth)acrylate, lauryl (meth)acrylate, cetyl (meth)acrylate, stearyl (meth)acrylate, phenyl (meth)acrylate, benzyl (meth)acrylate, etc.;

alkoxyalkyl (meth)acrylates or aryloxyalkyl (meth)acrylates such as 2-methoxyethyl (meth)acrylate, 2-ethoxyethyl (meth)acrylate, 4-methoxybutyl (meth)acrylate, 2-methoxypropyl (meth)acrylate, 3-methoxypropyl (meth)acrylate, 2-propoxyethyl (meth)acrylate, 2-butoxyethyl (meth)acrylate, isobutoxybutyl
 5 diglycol (meth)acrylate, 2-phenoxyethyl (meth)acrylate, etc.;

hydroxyalkyl (meth)acrylates such as hydroxymethyl (meth)acrylate, 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, 4-hydroxybutyl (meth)acrylate, 2-hydroxy-3-phenoxypropyl (meth)acrylate, etc.;

organosiloxane group-containing (meth)acrylates;

10 hydroxy group-, amide group- or ether group-containing (meth)acrylates such as (meth)acrylamide, polyethylene glycol mono(meth)acrylate, methoxypolyethylene glycol mono(meth)acrylate, etc.; and

aromatic vinyl compounds such as styrene, 2-methylstyrene, 3-methylstyrene, 4-methylstyrene, 2,4-dimethylstyrene, 4-tert-butylstyrene,
 15 5-tert-butyl-2-methylstyrene, etc. One of these polymerizable monomers may be used singly or two or more thereof may be used in combination.

In the present invention, "(meth)acrylamide" means "acrylamide or methacrylamide".

[0014]

20 Among the polymerizable monomers having a polymerizable double bond, alkyl (meth)acrylates and alkoxyalkyl (meth)acrylates are preferred; and methyl methacrylate (MMA), ethyl acrylate (EA), butyl acrylate (BA), 2-methoxyethyl acrylate (MEA), and 2-methoxyethyl methacrylate (MEMA) are preferred.

[0015]

25 As the polymerizable monomer having a polymerizable double bond, further, an anionic unsaturated monomer or a cationic unsaturated monomer may be used.

The anionic unsaturated monomer includes carboxy group-containing unsaturated monomers such as (meth)acrylic acid, maleic acid, maleic anhydride,
 30 itaconic acid, crotonic acid, etc.; and sulfonic acid group-containing unsaturated monomers such as styrenesulfonic acid, 3-(methacryloyloxy)propanesulfonic acid, acrylamidepropanesulfonic acid, etc.

These anionic unsaturated monomers may be partially or completely neutralized before use. Neutralization may be carried out in the state of
 35 monomers or may be carried out after formation into polymers.

Examples of the base to be used for neutralization include alkali metal hydroxides such as potassium hydroxide, sodium hydroxide, etc.; ammonia; and amine compounds such as triethanolamine, trimethylamine, etc.

[0016]

5 The cationic unsaturated monomer includes one or more selected from amino group-containing unsaturated monomers and quaternary ammonium base-containing unsaturated monomers.

 The amino group-containing unsaturated monomers include N,N-dimethylaminoethyl (meth)acrylate, N,N-diethylaminoethyl (meth)acrylate,
 10 N,N-dimethylaminopropyl (meth)acrylate, N,N-diethylaminopropyl (meth)acrylate, N,N-dimethylaminoethyl(meth)acrylamide, N,N-diethylaminoethyl(meth)acrylamide, N,N-dimethylaminopropyl(meth)acrylamide, N,N-diethylaminopropyl(meth)acrylamide, 2-vinylpyridine, 4-vinylpyridine, and
 15 structures formed by neutralizing these with an acid represented by H^+X^- .

 The quaternary ammonium base-containing unsaturated monomers include (meth)acryloyloxyethyltrimethyl ammonium, (meth)acryloyloxypropyltrimethylammonium, (meth)acryloylaminoethyltrimethylammonium,
 20 (meth)acryloylaminopropyltrimethylammonium, diallyldimethylammonium, 1-ethyl-4-vinylpyridinium, 1,2-dimethyl-5-vinylpyridinium and the like having X^- as the counter ion.

X^- represents an anion, and is preferably a halide ion, more preferably a chloride ion.

25 [0017]

[Method for Producing Silylacrylic Copolymer (A)]

 The silylacrylic copolymer (A) can be produced, for example, according to the following process.

 First, a solvent is put into a reactor, and heated up to about 80 to 120°C,
 30 and while the temperature is kept as such, a mixed liquid of the above-mentioned triisopropylsilyl (meth)acrylate, the above-mentioned, polymerizable double bond-having polymerizable monomer, a polymerization initiator, a chain transfer agent, a solvent and others is dropwise added thereto to attain polymerization reaction, thereby obtaining a silylacrylic copolymer (A).

35 The proportion of each content (by mass) of the constituent unit derived

from each monomer in the silylacrylic copolymer (A) may be considered to be the same as the proportion of the charge-in amount (by mass) of each of the above-mentioned monomers used in the polymerization reaction.

[0018]

5 The polymerization initiator usable in production of the silylacrylic copolymer (A) is not specifically limited, and various radical polymerization initiators can be used. Specifically, there are mentioned benzoyl peroxide, hydrogen peroxide, cumene hydroperoxide, tert-butyl hydroperoxide, potassium persulfate, sodium persulfate, 2,2'-azobis(isobutyronitrile) [AIBN],
10 2,2'-azobis(2-methylbutyronitrile) [AMBN], 2,2'-azobis(2,4-dimethylvaleronitrile) [ADVN], tert-butyl peroxyoctoate [TBPO], etc. One of these polymerization initiators may be used singly or two or more thereof may be used in combination. The radical polymerization initiator may be added to the reaction system only at the start of reaction, or may be added to the reaction system both at the start of
15 reaction and during reaction.

The amount of the polymerization initiator in production of the silylacrylic copolymer (A) is preferably 0.5 to 20 parts by mass relative to 100 parts by mass of the total of the monomers.

[0019]

20 The chain transfer agent usable in production of the silylacrylic copolymer (A) is not specifically limited, and examples thereof include α -methylstyrene dimer, thioglycolic acid, diterpene, terpinolen, γ -terpinene; mercaptans such as tert-dodecylmercaptan, n-dodecylmercaptan, etc.; halides such as carbon tetrachloride, methylene chloride, bromoform, bromotrichloroethane, etc.;
25 secondary alcohols such as glycerin, etc.; and others. One of these chain transfer agents may be used singly or two or more thereof may be used in combination.

In the case where a chain transfer agent is used in production of the silylacrylic copolymer (A), the amount thereof to be used is preferably 0.1 to 5 parts by mass relative to 100 parts by mass of the total of the monomers.

30 [0020]

Examples of the solvent usable in production of the silylacrylic copolymer (A) includes polyalcohol monoalkyl ethers such as propylene glycol monomethyl ether, dipropylene glycol monobutyl ether, dipropylene glycol monomethyl ether, tripropylene glycol monomethyl ether, tripropylene glycol monobutyl ether, etc.;
35 aromatic hydrocarbon solvents such as toluene, xylene, mesitylene, etc.; and

water, etc.

In the case where a solvent is used in production of the silylacrylic copolymer (A), the amount thereof to be used is, though not specifically limited thereto, preferably 5 to 150 parts by mass relative to 100 parts by mass of the total of the monomers.

[0021]

The ratio by mass of the constituent unit (a1) to the constituent unit (a2) [(a1)/(a2)] is preferably 40/60 to 95/5, more preferably 42/58 to 85/15, even more preferably 43/57 to 75/25, still more preferably 44/56 to 70/30. The ratio by mass [(a1)/(a2)] may be calculated from the charge-in ratio of each monomer in producing the copolymer.

[0022]

[Weight Average Molecular Weight of Silylacrylic Copolymer (A)]

The weight average molecular weight (Mw) of the silylacrylic copolymer (A) is preferably 5,000 to 100,000, more preferably 10,000 to 90,000, even more preferably 15,000 to 80,000, still more preferably 17,000 to 70,000, further more preferably 18,000 to 60,000. When the weight average molecular weight (Mw) of the silylacrylic copolymer falls within the above-mentioned range, the spray coating workability with the antifouling coating composition is improved and the physical properties of the coating film is also improved.

The weight average molecular weight (Mw) of the silylacrylic copolymer (A) indicates a value in gel permeation chromatography (GPC) as measured according to the method described in the section of Examples.

[0023]

[Viscosity of Silylacrylic Copolymer (A)]

The viscosity of the silylacrylic copolymer (A) is preferably 500 to 10,000 mPa·s, more preferably 1,000 to 7,000 mPa·s, even more preferably 1,500 to 6,000 mPa·s, still more preferably 1,800 to 5,000 mPa·s, further more preferably 2,000 to 4,800 mPa·s. When the viscosity of the silylacrylic copolymer (A) falls within the above-mentioned range, the spray coating workability with the antifouling coating composition is improved.

The viscosity of the silylacrylic copolymer (A) can be measured according to the method described in the section of Examples.

[0024]

[Content of Silylacrylic Copolymer (A)]

The content of the silylacrylic copolymer (A) in the antifouling coating composition is preferably 5% by mass or more, more preferably 10% by mass or more, even more preferably 13% by mass or more, still more preferably 15% by mass or more, further more preferably 16% by mass or more, and is preferably 40% by mass or less, more preferably 35% by mass or less, even more preferably 30% by mass or less, still more preferably 25% by mass or less, and further more preferably 23% by mass or less. When the content of the silylacrylic copolymer (A) falls within the above-mentioned range, a coating film capable of exhibiting excellent antifouling performance for a long period of time can be formed, and the coating film can maintain the strength thereof for a long period of time.

[0025]

<Lower Alcohol (B)>

The antifouling coating composition of the present invention contains a lower alcohol (B) having 1 to 3 carbon atoms (hereinafter this may be simply referred to as "lower alcohol (B)") for the purpose of reducing the consumption of the coating film not only under condition in contact with water at an ambient temperature of about 25°C but also under the condition in contact with water at a high temperature of about 30°C. In the present invention, the lower alcohol (B) is not included in the organic solvent (F) to be mentioned hereinunder.

Examples of the lower alcohol having 1 to 3 carbon atoms include methyl alcohol, ethyl alcohol, n-propyl alcohol and isopropyl alcohol. Among these, from the viewpoint of reducing the consumption under the condition in contact with water at a high temperature of about 30°C, ethyl alcohol is preferred.

[0026]

[Content of Lower Alcohol (B)]

The content of the lower alcohol (B) in the antifouling coating composition is 0.1 to 3% by mass. When the content of the lower alcohol (B) falls within the above-mentioned range, the consumption of the coating film under the condition in contact with water at a high temperature of about 30°C can be reduced. From the same viewpoint, the content of the lower alcohol (B) is preferably 0.2% by mass or more, more preferably 0.3% by mass or more, even more preferably 0.4% by mass or more, still more preferably 0.5% by mass or more, and is preferably 2.5% by mass or less, more preferably 2.0% by mass or less, even more preferably 1.5% by mass or less, still more preferably 1.0% by mass or less, further more preferably 0.9% by mass or less, and even further more preferably 0.8% by mass or

less.

[0027]

<Antifouling Agent (C) Including Copper Component and Zinc Component>

In the present invention, for the purpose of improving the antifouling performance of the coating composition, an antifouling agent (C) including a copper component and a zinc component (hereinafter this may be simply referred to as "antifouling agent (C)") is used.

The copper component in the antifouling agent (C) including a copper component and a zinc component may be any of an organic or inorganic component, and examples thereof include cuprous oxide, copper rhodanide, copper powder, copper pyrithione, copper thiocyanate, cupronickel, etc. Among these, cuprous oxide and copper pyrithione are preferred. On the other hand, the zinc component of the antifouling agent (C) including a copper component and a zinc component may be any of an organic or inorganic component, and includes zinc oxide, zinc pyrithione, zinc dimethyldithiocarbamate, zinc ethylenebis dithiocarbamate, bisdimethyldithiocarbamoyl zinc ethylenebis dithiocarbamate, etc. Among these, zinc oxide is preferred. In the antifouling agent (C), one of the copper components may be used singly or two or more thereof may be used in combination. In the antifouling agent (C), one of the zinc components may be used singly or two or more thereof may be used in combination. As the antifouling agent (C), preferably, cuprous oxide, copper pyrithione and zinc oxide are used in combination.

The content of the antifouling agent (C) including a copper component and a zinc component in the antifouling coating composition of the present invention is, from the viewpoint of improving the antifouling performance of the coating film, preferably 5 to 70% by mass, more preferably 10 to 60% by mass.

In the antifouling agent (C) including a copper component and a zinc component, the ratio of the copper component to the zinc component [copper component/zinc component] (by mass) is, from the viewpoint of reducing the consumption of the coating film also under the condition in contact with water at a high temperature of about 30°C, preferably in a range of 99/1 to 40/60, more preferably in a range of 97/3 to 50/50, even more preferably in a range of 95/5 to 60/40.

[0028]

The antifouling coating composition of the present invention may contain

any other antifouling agent than the antifouling agent (C) including a copper component and a zinc component (hereinafter this may be simply referred to as "the other antifouling agent than the antifouling agent (C)").

Examples of the other antifouling agent than the antifouling agent (C) include medetomidine, 4-bromo-2-(4-chlorophenyl)-5-(trifluoromethyl)-1H-pyrrole-3-carbonitrile, 4,5-dichloro-2-n-octyl-4-isothiazolin-3-one, borane-nitride base adducts (pyridine-trifluorophenylborane, 4-isopropylpyridine-diphenylmethylborane, etc.), ($\pm$)-4-[1-(2,3-dimethylphenyl)ethyl]-1H-imidazole, N,N-dimethyl-N'-(3,4-dichlorophenyl)urea, N-(2,4,6-trichlorophenyl)maleimide, 2-methylthio-4-tert-butylamino-6-cyclopropylamino-1,3,5-triazine, 2,4,5,6-tetrachloroisophthalonitrile, bisdimethyldithiocarbamoyl zinc ethylenebis dithiocarbamate, chloromethyl-n-octyl disulfide, N',N'-dimethyl-N'-phenyl-(N-fluorodichloromethylthio)sulfamide, N',N'-dimethyl-N'-p-tolyl(N-fluorodichloromethylthio)sulfamide, tetraalkylthiuram disulfides, zinc dimethyl dithiocarbamate, zinc ethylenebis dithiocarbamate, 2,3-dichloro-N-(2',6'-diethylphenyl)maleimide, 2,3-dichloro-N-(2'-ethyl-6'-methylphenyl)maleimide, etc. One of these other antifouling agents than the antifouling agent (C) may be used singly or two or more thereof may be used in combination.

The total content of the antifouling agent (C) and the other antifouling agents than the antifouling agent (C) in the antifouling coating composition of the present invention is, from the viewpoint of improving the antifouling performance of the coating film, preferably 5 to 70% by mass, more preferably 10 to 60% by mass.

[0029]

<Monocarboxylic Acid Compound (D)>

In the present invention, for the purpose of improving the surface renewability and the waterproofness of the coating film, a monocarboxylic acid compound (D) is used.

Preferred examples of the monocarboxylic acid compound (D) include a compound having a saturated or unsaturated aliphatic hydrocarbon group having 10 to 40 carbon atoms and substituted with one carboxy group, a compound having a saturated or unsaturated alicyclic hydrocarbon group having 3 to 40 carbon atoms and substituted with one carboxy group, and compounds of these

substitution products substituted with one carboxyl group.

Above all, trimethylisobutenylcyclohexene-carboxylic acid, versatic acid, palmitic acid, stearic acid, oleic acid, linolic acid, linolenic acid, neoabietic acid, pimaric acid, dehydroabietic acid, 12-hydroxystearic acid, naphthenic acid, and
5 metals salts thereof are preferred. In addition, rosin and rosin derivatives mainly consisting of a rosin acid such as abietic acid, palustric acid, isopimaric acid or the like are also preferred.

Examples of the trimethylisobutenylcyclohexene-carboxylic acid include a reaction product of 2,6-dimethylocta-2,4,6-triene and methacrylic acid, and this
10 consists of mainly 1,2,3-trimethyl-5-(2-methylprop-1-en-1-yl)cyclohex-3-ene-1-carboxylic acid and 1,4,5-trimethyl-2-(2-methylprop-1-en-1-yl)cyclohex-3-ene-carboxylic acid (85% by mass or more).

Rosin and rosin derivatives include rosins such as gum rosin, wood rosin,
15 tall oil rosin, etc.; rosin derivatives such as hydrogenated rosin, disproportionated rosin, etc.; etc.

The content of the monocarboxylic acid compound (D) in the antifouling coating composition of the present invention is preferably 0.1 to 50% by mass, more preferably 1 to 30% by mass, even more preferably 2 to 10% by mass.

20 [0030]

<Optional Components>

As needed and in addition to the silylacrylic copolymer (A), the lower alcohol (B), the antifouling agent (C) including a copper component and a zinc component, and the monocarboxylic acid compound (D), the antifouling coating
25 composition of the present invention may contain, a pigment (E), an organic solvent (F), a liquid behavior improving agent (anti-sagging, anti-settling) (G), a plasticizer (H), a dehydrating agent (I), etc.

[0031]

[Pigment (E)]

30 In the present invention, for the purpose of coloration of the coating film and masking of the substrate material, and for the purpose of adequately controlling the coating film strength and of further improving the antifouling performance, a pigment (E) may be used.

Examples of the pigment (E) include extender pigments such as talc, mica,
35 clay, potassium feldspar, calcium carbonate, kaolin, alumina white, white carbon,

aluminum hydroxide, magnesium carbonate, barium carbonate, barium sulfate, calcium sulfate, zinc sulfide, etc.; and coloring pigments such as red iron oxide, titanium white (titanium oxide), yellow iron oxide, carbon black, naphthol red, phthalocyanine blue, etc., and above all, talc and red iron oxide are preferred.

5 One of these pigments may be used singly or two or more thereof may be used in combination.

In the case where the antifouling coating composition of the present invention contains a pigment (E), the content of the pigment (E) in the antifouling coating composition is preferably 1 to 30% by mass, more preferably 4 to 25% by
10 mass, even more preferably 7 to 20% by mass.

Some copper-based and zinc-based antifouling agents such as cuprous oxide, zinc oxide, copper pyrithione, zinc pyrithione and the like may have both a function as an antifouling agent and a function as a pigment, but in the present invention, these are dealt with as the antifouling agent (C) including a copper
15 component and a zinc component.

[0032]

[Organic Solvent (F)]

In the present invention, an organic solvent (F) may be used for the purpose of keeping the viscosity of the antifouling coating composition small and
20 for the purpose of improving spraying atomization performance and spray coating workability.

As the organic solvent (F), any aromatic hydrocarbon-based, aliphatic hydrocarbon-based, alicyclic hydrocarbon-based, ketone-based, ester-based, alcohol-based and the like organic solvents may be used, and aromatic
25 hydrocarbon-based organic solvents are preferred. One of these organic solvents may be used singly or two or more thereof may be used in combination.

Examples of the aromatic hydrocarbon-based organic solvent include toluene, xylene, styrene, mesitylene, etc.

Examples of the aliphatic hydrocarbon-based organic solvent include
30 pentane, hexane, heptane, octane, etc.

Examples of the alicyclic hydrocarbon-based organic solvent include cyclohexane, methylcyclohexane, ethylcyclohexane, etc.

Examples of the ketone-based organic solvent include acetylacetone, acetone, methyl ethyl ketone, methyl isobutyl ketone, dimethyl carbonate, etc.

35 Examples of the ester-based organic solvent include ethyl acetate, butyl

acetate, propylene glycol monomethyl ether acetate, etc.

Examples of the alcohol-based organic solvent include n-butanol, propylene glycol monomethyl ether, etc.

5 In the case where the antifouling coating composition of the present invention contains an organic solvent (F), a preferred amount of the content of the organic solvent (F) in the antifouling coating composition may be determined depending on the desired viscosity of the antifouling coating composition in accordance with the coating mode with the composition, but is, in general, preferably 1 to 50% by mass. When the content is too much, there may occur
10 some failures of anti-sagging performance degradation, etc.

[0033]

[Liquid Behavior Improving Agent (anti-sagging, anti-settling) (G)]

In the present invention, a liquid behavior improving agent (G) may be used for the purpose of controlling the viscoelasticity of the antifouling coating
15 composition and for attaining anti-sagging and anti-settling effects. The liquid behavior improving agent (G) includes organic clay waxes (Al, Ca and Zn stearates, lecithin salts, alkylsulfonates, etc.), organic waxes (polyethylene wax, polyethylene oxide wax, amide wax, polyamide wax, hydrogenated castor oil wax, etc.), mixtures of organic clay wax and organic wax, synthetic fine powder silica,
20 etc. One of these liquid behavior improving agents may be used singly or two or more thereof may be used in combination.

As the liquid behavior improving agent (G), commercial products may be used, and examples thereof include "Disparlon 305", "Disparlon 4200-20" and "Disparlon A630-20X" manufactured by Kusumoto Chemicals, Ltd., etc.

25 In the case where the antifouling coating composition of the present invention contains a liquid behavior improving agent (G), the content of the liquid behavior improving agent (G) in the antifouling coating composition is, in general, preferably 0.01 to 10% by mass, more preferably 0.1 to 3% by mass.

[0034]

30 [Plasticizer (H)]

With respect to the antifouling coating composition of the present invention, a plasticizer (H) may be used for the purpose of improving the cracking resistance and the waterproofness of the coating film and preventing discoloration thereof.

35 Examples of the plasticizer (H) include n-paraffin, chloroparaffin, terpene

phenol, tricresyl phosphate (TCP), polyvinyl ethyl ether, etc. Above all, chloroparaffin and terpene phenol are preferred, and chloroparaffin is more preferred. One of these plasticizers may be used singly or two or more thereof may be used in combination.

5 As the plasticizer (H), commercial products may be used, and examples of the n-paraffin include "n-Paraffin" manufactured by Nippon Oil Corporation, etc.; and examples of the chloroparaffin include "Toyoparax A-40/A-50/A-70/A-145/A-150" manufactured by Tosoh Corporation, etc.

10 In the case where the antifouling coating composition of the present invention contains a plasticizer (H), the content of the plasticizer (H) in the antifouling coating composition is preferably 0.1 to 10% by mass.

[0035]

[Dehydrating Agent (I)]

15 In the present invention, a dehydrating agent (I) may be used for the purpose of improving the storage stability of the antifouling coating composition.

Examples of the dehydrating agent (I) include alkoxysilanes, zeolite known as a general name of "Molecular Sieve", alumina, ortho esters such as alkyl orthoformates, etc., orthoboric acid, isocyanates, gypsum, ethyl silicate, etc. One of these dehydrating agents may be used singly or two or more thereof may be used in combination.

20 In the case where the antifouling coating composition of the present invention contains a dehydrating agent (I), the content of the dehydrating agent (I) in the antifouling coating composition is preferably 0.1 to 10% by mass, more preferably 0.2 to 2% by mass. When the content of the dehydrating agent (I) falls within the above-mentioned range, the antifouling coating composition may keep good storage stability.

[0036]

<Method for Producing Antifouling Coating Composition>

30 The antifouling coating composition of the present invention can be prepared using the same apparatus and means as those for known ordinary antifouling coating compositions. Specifically, while a solution or a dispersion obtained by mixing a solution of a silylacrylic copolymer (A) that has been prepared previously, an antifouling agent (C) including a copper component and a zinc component, and a monocarboxylic acid compound (D), and, as needed, other additives and the like, a lower alcohol (B) is added thereto, and further stirred

and mixed to prepare the composition.

[0037]

[Coating Film and Substrate with Coating Film]

5 The coating film of the present invention is one formed by curing the antifouling coating composition of the present invention. Specifically, for example, the antifouling coating composition of the present invention is applied to a substrate or the like, and then cured to form a coating film.

10 The coating method with the antifouling coating composition of the present invention includes known methods of a method using a brush, a roller or a spray, etc.

The antifouling coating composition applied according to the above-mentioned method can be cured, for example, by leaving it under a condition of 25°C for 0.5 to 14 days or so to form a coating film. Curing the antifouling coating composition may be attained by blowing under heat.

15 The thickness of the coating film after cured of the present invention is, for example, from the viewpoint of improving the coating film strength, preferably 30 to 1,000 μm or so. As the method for forming the coating film having such a thickness, there may be mentioned a method of one-time or plural-times coating with the antifouling coating composition where the coating thickness in one time is generally 10 to 300 μm , preferably 30 to 200 μm .

20 [0038]

The substrate with a coating film of the present invention has the above-mentioned coating film on a substrate.

25 The method for producing the substrate with a coating film of the present invention is not specifically limited. The substrate with a coating film according to the present invention can be produced, for example, according to a method that includes a step of applying the antifouling coating composition on a substrate or impregnating a substrate with the antifouling coating composition to give an applied material or impregnated material, and a step of curing the antifouling
30 coating composition which has been applied on the substrate or which the substrate has been impregnated with, or a method that includes a step of attaching a coating film formed by curing the antifouling coating composition to a substrate.

35 Specifically, as the method for obtaining an applied material or an impregnated material by applying the antifouling coating composition or

impregnating therewith, there may be mentioned a method of fully stirring the antifouling coating composition and then applying it on a substrate or impregnating a substrate with it by spraying or any other means.

On the other hand, as the method of curing the antifouling coating composition which has been applied on a substrate or which a substrate has been impregnated with, a method of drying the coated material or the impregnated material to cure the coating composition is preferred, and specifically, there may be mentioned a method of curing the composition by leaving it in air at an ambient temperature for about 0.5 to 14 days or by applying forced air blowing thereto under heat. According to the method, the substrate with a coating film, which includes the coating film on a substrate, can be produced with ease.

[0039]

Regarding the method of attaching the coating film formed by curing the antifouling coating composition to a substrate, for example, there may be mentioned a method of attaching a film including the coating film formed by curing the antifouling coating composition to a substrate using the known technique described in JP 2013-129724 A. According to the method, a substrate with a coating film in which the substrate is covered with the coating film can be produced.

[0040]

The antifouling coating composition of the present invention can be used for maintaining the antifouling function of a substrate for a long period of time in a broad industrial field covering ships, fishery, pipelines, underwater installations, diving goods, underwater propellers, power generation, port/civil engineering constructions, etc. Examples of the substrate include ships (containerships, large-scale steel-hulled boats such as tankers, etc., hull outer panels for fish boats, FRP boats, wooden vessels, yachts, etc., and newly constructed ships or repaired ships), fishery materials (ropes, fish nets, fishing gears, floats, buoys, etc.), oil pipelines, water pipelines, circulating water pipes, diver suits, swimming goggles, oxygen cylinders, swimwear, torpedoes, underwater constructions such as feed-water and drainage ports for heat power plants or nuclear power plants, seawater utilization equipments (seawater pumps, etc.), mega-floats, bay area roads, undersea tunnels, port facilities, sludge diffusion-preventing films in various marine civil engineering works for canals, waterways, etc., etc. Among these, ships are preferred for the substrate.

[0041]

The antifouling coating composition of the present invention may be directly applied on a substrate or impregnated into a substrate. Also in the case of directly applying to a substrate whose material is formed of a fiber-reinforced plastic (FRP), iron steel, wood, aluminum alloy or the like for feed-water and drainage ports for nuclear power plants, mega-floats, ships and the like, the antifouling coating composition of the present invention can be so controlled as to have good adhesiveness to the surfaces of these substrates (materials).

In addition, the substrate that is an object to which the antifouling coating composition is applied may be one already coated with a primary coating material on the surface thereof. Specifically, the antifouling coating composition of the present invention may be applied to the surface of a substrate previously coated with an undercoated material (undercoat) such as an anticorrosive agent, a primer or the like. Further, the antifouling coating composition of the present invention may be applied to the surface of a substrate that has been already coated with a conventional coating material or has been already coated with the antifouling coating composition of the present invention, for repairing. The kind of the coating material that is to be in direct contact with the antifouling coating composition of the present invention is not specifically limited.

Examples

[0042]

The present invention is described further specifically based on Examples, but the present invention is not limited to these Examples.

[0043]

<Production of Silylacrylic Copolymer (A)>

[Production Example 1: Production of Silylacrylic Copolymer (A1)]

Fifty-three parts by mass of xylene was put into a reactor equipped with a stirrer, a reflux condenser, a thermometer, a nitrogen introducing duct and a dropping funnel, and while xylene was stirred with the stirrer in a nitrogen atmosphere, this was heated until the temperature of xylene in the reactor reached 85°C under an atmospheric pressure. While the temperature of xylene in the reactor was kept at 85°C, a monomer mixture of 45 parts by mass of TIPSMA (triisopropylsilyl methacrylate), 35 parts by mass of MEMA (2-methoxyethyl methacrylate), 15 parts by mass of MMA (methyl methacrylate),

5 parts by mass of BA (butyl acrylate) and 1 part by mass of 2,2'-azobis(2-methylbutyronitrile) was added into the reactor through the dropping funnel over 2 hours.

Next, further, 0.5 parts by mass of tert-butyl peroxyoctoate was added into the reactor, and while the liquid temperature in the reactor was kept at 85°C under an atmospheric pressure, this was kept stirred with the stirrer for 2 hours, and then the liquid temperature in the reactor was raised from 85°C up to 110°C, and this was heated for 1 hour. Subsequently, 14 parts by mass of xylene was added into the reactor to lower the liquid temperature in the reactor, and at the time when the liquid temperature reached 40°C, the stirring was stopped to give a silylacrylic copolymer (A1). The characteristics of the silylacrylic copolymer (A1) are shown in Table 1.

[0044]

[Production Examples 2 to 4: Production of Silylacrylic Copolymers (A2) to (A4)]

Silylacrylic copolymers (A2) to (A4) were produced through polymerization in the same manner as in Production Example 1 except that the charge-in amount of each monomer was changed as in Table 1. The characteristics of the silylacrylic copolymers (A2) to (A4) are shown in Table 1.

[0045]

Methods for measuring the heating residue, the weight average molecular weight (Mw) and the viscosity of the resultant silylacrylic copolymers (A1) to (A4) are as mentioned below.

<Method for calculation of heating residue (mass NV)>

One gram of the silylacrylic copolymer (A) was weighed on a flat-bottom dish, and uniformly spread thereon using a wire having a known mass, dried at 125°C for 1 hour, and then the masses of the residue and the wire were measured to calculate the heating residue (% by mass).

[0046]

<Measurement of weight average molecular weight (Mw) of silylacrylic copolymer (A)>

The weight average molecular weight (Mw) of the silylacrylic copolymer (A) was measured through gel permeation chromatography (GPC) using a measurement device of "HLC-8120GPC" manufactured by Tosoh Corporation, two separation columns of "TSK-gel α -type" (α -M) manufactured by Tosoh Corporation, and an eluent of dimethylformamide (DMF). The weight average molecular

weight (Mw) of the silylacrylic copolymer (A) is a polystyrene-equivalent conversion.

[0047]

<Condition for measurement of viscosity>

- 5 The viscosity of the silylacrylic copolymer (A) was measured, using a B-type viscometer [manufactured by Tokyo Keiki Inc.) at a liquid temperature of 25°C (unit: mPa·s).

[0048]

Table 1

			Production Example of Silylacrylic Copolymer (A)			
			1	2	3	4
Silylacrylic Copolymer (A)			A1	A2	A3	A4
Composition (part by mass)	(a1)	TIPSMA	45	60	60	
		TIPSA				60
	(a2)	MEMA	35	25		
		MEA			25	25
		MMA	15	10	15	10
		BA	5	5		5
2,2'-Azobis(2-methylbutyronitrile)			1	1	1	1
t-Butyl peroxyoctoate			0.5	0.5	0.5	0.5
Ratio by mass [(a1)/(a2)]			45/55	60/40	60/40	60/40
Characteristics	Heating Residue (% by mass)		59.8	59.9	60.3	55.5
	Weight Average Molecular Weight [Mw]		50,516	39,880	39,637	40,332
	Viscosity (mPa·s)		4,470	3,580	1,842	880

10 [0049]

Abbreviations in Table 1 are as follows.

TIPSMA: triisopropylsilyl methacrylate

TIPSA: triisopropylsilyl acrylate

MEMA: 2-methoxyethyl methacrylate

- 15 MEA: 2-methoxyethyl acrylate

MMA: methyl methacrylate

BA: butyl acrylate

<Production of Antifouling Coating Composition>

[Examples 1 to 14 and Comparative Examples 1 to 11]

- 20 Compounding ingredients:

The compounding ingredients used in the antifouling coating composition are shown in Table 2.

[0050]

Table 2

	Product Name	Solid Content (% by mass)
Antifouling Agent (C)	Copper pyrithione Product name "Copper Omadine" (manufactured by Lonza Japan Ltd.)	100
	Cuprous oxide NC301 (manufactured by Nisshin Chemco Ltd.)	100
	Zinc oxide (manufactured by HakusuiTech Co., Ltd.)	100
Monocarboxylic acid Compound (D)	WW Rosin (made in China)	100
Pigment (E)	Talc FC-1 (manufactured by Fukuoka Talc Co., Ltd.)	100
	Red Iron Oxide 404 (manufactured by Toda Kogyo Corp.)	100
Liquid Behavior Improving Agent (G)	Disparlon 4200-20 (manufactured by Kusumoto Chemicals, Ltd.)	20
	Disparlon A630-20X (manufactured by Kusumoto Chemicals, Ltd.)	20
Dehydrating Agent (I)	Gypsum D-1 (manufactured by Noritake Company Ltd.)	100
	Ethyl silicate 28 (manufactured by Colcoat Co., Ltd.)	97

[0051]

Production of Antifouling Coating Composition

According to the formulation (part by mass) shown in Tables 3 to 6, the compounding ingredients were mixed and stirred to produce antifouling coating compositions. The antifouling coating compositions were evaluated as follows. The results are shown in Tables 3 to 6.

[0052]

[Evaluation of storage stability at 50°C]

Immediately after production, each antifouling coating composition was left in a constant-temperature unit at 50°C, and the viscosity thereof was measured at intervals of one week. The viscosity immediately after production and the viscosity after storage (both were controlled to have a coating composition temperature of 23°C) were compared to confirm the increase in the viscosity. For measurement of the viscosity, a Stormer viscometer (unit Ku). The measurement was carried out for 4 weeks, and the difference between the viscosity after 4 weeks and the viscosity after one week was referred to as a viscosity increase rate. Samples having a lower viscosity increase rate have better storage stability.

[0053]

[Evaluation of consumption at 25°C]

The antifouling coating composition of Examples and Comparative Examples was applied at an ambient temperature to a polyvinyl chloride panel (length 50 mm × width 50 mm) so as to have a dry thickness of 100 μm, using a film applicator having a slit of 0.7 mm, and left at an ambient temperature for 1 day to produce a test panel with a coating film.

The test panel with a coating film was immersed for 1 month in seawater controlled at 25°C under the condition that the water flow velocity above the test panel corresponds to about 15 knots according to calculation. After one-month immersion, the film thickness was measured using a noncontact-type laser thickness meter. The difference between the film thickness before immersion and the film thickness after immersion was calculated to determine the consumption. Further, under the above-mentioned condition, the test panel was immersed for 2 to 6 months, and the consumption was determined in the same manner as above.

In this evaluation, smaller values indicate lower consumption.

[0054]

[Evaluation of consumption at 30°C]

The consumption at 30°C was determined in the same manner as in the evaluation of consumption at 25°C, except that the panel with a coating film was immersed in seawater controlled at 30°C.

Also in this evaluation, smaller values indicate lower consumption, and a value of the ratio [consumption at 30°C/consumption at 25°C] is preferably nearer to 1.

[0055]

Table 3

			Example						
			1	2	3	4	5	6	7
Formulation (% by mass)	Silylacrylic Copolymer (A)	A1	18				18	18	18
		A2		18					
		A3			18				
		A4				18			
	Lower Alcohol (B)	Methyl Alcohol							0.5
		Ethyl Alcohol	0.5	0.5	0.5	0.5	0.3	0.7	
		Isopropyl Alcohol							
		n-Propyl Alcohol							
	Alcohol	n-Butyl Alcohol							
		n-Hexanol							
		Octyl Alcohol							
	Antifouling Agent (C)	Copper Pyrithione	2	2	2	2	2	2	2
		Cuprous Oxide NC301	50	50	50	50	50	50	50
		Zinc Oxide	4	4	4	4	4	4	4
	Monocarboxylic Acid Compound (D)	WW Rosin	4	4	4	4	4	4	4
	Pigment (E)	Talc FC-1	4	4	4	4	4	4	4
		Red Iron Oxide 404	3	3	3	3	3	3	3
	Organic Solvent (F)	Xylene	11.5	11.5	11.5	11.5	11.5	11.3	11.5
		Methyl isobutyl ketone							
		Methyl ethyl ketone							
		Butyl acetate							
		Ethyl acetate							
	Liquid Behavior Improving Agent (G)	Disparlon 4200-20	1	1	1	1	1	1	1
		Disparlon A630-20X	1	1	1	1	1	1	1
	Dehydrating Agent (I)	Gypsum D-1	1	1	1	1	1	1	1
		Ethyl Silicate 28							
	Total		100	100	100	100	100	100	100
Evaluation	Storage Stability at 50°C [unit = Ku]	after 1 week	91	89	92	87	89	89	87
		after 2 weeks	91	90	94	88	90	91	88
		after 3 weeks	92	92	95	88	91	91	90
		after 4 weeks	94	95	96	91	93	93	93
		viscosity increase rate	+3	+6	+4	+4	+4	+4	+6
	Consumption at 25°C [unit = μm]	after 1 month	3.7	3.3	4.3	4.3	3.9	4.3	4.2
		after 2 months	6.8	8.7	8.7	8.8	7.4	8.6	9.1
		after 3 months	10.5	11.3	13.3	14.3	11.3	10.4	11.3
		after 4 months	13.3	15.3	17.2	19.8	16.8	14.3	15.7
		after 5 months	17.8	20.5	23.4	25.4	21.3	19.8	21.3
		after 6 months	24.3	28.7	30.5	32.3	27.8	26.5	26.8
		monthly average	4.05	4.78	5.08	5.38	4.63	4.42	4.47
	Consumption at 30°C [unit = μm]	after 1 month	4.8	4.3	5.6	5.8	4.2	5.7	4.8
		after 2 months	7.8	9.8	9.8	10.8	8.1	9.5	8.8
		after 3 months	11.3	14.5	15.7	16.8	13.4	12.4	14.5
		after 4 months	15.6	17.8	19.8	25.6	17.8	16.8	19.8
		after 5 months	21.3	23.4	25.6	34.5	23.4	23.7	25.6
		after 6 months	27.8	30.1	33.4	42.3	28.8	28.3	30.4
		monthly average	4.63	5.02	5.57	7.05	4.80	4.72	5.07
	Ratio of Monthly Average Consumption [30°C /25°C]		1.14	1.05	1.10	1.31	1.04	1.07	1.13

[0056]

Table 4

			Example						
			8	9	10	11	12	13	14
Formulation (% by mass)	Silylacrylic Copolymer (A)	A1	18	18	18		18	18	
		A2				18			18
		A3							
		A4							
	Lower Alcohol (B)	Methyl Alcohol					0.3		
		Ethyl Alcohol			0.5	0.5		1	2
		Isopropyl Alcohol	0.5						
		n-Propyl Alcohol		0.5					
	Alcohol	n-Butyl Alcohol							
		n-Hexanol							
		Octyl Alcohol							
	Antifouling Agent (C)	Copper Pyrithione	2	2	2	2	2	2	2
		Cuprous Oxide NC301	50	50	50	50	50	50	50
		Zinc Oxide	4	4	4	4	4	4	4
	Monocarboxylic Acid Compound (D)	WW Rosin	4	4	4	4	4	4	4
	Pigment (E)	Talc FC-1	4	4	4	4	4	4	4
		Red Iron Oxide 404	3	3	3	3	3	3	3
	Organic Solvent (F)	Xylene	11.5	11.5	11.5	11.5	11.7	11	10
		Methyl isobutyl ketone							
		Methyl ethyl ketone							
		Butyl acetate							
		Ethyl acetate							
	Liquid Behavior Improving Agent (G)	Disparlon 4200-20	1	1	1	1	1	1	1
		Disparlon A630-20X	1	1	1	1	1	1	1
	Dehydrating Agent (I)	Gypsum D-1	1	1			1	1	1
		Ethyl Silicate 28			1	1			
	Total		100	100	100	100	100	100	100
Evaluation	Storage Stability at 50°C [unit = Ku]	after 1 week	89	87	88	87	88	92	89
		after 2 weeks	89	88	90	88	88	95	94
		after 3 weeks	91	88	91	88	89	113	108
		after 4 weeks	92	91	94	89	91	116	121
		viscosity increase rate	+3	+4	+6	+2	+3	+24	+32
	Consumption at 25°C [unit = μm]	after 1 month	3.9	4.1	4.3	3.9	4.2	4.1	4.9
		after 2 months	7.8	7.9	8.8	7.8	8.3	7.8	9.8
		after 3 months	12.3	10.3	11.3	10.4	12.3	11.3	13.5
		after 4 months	16.3	12.9	15.6	14.6	15.6	15.8	17.8
		after 5 months	20.4	16.8	19.8	18.9	20.3	20.4	22.3
		after 6 months	26.7	23.9	24.5	24.3	25.7	25.6	29.8
		monthly average	4.45	3.98	4.08	4.05	4.28	4.27	4.97
	Consumption at 30°C [unit = μm]	after 1 month	5.1	4.8	4.9	5.3	5.3	5.7	5.1
		after 2 months	9.8	8.1	9.8	9.8	9.7	9.8	10.3
		after 3 months	15.5	12.3	14.5	13.4	14.3	12.3	14.5
		after 4 months	21.3	15.8	21.3	16.7	19.8	17.8	19.8
		after 5 months	26.7	22.5	16.7	24.5	24.5	22.3	24.5
		after 6 months	32.3	26.9	30.4	29.8	30.5	27.5	32.3
		monthly average	5.38	4.48	5.07	4.97	5.08	4.58	5.38
	Ratio of Monthly Average Consumption [30°C /25°C]		1.21	1.13	1.24	1.23	1.19	1.07	1.08

[0057]

Table 5

			Comparative Example					
			1	2	3	4	5	6
Formulation (% by mass)	Silylacrylic Copolymer (A)	A1	18				18	18
		A2		18				
		A3			18			
		A4				18		
	Lower Alcohol (B)	Methyl Alcohol						
		Ethyl Alcohol						
		Isopropyl Alcohol						
		n-Propyl Alcohol						
	Alcohol	n-Butyl Alcohol						
		n-Hexanol						
		Octyl Alcohol						
	Antifouling Agent (C)	Copper Pyrithione	2	2	2	2	2	2
		Cuprous Oxide NC301	50	50	50	50	50	50
		Zinc Oxide	4	4	4	4	4	4
	Monocarboxylic Acid Compound (D)	WW Rosin	4	4	4	4	4	4
	Pigment (E)	Talc FC-1	4	4	4	4	4	4
		Red Iron Oxide 404	3	3	3	3	3	3
	Organic Solvent (F)	Xylene	12	12	12	12	11.5	11.5
		Methyl isobutyl ketone					0.5	
		Methyl ethyl ketone						0.5
		Butyl acetate						
		Ethyl acetate						
	Liquid Behavior Improving Agent (G)	Disparlon 4200-20	1	1	1	1	1	1
		Disparlon A630-20X	1	1	1	1	1	1
	Dehydrating Agent (I)	Gypsum D-1	1	1	1	1	1	1
		Ethyl Silicate 28						
	Total		100	100	100	100	100	100
Evaluation	Storage Stability at 50°C [unit = Ku]	after 1 week	88	91	87	88	88	86
		after 2 weeks	88	92	88	89	92	89
		after 3 weeks	89	92	90	92	96	93
		after 4 weeks	90	93	91	94	101	99
		viscosity increase rate	+2	+2	+4	+6	+13	+13
	Consumption at 25°C [unit = μm]	after 1 month	3.1	2.8	3.9	4.1	3.7	3.9
		after 2 months	5.4	5.9	7.7	9.3	6.9	5.3
		after 3 months	9.8	9.7	11.3	13.7	10.4	10.3
		after 4 months	13.2	13.4	16.7	18.8	14.5	13.5
		after 5 months	18.8	17.8	23.4	24.8	19.8	17.9
		after 6 months	23.5	24.5	29.8	31.8	26.7	22.7
		monthly average	3.92	4.08	4.97	5.30	4.45	3.78
	Consumption at 30°C [unit = μm]	after 1 month	5.9	4.3	5.3	5.8	4.9	5.3
		after 2 months	11.5	9.8	10.8	11.8	9.8	10.9
		after 3 months	17.8	15.5	18.7	20.5	17.8	18.3
		after 4 months	23.5	23.4	27.6	29.8	23.3	24.1
		after 5 months	29.8	30.5	35.6	36.9	31.7	30.1
		after 6 months	34.5	36.7	45.6	50.8	44.5	35.6
		monthly average	5.75	6.12	7.60	8.47	7.42	5.93
	Ratio of Monthly Average Consumption [30°C /25°C]		1.47	1.50	1.53	1.60	1.67	1.57

[0058]

Table 6

			Comparative Example				
			7	8	9	10	11
Formulation (% by mass)	Silylacrylic Copolymer (A)	A1	18	18	18	18	18
		A2					
		A3					
		A4					
	Lower Alcohol (B)	Methyl Alcohol					
		Ethyl Alcohol					
		Isopropyl Alcohol					
		n-Propyl Alcohol					
	Alcohol	n-Butyl Alcohol			0.5		
		n-Hexanol				0.5	
		Octyl Alcohol					0.5
	Antifouling Agent (C)	Copper Pyrithione	2	2	2	2	2
		Cuprous Oxide NC301	50	50	50	50	50
		Zinc Oxide	4	4	4	4	4
	Monocarboxylic Acid Compound (D)	WW Rosin	4	4	4	4	4
	Pigment (E)	Talc FC-1	4	4	4	4	4
		Red Iron Oxide 404	3	3	3	3	3
	Organic Solvent (F)	Xylene	11.5	11.5	11.5	11.5	11.5
		Methyl isobutyl ketone					
		Methyl ethyl ketone					
		Butyl acetate	0.5				
		Ethyl acetate		0.5			
	Liquid Behavior Improving Agent (G)	Disparlon 4200-20	1	1	1	1	1
		Disparlon A630-20X	1	1	1	1	1
	Dehydrating Agent (I)	Gypsum D-1	1	1	1	1	1
		Ethyl Silicate 28					
	Total		100	100	100	100	100
Evaluation	Storage Stability at 50°C [unit = Ku]	after 1 week	86	89	87	88	89
		after 2 weeks	87	90	89	90	91
		after 3 weeks	89	93	91	90	91
		after 4 weeks	91	95	93	91	93
		viscosity increase rate	+5	+6	+4	+3	+4
	Consumption at 25°C [unit = μm]	after 1 month	4.2	3.9	4.5	3.7	3.9
		after 2 months	7.9	6.1	9.1	6.1	5.8
		after 3 months	13.6	9.6	14.5	9.7	9.5
		after 4 months	18.7	13.3	19.5	14.1	14.3
		after 5 months	22.3	19.1	24.5	19.3	18.3
		after 6 months	27.8	24.1	29.8	26.3	25.4
		monthly average	4.63	4.02	4.97	4.38	4.23
	Consumption at 30°C [unit = μm]	after 1 month	5.7	5.6	5.1	5.7	6.2
		after 2 months	12.3	12.5	9.8	12.1	12.3
		after 3 months	19.7	16.3	16.7	19.3	19.5
		after 4 months	28.9	24.5	25.6	25.3	25.5
		after 5 months	36.9	29.5	31.6	30.1	30.2
		after 6 months	45.6	34.9	44.3	36.4	35.6
		monthly average	7.60	5.82	7.38	6.07	5.93
	Ratio of Monthly Average Consumption [30°C /25°C]		1.64	1.45	1.49	1.38	1.40

[0059]

As obvious from the results of Examples and Comparative Examples,

according to the present invention, there can be provided an antifouling coating composition capable of forming a coating film that can reduce not only the consumption thereof under the condition in contact with water at an ambient temperature of about 25°C but also the consumption thereof under the condition
5 in contact with water at a high temperature of about 30°C, and which can maintain the physical properties thereof for a long period of time.

Industrial Applicability

[0060]

10 The antifouling coating composition of the present invention can reduce not only the consumption of the coating film under the condition in contact with water at an ambient temperature of about 25°C but also the consumption thereof under the condition in contact with water at a high temperature of about 30°C. Consequently, the antifouling coating composition can maintain the physical
15 properties of the coating film formed on the surfaces of structures that drive forward underwater such as ships and others, and the surfaces of structures installed underwater and others, and also the coating film formed on the inner surfaces of tubular structures such as pipelines and others, for a long period of time.

CLAIMS

[Claim 1]

5 An antifouling coating composition comprising (A) a silylacrylic copolymer having a constituent unit (a1) derived from a triisopropylsilyl (meth)acrylate and a constituent unit (a2) derived from a polymerizable monomer having a polymerizable double bond, (B) a lower alcohol having 1 to 3 carbon atoms, (C) an antifouling agent including a copper component and a zinc component, and (D) a monocarboxylic acid compound, the content of the lower alcohol (B) in the
10 antifouling coating composition being from 0.1 to 3% by mass.

[Claim 2]

The antifouling coating composition according to claim 1, wherein the ratio by mass of the constituent unit (a1) to the constituent unit (a2) [(a1)/(a2)] is from 40/60 to 95/5.

15 [Claim 3]

The antifouling coating composition according to claim 1 or 2, wherein the content of the silylacrylic copolymer (A) in the antifouling coating composition is from 5 to 40% by mass.

[Claim 4]

20 The antifouling coating composition according to any of claims 1 to 3, wherein the weight average molecular weight (Mw) of the silylacrylic copolymer (A) is from 5,000 to 100,000.

[Claim 5]

25 A coating film formed by curing the antifouling coating composition of any of claims 1 to 4.

[Claim 6]

A substrate with a coating film, comprising the coating film of claim 5 on a substrate.

[Claim 7]

30 The substrate with a coating film according to claim 6, wherein the substrate is a ship.

[Claim 8]

35 A method for producing a substrate with a coating film, comprising (1) a step of applying the antifouling coating composition of any of claims 1 to 4 on a substrate or impregnating a substrate with the antifouling coating composition of

any of claims 1 to 4 to give an applied material or impregnated material, and (2) a step of curing the antifouling coating composition by drying the applied material or impregnated material.