

DESCRIPTION

Title of Invention:

MULTILAYER ANTIFOULING COATING FILM, SUBSTRATE WITH MULTILAYER ANTIFOULING COATING FILM AND METHOD FOR PRODUCING SAME, COATING MATERIAL KIT FOR FORMING MULTILAYER ANTIFOULING COATING FILM, UPPER-LAYER ANTIFOULING COATING COMPOSITION, AND ANTIFOULING METHOD

Technical Field

[0001]

The present invention relates to a multilayer antifouling coating film, a substrate with a multilayer antifouling coating film and a method for producing the substrate, a coating material kit for forming a multilayer antifouling coating film, an upper-layer antifouling coating composition, and an antifouling method.

Background Art

[0002]

Ships, submarine structures and articles used in water such as fishing nets are desired to be resistant to adhesion of aquatic organisms thereto so as not to interfere with the functions thereof. Heretofore, for the purpose of preventing adhesion of such organisms, synthesis and evaluation of a large number of biocidal or biorepellent organic compounds, namely organic antifouling agents have been made. Typical examples of such organic antifouling agents include 4-bromo-2-(4-chlorophenyl)-5-(trifluoromethyl)-1H-pyrrole-3-carbonitrile (also known as tralopyril) described in PTL 1 and 4,5-dichloro-2-n-octyl-4-isothiazolin-3-one (also known as DCOIT) described in PTL 2.

On the other hand, for taking advantage of the effect of such an antifouling agent, use of a self-grinding antifouling coating film that uses a hydrolyzable polymer is being investigated. As for a self-grinding antifouling coating film, the hydrolyzable polymer therein is hydrolyzed at the coating film surface that is in contact with water and the hydrophilized layer is ground by streams of water, and according to such a process, the coating film surface is continuously renewed. The above-mentioned antifouling agent gradually

diffuses from the coating film surface into water and therefore the concentration thereof at the coating film surface lowers, but by combination with such a self-grinding antifouling coating film, the problem can be solved. For example, PTL 3 discloses an antifouling coating composition that contains two or more kinds of antifouling agents each containing tralopyril, and an acrylic resin having a specific group in the side chain.

Citation List

Patent Literature

[0003]

PTL 1: WO95/5739

PTL 2: WO95/32862

PTL 3: WO2011/158358

Summary of Invention

Technical Problem

[0004]

However, in such an antifouling coating composition containing an antifouling agent and a hydrolyzable polymer, especially when the antifouling agent is an organic antifouling agent that is soluble in a solvent generally contained in an antifouling coating composition, there often occurs a problem in that, when the antifouling coating composition is applied and dried to form an antifouling coating film and when the drying is carried out in an external environment, especially at a high temperature, the antifouling agent is eccentrically located around the surface of the coating film. A specific cause of the problem is not clear. However, when an antifouling agent is eccentrically located around the surface of a coating film, there may occur some abnormality in the appearance of the coating film. Additionally, as an especially serious problem, a large amount of the antifouling agent in the coating film is consumed owing to coating film renewal in the initial stage in using the coating film and, consequently in continuous use of the coating film later on, the antifouling agent concentration may be lower than the planned one, therefore causing a risky problem of reduction in long-term antifouling performance.

[0005]

In light of such problems, objects of the present invention are to provide a

multilayer antifouling coating film which is free from a problem of poor appearance owing to eccentric location of an antifouling agent in the surface of the coating film and which can exhibit high antifouling performance for a long period of time even under a high fouling load condition, to provide a substrate with a multilayer antifouling coating film using the multilayer antifouling coating film and a method for producing the substrate, and to provide an antifouling method. Further objects of the present invention are to provide a coating material kit for forming a multilayer antifouling coating film, and an upper-layer antifouling coating composition.

Solution to Problem

[0006]

As a result of assiduous studies, the present inventors have found that the above-mentioned problems can be solved by using a multilayer antifouling coating film that satisfies the specific requirements mentioned below, and have completed the present invention.

[0007]

The present invention relates to the following [1] to [15].

[1] A multilayer antifouling coating film including an underlayer antifouling coating film (X) and an upper-layer antifouling coating film (Y) which are layered on each other, wherein the underlayer antifouling coating film (X) contains a hydrolyzable polymer (A1) and an organic antifouling agent (B1), the upper-layer antifouling coating film (Y) contains a hydrolyzable polymer (A2), and the organic antifouling agent (B1) is at least one selected from 4-bromo-2-(4-chlorophenyl)-5-(trifluoromethyl)-1H-pyrrole-3-carbonitrile and 4,5-dichloro-2-n-octyl-4-isothiazolin-3-one.

[2] The multilayer antifouling coating film according to [1], wherein at least one of the hydrolyzable polymer (A1) and the hydrolyzable polymer (A2) has a constituent unit derived from a silyl ester group-containing monomer (a11).

[3] The multilayer antifouling coating film according to [2], wherein the silyl ester group-containing monomer (a11) is represented by the following formula (1-1).

[0008]



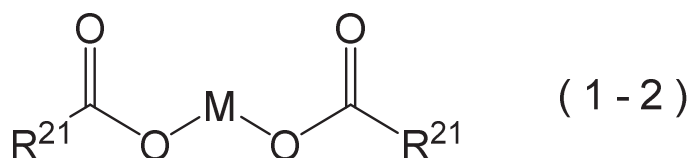
In the formula (1-1), R¹¹ represents a hydrogen atom or a methyl group; and R¹², R¹³ and R¹⁴ each independently represent a monovalent hydrocarbon group.

[0009]

[4] The multilayer antifouling coating film according to any one of [1] to [3], wherein at least one of the hydrolyzable polymer (A1) and the hydrolyzable polymer (A2) has a constituent unit derived from a metal ester group-containing monomer (a12).

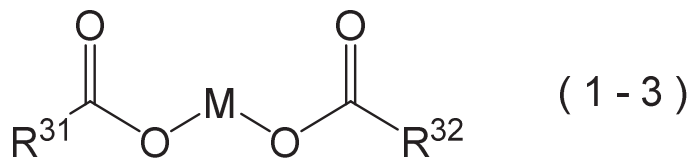
[5] The multilayer antifouling coating film according to [4], wherein the metal ester group-containing monomer (a12) contains at least one of a monomer (a121) represented by the following formula (1-2) and a monomer (a122) represented by the following formula (1-3).

[0010]



In the formula (1-2), R²¹ each independently represents a monovalent group containing a terminal ethylenically unsaturated group; and M represents a metal.

[0011]



In the formula (1-3), R³¹ represents a monovalent group containing a terminal ethylenically unsaturated group; R³² represents a monovalent organic group having 1 to 30 carbon atoms containing no terminal ethylenically unsaturated group; and M represents a metal.

[0012]

[6] A substrate with a multilayer antifouling coating film, which is one

covered with the multilayer antifouling coating film according to any one of [1] to [5].

[7] The substrate with a multilayer antifouling coating film according to [6], wherein the substrate is an underwater structure, a ship or a fishing gear.

[8] An antifouling method including using the multilayer antifouling coating film according to any one of [1] to [5].

[9] A method for producing a substrate with a multilayer antifouling coating film, including: a step of applying an underlayer antifouling coating composition (x) onto a substrate to form an underlayer antifouling coating film (X) thereon, and a step of applying an upper-layer antifouling coating composition (y) onto the underlayer antifouling coating film (X) to form an upper-layer antifouling coating film (Y) thereon, wherein the underlayer antifouling coating composition (x) contains a hydrolyzable polymer (A1) and an organic antifouling agent (B1), the organic antifouling agent (B1) is at least one selected from 4-bromo-2-(4-chlorophenyl)-5-(trifluoromethyl)-1H-pyrrole-3-carbonitrile and 4,5-dichloro-2-n-octyl-4-isothiazolin-3-one, and the upper-layer antifouling coating composition (y) contains a hydrolyzable polymer (A2) and an organic solvent (C2).

[10] The method for producing a substrate with a multilayer antifouling coating film according to [9], wherein the organic solvent (C2) is a solvent which the polymer (B1) contained in the underlayer antifouling coating composition (x) is soluble in.

[11] The method for producing a substrate with a multilayer antifouling coating film according to [9] or [10], wherein the organic solvent (C2) contains one or more selected from the group consisting of a hydrocarbon organic solvent, an alcohol organic solvent, a ketone organic solvent and an ester organic solvent.

[12] The method for producing a substrate with a multilayer antifouling coating film according to any one of [9] to [11], wherein the upper-layer antifouling coating composition (y) does not substantially contain an organic antifouling agent selected from 4-bromo-2-(4-chlorophenyl)-5-(trifluoromethyl)-1H-pyrrole-3-carbonitrile and 4,5-dichloro-2-n-octyl-4-isothiazolin-3-one.

[13] The method for producing a substrate with a multilayer antifouling coating film according to any one of [9] to [12], wherein the upper-layer antifouling coating composition (y) does not substantially contain an

antifouling agent.

[14] A coating material kit for forming a multilayer antifouling coating film, including an underlayer antifouling coating composition (x) containing a hydrolyzable polymer (A1) and an organic antifouling agent (B1), and an upper-layer antifouling coating composition (y) containing a hydrolyzable polymer (A2) and an organic solvent (C2), wherein the organic antifouling agent (B1) is at least one selected from 4-bromo-2-(4-chlorophenyl)-5-(trifluoromethyl)-1H-pyrrole-3-carbonitrile and 4,5-dichloro-2-n-octyl-4-isothiazolin-3-one, and the organic antifouling agent (B1) contained in the underlayer antifouling coating composition (x) is soluble in the organic solvent (C2).

[15] An upper-layer antifouling coating composition, which is applied onto the surface of an underlayer antifouling coating film (X) containing a hydrolyzable polymer (A1) and an organic antifouling agent (B1), wherein the upper-layer antifouling coating composition contains a hydrolyzable polymer (A2) and an organic solvent (C2), the organic antifouling agent (B1) is at least one selected from 4-bromo-2-(4-chlorophenyl)-5-(trifluoromethyl)-1H-pyrrole-3-carbonitrile and 4,5-dichloro-2-n-octyl-4-isothiazolin-3-one, and the organic solvent (C2) is a solvent which the organic antifouling agent (B1) contained in the underlayer coating film (X) is soluble in.

Advantageous Effects of Invention

[0013]

According to the present invention, there can be provided a multilayer antifouling coating film which is free from a problem of poor appearance owing to eccentric location of an antifouling agent in the surface of the coating film and which can exhibit high antifouling performance for a long period of time even under a high fouling load condition, a substrate with a multilayer antifouling coating film using the multilayer antifouling coating film and a method for producing the substrate, and an antifouling method. Further, according to the present invention, there can also be provided a coating material kit for forming a multilayer antifouling coating film that is used for producing the antifouling coating film, and an upper-layer antifouling coating composition.

Description of Embodiments

[0014]

[Multilayer antifouling coating film, substrate with multilayer antifouling coating film, and method for producing the substrate]

The multilayer antifouling coating film of the present invention is a multilayer antifouling coating film including an underlayer antifouling coating film (X) and an upper-layer antifouling coating film (Y) which are layered on each other, wherein the underlayer antifouling coating film (X) contains a hydrolyzable polymer (A1) and an organic antifouling agent (B1), the upper-layer antifouling coating film (Y) contains a hydrolyzable polymer (A2), and the organic antifouling agent (B1) is at least one selected from 4-bromo-2-(4-chlorophenyl)-5-(trifluoromethyl)-1H-pyrrole-3-carbonitrile and 4,5-dichloro-2-n-octyl-4-isothiazolin-3-one.

The substrate with a multilayer antifouling coating film of the present invention is such that a substrate is covered with the multilayer antifouling coating film of the present invention.

Further, the method for producing a substrate with a multilayer antifouling coating film of the present invention includes: a step of applying an underlayer antifouling coating composition (x) onto a substrate to form an underlayer antifouling coating film (X) thereon, and a step of applying an upper-layer antifouling coating composition (y) onto the underlayer antifouling coating film (X) to form an upper-layer antifouling coating film (Y) thereon, wherein the underlayer antifouling coating composition (x) contains a hydrolyzable polymer (A1) and an organic antifouling agent (B1), the organic antifouling agent (B1) is at least one selected from 4-bromo-2-(4-chlorophenyl)-5-(trifluoromethyl)-1H-pyrrole-3-carbonitrile and 4,5-dichloro-2-n-octyl-4-isothiazolin-3-one, and the upper-layer antifouling coating composition (y) contains a hydrolyzable polymer (A2) and an organic solvent (C2).

Preferably, the substrate with a multilayer antifouling coating film of the present invention is one produced according to the production method for a substrate with a multilayer antifouling coating film of the present invention. Also preferably, the multilayer antifouling coating film of the present invention is formed of the underlayer antifouling coating composition (x) and the upper-layer antifouling coating composition (y) that are used in the production method for a substrate with a multilayer antifouling coating film.

[0015]

According to the present invention, there can be provided a multilayer antifouling coating film which is free from a problem of poor appearance owing to eccentric location of an antifouling agent in the surface of the coating film and which can exhibit high antifouling performance for a long period of time even under a high fouling load condition, a substrate with a multilayer antifouling coating film using the multilayer antifouling coating film and a method for producing the substrate, and an antifouling method. Further, according to the present invention, there can also be provided a coating material kit for forming a multilayer antifouling coating film that is used for producing the antifouling coating film, and an upper-layer antifouling coating composition.

[0016]

In the case where an antifouling coating film is formed using an already-existing antifouling coating material as shown in PTLs 1 to 3, there often occurs a problem that an organic antifouling agent may be eccentrically located around the surface of the coating film in some external environments. As a result of assiduous studies, the present inventors have found that when an underlayer antifouling coating film (X) contains a hydrolyzable polymer (A1) and a specific organic antifouling agent (B1), and further when an upper-layer antifouling coating film (Y) containing a hydrolyzable polymer (A2) is formed on the underlayer antifouling coating film (X), the organic antifouling agent can be prevented from being eccentrically located around the surface of the multilayer antifouling coating film, a problem of poor appearance of the resultant multilayer antifouling coating film can be prevented from occurring, and further even under a high fouling load condition, the coating film can exhibit high antifouling performance for a long period of time, and have completed the present invention.

While details of the functional mechanism of the aforementioned effects is not quite clear, a part thereof can be estimated as follows. Specifically, it is estimated that, even when the organic antifouling agent (B1) that the underlayer antifouling coating film (X) contains is eccentrically located around the surface of the underlayer antifouling coating film (X) in forming the underlayer antifouling coating film (X), the organic antifouling agent (B1) can be prevented from being eccentrically located around the surface of the multilayer antifouling coating film as a whole, by providing the upper-layer antifouling coating film (Y) on the underlayer antifouling coating film (X), and therefore the resultant multilayer

antifouling coating film can be prevented from having poor appearance.

In addition, it is estimated that, in the multilayer antifouling coating film, the organic antifouling agent (B1) can be continuously supplied from the underlayer antifouling coating film (X) into the upper-layer antifouling coating film (Y), and therefore the multilayer antifouling coating film can exhibit high antifouling performance for a long period of time from the initial stage thereof. The underlayer antifouling coating film (X) and the upper-layer antifouling coating film (Y) both contain a hydrolyzable polymer, and therefore can still exhibit antifouling performance by the coating film renewing property that the underlayer antifouling coating film (X) and the upper-layer antifouling coating film (Y) have. In particular, it is estimated that, when the upper-layer antifouling coating composition (y) for forming the upper-layer antifouling coating film (Y) contains an organic solvent (C2) and when the organic solvent (C2) can dissolve the organic antifouling agent (B1) that the underlayer antifouling coating film (X) contains, the organic antifouling agent (B1) can be infiltrated into the upper-layer antifouling coating composition (y) when the upper-layer antifouling coating composition (y) is applied onto the underlayer antifouling coating film (X) and therefore a suitable amount of the organic antifouling agent (B1) can be supplied to the upper-layer antifouling coating film (Y), and consequently, the multilayer antifouling coating film can exhibit high antifouling performance from the initial stage thereof.

In addition, it is considered that, unlike an ordinary antifouling coating film where an organic antifouling agent is uniformly distributed in the film or is eccentrically located toward the surface layer thereof, the multilayer antifouling coating film of the present invention has a concentration gradient state such that the concentration of the organic antifouling agent (B1) therein increases toward the underlayer direction, and it is estimated that, in point of dissipation by diffusion of an organic antifouling agent from the coating film in water, the concentration of the organic antifouling agent (B1) can be kept high when the coating film renewal from the upper-layer toward the underlayer has reached the under layer, and consequently the antifouling performance of the multilayer antifouling coating film of the present invention can be bettered.

Hereinunder the underlayer antifouling coating film (X), and the underlayer antifouling coating composition (x) favorable for forming the underlayer antifouling coating film (X), and the upper-layer antifouling coating

film (Y), and the upper-layer antifouling coating composition (y) favorable for forming the upper-layer antifouling coating film (Y) are described.

In the following description, the underlayer antifouling coating composition (x) and the upper-layer antifouling coating composition (y) may be collectively referred to as an antifouling coating composition or a coating composition. Like the hydrolyzable polymer (A1) which means the hydrolyzable polymer that the underlayer antifouling coating composition (x) contains, and the hydrolyzable polymer (A2) which means the hydrolyzable polymer that the upper-layer antifouling coating composition (y) contains, each component that the underlayer antifouling coating composition (x) contains is given a number 1 (one) after the alphabet that expresses the component, and each component that the upper-layer antifouling coating composition (y) contains is given a number 2 (two) after the alphabet that expresses the component; and in the case of collectively naming them, the alphabet expression for the component is given no number symbol, as that for a hydrolyzable polymer (A).

[0017]

<Underlayer antifouling coating film (X), and underlayer antifouling coating composition (x), and upper-layer antifouling coating film (Y), and upper-layer antifouling coating composition (y)>

The multilayer antifouling coating film of the present invention includes an underlayer antifouling coating film (X) and an upper-layer antifouling coating film (Y) which are layered on each other. Preferably, the underlayer antifouling coating film (X) and the upper-layer antifouling coating film (Y) are adjacent layers.

The underlayer antifouling coating film (X) contains a hydrolyzable polymer (A1) and an organic antifouling agent (B1), and the upper-layer antifouling coating film (Y) contains a hydrolyzable polymer (A2).

The underlayer antifouling coating composition (x) favorably used for forming the underlayer antifouling coating film (X) contains a hydrolyzable polymer (A1) and an organic antifouling agent (B1), and preferably further contains an organic solvent (C1).

The upper-layer antifouling coating film (Y) contains a hydrolyzable polymer (A2).

The upper-layer antifouling coating composition (y) favorably used for forming the upper-layer antifouling coating film (Y) preferably contains an

organic solvent (C2) in addition to the hydrolyzable polymer (A2).

The components used in the antifouling coating films and the antifouling coating compositions will be described below.

[0018]

(Hydrolyzable polymer (A1) and hydrolyzable polymer (A2))

In the present invention, the underlayer antifouling coating film (X) contains a hydrolyzable polymer (A1), and the upper-layer antifouling coating film (Y) contains a hydrolyzable polymer (A2). Here, as described above, the hydrolyzable polymer (A1) and the hydrolyzable polymer (A2) are collectively referred to as a hydrolyzable polymer (A).

Since the underlayer antifouling coating film (X) and the upper-layer antifouling coating film (Y) contain a hydrolyzable polymer (A), the coating films are given suitable water resistance and antifouling performance owing to coating film renewal.

[0019]

The hydrolyzable polymer (A) has (i) a constituent unit derived from a hydrolyzable group-containing monomer (a1), and further preferably has (ii) a constituent unit derived from any other monomer (a2).

In the present invention, "a polymer having a constituent unit derived from (a)" means a polymer in which (a) has been introduced through polymerization reaction or chain transfer. Accordingly, for example, in the case where the monomer (a2) has a mercapto group, the radical polymerization terminal draws H from -SH and the resultant -S· (S radical) initiates polymerization and is introduced into the hydrolyzable polymer, and also in such a case, the hydrolyzable polymer (A) has a constituent unit derived from any other monomer (a2).

The constituent units are described below.

[0020]

[(i) Constituent unit derived from hydrolyzable group-containing monomer (a1)]

The hydrolyzable polymer (A) has (i) a constituent unit derived from a hydrolyzable group-containing monomer (a1).

Preferred examples of the hydrolyzable group-containing monomer (a1) include a silyl ester group-containing monomer (a11) or a metal ester group-containing monomer (a12).

Preferably, the antifouling coating composition contains a hydrolyzable

polymer (A) having a constituent unit derived from a silyl ester group-containing monomer (a11) from the viewpoint of bettering the antifouling performance of the multilayer antifouling coating film to be produced and bettering the interlayer adhesiveness between the upper-layer antifouling coating film (Y) and the underlayer antifouling coating film (X).

[0021]

Also preferably, the antifouling coating compositions contain a hydrolyzable polymer (A) having a constituent unit derived from a metal ester group-containing monomer (a12) from the viewpoint of bettering the antifouling performance of the multilayer antifouling coating film to be produced and bettering the film physical properties of the antifouling coating film.

The content of the constituent unit derived from the hydrolyzable monomer (a1) in the hydrolyzable polymer (A) is preferably 3 to 80 parts by mass, more preferably 5 to 70 parts by mass, based on the total constituent units, 100 parts by mass, of the hydrolyzable polymer.

[0022]

-Silyl ester group-containing monomer (a11)-

Preferably, the silyl ester group-containing monomer (a11) contains a compound represented by the following formula (1-1).

[0023]



In the formula (1-1), R¹¹ represents a hydrogen atom or a methyl group; and R¹², R¹³ and R¹⁴ each independently represent a monovalent hydrocarbon group.

[0024]

In the formula (1-1), R¹¹ represents a hydrogen atom or a methyl group, and is, from the viewpoint of bettering long-term antifouling performance and water resistance of the antifouling coating film, preferably a methyl group.

In the formula (1-1), R¹², R¹³ and R¹⁴ each independently represent a monovalent hydrocarbon group. Such a hydrocarbon group includes a linear, branched or cyclic alkyl group, and an aryl group. The alkyl group preferably has 1 to 12 carbon atoms, more preferably 1 to 8 carbon atoms, and even more

preferably 1 to 4 carbon atoms. The aryl group preferably has 6 to 14 carbon atoms, more preferably 6 to 10 carbon atoms. From the viewpoint of imparting suitable hydrolyzability to the antifouling coating film to thereby better the long-term antifouling performance and the water resistance of the film, preferably, R^{12} to R^{14} each are selected from an isopropyl group, an n-propyl group, a sec-butyl group, an n-butyl group and a phenyl group, and more preferably all of R^{12} to R^{14} are isopropyl groups.

Namely, the silyl ester group-containing monomer (a11) is especially preferably triisopropylsilyl (meth)acrylate, and most preferably triisopropylsilyl methacrylate.

[0025]

In the case where the hydrolyzable polymer (A) has a constituent unit derived from the monomer (a11), the amount of the constituent unit derived from the monomer (a11) relative to all the constituent units, 100 parts by mass, is, from the viewpoint of bettering the water resistance of the antifouling coating film, preferably 10 to 90 parts by mass, more preferably 40 to 80 parts by mass, even more preferably 45 to 70 parts by mass, and further more preferably 45 to 65 parts by mass.

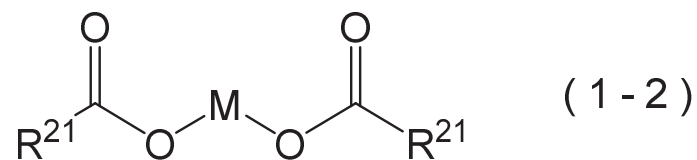
The ratio of each content (mass) of the constituent units derived from the monomers in the hydrolyzable polymer (A) may be considered to be the same as the ratio of the charged amount (mass) of the monomers (reaction raw materials) used in polymerization.

[0026]

-Metal ester group-containing monomer (a12)-

In the present invention, the hydrolyzable group-containing monomer (a1) preferably contains a metal ester group-containing monomer (a12), and the metal ester group-containing monomer preferably contains at least one of a monomer (a121) represented by the following formula (1-2) and a monomer (a122) represented by the following formula (1-3).

[0027]



In the formula (1-2), R^{21} each independently represents a monovalent

group containing a terminal ethylenically unsaturated group; and M represents a metal.

[0028]

Examples of the metal to constitute the metal ester group include magnesium, calcium, neodymium, titanium, zirconium, iron, ruthenium, cobalt, nickel, copper, zinc, and aluminum.

In the formula (1-2), M is a divalent metal, and from among the aforementioned metals, a divalent metal may be appropriately selected for use for M. Among these, Group 10 to 12 metals such as nickel, copper and zinc are preferred; copper and zinc are more preferred; and zinc is even more preferred.

[0029]

In the formula (1-2), R^{21} represents a monovalent group containing a terminal ethylenically unsaturated group ($CH_2=C<$), and the carbon number of R^{21} is preferably 2 to 50, more preferably 2 to 30, even more preferably 2 to 10, and further more preferably 2 to 6. So far as having a terminal ethylenically unsaturated group, R^{21} may have an ethylenically unsaturated group in any other than the terminal, but preferably has an ethylenically unsaturated group only at the terminal.

Preferably, R^{21} is an unsaturated aliphatic hydrocarbon group having a terminal ethylenically unsaturated group, and in which the unsaturated aliphatic hydrocarbon group may have an ester bond, an amide bond, and an ether bond in the carbon chain thereof. Specifically, examples of R^{21} include groups resulting from removal of a carboxy group from an aliphatic unsaturated monocarboxylic acid having a terminal ethylenically unsaturated group, such as acrylic acid (2-propenoic acid), methacrylic acid (2-methyl-2-propenoic acid), 3-butenic acid, 4-pentenic acid, 10-undecenoic acid, 3-(meth)acryloyloxypropionic acid, and 3-(meth)acryloyloxy-2-methylpropionic acid. Other examples thereof include groups resulting from removal of one carboxy group from an aliphatic unsaturated dicarboxylic acid having a terminal ethylenically unsaturated group such as itaconic acid.

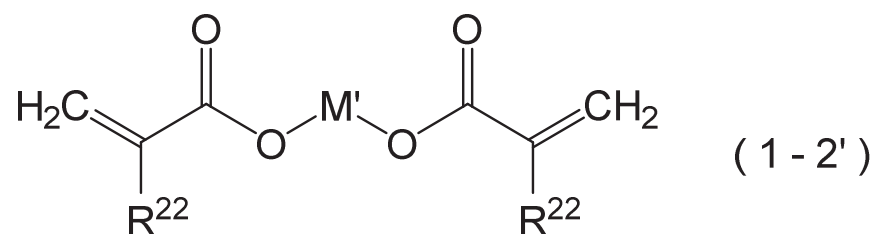
Among these, R^{21} is preferably a group resulting from removal of a carboxy group from an aliphatic unsaturated monocarboxylic acid having a terminal ethylenically unsaturated group, more preferably a group resulting from removal of a carboxy group from an acrylic acid, a methacrylic acid or a (meth)acryloyloxyalkylcarboxylic acid, and even more preferably a group

resulting from removal of a carboxy group from an acrylic acid or a methacrylic acid.

[0030]

Such a monomer (a121) is preferably a monomer (a121') represented by the following formula (1-2').

[0031]

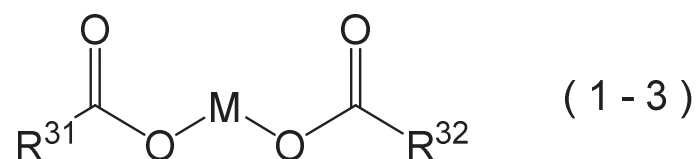


In the formula (1-2'), R²² each independently represents a hydrogen atom or a methyl group; and M' represents copper or zinc.

[0032]

Examples of the monomer (a121) represented by the formula (1-2) include zinc diacrylate, zinc dimethacrylate, zinc acrylate(methacrylate), zinc di(3-acryloyloxypropionate), zinc di(3-methacryloyloxypropionate), zinc di(3-(meth)acryloyloxy-2-methylpropionate), copper diacrylate, copper dimethacrylate, copper acrylate(methacrylate), copper di(3-acryloyloxypropionate), copper di(3-methacryloyloxypropionate), and copper di(3-(meth)acryloyloxy-2-methylpropionate).

[0033]



In the formula (1-3), R³¹ represents a monovalent group containing a terminal ethylenically unsaturated group; R³² represents a monovalent organic group having 1 to 30 carbon atoms containing no terminal ethylenically unsaturated group; and M represents a metal.

[0034]

In the formula (1-3), R³¹ represents a monovalent group containing a terminal ethylenically unsaturated group. For R³¹, the same groups as those of R²¹ in the formula (1-2) are exemplified, and the preferred embodiments thereof are also the same as those of R²¹.

In the formula (1-3), R^{32} represents a monovalent organic group having 1 to 30 carbon atoms containing no terminal ethylenically unsaturated group. Examples of R^{32} include an aliphatic hydrocarbon group having 1 to 30 carbon atoms, an alicyclic hydrocarbon group having 3 to 30 carbon atoms and an aromatic hydrocarbon group having 6 to 30 carbon atoms, each containing no terminal ethylenically unsaturated group. These groups may have a substituent. Examples of the substituent include a hydroxy group.

The aliphatic hydrocarbon group may be linear or branched, and may be a saturated aliphatic hydrocarbon group or an unsaturated aliphatic hydrocarbon group. In the case where R^{32} is an unsaturated aliphatic hydrocarbon group, R^{32} does not have a terminal ethylenically unsaturated group. The carbon number of the aliphatic hydrocarbon group is 1 to 30, preferably 1 to 28, more preferably 1 to 26, and even more preferably 1 to 24. The aliphatic hydrocarbon group may be further substituted with an alicyclic hydrocarbon group or an aromatic hydrocarbon group.

The alicyclic hydrocarbon group may be a saturated alicyclic hydrocarbon group, or an unsaturated alicyclic hydrocarbon group. The carbon number of the alicyclic hydrocarbon group is 3 to 30, preferably 4 to 20, more preferably 5 to 16, and even more preferably 6 to 12. The alicyclic hydrocarbon group may be further substituted with an aliphatic hydrocarbon group or an aromatic hydrocarbon group.

The carbon number of the aromatic hydrocarbon group is 6 to 30, preferably 6 to 24, more preferably 6 to 18, and even more preferably 6 to 10. The aromatic hydrocarbon group may be further substituted with an aliphatic hydrocarbon group or an alicyclic hydrocarbon group.

[0035]

R^{32} is preferably an organic acid residue formed of a monobasic acid, and specifically, examples thereof include groups resulting from removal of a carboxy group from an organic acid selected from the group consisting of versatic acid, palmitic acid, stearic acid, isostearic acid, oleic acid, linoleic acid, linolenic acid, abietic acid, neoabietic acid, pimaric acid, dehydroabietic acid, 12-hydroxystearic acid, and naphthenic acid.

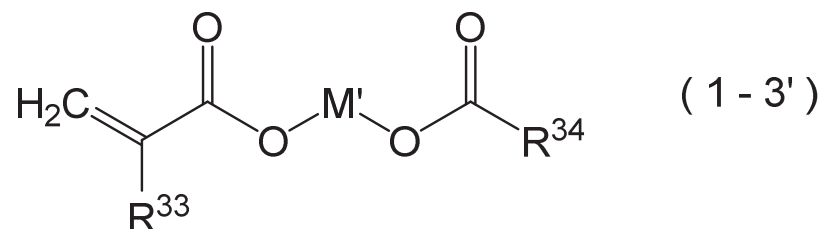
Among these, groups resulting from removal of a carboxy group from abietic acid, versatic acid and naphthenic acid are preferred; and groups resulting from removal of a carboxy group from abietic acid and versatic acid are more

preferred.

[0036]

Such a monomer (a122) is preferably a monomer (a122') represented by the following formula (1-3').

[0037]



In the formula (1-3'), R³³ represents a hydrogen atom or a methyl group; R³⁴ represents a monovalent organic group having 1 to 30 carbon atoms containing no terminal ethylenically unsaturated group; and M' represents copper or zinc.

[0038]

Examples of the monomer (a122) represented by the formula (1-3) include zinc 3-(meth)acryloyloxypropionate (rosin), zinc 3-(meth)acryloyloxypropionate (versatate), zinc (meth)acrylate (rosin), zinc (meth)acrylate (versatate), zinc (meth)acrylate (naphthenate), copper 3-(meth)acryloyloxypropionate (rosin), copper 3-(meth)acryloyloxypropionate (versatate), copper (meth)acrylate (rosin), copper (meth)acrylate (versatate), and copper (meth)acrylate (naphthenate).

In the case where the hydrolyzable polymer (A) has a constituent unit derived from the monomer (a122) represented by the formula (1-3), the hydrolyzable polymer (A) preferably has a constituent unit formed through polymerization of the terminal ethylenically unsaturated group alone in the polymerizable compound (monomer (a122)) represented by the formula (1-3).

In the case where the hydrolyzable polymer (A) has a constituent unit derived from the monomer (a121) or (a122), the total content of the constituent units derived from the monomers (a121) and (a122) is, from the viewpoint of bettering the antifouling performance and the water resistance of the antifouling coating film, preferably 3 to 40 parts by mass, more preferably 5 to 30 parts by mass, relative to 100 parts by mass of all the constituent units.

[0039]

[(ii) Constituent unit derived from other monomer (a2)]

In the present invention, the hydrolyzable polymer (A) preferably contains

a constituent unit derived from any other monomer (a2).

As the other monomer (a2), any monomer copolymerizable with the monomer (a1) can be used with no limitation. Among these, the other monomer is preferably an ethylenically unsaturated compound.

Examples of the other monomer (a2) include:

a polyorganosiloxane block-containing monomer (a21);

an alkyl (meth)acrylate or an aryl (meth)acrylate, such as methyl (meth)acrylate, ethyl (meth)acrylate, n-propyl (meth)acrylate, isopropyl (meth)acrylate, n-butyl (meth)acrylate, isobutyl (meth)acrylate, tert-butyl (meth)acrylate, pentyl (meth)acrylate, hexyl (meth)acrylate, cyclohexyl (meth)acrylate, n-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, and benzyl (meth)acrylate;

an alkoxyalkyl (meth)acrylate, such as 2-methoxyethyl (meth)acrylate, 2-ethoxyethyl (meth)acrylate, 4-methoxybutyl (meth)acrylate, 3-methoxy-n-propyl (meth)acrylate, 2-propoxyethyl (meth)acrylate, 2-butoxyethyl (meth)acrylate, isobutoxybutyldiglycol (meth)acrylate, 2-phenoxyethyl (meth)acrylate, methoxypolyethylene glycol (meth)acrylate, ethoxypolyethylene glycol (meth)acrylate, butoxypolyethylene glycol (meth)acrylate, and phoxypolyethylene glycol (meth)acrylate;

a hydroxyalkyl (meth)acrylate, such as hydroxymethyl (meth)acrylate, 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, 4-hydroxybutyl (meth)acrylate, and 2-hydroxy-3-phenoxypropyl (meth)acrylate;

glycidyl (meth)acrylate; and

a vinyl compound, such as styrene, α -methylstyrene, vinyl acetate, vinyl benzoate, vinyltoluene, acrylonitrile, vinylpyridine, vinylpyrrolidone, and vinyl chloride. From the viewpoint of bettering antifouling performance such as slime resistance, a polyorganosiloxane block-containing monomer (a21) is preferably contained. These monomers may be used alone or as a combination of two or more kinds thereof.

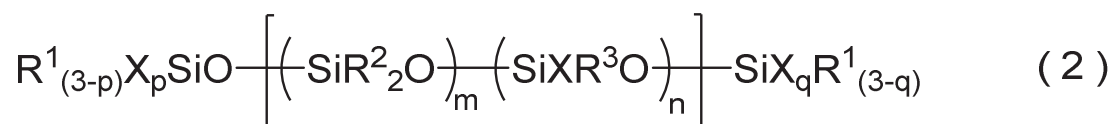
[0040]

The polyorganosiloxane block-containing monomer (a21) is a monomer having a polyorganosiloxane block and having a polymerizable unsaturated group and/or a chain transferable reactive group such as a thiol group, and acts to

introduce a polyorganosiloxane block into the hydrolyzable polymer (A) to be formed especially to improve the antifouling performance such as slime resistance of the resultant polymer.

The polyorganosiloxane block-containing monomer (a21) is preferably represented by the following formula (2).

[0041]



In the formula (2), R^1 , R^2 and R^3 each independently represent a monovalent hydrocarbon group; X each independently represents a (meth)acryloyloxyalkyl group or a mercaptoalkyl group; m represents 1 or more; n represents 0 or more; and p and q each independently represent 0 or 1, provided that $n + p + q$ is 1 or more.

[0042]

In the formula (2), R^1 , R^2 and R^3 each independently represent a monovalent hydrocarbon group, and the hydrocarbon group includes a linear, branched or cyclic alkyl group, and an aryl group. The carbon number of the alkyl group is preferably 1 to 12, more preferably 1 to 8, and even more preferably 1 to 4. The carbon number of the aryl group is preferably 6 to 14, and more preferably 6 to 10. From the viewpoint of polymerization easiness, R^1 , R^2 and R^3 each are preferably an alkyl group such as a methyl group or a butyl group.

In the formula (2), X each independently represents a (meth)acryloyloxyalkyl group or a mercaptoalkyl group, and from the viewpoint of uniform polymerization progression, a (meth)acryloyloxyalkyl group is preferred; and from the viewpoint of reducing the viscosity of the polymer to be formed to facilitate the handling thereof, a mercaptoalkyl group is also preferred. Such X includes a (meth)acryloyloxyethyl group, a (meth)acryloyloxypropyl group, a (meth)acryloyloxybutyl group, a mercaptomethyl group, a mercaptoethyl group, a mercaptopropyl group and a mercaptobutyl group.

In the formula (2), m is 1 or more, n is 0 or more, and p and q each independently are 0 or 1, provided that $n + p + q$ is 1 or more.

m and n mean an average molar number of repeating units (SiR^2_2O) and $(SiXR^3O)$, respectively.

In the formula (2), $m + n$ is preferably 2 or more.

[0043]

In this description, in the case where two or more different repeating units are described in parallel between parentheses [], the repeating units may repeat in any form or order of a random configuration, an alternate configuration or a block configuration. Namely, for example, a formula $-(Y_3-Z_3)-$ (where Y and Z each indicate a repeating unit) may be in any form of a random configuration of $-YYZYZZ-$, or an alternate configuration of $-YZYZYZ-$ or a block configuration of $-YYYYZZ-$ or $-ZZZYYY-$.

[0044]

As one embodiment, the hydrolyzable polymer (A) preferably has a constituent unit derived from a monomer (a211) of the formula (2) where n is 0, p is 1 and q is 0.

An antifouling coating composition containing a hydrolyzable polymer (A) having a constituent unit derived from such a monomer (a211) is preferred since the composition can form an antifouling coating film having an especially excellent antifouling performance.

In such a monomer (a211), m is preferably 3 to 200, more preferably 5 to 70 from the viewpoint of polymerization easiness.

As such a monomer (a211), commercial products may be used, and examples thereof include FM-0711 (one-terminal methacryloyloxyalkyl-modified organopolysiloxane, number-average molecular weight $M_n = 1,000$), FM-0721 (one-terminal methacryloyloxyalkyl-modified organopolysiloxane, number-average molecular weight $M_n = 5,000$) and FM-0725 (one-terminal methacryloyloxyalkyl-modified organopolysiloxane, number-average molecular weight $M_n = 10,000$) all manufactured by JNC Corporation; and X-22-174ASX (one-terminal methacryloyloxyalkyl-modified organopolysiloxane, functional group equivalent 900 g/mol), KF-2012 (one-terminal methacryloyloxyalkyl-modified organopolysiloxane, functional group equivalent 4,600 g/mol) and X-22-2426 (one-terminal methacryloyloxyalkyl-modified organopolysiloxane, functional group equivalent 12,000 g/mol) all manufactured by Shin-Etsu Chemical Co., Ltd.

[0045]

As another embodiment, the hydrolyzable polymer (A) preferably has a constituent unit derived from a monomer (a212) of the formula (2) where n is 0, p and q are 1.

An antifouling coating composition containing a hydrolyzable polymer (A) having a constituent unit derived from such a monomer (a212) is preferred since the interlayer adhesiveness in the multilayer antifouling coating film to be formed tends to better.

In such a monomer (a212), m is preferably 3 to 200, more preferably 5 to 70 from the viewpoint of polymerization easiness.

As such a monomer (a212), commercial products may be used, and examples thereof include FM-7711 (both-terminal methacryloyloxyalkyl-modified organopolysiloxane, number-average molecular weight $M_n = 1,000$), FM-7721 (both-terminal methacryloyloxyalkyl-modified organopolysiloxane, number-average molecular weight $M_n = 5,000$) and FM-7725 (both-terminal methacryloyloxyalkyl-modified organopolysiloxane, number-average molecular weight $M_n = 10,000$) all manufactured by JNC Corporation; and X-22-164 (both-terminal methacryloyloxyalkyl-modified organopolysiloxane, functional group equivalent 190 g/mol), X-22-164AS (both-terminal methacryloyloxyalkyl-modified organopolysiloxane, functional group equivalent 450 g/mol), X-22-164A (both-terminal methacryloyloxyalkyl-modified organopolysiloxane, functional group equivalent 860 g/mol), X-22-164B (both-terminal methacryloyloxyalkyl-modified organopolysiloxane, functional group equivalent 1630 g/mol), X-22-164C (both-terminal methacryloyloxyalkyl-modified organopolysiloxane, functional group equivalent 2,370 g/mol), X-22-164E (both-terminal methacryloyloxyalkyl-modified organopolysiloxane, functional group equivalent 3,900 g/mol), and X-22-167B (both-terminal mercaptoalkyl-modified organopolysiloxane, functional group equivalent 1,670 g/mol) all manufactured by Shin-Etsu Chemical Co., Ltd.

[0046]

As still another embodiment, the hydrolyzable polymer (A) preferably has a constituent unit derived from a monomer (a213) of the formula (2) where X is a mercaptoalkyl group, and n is 1 or more.

A hydrolyzable polymer (A) having a constituent unit derived from such a monomer (a213) is preferred since the resulting composition has a low viscosity and is easy to handle.

In such a monomer (a213), m is preferably 50 to 1,000, and n is preferably 1 to 30, from the viewpoint of easiness in polymerization.

As such a monomer (a213), commercial products may be used, and

examples thereof include KF-2001 (side chain-mercaptoalkyl-modified organopolysiloxane, functional group equivalent 1,900 g/mol) and KF-2004 (side chain-mercaptoalkyl-modified organopolysiloxane, functional group equivalent 30,000 g/mol) both manufactured by Shin-Etsu Chemical Co., Ltd.

[0047]

From the viewpoint of antifouling performance and water resistance under dry-wet alternate conditions and also from the viewpoint of interlayer adhesiveness of the antifouling coating film, the content of the constituent unit derived from the monomer (a21) in the hydrolyzable polymer (A) is preferably 0.5 to 60 parts by mass relative to 100 parts by mass of all the constituent units therein, more preferably 1 to 50 parts by mass, even more preferably 2 to 50 parts by mass, and further more preferably 5 to 50 parts by mass.

[0048]

The hydrolyzable polymer (A) can be obtained by synthesis from a hydrolyzable group-containing monomer (a1) and optionally any other monomer (a2) according to a known method.

For example, in the case where the hydrolyzable group-containing monomer (a1) contains the above-mentioned monomer (a121) or (a122), for example, an inorganic metal compound (preferably a copper or zinc oxide, hydroxide or chloride) and an organic acid such as methacrylic acid or acrylic acid or an ester thereof are reacted by heating with stirring in the presence of an organic solvent or water at a temperature not higher than the decomposition temperature of the metal salt according to a known method to synthesize the polymer.

More specifically, first, a mixture prepared by mixing a solvent and a metal component such as zinc oxide is stirred with heating at around 50 to 80°C, and a mixture of an organic acid such as methacrylic acid or acrylic acid or an ester thereof, and water is dropwise added thereto, and further stirred to give a monomer (a121) or (a122).

Next, a solvent is put into a newly prepared reactor and heated at around 80 to 120°C, and a mixture of the monomer (a121) or (a122), and any other monomer (a2), a polymerization initiator, a chain transfer agent and a solvent is dropwise added thereto, and polymerization is carried out to provide the metal ester group-containing hydrolyzable polymer (A).

[0049]

The polymerization initiator usable in producing the hydrolyzable polymer (A) is not specifically limited, and various radical polymerization initiators can be used. Specific examples thereof include benzoyl peroxide, hydrogen peroxide, cumene hydroperoxide, tert-butyl hydroperoxide, potassium persulfate, sodium persulfate, 2,2'-azobis(isobutyronitrile) (AIBN), 2,2'-azobis(2-methylbutyronitrile) (AMBN), 2,2'-azobis(2,4-dimethylvaleronitrile) (ADVN), and tert-butyl peroctoate (TBPO). The polymerization initiators may be used alone or as a combination of two or more kinds thereof. The radical polymerization initiator may be added into the reaction system only at the start of the reaction, or may be added into the reaction system both at the start of the reaction and in the course of the reaction.

The amount of the polymerization initiator to be used in the production of the hydrolyzable polymer (A) is preferably from 0.1 to 20 parts by mass per 100 parts by mass in total of the monomers.

[0050]

The chain transfer agent that can be used for the production of the hydrolyzable polymer (A) is not particularly limited, and examples thereof include α -methylstyrene dimer, thioglycolic acid, diterpene, terpinolene, γ -terpinene; mercaptans, such as tert-dodecylmercaptan and n-dodecylmercaptan; a halide, such as carbon tetrachloride, methylene chloride, bromoform, and bromotrichloroethane; and a secondary alcohol, such as isopropanol and glycerol. The chain transfer agents may be used alone or as a combination of two or more kinds thereof.

In the case where the chain transfer agent is used in the production of the hydrolyzable polymer (A), the amount thereof used is preferably from 0.1 to 5 parts by mass per 100 parts by mass in total of the monomers.

[0051]

Examples of the solvent that can be used for the production of the hydrolyzable polymer (A) include an aromatic solvent, such as toluene, xylene, and mesitylene; an alcohol, such as propanol, butanol, propylene glycol monomethyl ether, and dipropylene glycol monomethyl ether; a ketone, such as methyl ethyl ketone, methyl isobutyl ketone, and methyl amyl ketone; an ester, such as ethyl acetate and butyl acetate; and water.

[0052]

Preferably, the number-average molecular weight (M_n) and the weight-average molecular weight (M_w) of the hydrolyzable polymer (A) are

appropriately controlled in consideration of the viscosity and the storage stability of the antifouling coating composition and of the elution rate (renewability) of the resultant antifouling coating film.

The number-average molecular weight (M_n) is preferably 1,000 to 100,000, more preferably 1,500 to 30,000. The weight-average molecular weight (M_w) is preferably 2,000 to 200,000, more preferably 3,000 to 60,000.

The number-average molecular weight (M_n) and the weight-average molecular weight (M_w) can be obtained through measurement by gel permeation chromatography and converting based on the standard polystyrene.

[0053]

One alone of the hydrolyzable polymer (A) may be used, or two or more kinds thereof may be used in combination.

The content of the hydrolyzable polymer (A) in the underlayer antifouling coating composition (x) and the upper-layer antifouling coating composition (y) is, from the viewpoint of bettering the coating workability with the antifouling coating composition and bettering the antifouling performance of the antifouling coating film, preferably 5% by mass or more, based on the solid content in the antifouling coating composition, more preferably 10% by mass or more, and is preferably 99% by mass or less, more preferably 95% by mass or less, even more preferably 90% by mass or less, and further more preferably 88% by mass or less.

In the present invention, in the case where the underlayer antifouling coating composition (x) or the upper-layer antifouling coating composition (y) contains two or more kinds of hydrolyzable polymers (A), the aforementioned content is a preferred range of the total content of the hydrolyzable polymers (A), and the same shall apply to the constituent components to be mentioned hereinafter.

[0054]

In the case where the hydrolyzable polymer (A) contains a constituent unit derived from a silyl ester group-containing monomer (a11), the content of the hydrolyzable polymer (A) based on the solid content of the underlayer antifouling coating composition (x) or the upper-layer antifouling coating composition (y) is preferably 5 to 60% by mass, more preferably 10 to 50% by mass, even more preferably 12 to 40% by mass.

In the case where the hydrolyzable polymer (A) has a constituent unit derived from a metal ester group-containing monomer, preferably the monomer

(a121) and/or the monomer (a122), the content of the hydrolyzable polymer (A) based on the solid content of the underlayer antifouling coating composition (x) or the upper-layer antifouling coating composition (y) is preferably 10 to 99% by mass, more preferably 15 to 95% by mass, even more preferably 20 to 90% by mass, and further more preferably 25 to 88% by mass.

[0055]

In the present invention where the hydrolyzable polymer (A) has a constituent unit derived from a polyorganosiloxane block-containing monomer (a21), preferably, the content ratio of the hydrolyzable polymer (A) in the antifouling coating film is increased for enhancing the slime resistance of the antifouling coating film that is estimated to be owed by the polyorganosiloxane.

In the present invention, in the case where the coating composition contains two or more kinds of hydrolyzable polymers (A), the aforementioned content is a preferred range of the total content of the hydrolyzable polymers (A), and the same shall apply to the constituent components to be mentioned hereinafter.

[0056]

(Organic antifouling agent (B1))

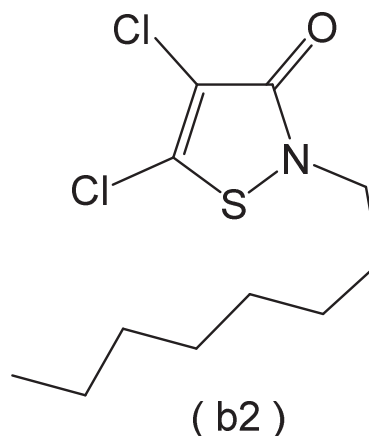
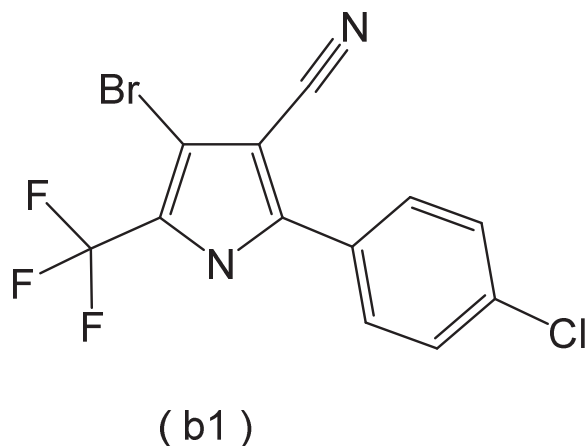
In the present invention, the underlayer antifouling coating film (X) and the underlayer antifouling coating composition (x) contain an organic antifouling agent (B1), and the organic antifouling agent is at least one selected from 4-bromo-2-(4-chlorophenyl)-5-(trifluoromethyl)-1H-pyrrole-3-carbonitrile and 4,5-dichloro-2-n-octyl-4-isothiazolin-3-one.

Here,

4-bromo-2-(4-chlorophenyl)-5-(trifluoromethyl)-1H-pyrrole-3-carbonitrile is represented by the following formula (b1) and is referred to as tralopyril.

4,5-Dichloro-2-n-octyl-4-isothiazolin-3-one is represented by the following formula (b2) and is referred to as DCOIT.

[0057]



[0058]

The organic antifouling agent (B1) is at least one selected from tralopyril and DCOIT, and especially from the viewpoint of improving antifouling performance against barnacles, preferably the antifouling agent contains tralopyril, and especially from the viewpoint of improving antifouling performance against slime, a cell secretion, also preferably the antifouling agent contains DCOIT.

One alone of the organic antifouling agent (B1) may be used, or two or more kinds thereof may be used in combination. Namely, tralopyril or DCOIT may be used alone, or tralopyril and DCOIT may be used in combination.

The total content of the organic antifouling agent (B1) in the underlayer antifouling coating composition (x) can be selected in any desired manner depending on the efficacy and the cost of the organic antifouling agent to be used, and can be preferably 0.1 to 50% by mass based on the solid content of the underlayer antifouling coating composition (x), but from the viewpoint of imparting excellent antifouling performance and physical properties to the multilayer antifouling coating film, the total content is more preferably 1 to 30% by mass, even more preferably 3 to 20% by mass. The total content of the organic antifouling agent (B1) in the underlayer antifouling coating film (X) is, from the viewpoint of imparting excellent antifouling performance and physical properties to the multilayer antifouling coating film, preferably 0.1 to 50% by mass, more preferably 1 to 30% by mass, even more preferably 3 to 20% by mass. The content of the organic antifouling agent (B1) in the underlayer antifouling coating film (X) varies, depending on dissolution thereof in the organic solvent (C2) that an upper-layer antifouling coating composition (y) contains in forming an

upper-layer antifouling coating film (Y) and on supply of the organic antifouling agent (B1) from the underlayer antifouling coating film (X) to the upper-layer antifouling coating film (Y) in the multilayer antifouling coating film. Accordingly, most suitably, the content of the organic antifouling agent (B1) is defined based on the solid content of the underlayer antifouling coating composition (x).

[0059]

In the case where the underlayer antifouling coating composition (x) contains tralopyril as the organic antifouling agent (B1), the content of tralopyril therein is, from the viewpoint of improving antifouling performance and coating film physical properties of the multilayer antifouling coating film and improving interlayer adhesiveness of the film, preferably 1 to 30% by mass, more preferably 3 to 20% by mass based on the solid content of the underlayer antifouling coating composition (x). In the case where the underlayer antifouling coating composition (x) contains DCOIT as the organic antifouling agent (B1), the content of DCOIT therein is, from the same viewpoints as above, preferably 0.5 to 15% by mass, more preferably 1 to 12% by mass, even more preferably 2 to 10% by mass based on the solid content of the underlayer antifouling coating composition (x).

[0060]

The underlayer antifouling coating composition (x) may contain any other organic antifouling agent (B'1) in addition to tralopyril and DCOIT as an organic antifouling agent. The other organic antifouling agent (B'1) is a compound having antifouling performance and does not contain a metal element. Boron of a semi-metal does not correspond to a metal element.

The other organic antifouling agent (B'1) includes borane-nitrogen base adducts such as pyridine triphenylborane and 4-isopropylpyridine diphenylmethyl borane, and (+/-)-4-[1-(2,3-dimethylphenyl)ethyl]-1H-imidazole (also called medetomidine), N,N-dimethyl-N'-(3,4-dichlorophenyl)urea (also called Diuron), N-(2,4,6-trichlorophenyl)maleimide, 2,4,5,6-tetrachloroisophthalonitrile, 2-methylthio-4-tert-butylamino-6-cyclopropylamino-1,3,5-triazine (also called Cybutryne), chloromethyl-n-octyl disulfide, N,N'-dimethyl-N'-phenyl-(N-fluorodichloromethylthio)sulfamide (also called Dichlofluanid), tetraalkylthiuram disulfide (also called TMTD), 2,3-dichloro-N-(2',6'-diethylphenyl)maleimide, and 2,3-dichloro-N-(2'-ethyl-6'-methylphenyl)maleimide.

A case where the other organic antifouling agent forms a salt in the antifouling coating composition or in the antifouling coating film is not excluded, and even in such a case of adding a salt thereof, the salt corresponds to the organic antifouling agent.

[0061]

In the present invention, the upper-layer antifouling coating composition (y) may optionally contain an organic antifouling agent (B2) of at least one selected from tralopyril and DCOIT, or any other organic antifouling agent (B'2) within a range not interfering with the objects of the present invention. Examples of the other organic antifouling agent (B'2) include the same compounds as those for the other organic antifouling agent (B'1).

When the upper-layer antifouling coating composition (y) contains an organic antifouling agent (B2) and/or the other organic antifouling agent (B'2), the antifouling performance of the multilayer antifouling coating film can be improved more.

In the case where the upper-layer antifouling coating composition (y) contains an organic antifouling agent (B2), from the viewpoint of resource saving, the content of the organic antifouling agent (B2) in the upper-layer antifouling coating composition (y) is preferably such that the content of the organic antifouling agent in the upper-layer antifouling coating film (Y) is lower than the content of the organic antifouling agent in the underlayer antifouling coating film (X). Also preferably, from the viewpoint of not forming precipitates on the surface of the antifouling coating film, the upper-layer antifouling coating composition (y) does not substantially contain the organic antifouling agent (B2).

In the present invention, the wording "a coating composition does not substantially contain a substance" means that the concentration of the substance in the solid content of the coating composition is less than 0.1% by mass, preferably 0.05% by mass or less, more preferably 0.03% by mass or less, even more preferably 0.01% by mass or less.

[0062]

Especially in the case where the upper-layer antifouling coating composition (y) contains a hydrolyzable polymer (A2) having a constituent unit derived from the above-mentioned silyl ester group-containing monomer (a11) and where an organic antifouling agent such as tralopyril, or a borane-nitrogen base adduct such as pyridine triphenylborane or 4-isopropylpyridine diphenylmethyl

borane, or a nitrogen-containing heterocyclic compound such as medetomidine is used along with the polymer, there may occur some trouble of viscosity increase with time of the coating composition, and therefore preferably, the composition of the type does not substantially contain any of these.

[0063]

In the case where the upper-layer antifouling coating composition (y) contains an organic antifouling agent (B2) and/or any other organic antifouling agent (B'2), the content thereof is, based on the solid content of the upper-layer antifouling coating composition (y), preferably 0.1% by mass to 10% by mass, more preferably 0.3% by mass to 5% by mass.

The upper-layer antifouling coating film (Y) contains not only the organic antifouling agent (B2) and the other organic antifouling agent (B'2) that the upper-layer antifouling coating composition (y) contains but also the organic antifouling agent (B1) and the other organic antifouling agent (B'1) that have released from the underlayer antifouling coating film (X) in coating with the upper-layer antifouling coating composition (y) and also the organic antifouling agent (B1) and the other organic antifouling agent (B'1) that have transferred from the underlayer antifouling coating film (X) after the multilayer antifouling coating film has been formed. Accordingly, even in such a case that the upper-layer antifouling coating composition (y) does not substantially contain an organic antifouling agent (B2) and any other organic antifouling agent (B'2), the upper-layer antifouling coating film (Y) contains an organic antifouling agent.

[0064]

(Organic solvent (C2))

In the present invention, the upper-layer antifouling coating composition (y) preferably contains an organic solvent (C2) for the purpose of extracting the organic antifouling agent (B1) from the underlayer antifouling coating film (X) and for the purpose of controlling the viscosity of the upper-layer antifouling coating composition (y). The upper-layer antifouling coating composition (y) may contain a solvent used in preparing the hydrolyzable polymer (A2) as the organic solvent (C2), and may contain a solvent separately added in mixing the hydrolyzable polymer (A2) and any other optional component added thereto.

In the present invention, a solvent in which the organic antifouling agent (B1) is soluble is preferably selected as the organic solvent (C2). In the present invention, "soluble" means that the solubility at 23°C is 1 g/L or more.

Preferably, the organic solvent (C2) contains one such that the solubility at 23°C of the organic antifouling agent (B1) therein is 10 g/L or more, more preferably 100 g/L or more.

The solubility can be determined, for example, according to the following method.

100 g of a solute whose solubility is to be determined and 1 L of a solvent are fully stirred in a container to give a uniform suspension, and the concentration of the solute in the supernatant is measured according to a measurement method of HPLC or the like to thereby determine the solubility of the solute. In the case where the mixture is a uniform solution, the solubility is 100 g/L or more.

[0065]

The organic solvent (C2) includes a hydrocarbon organic solvent such as xylene, toluene and ethylbenzene; a ketone organic solvent such as methyl ethyl ketone, cyclohexane, 4-methyl-2-pentanone (also called methyl isobutyl ketone), and 2-heptanone (also called methyl amyl ketone); an aliphatic (having a carbon number of 1 to 10, preferably 2 to 5) alcohol organic solvent such as ethanol, isopropyl alcohol, n-butanol, isobutanol, propylene glycol monomethyl ether and ethylene glycol; and an ester organic solvent such as ethyl acetate, n-propyl acetate, isopropyl acetate, n-butyl acetate, and isobutyl acetate. From the viewpoint of evaporation speed, easy handleability and easy availability of raw materials, xylene, n-butanol, isobutanol, propylene glycol monomethyl ether, n-butyl acetate, isobutyl acetate and 2-heptanone are preferred.

[0066]

The organic solvent (C2) that the upper-layer antifouling coating composition (y) contains is, from the viewpoint of effective supply of the organic antifouling agent (B1) from the underlayer antifouling coating film to the upper-layer antifouling coating film (Y), preferably one that contains the above-mentioned ester organic solvent or the ketone organic solvent, and more preferably one containing an ester organic solvent.

In the case where the upper-layer antifouling coating composition (y) contains an ester organic solvent or a ketone organic solvent as the organic solvent (C2), the content thereof is preferably 1 to 50% by mass, more preferably 2 to 30% by mass in the upper-layer antifouling coating composition (y).

[0067]

In the case where the organic antifouling agent (B1) that the underlayer antifouling coating film (X) contains is to contain 4-bromo-2-(4-chlorophenyl)-5-(trifluoromethyl)-1H-pyrrole-3-carbonitrile (also called tralopyril), especially preferably the coating composition contains the above-mentioned alcohol organic solvent, ester organic solvent or ketone organic solvent from the viewpoint of supply of tralopyril to the upper-layer antifouling coating film (Y) in addition to the above-mentioned viewpoint, and above all, the coating composition preferably contains an ester organic solvent from the viewpoint of reducing the viscosity of the upper-layer antifouling coating composition (y) to secure an easy coating operation. In the case where the underlayer antifouling coating film (X) contains tralopyril and where the upper-layer antifouling coating composition (y) contains an alcohol organic solvent, an ester organic solvent or a ketone organic solvent, the content thereof is preferably 2 to 50% by mass, more preferably 5 to 30% by mass in the upper-layer antifouling coating composition (y).

[0068]

One alone of the organic solvent (C2) may be used, or two or more kinds thereof may be used in combination.

In the present invention, the organic solvent (C2) that the upper-layer antifouling coating composition (y) contains can dissolve the organic antifouling agent (B1) containing the underlayer antifouling coating film (X) and the underlayer antifouling coating composition (x). Here, the wording that the organic solvent (C2) can dissolve the organic antifouling agent (B1) means that, when the organic solvent (C2) contains two or more kinds of organic solvents, the organic solvent (C2) satisfies at least any of (i) the antifouling agent is soluble in the organic solvent whose content (% by mass) is the highest in the organic solvent (C2), or (ii) the antifouling agent is soluble in all the organic solvent (C2) of a mixture of two or more kinds of organic solvents that the upper-layer antifouling coating composition (y) contains. As described above, "soluble" means that the solubility at 23°C is 1 g/L or more, preferably 10 g/L or more, more preferably 100 g/L or more.

[0069]

In the present invention, the content of the organic solvent (C2) in the upper-layer antifouling coating composition (y) is, from the viewpoint of coating operability of the upper-layer coating composition (y), dryability of the coating

film and environmental emission, and from the viewpoint of supply of the organic antifouling agent (B1) from the underlayer antifouling coating film (X) to the upper-layer antifouling coating film (Y), preferably 5 to 90% by mass, more preferably 10 to 90% by mass, even more preferably 20 to 80% by mass, and further more preferably 40 to 70% by mass.

[0070]

In the present invention, the underlayer antifouling coating composition (x) may also contain an organic solvent (C1). Examples of the organic solvent (C1) include the same as those of the organic solvent (C2) that the upper-layer antifouling coating composition (y) contains.

The content of the organic solvent (C1) in the underlayer antifouling coating composition (x) is preferably 5 to 90% by mass, more preferably 10 to 70% by mass.

[0071]

(Other components)

In the present invention, the underlayer antifouling coating composition (x) and the upper-layer antifouling coating composition (y) may contain any other component in addition to the above-mentioned components.

[Other antifouling agent (D)]

The coating composition of the present invention may further contain any other antifouling agent (D) for the purpose of further improving the antifouling performance of the coating film to be formed. In the present invention, the other antifouling agent (D) includes other antifouling agents than the above-mentioned organic antifouling agent (B) and the other organic antifouling agent (B'). The organic antifouling agent (B), the other organic antifouling agent (B') and the other antifouling agent (D) will be collectively referred to as an antifouling agent.

As described above, the multilayer antifouling coating film of the present invention exhibits excellent antifouling performance owing to optimum utilization of the organic antifouling agent (B1) derived from the underlayer antifouling coating film (X), but especially when the upper-layer antifouling coating composition (y) contains any other antifouling agent (D), the antifouling performance of the multilayer antifouling coating film can be further more improved. In one aspect of the present invention, such an antifouling agent that is naturally required for attaining antifouling performance enough for use even in high-fouling environments can be saved, and the present invention attains the

effect of reducing emission of such an antifouling agent in external environments.

In the case where the underlayer coating composition (x) contains the other antifouling agent (D), the coating film can exhibit good antifouling performance in a situation where the coating film is required to have antifouling performance.

[0072]

Examples of the other antifouling agent (D) include cuprous oxide, copper oxide, copper (metal copper), copper thiocyanate (also called copper rhodanide), and metal pyrithiones such as copper pyrithione and zinc pyrithione; bisdimethyldithiocarbamoyl zinc ethylenebisdithiocarbamate (also called polycarbamate), zinc dimethyl dithiocarbamate (also called Ziram), and zinc ethylene bisdithiocarbamate. Above all, the coating composition preferably contains any of cuprous oxide, and metal pyrithiones such as copper pyrithione and zinc pyrithione.

Among these, cuprous oxide having an average particle size of approximately 0.1 to 30 μm is preferred since it can exhibit long-term antifouling performance; and cuprous oxide surface-treated with any of glycerol, stearic acid, lauric acid, sucrose, lecithin or mineral oil is preferred from the viewpoint of long-term stability in storage. Examples of commercial products of such cuprous oxide include NC-301 (manufactured by NC TECH Co., Ltd.), NC-803 (manufactured by NC TECH Co., Ltd.), Red Copp97N Premium (manufactured by AMERICAN CHEMET Co.), Purple Copp (manufactured by AMERICAN CHEMET Co.), and LoLoTint97 (manufactured by AMERICAN CHEMET Co.).

[0073]

One kind alone of the other antifouling agent (D) may be used or two or more kinds thereof may be used in combination.

In the present invention, in the case where the antifouling coating composition contains the other antifouling agent (D), the total content thereof can be selected in any desired manner from the viewpoint of the effect and the easy availability of the compound to be used, but from the viewpoint of bettering the antifouling performance and the physical properties of the multilayer antifouling coating film to be formed and from the viewpoint of reducing environmental load, the content is preferably 0.1 to 90% by mass based on the solid content of each antifouling coating composition.

In the case where the underlayer antifouling coating composition (x) or the

upper-layer antifouling coating composition (y) each contain cuprous oxide or copper rhodanide, the total content thereof is, based on the solid content of each coating composition, preferably 10 to 80% by mass, more preferably 30 to 70% by mass.

In the case where the underlayer antifouling coating composition (x) or the upper-layer antifouling coating composition (y) each contain zinc pyrithione or copper pyrithione, the total content thereof is, based on the solid content of each coating composition, preferably 0.5 to 30% by mass, more preferably 1 to 20% by mass.

[0074]

[Other pigment (E)]

The coating composition of the present invention may contain any other pigment (E) than the antifouling agent for the purpose of coloring a coating film, concealing a base, or adjusting to an appropriate coating strength.

Examples of the other pigment (E) include extender pigments such as zinc oxide, talc, mica, clay, potassium feldspar, calcium carbonate, kaolin, alumina white, white carbon, aluminum hydroxide, magnesium carbonate, barium carbonate, barium sulfate, calcium sulfate, and zinc sulfide; and color pigments such as Bengal red (red iron oxide), titanium white (titanium oxide), yellow iron oxide, carbon black, naphthol red, and phthalocyanine blue, and among these, zinc oxide or talc is preferably contained. One kind alone of these pigments may be used or two or more kinds thereof may be used in combination.

In the case where the coating composition of the present invention contains the other pigment (E), the preferred content thereof may be determined depending on the desired concealing performance of the formed antifouling coating film and on the desired viscosity of the antifouling coating composition, and is preferably 1 to 60% by mass based on the solid content of the coating composition.

[0075]

[Monocarboxylic acid compound (F)]

The coating composition of the present invention may contain a monocarboxylic acid compound (F).

In the present invention, the monocarboxylic acid compound (F) enhances the renewability of the formed coating film from the surface thereof in water. In the case where the coating film contains an antifouling agent, the discharge

thereof to water is accelerated by the monocarboxylic acid compound to facilitate the enhancement of the antifouling performance of the coating film, and furthermore the monocarboxylic acid compound has a function of imparting an appropriate water resistance to the coating film.

As the monocarboxylic acid compound (F), assuming that the monocarboxylic acid compound is represented by R-COOH, for example, R preferably represents a saturated or unsaturated aliphatic hydrocarbon group having 10 to 40 carbon atoms, a saturated or unsaturated alicyclic hydrocarbon group having 3 to 40 carbon atoms, or a group obtained by allowing these groups to have a substituent.

[0076]

Specifically, preferred examples thereof include abietic acid, neoabietic acid, dehydroabietic acid, palustric acid, isopimaric acid, pimaric acid, trimethylisobutenylcyclohexenecarboxylic acid, versatic acid, stearic acid, and naphthenic acid.

A rosin compound containing abietic acid, palustric acid, isopimaric acid, and the like as a major component is also preferred. Examples of the rosin compound include rosin, such as gum rosin, wood rosin, and tall oil rosin, a rosin derivative, such as hydrogenated rosin, disproportionated rosin, and a rosin metal salt, and pine tar.

Examples of the trimethylisobutenylcyclohexenecarboxylic acid include a reaction product of 2,6-dimethylocta-2,4,6-triene and methacrylic acid, which contains 1,2,3-trimethyl-5-(2-methylprop-1-en-1-yl)cyclohexa-3-ene-1-carboxylic acid and 1,4,5-trimethyl-2-(2-methylprop-1-en-1-yl)cyclohexa-3-ene-1-carboxylic acid as a major component (85% by mass or more).

[0077]

In the present invention, a part or all of the monocarboxylic acid compound (F) may form a metal ester. Examples of the metal ester include a zinc ester and a copper ester, which may be formed in advance before the production of the coating composition or may be formed through reaction with the other coating component in the production of the coating composition.

[0078]

One kind alone of the monocarboxylic acid compound (F) and/or a metal ester thereof may be used or two or more kinds thereof may be used in combination.

In the case where the coating composition of the present invention contains a monocarboxylic acid compound (F) and/or a metal ester thereof, from the viewpoint of the coating workability with the coating composition or of the water resistance of the antifouling coating film, the content thereof based on the solid content of the coating composition is preferably 0.1 to 50% by mass, and more preferably 1 to 20% by mass.

[0079]

[Dehydrating Agent (G)]

The coating composition of the present invention may contain a dehydrating agent (G) for the purpose of enhancing the storage stability thereof. Examples of the dehydrating agent (G) include synthetic zeolite, anhydrate gypsum (calcium sulfate), and hemihydrate gypsum (also called calcined gypsum) as an inorganic dehydrating agent; and alkoxysilanes such as tetramethoxysilane, tetraethoxysilane, tetrabutoxysilane, tetraphenoxysilane, methyltriethoxysilane, dimethyldiethoxysilane, and trimethylethoxysilane, or condensation products thereof, and alkyl orthoformates such as methyl orthoformate and ethyl orthoformate, as an organic dehydrating agent. One kind alone of the dehydrating agent (G) may be used, or two or more kinds thereof may be used in combination.

In the case where the coating composition of the present invention contains the dehydrating agent (G), the content thereof is preferably 0.1 to 20% by mass based on the solid content of the coating composition, and more preferably 0.2 to 15% by mass.

[0080]

[Plasticizer (H)]

The coating composition of the present invention may contain a plasticizer (H) for the purpose of imparting plasticity to the antifouling coating film.

Examples of the plasticizer (H) include tricresyl phosphate (TCP), dioctyl phthalate (DOP), and diisodecyl phthalate (DIDP). One kind alone of the plasticizer may be used or two or more kinds thereof may be used in combination.

In the case where the coating composition of the present invention contains the plasticizer (H), the content thereof is preferably 0.1 to 10% by mass based on the solid content of the coating composition, and more preferably 0.5 to 5% by mass. In the case where the content of the plasticizer (H) is in the range, the plasticity of the coating film can be kept good.

[0081]

[Anti-sagging agent/anti-settling agent (I)]

The coating composition of the present invention may contain an anti-sagging agent/anti-settling agent (I) for the purpose of controlling the viscosity of the coating composition.

Examples of the anti-sagging agent/anti-settling agent (I) include organoclay wax (such as stearate salts, lecithin salts, and alkyl sulfonates of Al, Ca, and Zn), organic wax (such as polyethylene wax, oxidized polyethylene wax, amide wax, polyamide wax, and hydrogenated castor oil wax), a mixture of organoclay wax and organic wax, and synthetic fine powder silica.

The anti-sagging agent/anti-settling agent (I) used may be a commercially available product, and examples thereof include "Disparlon 305", "Disparlon 4200-20", "Disparlon A630-20X", and "Disparlon 6900-20X" all manufactured by Kusumoto Chemicals, Ltd., and "A-S-A D-120", manufactured by Itoh Oil Chemicals, Co., Ltd.

[0082]

One kind alone of the anti-sagging agent/anti-settling agent (I) may be used or two or more kinds thereof may be used in combination.

In the case where the coating composition of the present invention contains the anti-sagging agent/anti-settling agent (I), the content thereof is preferably 0.1 to 10% by mass based on the solid content of the coating composition, and more preferably 0.2 to 3% by mass.

[0083]

[Binder component (J)]

The coating composition of the present invention may contain a binder component (J) for the purpose of imparting water resistance, crack resistance and strength to the formed antifouling coating film.

Examples of the binder component (J) include a chlorinated paraffin, an n-paraffin, a polyester polymer, a terpene phenol resin, a petroleum resin, and a ketone resin. Among these, a chlorinated paraffin, a polyester polymer and a petroleum resin are preferred.

One kind alone of the binder component (J) may be used or two or more kinds thereof may be used in combination.

[0084]

The chlorinated paraffin may have any of a linear or branched molecular

structure, and may be liquid or solid (for example, powdery) at room temperature (e.g., 23°C).

Preferably, the chlorinated paraffin has 8 to 30 carbon atoms, more preferably 10 to 26 carbon atoms on average in one molecule. The antifouling coating composition containing such a chlorinated paraffin can form an antifouling coating film that may hardly crack (break) or peel. When the average carbon number is less than 8, the effect of preventing the coating film from cracking will be insufficient.

The viscosity of the chlorinated paraffin (measurement temperature 25°C) is preferably 1 poise or more, more preferably 1.2 poise or more, and the specific gravity (25°C) thereof is preferably 1.05 to 1.80 g/cm³, more preferably 1.10 to 1.70 g/cm³.

The chlorination degree (chlorine content) of the chlorinated paraffin is generally 35 to 70 parts by mass based on the chlorinated paraffin as 100 parts by mass, preferably 35 to 65 parts by mass. The coating composition containing a chlorinated paraffin having such a chlorination degree can form a coating film that may hardly crack (break) or peel.

[0085]

The polyester polymer is obtained through reaction of one or more polyalcohols, one or more polycarboxylic acids and/or anhydrides thereof, and optionally any other component, for which any kinds of components may be used in any desired amount, and depending on the combination thereof, the hydroxyl value/acid value and the viscosity of the resultant polymer can be controlled.

Examples of the polyalcohol include propylene glycol, glycerol, ethylene glycol, neopentyl glycol, 1,6-hexanediol, trimethylolpropane (TMP), pentaerythritol, sorbitol; and polyalkylene glycol such as diethylene glycol. From easy availability of raw materials, propylene glycol, ethylene glycol, neopentyl glycol, glycerol and TMP are preferred. Two or more kinds of such polyalcohols may be used in combination.

Examples of the polycarboxylic acid and/or anhydride thereof include malonic acid, maleic acid, fumaric acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, 1,9-nonamethylenedicarboxylic acid, 1,10-decamethylenedicarboxylic acid, 1,11-undecamethylenedicarboxylic acid, 1,12-dodecamethylenedicarboxylic acid, cyclohexanedicarboxylic acid, decahydronaphthalenedicarboxylic acid, terephthalic acid, isophthalic acid,

phthalic acid, hexahydrophthalic acid, succinic acid, and anhydrides thereof. Phthalic anhydride, adipic acid, isophthalic acid and hexahydrophthalic anhydride are preferred.

From the viewpoint of the storage stability of the coating composition, the antifouling performance of the coating film and the imparting suitable hydrophilicity to the film, the hydroxyl value of the solid content of the polyester polymer is preferably 50 to 150 mgKOH/g, more preferably 80 to 120 mgKOH/g.

Dissolved in a solvent, the polyester polymer may be used as a solution thereof (hereinafter this may be referred to as a polyester polymer solution). As the solvent, those mentioned for the organic solvent (C1) may be used.

From the viewpoint of reducing the viscosity of the coating composition, the polyester polymer solution preferably has 3,000 mPa·s or less at 25°C, more preferably 1,000 mPa·s or less.

The polyester polymer solution may contain unreacted raw materials.

The petroleum resin includes C5-base, C9-base, styrene-base and dichloropentadiene-base resins, and hydrogenated products thereof.

[0086]

Commercial products may be used for the binder component (J), and examples thereof include "Toyoparax C-70/A-50/A-70/A-145/A-150/150" by Tosoh Corporation for the chlorinated paraffin; "Teslac 2474" by Hitachi Chemical Company, Ltd. for the polyester polymer; and "Quintone 1500" and "Quintone 1700" both by Zeon Corporation for the petroleum resin.

In the case where the coating composition of the present invention contains the binder component (J), the content thereof is preferably 0.1 to 10% by mass based on the solid content of the coating composition.

[0087]

(Production method for underlayer antifouling coating composition (x) and upper-layer antifouling coating composition (y))

The underlayer antifouling coating composition (x) and the upper-layer antifouling coating composition (y) of the present invention can be produced using the same apparatus and method as those for known ordinary coating materials.

Specifically, the upper-layer antifouling coating composition (y) can be produced by preparing a hydrolyzable polymer (A2), and then adding a solution of the hydrolyzable polymer (A2) and an organic solvent (C2) and optionally any other additive components all at a time or sequentially, stirring and mixing.

[0088]

(Preferred combination of underlayer antifouling coating composition (x) and upper-layer antifouling coating composition (y))

In the present invention, the underlayer antifouling coating composition (x) and the upper-layer antifouling coating composition (y) may be in any of the following embodiments (i) to (vii). In addition, the underlayer antifouling coating composition (x) or the upper-layer antifouling coating composition (y) may contain, as the hydrolyzable polymer (A), both a hydrolyzable polymer having a constituent unit derived from a silyl ester group-containing monomer and a hydrolyzable polymer having a constituent unit derived from a metal ester group-containing monomer.

(i) The hydrolyzable polymer (A) that the underlayer antifouling coating composition (x) and the upper-layer antifouling coating composition (y) contain each has a constituent unit derived from a silyl ester group-containing monomer (a11).

(ii) The hydrolyzable polymer (A) that the underlayer antifouling coating composition (x) and the upper-layer antifouling coating composition (y) contain each has a constituent unit derived from a metal ester group-containing monomer (a12).

(iii) The hydrolyzable polymer (A1) that the underlayer antifouling coating composition (x) contains has a constituent unit derived from a silyl ester group-containing monomer (a11), and the hydrolyzable polymer (A2) that the upper-layer antifouling coating composition (y) contains has a constituent unit derived from a metal ester group-containing monomer (a12).

(iv) The hydrolyzable polymer (A1) that the underlayer antifouling coating composition (x) contains has a constituent unit derived from a metal ester group-containing monomer (a12), and the hydrolyzable polymer (A2) that the upper-layer antifouling coating composition (y) contains has a constituent unit derived from a silyl ester group-containing monomer (a11).

[0089]

Especially preferably, the underlayer antifouling coating composition (x) and the upper-layer antifouling coating composition (y) are in any of the following embodiments (v) to (vii).

(v) The underlayer antifouling coating composition (x) contains 4-bromo-2-(4-chlorophenyl)-5-(trifluoromethyl)-1H-pyrrole-3-carbonitrile as the

organic antifouling agent (B1), and the hydrolyzable polymer (A2) that the upper-layer antifouling coating composition (y) contains has a constituent unit derived from a metal ester group-containing monomer (a12).

(vi) The underlayer antifouling coating composition (x) contains 4,5-dichloro-2-n-octyl-4-isothiazolin-3-one as the organic antifouling agent (B1), and the hydrolyzable polymer (A2) that the upper-layer antifouling coating composition (y) contains has a constituent unit derived from a metal ester group-containing monomer (a12).

(vii) The underlayer antifouling coating composition (x) contains 4,5-dichloro-2-n-octyl-4-isothiazolin-3-one as the organic antifouling agent (B1), and the hydrolyzable polymer (A2) that the upper-layer antifouling coating composition (y) contains has a constituent unit derived from a silyl ester group-containing monomer (a11).

[0090]

In any of the above-mentioned embodiments, as described above, preferably, the upper-layer antifouling coating composition (y) does not substantially contain an organic antifouling agent (B2) and any other organic antifouling agent (B'2), and more preferably does not contain them, from the viewpoint of preventing the upper-layer antifouling coating film from having a poor appearance.

Among the above-mentioned embodiments, preferred is one (the embodiment (ii)) where the hydrolyzable polymer that the underlayer antifouling coating composition (x) and the upper-layer antifouling coating composition (y) contains each has a constituent unit derived from a metal ester group-containing monomer. In the case of the embodiment (ii), preferably, the upper-layer antifouling coating composition (y) does not contain an organic antifouling agent (B2) and any other organic antifouling agent (B'2), and in addition thereto, also does not contain any other antifouling agent (D), from the viewpoint of interlayer adhesiveness.

[0091]

(Production method for substrate with multilayer antifouling coating film)

A method for producing a substrate with a multilayer antifouling coating film includes a step of applying an underlayer antifouling coating composition (x) onto a substrate to form an underlayer antifouling coating film (X) thereon, and a step of applying an upper-layer antifouling coating composition (y) onto the

underlayer antifouling coating film (X) to form an upper-layer antifouling coating film (Y) thereon.

As the underlayer antifouling coating composition (x) and the upper-layer antifouling coating composition (y), the above-mentioned underlayer antifouling coating composition (x) and the upper-layer antifouling coating composition (y) are used.

[0092]

The method of applying an underlayer antifouling coating composition (x) onto a substrate is not specifically limited, and the composition may be applied onto a substrate according to a known method such as a method of using a brush, a roller or a spray.

The applied underlayer antifouling coating composition (x) is dried to form an underlayer antifouling coating film (X). The underlayer antifouling coating composition (x) that has been applied according to the above-mentioned method is left, for example, under a condition of 25°C, preferably for 1 hour to 14 days or so, more preferably 1 day to 7 days or so to be dried to form an underlayer antifouling coating film (X). Drying the underlayer antifouling coating composition (x) may be carried out with blowing under heat.

[0093]

The thickness of the underlayer antifouling coating film (X) may be arbitrarily selected depending on the antifouling performance and the coating film strength demanded of the underlayer antifouling coating film (X) and a period of use, and is preferably 10 to 1,000 μm or so, but from the viewpoint of antifouling performance of the multilayer antifouling coating film, easiness in coating film formation and resource saving, the thickness is more preferably 50 to 400 μm , even more preferably 70 to 200 μm .

As a method for forming the underlayer antifouling coating film (X) having the thickness, there may be mentioned a method of applying the underlayer antifouling coating composition (x) once or more to a thickness per one-time applying of preferably 10 to 300 μm . In the case where the underlayer antifouling coating film (X) is formed by applying the underlayer antifouling coating composition (x) more than once, two or more underlayer antifouling coating compositions (x) differing in point of the compositional formulation may be layered.

[0094]

The substrate to which the underlayer antifouling coating composition (x) is applied may be previously coated with a coating film such as a primer layer, or may be roughened by sand blasting treatment, and the kind of the coating film with which the underlayer antifouling coating film (X) is to be kept in direct contact is not specifically limited.

[0095]

The method for producing a substrate with a multilayer antifouling coating film of the present invention includes a step applying an upper-layer antifouling coating composition (y) onto the underlayer antifouling coating film (X) formed on the substrate, to thereby form an upper-layer antifouling coating film (Y) thereon.

The method of applying an upper-layer antifouling coating composition (y) is not specifically limited, and the composition may be applied according to the same method as that for applying the above-mentioned underlayer antifouling coating composition (x), and the applied upper-layer antifouling coating composition (y) is dried to form an upper-layer antifouling coating film (Y). The drying condition for the upper-layer antifouling coating composition (y) is not specifically limited, but preferably, the drying condition is such that the coated substrate is kept under a condition of higher than 0°C for a period of from coating with the upper-layer antifouling coating composition (y) to before the use thereof, and more preferably under a condition of higher than 10°C for such a period of time. Under the drying condition, the resulting multilayer antifouling coating film can have a good appearance, and can exhibit good physical properties and antifouling performance.

The drying of the upper-layer antifouling coating composition (y) may be carried out, for example, under the condition of an average temperature of 25°C generally for 1 hour to 14 days, preferably 1 to 7 days or so, and the drying may be carried out with heating or blowing.

[0096]

Prior to coating with the upper-layer antifouling coating composition (y), the underlayer antifouling coating film (X) may be pretreated for surface roughening with a sand paper or for surface washing with high-pressure water, and so far as the requirements for the present invention are satisfied, a fresh upper-layer antifouling coating composition (y) may be newly applied onto the underlayer antifouling coating film (X) on which the upper-layer antifouling

coating film (Y) of the multilayer antifouling coating film of the present invention has been completely worn away and the underlayer antifouling coating film (X) has been exposed out, or onto the antifouling coating film that has been already used for a certain period of time for antifouling undersea, thereby to newly form a multilayer antifouling coating film.

[0097]

The thickness of the upper-layer antifouling coating film (Y) may be arbitrarily selected depending on the renewal rate of the upper-layer antifouling coating film (Y) and a period of use, and is preferably 40 to 1,500 μm or so, but from the viewpoint of antifouling performance and coating film strength of the multilayer antifouling coating film, and easiness in coating film formation, the thickness is more preferably 60 to 800 μm , even more preferably 80 to 600 μm . As a method for forming the coating film having the thickness, there may be mentioned a method of applying the upper-layer antifouling coating composition (y) once or more to a thickness per one-time applying of preferably 30 to 500 μm , more preferably 50 to 200 μm .

[0098]

The substrate with a multilayer antifouling coating film of the present invention can be produced by forming the above-mentioned multilayer antifouling coating film on a substrate according to the above-mentioned method.

The multilayer antifouling coating film of the present invention can be utilized for retaining the antifouling performance of a substrate for a prolonged period of time in a wide range of industrial fields including ships, fishery, marine structures, and the like. Examples of the substrate include a ship (such as an outside shell of a ship's hull of a large scale steel-hulled ship, e.g., a container ship and a tanker, a fishing boat, an FRP boat, a wooden boat, a yacht, and the like, and a newly built ship and a repaired ship), a fishing material (such as a rope, a fishing net, a fishing gear, a float, and a buoy), and a marine structure, such as a mega-float. Among these, the substrate is preferably selected from the group consisting of a ship, an underwater structure, and a fishing gear, is more preferably selected from the group consisting of a ship and an underwater structure, and is further preferably a ship.

[0099]

[Antifouling method, coating material kit for forming multilayer antifouling coating film, and upper-layer antifouling coating composition]

The antifouling method of the present invention uses the multilayer antifouling coating film mentioned above, and is a method for antifouling by providing the multilayer antifouling coating film of the present invention on various substrates.

The coating material kit for forming a multilayer antifouling coating film of the present invention includes at least the above-mentioned underlayer antifouling coating composition (x) and the upper-layer antifouling coating composition (y). The coating material kit for forming a multilayer antifouling coating film of the present invention may be a kit of three or more coating compositions prepared by combining the underlayer antifouling coating composition (x) and the upper-layer antifouling coating composition (y) and, in addition thereto, a primer layer forming coating composition.

Further, the upper-layer antifouling coating composition of the present invention is the above-mentioned upper-layer antifouling coating composition (y), and is favorably used for forming an upper-layer antifouling coating film (Y) on an underlayer antifouling coating film (X) formed of an underlayer antifouling coating composition (x).

Examples

[0100]

The present invention will be described more specifically with reference to examples below, but the present invention is not whatsoever limited to the examples. In the following, the "part" means part by mass as long as it does not counter the spirit of the present invention.

The "solid contents" of the components used in the examples each mean a component obtained from removal of the volatile component contained as a solvent from the component, and mean a component that is obtained by drying the component in a hot air dryer at 125°C for 1 hour.

[0101]

[Production of hydrolyzable polymer (A)]

<Production Example 1: Production of hydrolyzable polymer solution (A-1)>

43 parts by mass of xylene, 10 parts by mass of triisopropylsilyl methacrylate and 2 parts by mass of KF-2001 (by Shin-Etsu Chemical Co., Ltd.) were put into a reaction vessel equipped with a stirrer, a condenser, a thermometer, a dropping device, a nitrogen introducing tube, and a heating and

cooling jacket, and heated with stirring under a temperature condition of $80 \pm 5^{\circ}\text{C}$ in a nitrogen stream atmosphere. While kept at the temperature, a mixture of 50 parts by mass of triisopropylsilyl methacrylate, 8 parts by mass of KF-2001 (by Shin-Etsu Chemical Co., Ltd.), 25 parts by mass of 2-methoxyethyl methacrylate, 5 parts by mass of methyl methacrylate and 2.0 parts by mass of 2,2'-azobisisobutyronitrile (AIBN) was dropwise added to the reaction vessel through the dropping device over 2 hours. Subsequently, this was stirred at the temperature for 2 hours, and then 0.4 parts by mass of AIBN was added thereto and heated up to 105°C over 3 hours, and thereafter 24 parts by mass of xylene was added to give a colorless transparent hydrolyzable polymer solution (A-1).

The formulation of the monomer mixture used, and the characteristic values of the hydrolyzable polymer solution (A-1) are shown in Table 1.

[0102]

<Production Examples 2 to 4: Production of hydrolyzable polymer solutions (A-2) to (A-4)>

Hydrolyzable polymer solutions (A-2) to (A-4) were produced in the same manner as in Production Example 1 except that the charging ratio of the monomer mixture used in Production Example 1, the kind and the amount of the polymerization initiator used in dropwise adding and the charging order were appropriately adjusted.

The constitution of the monomer mixture used, and the characteristic values of the hydrolyzable polymer solutions (A-2) to (A-4) and the polymers contained therein, as measured according to the methods described below, are shown in Table 1.

[0103]

Table 1 - Production Examples (silyl ester group-containing hydrolyzable polymer solutions)

			Production Example 1	Production Example 2	Production Example 3	Production Example 4
			(A-1)	(A-2)	(A-3)	(A-4)
Monomer Mixture	Silyl ester group-containing monomer (a11)	triisopropylsilyl methacrylate	60.0	60.0	45.0	50.0
		triisopropylsilyl acrylate			30.0	
	Other Monomers (a2)	KF-2001* ¹	10.0			
		FM-0711* ²				10.0
		2-methoxyethyl acrylate		15.0		
		2-methoxyethyl methacrylate	25.0			20.0
		methyl methacrylate	5.0	25.0	20.0	20.0
Total (parts by mass)		100.0	100.0	100.0	100.0	
Physical Properties	Solid content (% by mass)		59.2	60.4	60.6	59.2
	Viscosity (mPa·s/25°C)		709	2,473	2,690	1,839
	Number-average molecular weight (Mn)		4,600	10,100	9,700	7,900
	Weight-average molecular weight (Mw)		38,500	40,300	49,200	36,360

[0104]

The components in Table 1 are as follows.

*1 KF-2001: by Shin-Etsu Chemical Co., Ltd., side chain mercaptoalkyl-modified organopolysiloxane, functional group equivalent = 1,900 g/mol

*2 FM-0711: by JNC Corporation, one-terminal methacryloyloxyalkyl-modified organopolysiloxane, number-average molecular weight Mn = 1,000

[0105]

Measurement methods of the viscosity of the resultant polymer solutions (A-1) to (A-4), and the number-average molecular weight (Mn) and the weight-average molecular weight (Mw) of the polymers contained in the solutions are as mentioned below.

(Viscosity of Polymer Solution)

The viscosity at 25°C of the polymer solution was measured using an E-type viscometer (manufactured by Toki Sangyo Co., Ltd.).

[0106]

(Measurement of Number-Average Molecular Weight (Mn) and Weight-Average Molecular Weight (Mw) of Polymer)

The number-average molecular weight (Mn) and the weight-average

molecular weight (Mw) of the polymer were measured through GPC (gel permeation chromatography) under the condition mentioned below.

GPC Condition

Apparatus: "HLC-8120GPC", manufactured by Tosoh Corporation

Columns: "Super H2000+H4000", manufactured by Tosoh Corporation, 6 mm (inner diameter), each 15 cm (length)

Eluent: tetrahydrofuran (THF)

Flow Rate: 0.500 ml/min

Detector: RI

Column thermostat chamber temperature: 40°C

Standard Material: polystyrene

Sample Preparation Method: A small amount of calcium chloride was added to the polymer solution prepared in each Production Example for dehydration, then filtered through a membrane filter, and the filtered solution was a sample for GPC measurement.

[0107]

<Production Examples 5 to 7: Hydrolyzable polymer solutions (A-5) to (A-7)>

[Production Example M1: Production of metal ester group-containing monomer mixture (a12-1)]

85.4 parts of PGM (propylene glycol monomethyl ether) and 40.7 parts of zinc oxide were put into a four-neck flask equipped with a condenser, a thermometer, a dropping funnel and a stirrer, and heated up to 75°C with stirring. Subsequently, a mixture of 43.1 parts of methacrylic acid, 36.1 parts of acrylic acid, and 5 parts of water was added dropwise thereto through the dropping funnel at a constant dropping rate over 3 hours. Further, this was stirred for 2 hours, and then 36 parts of PGM was added thereto to give a transparent metal ester group-containing monomer mixture (a12-1). The solid content was 44.8% by mass.

[0108]

<Production Example 5: Production of hydrolyzable polymer solution (A-5)>

15 parts of PGM, 65 parts of xylene, and 4 parts of ethyl acrylate were put into a four-neck flask equipped with a condenser, a thermometer, a dropping funnel and a stirrer, and heated up to 100°C with stirring. Subsequently, a transparent mixture of 32.3 parts of methyl methacrylate, 13.9 parts of ethyl acrylate, 40 parts of FM-0711 (product name, manufactured by JNC Corporation),

21.7 parts of the metal ester group-containing monomer mixture (a12-1) in Production Example M1, 10 parts of xylene, 1.2 parts of a chain transfer agent (Nofmer MSD (product name) manufactured by NOF Corporation, α -methylstyrene dimer), 2.5 parts of AIBN, and 0.8 parts of 2,2'-azobis(2-methylbutyronitrile) (AMBN) was dropwise added thereto through the dropping funnel at a constant rate over 6 hours. After dropwise addition, 0.5 parts of tert-butyl peroctoate and 10 parts of xylene were dropwise added over 30 minutes, and further stirred for 1 hour and 30 minutes, and thereafter 10.1 parts of xylene was added to give a pale yellow transparent hydrolyzable polymer solution (A-5).

[0109]

<Production Example 6: Production of hydrolyzable polymer solution (A-6)>

15 parts of PGM, 65 parts of xylene, and 4 parts of ethyl acrylate were put into a four-neck flask equipped with a condenser, a thermometer, a dropping funnel and a stirrer, and heated up to 100°C with stirring. Subsequently, a transparent mixture of 32.3 parts of methyl methacrylate, 43.9 parts of ethyl acrylate, 10 parts of FM-0721 (product name, manufactured by JNC Corporation), 21.7 parts of the metal ester group-containing monomer mixture (a12-1) in Production Example M1, 10 parts of xylene, 1.2 parts of a chain transfer agent (Nofmer MSD (product name) manufactured by NOF Corporation, α -methylstyrene dimer), 2.5 parts of AIBN, and 3 parts of AMBN was dropwise added thereto through the dropping funnel at a constant rate over 6 hours. After dropwise addition, 0.5 parts of t-butyl peroctoate and 10 parts of xylene were dropwise added over 30 minutes, and further stirred for 1 hour and 30 minutes, and thereafter 10.1 parts of xylene was added to give a pale yellow transparent hydrolyzable polymer solution (A-6).

[0110]

<Production Example 7: Production of hydrolyzable polymer solution (A-7)>

15.0 parts of PGM, 60.0 parts of xylene, and 4.0 parts of ethyl acrylate were put into a reactor equipped with a stirrer, a condenser, a thermometer, a dropping device, a nitrogen introducing duct and a heating-cooling jacket, and heated up to $100 \pm 5^\circ\text{C}$ with stirring. While kept at the temperature, a mixture of 40.2 parts of the metal ester group-containing monomer mixture (a12-1) obtained in Production Example M1, 15.0 parts of methyl methacrylate, 48.0 parts of ethyl acrylate, 15.0 parts of n-butyl acrylate, 2.5 parts of a polymerization

initiator AIBN, 6.5 parts of a polymerization initiator AMBN, 1.2 parts of a chain transfer agent "Nofmer MSD" and 10.0 parts of xylene was dropwise added to the reactor through the dropping device over 6 hours. After dropwise addition, 0.5 parts of a polymerization initiator, t-butyl peroctoate and 7.0 parts of xylene were dropwise added over 30 minutes, and further stirred for 1 hour and 30 minutes, and thereafter 8.0 parts of xylene was added to give a pale yellow transparent hydrolyzable polymer solution (A-7).

The constitutions of the monomer components of the hydrolyzable polymer solutions (A-5) to (A-7) and the characteristic values of the hydrolyzable polymer solutions (A-5) to (A-7) are summarized in Table 2. The viscosity, the number-average molecular weight, and the weight-average molecular weight were measured like those of the hydrolyzable polymer solution (A-1), and the zinc content (% by mass) was measured with an atomic absorption spectrophotometer (by Shimadzu Corporation, AA6800 (product name)).

[0111]

Table 2 - Production Examples (metal ester group-containing hydrolyzable polymer solutions)

			Production Example 5	Production Example 6	Production Example 7
			(A-5)	(A-6)	(A-7)
Monomer Mixture	Metal Ester Group-Containing Monomer (a12) (The unparenthesized numerical value is part by mass of the reaction liquid, and the parenthesized numerical value is part by mass of monomer.)	Monomer- containing mixture (a12-1)	21.7 (9.7)	21.7 (9.7)	40.2 (18.1)
	Other Monomers (a2)	FM-0711*2	40.0		
		FM-0721*3		10.0	
		methyl methacrylate	32.3	32.3	15.0
		ethyl acrylate	17.9	47.9	52.0
Physical Properties	Solid content (% by mass)		45.1	45.7	46.4
	Viscosity (mPa·s/25°C)		6,100	4,900	400
	Zinc content (% by mass)		1.3	1.3	2.5
	Number-average molecular weight (Mn)		1,450	1,120	900
	Weight-average molecular weight (Mw)		8,800	6,800	5,200

[0112]

The components in Table 2 are as follows.

*2 FM-0711: by JNC Corporation, one-terminal methacryloyloxyalkyl-modified organopolysiloxane, number-average molecular weight $M_n = 1,000$

*3 FM-0721: by JNC Corporation, one-terminal methacryloyloxyalkyl-modified organopolysiloxane, number-average molecular weight $M_n = 5,000$

[0113]

[Production of underlayer antifouling coating composition (x), upper-layer antifouling coating composition (y), and multilayer antifouling coating film]

Constituent components:

The constituent components used in an underlayer antifouling coating composition (x) and an upper-layer antifouling coating composition (y) are shown in Table 3.

[0114]

Table 3 (1/2) · List of Components

		Components	Manufacturing Companies, Product Names, Chemical Formulae, and Characteristics	Abbreviations
(B)	Organic Antifouling Agent	tralopyril	by Janssen PMP, "Econea Technical" chemical name: 4-bromo-2-(4-chlorophenyl)-5-(trifluoromethyl)-1H-pyrrole-3-carbonitrile	EC
		DCOIT	by Rohm & Haas Japan, "SEA NINE 211N" chemical name: 4,5-dichloro-2-n-octyl-4-isothiazolin-3-one solid content 30% by mass xylene solution	SN
(B')	Other Organic Antifouling Agent	PK	by Hokko Chemical Industry Co., Ltd. chemical name: pyridine triphenylborane	PK
		medetomidine	by I-Tech AB, "Selektope" chemical name: (+/-)-4-[1-(2,3-dimethylphenyl)ethyl]-1H-imidazole	MD
(C)	Organic Solvent	xylene	-	Xy
		propylene glycol monomethyl ether	-	PGM
		n-butanol	-	NBA
		n-butyl acetate	-	NAC
		isobutyl acetate	-	IAC
		2-heptanone	-	HPN
(D)	Other Antifouling Agent	cuprous oxide	by NC Tech Co., Ltd., "Cuprous oxide NC-301"	-
		copper pyrithione	by Arch UK Biocides Ltd., "Copper Omadine Powder" chemical formula: $\text{Cu}(\text{-S-C}_5\text{H}_4\text{N-O-})_2$	-
		zinc pyrithione	by Arch UK Biocides Ltd., "Zinc Omadine Powder" chemical formula: $\text{Zn}(\text{-S-C}_5\text{H}_4\text{N-O-})_2$	-

[0115]

Table 3 (2/2) - List of Components

		Components	Manufacturing Companies, Product Names, Chemical Formulae, and Characteristics	Abbreviations
(E)	Other Pigments	zinc oxide	by Hokusui Tech Co., Ltd. "Zinc Oxides JIS#3"	-
		talc	by Takehara Kagaku Kogyo Co., Ltd. "TTK Talc"	-
		titanium oxide	by Ishihara Sangyo Kaisha, Ltd. "Tipaque PFC105"	-
		red iron oxide	by Morishita Bengara Kogyo Co., Ltd. "Bengara No. 404"	-
(F)	Monocarboxylic Acid Compound	rosin	WW rosin (made in China)	-
		versatic acid	by Japan Epoxy Resin "Versatic 10", neodecanoic acid	-
(G)	Dehydrating Agent	calcium sulfate	-	-
		alkoxysilane	by Colcoat Co., Ltd. "Ethyl Silicate 28"	-
(H)	Plasticizer	TCP	by Kyowa Hakko Kogyo Kabushiki Kaisha tricresyl phosphate	-
(I)	Anti-Sagging Agent/ Anti-Settling Agent	fatty acid amide wax	by Kusumoto Chemicals, Ltd. "Disperlon 6900-20X" solid content 20% by mass xylene dispersion	-
(J)	Binder Component	chlorinated paraffin	by Tosoh Corporation "Toyoparax 150"	-
		polyester polymer	by Hitachi Chemical Company, Ltd. "Teslac 2474", Mn 2,000 constituent component: neopentyl glycol/ ethylene glycol/isophthalic acid/adipic acid hydroxyl value 120 mgKOH/g	-
(K)	Epoxy Resin	#1001 epoxy resin	by Mitsubishi Chemical Corporation, "jER 001-75X" bisphenol A-type epoxy resin epoxy equivalent 450 to 500 solid content 75% by mass xylene solution	-
(L)	Epoxy Resin Curing Agent	amine-type curing agent 1	by DIC Corporation, "Luckamide TD966" polyamidoamine, active hydrogen equivalent 380 g/eq	-
		amine-type curing agent 2	by Air Products and Chemicals, Inc. "Ancamine 2432" modified aliphatic polyamine (containing MXDA) amine value 370	-

[0116]

Both tralopyril and DCOIT are soluble in xylene and propylene glycol monomethyl ether. The solubility of tralopyril was 1 g/L or more in xylene, and 100 g/L or more in propylene glycol monomethyl ether; DCOIT was 100 g/L or more in xylene and propylene glycol monomethyl ether.

[0117]

<Production of underlayer antifouling coating composition (x) and upper-layer antifouling coating composition (y)>

At the blending ratio (parts by mass) shown in Table 4 and Table 5, the constituent components were mixed with stirring to give an underlayer antifouling coating composition (x) and an upper-layer antifouling coating composition (y). The blending amount of each component shown in Table 4 and Table 5 indicates the blending amount on a wet-weight basis thereof. For example, in the upper-layer antifouling coating composition (y-1), the blending amount of the fatty acid amide wax on a wet-weight basis thereof (as a whole) is 2.0 parts by mass and the solid content thereof is 20%, and therefore the blending amount of the fatty acid amide wax itself as an active ingredient is 0.4 parts by mass.

The upper-layer antifouling coating composition (y-9) was a silicone coating composition (product name "CMP Bioclean HB", by Chugoku Marine Paints, Ltd., not containing a hydrolyzable polymer (A) and an organic antifouling agent (B)), and the underlayer antifouling coating composition (x-8) was prepared by mixing 3 parts by mass of tralopyril and 10 parts by mass of 2-heptanone with 100 parts by mass of the upper-layer antifouling coating composition (y-9).

[0118]

Table 4 - Underlayer Antifouling Coating Composition (x)

				Underlayer Antifouling Coating Composition						
				x-1	x-2	x-3	x-4	x-5	x-6	x-7
Blending Amount (part by mass)		(A) *4	hydrolyzable polymer (A-1) (solid content 59.2%)		22.0	22.0				
			hydrolyzable polymer (A-6) (solid content 45.7%)				34.0	34.0		
			hydrolyzable polymer (A-7) (solid content 46.4%)						36.0	36.0
		(B)	tralopyril	6.0					6.0	
			DCOIT (solid content 30%)		5.0		3.0			
		(B')	medetomidine				0.1			
		(C)	xylene	5.0	12.0	15.5	5.9	7.0	9.0	9.0
			propylene glycol monomethyl ether	5.0			3.0	3.0	3.0	3.0
			2-heptanone	9.0						
		(D)	cuprous oxide		40.0	41.5	30.0	32.0		
			copper pyrithione		2.0	2.0	2.0	2.0		
			zinc pyrithione						6.0	
		(E)	zinc oxide	5.0	5.0	5.0	10.0	10.0	22.0	28.0
			talc	19.0	5.0	5.0	3.0	3.0	8.0	8.0
			titanium oxide	2.0			1.0	1.0		
			red iron oxide		2.0	2.0	3.0	3.0	3.0	3.0
		(F)	rosin		5.0	5.0				
			versatic acid						1.5	1.5
		(G)	alkoxysilane		0.5	0.5				
		(I)	fatty acid amide wax (solid content 20%)	5.0	1.5	1.5	5.0	5.0	3.5	3.5
		(J)	chlorinated paraffin	2.0					2.0	2.0
		(K)	#1001 epoxy resin (solid content 75%)	29.0						
		Curing Agent Component	(L)	amine-type curing agent 1	4.0					
	amine-type curing agent 2			4.0						
	(C)		xylene	3.0						
			propylene glycol monomethyl ether	2.0						
			Total (part by mass)	100.0	100.0	100.0	100.0	100.0	100.0	94.0
	Solid Ratio (% by mass) of Coating Composition				64.8	74.3	74.3	66.5	67.5	65.9
Component (A)	component (A) (as code name) in coating composition			-	A-1	A-1	A-6	A-6	A-7	A-7
	total content (% by mass) of component (A) based on solid content of coating composition			0.0	17.5	17.5	23.4	23.0	25.3	27.9
Components (B) and (B')	component (B) and component (B') (as code name) in coating composition			EC	SN	-	SN MD	-	EC	-
	total content (% by mass) of component (B) and component (B') based on solid content of coating composition			9.3	2.0	0.0	1.5	0.0	9.1	0.0

*4: Containing the organic solvent (C) used in producing the component (A).

[0119]

Table 5 - Upper-Layer Antifouling Coating Composition (y)

			Upper-Layer Antifouling Coating Composition							
			y-1	y-2	y-3	y-4	y-5	y-6	y-7	y-8
Blending Amount (part by mass)	(A) *4	hydrolyzable polymer (A-2) (solid content 60.4%)	30.0							
		hydrolyzable polymer (A-3) (solid content 60.6%)		22.0						
		hydrolyzable polymer (A-4) (solid content 59.2%)			20.0					
		hydrolyzable polymer (A-5) (solid content 45.1%)				75.0				
		hydrolyzable polymer (A-6) (solid content 45.7%)					60.0		38.0	
		hydrolyzable polymer (A-7) (solid content 46.4%)						75.0		40.0
	(B')	PK								0.9
		medetomidine								0.1
	(C)	xylene	17.5	15.0	9.0	9.0	6.0	5.0	7.0	12.0
		propylene glycol monomethyl ether								6.0
		n-butanol							3.0	
		n-butyl acetate						6.0		2.0
		isobutyl acetate					6.0			
	(D)	cuprous oxide	30.0	42.0	50.0				30.0	
		copper pyrithione	1.0		1.5					1.0
	(E)	zinc oxide	12.0	5.0	7.0	5.0	15.0	5.0	12.0	23.8
		talc	3.0	3.0	3.0		5.0		3.0	5.0
		red iron oxide	3.0	3.0	3.0	5.0		3.0	3.0	3.0
	(F)	rosin	4.0	7.0	2.5					
		versatic acid					2.0			2.0
	(G)	calcium sulfate	1.0	1.0	1.0				1.0	
	(H)	TCP	1.0							
	(I)	fatty acid amide wax (solid content 20%)	2.0	2.0	2.0	6.0	5.0	4.0	3.0	3.6
	(J)	chlorinated paraffin polyester polymer			1.0		1.0	2.0		1.5
	Total (part by mass)			104.5	100.0	100.0	100.0	100.0	100.0	100.9
Solid Ratio (% by mass) of Coating Composition			70.4	74.7	81.2	45.0	51.4	45.6	67.0	56.1
Component (A)	component (A) (as code name) in coating composition	A-2	A-3	A-4	A-5	A-6	A-7	A-6	A-7	
	total content (% by mass) of component (A) based on solid content of coating composition	24.6	17.8	14.6	75.1	53.3	76.3	25.9	32.8	
Components (B) and (B')	component (B) and component (B') (as code name) in coating composition	-	-	-	-	-	-	-	PK MD	
	total content (% by mass) of component (B) and component (B') based on solid content of coating composition	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.8	
Component (C)	component (C) (as code name) in coating composition	Xy	Xy	Xy	Xy PGM	Xy PGM IAC	Xy PGM NAC	Xy PGM NBA	Xy PGM NAC	
	total content (% by mass) of component (C) based on solid content of coating composition	28.1	23.7	17.2	50.2	44.6	51.2	30.6	41.1	

*4: Containing the organic solvent (C) used in producing the component (A).

[0120]

[Examples 1 to 14, and Comparative Examples 1 to 6]

<Production of multilayer antifouling coating film>

An epoxy resin-based anti-corrosive coating composition (product name "BANNOH 500" by Chugoku Marine Paints, Ltd.) was applied to a sandblasted steel plate (length 300 mm × width 100 mm × thickness 3.2 mm) to have a dry film thickness of about 100 μm. Subsequently, the underlayer antifouling coating composition (x) produced according to Table 4 in a combination as shown in Table 6, Table 7 and Table 8 was applied once to have a dry film thickness of about 100 μm, and further on this, the upper-layer antifouling coating composition (y) produced according to Table 5 was applied once to have a dry film thickness of about 200 μm, and then dried under the condition of 25°C for 7 days to produce a test plate with a multilayer antifouling coating film. The three coating operations above were carried out at a pace of one coating operation a day, that is, in overpainting, the coating composition for the underlayer coating film was first applied, then dried under the condition of 25°C for at least 24 hours, and thereafter the coating composition for the upper-layer coating film was applied onto the underlayer coating film.

[0121]

[Examples 15 to 17]

Test plates with a multilayer antifouling coating film were produced using the underlayer antifouling coating composition (x-6) and the upper-layer antifouling coating composition (y-4) and in the same manner as that in producing the test plates of Examples 1 to 14 except that the dry film thickness of each coating composition could be as in Table 9.

[0122]

<Evaluation>

[Appearance]

The appearance of the multilayer antifouling coating films obtained in Examples 1 to 17 and Comparative Examples 1 to 6 were evaluated visually and, as a result, all the coating films were good without any failure such as appearance abnormality.

[0123]

[Barnacle-resistant immersion test]

The test plates of Examples 1 to 8, 15 to 17 and Comparative Examples 1

to 5 produced in the manner as above were immersed in seawater offshore Miyajima of Hiroshima prefecture at a position of about 0.5 meters below sea level in such a manner that the test surface could be horizontal to the sea surface and could face the sea bottom. Under the condition, the test plates were immersed statically for 3 months, and the area of the multilayer antifouling coating film occupied by barnacles (barnacles-occupied area of the multilayer antifouling coating film) was measured, and according to <Criteria for antifouling performance evaluation based on barnacles-occupied area> mentioned below, the antifouling performance (barnacle resistance) of the multilayer antifouling coating film was evaluated. The results are shown in Table 6, Table 7 and Table 9.

<Criteria for antifouling performance evaluation based on barnacles-occupied area>

5: The barnacles-occupied area was less than 1% of the entire test surface.

4: The barnacles-occupied area was 1% or more and less than 10% of the entire test surface.

3: The barnacles-occupied area was 10% or more and less than 30% of the entire test surface.

2: The barnacles-occupied area was 30% or more and less than 70% of the entire test surface.

1: The barnacles-occupied area was 70% or more of the entire test surface.

[0124]

[Accelerated slime resistance test]

The test plates of Examples 9 to 14 and Comparative Example 6 produced in the manner as above were immersed in Hiroshima Bay at a position of about 0.5 meters below sea level, as attached to a cylinder rotating in such a manner that the test surface could be at a speed of about 15 knots, under sun exposure condition. In 6 months from the start of immersion under the condition as above, the slime-occupied area of the antifouling coating film was measured, and according to <Criteria for antifouling performance evaluation based on slime-occupied area> mentioned below, the antifouling performance (slime resistance) of the multilayer antifouling coating film was evaluated. The results are shown in Table 8. Under the condition, the test plate is especially readily fouled by slime and botanical marine organisms because of the characteristics of the marine area in which the test plate is immersed and of the test condition.

<Criteria for antifouling performance evaluation based on slime-occupied area>

5: The total area occupied by slime in the test surface was less than 1% of the entire area.

4: The above area was 1% or more and less than 10% of the entire area.

3: The above area was 10% or more and less than 30% of the entire area.

2: The above area was 30% or more and less than 70% of the entire area.

1: The above area was 70% or more of the entire area.

[0125]

[Interlayer adhesiveness]

The test plates produced in the manner as above were immersed in seawater at 50°C for 1 month, then tested according to a knife cut test, and the interlayer adhesiveness thereof was evaluated according to the following criteria.

(Interlayer adhesiveness evaluation criteria)

5: No interlayer peeling was found at around the cut part.

4: The interlayer peeling area was less than 1 mm from the cut part.

3: The interlayer peeling area was 1 mm or more and less than 3 mm from the cut part.

2: The interlayer peeling area was 3 mm or more and less than 10 mm from the cut part.

1: The interlayer peeling area was 10 mm or more from the cut part.

The results are shown in Table 6 to Table 9.

[0126]

Table 6 - Multilayer Antifouling Coating Films and Evaluation Results thereof (1)

		Example			Comparative Example			
		1	2	3	1	2	3	4
Underlayer Antifouling Coating Composition (x)		x-2	x-4	x-6	x-1	x-3	x-5	x-7
Component (A)	component (A) (as code name) in coating composition	A-1	A-6	A-7	-	A-1	A-6	A-7
	total content (% by mass) of component (A) based on solid content of coating composition	17.5	23.4	25.3	0.0	17.5	23.0	27.9
Components (B) and (B')	components (B) and (B') (as code name) in coating composition	SN	SN MD	EC	EC	-	-	-
	total content (% by mass) of components (B) and (B') based on solid content of coating composition	2.0	1.5	9.1	9.3	0.0	0.0	0.0
Upper-Layer Antifouling Coating Composition (y)		y-5	y-5	y-5	y-5	y-5	y-5	y-5
Component (A)	component (A) (as code name) in coating composition	A-6	A-6	A-6	A-6	A-6	A-6	A-6
	total content (% by mass) of component (A) based on solid content of coating composition	53.3	53.3	53.3	53.3	53.3	53.3	53.3
Components (B) and (B')	components (B) and (B') (as code name) in coating composition	-	-	-	-	-	-	-
	total content (% by mass) of components (B) and (B') based on solid content of coating composition	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Component (C)	component (C) (as code name) in coating composition	Xy PGM IAC	Xy PGM IAC	Xy PGM IAC	Xy PGM IAC	Xy PGM IAC	Xy PGM IAC	Xy PGM IAC
	total content (% by mass) of component (C) based on solid content of coating composition	44.6	44.6	44.6	44.6	44.6	44.6	44.6
Evaluation Results	barnacle resistance	4	4	5	1	1	1	1
	interlayer adhesiveness	4	5	5	5	4	5	5

[0127]

Table 7 - Multilayer Antifouling Coating Films and Evaluation Results thereof (2)

		Example					Comparative Example
		4	5	6	7	8	5
Underlayer Antifouling Coating Composition (x)		x-4	x-6	x-6	x-4	x-6	x-8
Component (A)	component (A) (as code name) in coating composition	A-6	A-7	A-7	A-6	A-7	-
	total content (% by mass) of component (A) based on solid content of coating composition	23.4	25.3	25.3	23.4	25.3	0.0
Components (B) and (B')	components (B) and (B') (as code name) in coating composition	SN MD	EC	EC	SN MD	EC	EC
	total content (% by mass) of components (B) and (B') based on solid content of coating composition	1.5	9.1	9.1	1.5	9.1	3.3
Upper-Layer Antifouling Coating Composition (y)		y-4	y-4	y-6	y-7	y-8	y-9
Component (A)	component (A) (as code name) in coating composition	A-5	A-5	A-7	A-6	A-7	-
	total content (% by mass) of component (A) based on solid content of coating composition	75.1	75.1	76.3	25.9	32.8	0.0
Components (B) and (B')	components (B) and (B') (as code name) in coating composition	-	-	-	-	PK MD	-
	total content (% by mass) of components (B) and (B') based on solid content of coating composition	0.0	0.0	0.0	0.0	1.8	0.0
Component (C)	component (C) (as code name) in coating composition	Xy PGM	Xy PGM	Xy PGM NAC	Xy PGM NBA	Xy PGM NAC	Xy
	total content (% by mass) of component (C) based on solid content of coating composition	50.2	50.2	51.2	30.6	41.1	12.4
Evaluation Results	barnacle resistance	4	5	3	4	4	2
	interlayer adhesiveness	4	5	5	5	5	3

[0128]

Table 8 - Multilayer Antifouling Coating Films and Evaluation Results thereof (3)

		Example						Comparative Example
		9	10	11	12	13	14	6
Underlayer Antifouling Coating Composition (x)		x-2	x-2	x-4	x-2	x-4	x-4	x-8
Component (A)	component (A) (as code name) in coating composition	A-1	A-1	A-6	A-1	A-6	A-6	-
	total content (% by mass) of component (A) based on solid content of coating composition	17.5	17.5	23.4	17.5	23.4	23.4	0.0
Components (B) and (B')	components (B) and (B') (as code name) in coating composition	SN	SN	SN MD	SN	SN MD	SN MD	EC
	total content (% by mass) of components (B) and (B') based on solid content of coating composition	2.0	2.0	1.5	2.0	1.5	1.5	3.3
Upper-Layer Antifouling Coating Composition (y)		y-1	y-2	y-2	y-3	y-7	y-8	y-9
Component (A)	component (A) (as code name) in coating composition	A-2	A-3	A-3	A-4	A-6	A-7	-
	total content (% by mass) of component (A) based on solid content of coating composition	24.6	17.8	17.8	14.6	25.9	32.8	0.0
Components (B) and (B')	components (B) and (B') (as code name) in coating composition	-	-	-	-	-	PK MD	-
	total content (% by mass) of components (B) and (B') based on solid content of coating composition	0.0	0.0	0.0	0.0	0.0	1.8	0.0
Component (C)	component (C) (as code name) in coating composition	Xy	Xy	Xy	Xy	Xy PGM NBA	Xy PGM NAC	Xy
	total content (% by mass) of component (C) based on solid content of coating composition	28.1	23.7	23.7	17.2	30.6	41.1	12.4
Evaluation Results	slim resistance	4	4	5	4	4	4	2
	interlayer adhesiveness	4	4	4	4	5	5	3

[0129]

Table 9 - Multilayer Antifouling Coating Films and Evaluation Results thereof (4)

		Example		
		15	16	17
Underlayer Antifouling Coating Composition (x-6) thickness (μm)		approximately 40	approximately 100	approximately 100
Upper-Layer Antifouling Coating Composition (y-4) thickness (μm)		approximately 200	approximately 200	approximately 400
Evaluation Results	barnacle resistance	4	5	5
	interlayer adhesiveness	5	5	5

[0130]

As obvious from the results of Examples and Comparative Examples, the present invention can provide a multilayer antifouling coating film which has a good appearance and which can exhibit good antifouling performance and interlayer adhesiveness, and a substrate with a multilayer antifouling coating film having that multilayer antifouling coating film on a substrate.

CLAIMS

[Claim 1]

A multilayer antifouling coating film comprising an underlayer antifouling coating film (X) and an upper-layer antifouling coating film (Y) which are layered on each other, wherein:

the underlayer antifouling coating film (X) comprises a hydrolyzable polymer (A1) and an organic antifouling agent (B1),

the upper-layer antifouling coating film (Y) comprises a hydrolyzable polymer (A2), and

the organic antifouling agent (B1) is at least one selected from 4-bromo-2-(4-chlorophenyl)-5-(trifluoromethyl)-1H-pyrrole-3-carbonitrile and 4,5-dichloro-2-n-octyl-4-isothiazolin-3-one.

[Claim 2]

The multilayer antifouling coating film according to claim 1, wherein at least one of the hydrolyzable polymer (A1) and the hydrolyzable polymer (A2) has a constituent unit derived from a silyl ester group-containing monomer (a11).

[Claim 3]

The multilayer antifouling coating film according to claim 2, wherein the silyl ester group-containing monomer (a11) is represented by the following formula (1-1):



wherein R¹¹ represents a hydrogen atom or a methyl group; and R¹², R¹³ and R¹⁴ each independently represent a monovalent hydrocarbon group.

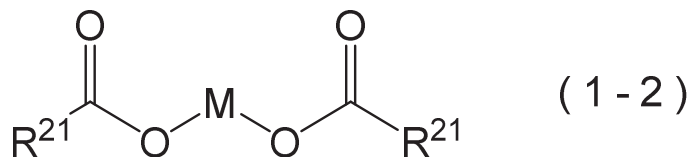
[Claim 4]

The multilayer antifouling coating film according to any one of claims 1 to 3, wherein at least one of the hydrolyzable polymer (A1) and the hydrolyzable polymer (A2) has a constituent unit derived from a metal ester group-containing monomer (a12).

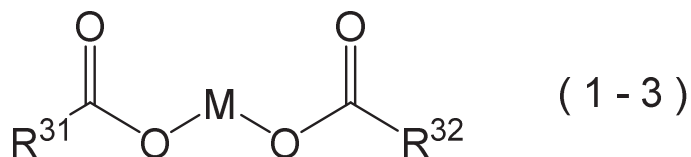
[Claim 5]

The multilayer antifouling coating film according to claim 4, wherein the metal ester group-containing monomer (a12) comprises at least one of a monomer

(a121) represented by the following formula (1-2) and a monomer (a122) represented by the following formula (1-3):



wherein R^{21} each independently represents a monovalent group containing a terminal ethylenically unsaturated group; and M represents a metal,



wherein R^{31} represents a monovalent group containing a terminal ethylenically unsaturated group; R^{32} represents a monovalent organic group having 1 to 30 carbon atoms containing no terminal ethylenically unsaturated group; and M represents a metal.

[Claim 6]

A substrate with a multilayer antifouling coating film, which is one covered with the multilayer antifouling coating film of any one of claims 1 to 5.

[Claim 7]

The substrate with a multilayer antifouling coating film according to claim 6, wherein the substrate is an underwater structure, a ship or a fishing gear.

[Claim 8]

An antifouling method comprising using the multilayer antifouling coating film of any one of claim 1 to 5.

[Claim 9]

A method for producing a substrate with a multilayer antifouling coating film, comprising:

a step of applying an underlayer antifouling coating composition (x) onto a substrate to form an underlayer antifouling coating film (X) thereon, and

a step of applying an upper-layer antifouling coating composition (y) onto the underlayer antifouling coating film (X) to form an upper-layer antifouling coating film (Y) thereon, wherein:

the underlayer antifouling coating composition (x) comprises a

hydrolyzable polymer (A1) and an organic antifouling agent (B1),

the organic antifouling agent (B1) is at least one selected from 4-bromo-2-(4-chlorophenyl)-5-(trifluoromethyl)-1H-pyrrole-3-carbonitrile and 4,5-dichloro-2-n-octyl-4-isothiazolin-3-one, and

the upper-layer antifouling coating composition (y) comprises a hydrolyzable polymer (A2) and an organic solvent (C2).

[Claim 10]

The method for producing a substrate with a multilayer antifouling coating film according to claim 9, wherein the organic solvent (C2) is a solvent which the polymer (B1) contained in the underlayer antifouling coating composition (x) is soluble in.

[Claim 11]

The method for producing a substrate with a multilayer antifouling coating film according to claim 9 or 10, wherein the organic solvent (C2) comprises one or more selected from the group consisting of a hydrocarbon organic solvent, an alcohol organic solvent, a ketone organic solvent and an ester organic solvent.

[Claim 12]

The method for producing a substrate with a multilayer antifouling coating film according to any one of claims 9 to 11, wherein the upper-layer antifouling coating composition (y) does not substantially contain an organic antifouling agent selected from 4-bromo-2-(4-chlorophenyl)-5-(trifluoromethyl)-1H-pyrrole-3-carbonitrile and 4,5-dichloro-2-n-octyl-4-isothiazolin-3-one.

[Claim 13]

The method for producing a substrate with a multilayer antifouling coating film according to any one of claims 9 to 12, wherein the upper-layer antifouling coating composition (y) does not substantially contain an antifouling agent.

[Claim 14]

A coating material kit for forming a multilayer antifouling coating film, comprising:

an underlayer antifouling coating composition (x) containing a hydrolyzable polymer (A1) and an organic antifouling agent (B1), and

an upper-layer antifouling coating composition (y) containing a hydrolyzable polymer (A2) and an organic solvent (C2), wherein:

the organic antifouling agent (B1) is at least one selected from 4-bromo-2-(4-chlorophenyl)-5-(trifluoromethyl)-1H-pyrrole-3-carbonitrile and 4,5-dichloro-2-n-octyl-4-isothiazolin-3-one, and

the organic antifouling agent (B1) contained in the underlayer antifouling coating composition (x) is soluble in the organic solvent (C2).

[Claim 15]

An upper-layer antifouling coating composition, which is applied onto the surface of an underlayer antifouling coating film (X) containing a hydrolyzable polymer (A1) and an organic antifouling agent (B1),

wherein the upper-layer antifouling coating composition comprises a hydrolyzable polymer (A2) and an organic solvent (C2), the organic antifouling agent (B1) is at least one selected from 4-bromo-2-(4-chlorophenyl)-5-(trifluoromethyl)-1H-pyrrole-3-carbonitrile and 4,5-dichloro-2-n-octyl-4-isothiazolin-3-one, and the organic solvent (C2) is a solvent which the organic antifouling agent (B1) contained in the underlayer coating film (X) is soluble in.