

DESCRIPTION

ANTIFOULING COATING COMPOSITION

TECHNICAL FIELD

[0001]

5 The present invention relates to an antifouling coating composition which, by containing an organopolysiloxane and an inorganic copper, can be sprayed while releasing less airborne spray dust to achieve excellent transfer efficiency of the coating gained by the substrate and can form antifouling films
10 having high antifouling properties.

BACKGROUND ART

[0002]

 Antifouling films formed from organopolysiloxane antifouling coating compositions are widely used to prevent
15 the attachment of aquatic organisms to objects such as marine vessels, underwater structures, fishing nets and fishing equipment. Films formed from organopolysiloxane antifouling coating compositions prevent macroorganisms such as barnacles and mussels from attaching or settling on the surface by means
20 of their characteristics such as low surface free energy and low elastic modulus. Further, demands exist for high antifouling performance also with respect to microorganisms, for example, the ability to prevent the attachment of slime which is a bacterial secretion in the form of film. An approach

being studied to meet such demands is to add bioactive antifouling agents such as cuprous oxide to antifouling coating compositions.

[0003]

5 Meanwhile, organopolysiloxane antifouling coating composition, particularly when sprayed, tend to be scattered as spray dust to the surrounding environment. As a result, the coating that has been sprayed goes off the target and is lost to other areas. The spray dust deposited to such unintended
10 areas serves as a hindrance in the spraying of the areas to cause problems such as poor adhesion and cissing of the newly sprayed coating. Thus, the spraying of an organopolysiloxane antifouling coating necessitates a careful protection of a wide area around the site of application from the deposition of dust.
15 This significantly decreases workability.

[0004]

As for organopolysiloxane antifouling coating compositions, for example, techniques described in Patent Literatures 1 to 4 are known. Patent Literature 1 discloses
20 an organopolysiloxane coating composition containing an antifouling agent wherein the antifouling agent is preferably copper or an inorganic copper compound. Patent Literature 2 describes that a polymer obtained by reacting a dimethylpolysiloxane having at least one hydroxyl group in the

molecule with an unsaturated isocyanate and further
copolymerizing the product with a desired vinyl monomer is used
in combination with an inorganic and/or organic antifouling
agent, the combined use making it possible to overcome defects
5 of traditional organopolysiloxane antifouling coatings and to
form practical solid films capable of preventing the attachment
of shellfishes in water over a long period of time. Patent
Literature 3 describes a fouling control coating composition
including a polysiloxane-based binder system, a
10 hydrophilic-modified polysiloxane and a biocide. Patent
Literature 4 describes an antifouling material which includes
a nitrogen-containing compound wherein the antifouling
material exhibits excellent repellent effects not only with
respect to slime-forming microorganisms but also for large
15 fouling organisms in water, and effectively prevents fouling
over a long period while being safe to the human body and
environmentally friendly.

[0005]

However, these techniques in the art are silent with
20 respect to the transfer efficiency of the coatings during
application, in particular, the control of the release of spray
dust.

CITATION LIST

PATENT LITERATURE

[0006]

Patent Literature 1: JP-A-2001-139816

Patent Literature 2: JP-A-H07-305001

Patent Literature 3: JP-A-2013-515122

5 Patent Literature 4: JP-A-H09-249507

SUMMARY OF INVENTION

TECHNICAL PROBLEM

[0007]

The present invention has been made in order to solve the
10 problems in the art discussed above. It is therefore an object
of the invention to provide an antifouling coating composition
which can form antifouling films having high antifouling
properties, has excellent transfer efficiency and can be
sprayed while releasing less spray dust.

15 SOLUTION TO PROBLEM

[0008]

The present inventors carried out extensive studies to
solve the problems discussed above. As a result, the present
inventors have found that the release of spray dust can be
20 unexpectedly controlled and excellent transfer efficiency is
attained with an antifouling coating composition including:

(A) an organopolysiloxane having two or more silanol
groups in the molecule,

(B) a crosslinking agent, and

(C) an inorganic copper. The present invention has been developed based on the finding.

[0009]

The inorganic copper (C) present in the antifouling
5 coating composition is preferably cuprous oxide and/or
metallic copper.

[0010]

Preferably, the antifouling coating composition further
includes copper pyrithione.

10 [0011]

Preferably, the antifouling coating composition further
includes an antifouling imparting agent (D) other than the
inorganic copper (C) and the copper pyrithione. The
antifouling imparting agent (D) is preferably a pyrithione salt
15 other than copper pyrithione.

[0012]

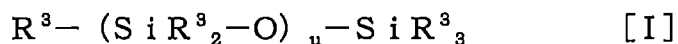
The antifouling coating composition preferably contains
the inorganic copper (C) in an amount of 0.5 to 60 wt%, and
more preferably 5 to 40 wt%.

20 [0013]

Preferably, the antifouling coating composition further
includes a silicone oil (E). The silicone oil (E) is preferably
an organopolysiloxane represented by the general formula [I]
below:

[0014]

[Chem. 1]



[0015]

5 (In the formula, R^3 independently at each occurrence represents a C_{1-10} alkyl group, an alkenyl group, an aryl group, an aralkyl group, an alkoxy group or a halogenated alkyl group; or a C_{2-100} polyoxyalkylene group optionally endcapped with a C_{1-10} hydrocarbon group, a hydroxyl group or a silyl group having
10 a condensation reactive group on the silicon atom, and u is an integer of 1 to 10,000.)

Preferably, the antifouling coating composition further includes a metallic curing catalyst (F) and/or an organic solvent (G).

15 [0016]

An antifouling film according to the present invention is obtained by curing the above antifouling coating composition.

[0017]

20 A method for producing antifouling films according to the present invention includes applying the above antifouling coating composition to form an antifouling film.

[0018]

An antifouling substrate according to the present

invention is obtained by coating a substrate with the above antifouling film. The substrate is preferably any of a marine vessel, an underwater structure and fishing equipment.

[0019]

5 A method for preventing substrates from fouling according to the present invention includes coating a surface of the substrate with the above antifouling film.

[0020]

10 A method for producing antifouling substrates according to the present invention includes a step of applying the above antifouling coating composition to a substrate, and a step of curing the antifouling coating composition spread on the substrate by the application step.

ADVANTAGEOUS EFFECTS OF INVENTION

15 [0021]

20 The organopolysiloxane antifouling coating compositions obtained according to the present invention can be sprayed while releasing less airborne dust, have excellent transfer efficiency and give antifouling films having high antifouling properties.

[0022]

 The antifouling coating compositions of the invention have excellent transfer efficiency and can be sprayed while releasing less airborne dust. The reduction in the release of

spray dust to the surrounding environment remedies problems such as poor adhesion and cissing of a coating or the like newly applied to the surrounding environment, and also makes it possible to save the coating time and the amount of the coating used.

BRIEF DESCRIPTION OF DRAWING

[0023]

[Fig. 1] Fig. 1 is a schematic view illustrating a device used in Examples to measure the ratio of dust released during spraying.

DESCRIPTION OF EMBODIMENTS

[0024]

-Antifouling coating compositions-

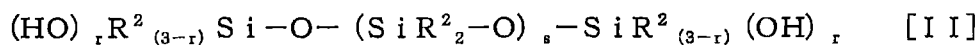
An antifouling coating composition according to the present invention includes (A) an organopolysiloxane having two or more silanol groups in the molecule, (B) a crosslinking agent, and (C) an inorganic copper. These ingredients will be described in order below.

⟨(A) Organopolysiloxanes having two or more silanol groups in the molecule⟩

Specifically, the organopolysiloxane (A) having two or more silanol groups in the molecule is suitably a compound represented by the general formula [II] below.

[0025]

[Chem. 2]



[0026]

In the general formula [II], R^2 independently at each
 5 occurrence represents a hydrogen atom, or a C_{1-10} alkyl group,
 an alkenyl group, an aryl group, an aralkyl group, an alkoxy
 group or a halogenated alkyl group.

[0027]

Examples of the alkyl groups include methyl group, ethyl
 10 group, propyl group, butyl group, pentyl group, hexyl group
 and heptyl group.

[0028]

Examples of the alkenyl groups include vinyl group, allyl
 group, propenyl group, isopropenyl group, butenyl group,
 15 isobutenyl group, pentenyl group, heptenyl group, hexenyl
 group and cyclohexenyl group.

[0029]

Examples of the aryl groups include phenyl group, tolyl
 group, xylyl group and naphthyl group.

20 [0030]

Examples of the aralkyl groups include benzyl group,
 2-phenylethyl group, 2-naphthylethyl group and diphenylmethyl
 group.

[0031]

Examples of the alkoxy groups include methoxy group, ethoxy group, propoxy group, butoxy group, methoxyethoxy group and ethoxyethoxy group.

[0032]

5 Examples of the halogenated alkyl groups include those groups resulting from partial or complete substitution of the above alkyl groups with halogen atoms such as fluorine atoms, chlorine atoms, bromine atoms and iodine atoms in place of hydrogen atoms.

10 [0033]

R^2 is preferably a methyl group.

[0034]

In the general formula [II], r is an integer of 1 to 3, and preferably 1.

15 [0035]

In the general formula [II], s is an integer of 10 to 10,000, and preferably 100 to 1,000.

[0036]

20 In the organopolysiloxane (A) having two or more silanol groups in the molecule, the weight average molecular weight measured by gel permeation chromatography (GPC) relative to polystyrenes is preferably 500 to 1,000,000, more preferably 5,000 to 100,000, and still more preferably 10,000 to 50,000. The viscosity at 23°C is preferably 20 to 100,000 mPa·s, more

preferably 100 to 10,000 mPa·s, and still more preferably 500 to 5,000 mPa·s. These weight average molecular weight and viscosity advantageously ensure that good workability will be obtained during the coating production and also that excellent
5 spray atomization properties, film curability and film strength will be obtained.

[0037]

In the antifouling coating composition, the organopolysiloxane (A) having two or more silanol groups in
10 the molecule is usually present in an amount of 20 to 90 wt%, and preferably 50 to 70 wt%. The proportion of the organopolysiloxane (A) relative to the weight of the solids present in the antifouling coating composition is usually 30 to 95 wt%, and preferably 60 to 90 wt%. This content of the
15 organopolysiloxane (A) ensures that the obtainable antifouling films will have good film strength and rubber elasticity and will exhibit antifouling properties over a long period of time.

[0038]

The organopolysiloxanes (A) having two or more silanol
20 groups in the molecule may be purchased in the market. Examples of such commercial products include "DMS-S35" (manufactured by GELEST).

<(B) Crosslinking agents>

The crosslinking agent (B) is preferably an organosilane

represented by the general formula [III] below which has two or more hydrolyzable groups in the molecule, and/or a partial hydrolytic condensate thereof.

[0039]

5 [Chem. 3]



[0040]

In the general formula [III], R^4 independently at each occurrence represents a hydrocarbon group having 1 to 6 carbon
10 atoms. Examples thereof include linear alkyl groups such as methyl group, ethyl group and propyl group, branched alkyl groups, cycloalkyl groups such as cyclohexyl group, alkenyl groups such as vinyl group, and aryl groups such as phenyl group, with methyl group and ethyl group being preferable.

15 [0041]

In the general formula [III], Y independently at each occurrence represents a hydrolyzable group. Examples thereof include alkoxy groups, ketoxime groups, acyloxy groups, alkenyloxy groups, amino groups, amide groups and aminoxy
20 groups, with alkoxy groups and ketoxime groups being preferable.

[0042]

Preferred alkoxy groups are those having a total of 1 to 10 carbon atoms. An oxygen atom may be present between at least

one pair of adjacent carbon atoms. Examples include methoxy group, ethoxy group, propoxy group, butoxy group, methoxyethoxy group and ethoxyethoxy group.

[0043]

5 Examples of the ketoxime groups (also referred to as ketoxime groups) include dimethylketoxime group, methylethylketoxime group, diethylketoxime group, methylisopropylketoxime group, cyclopentanoxime group and cyclohexanoxime group.

10 [0044]

 Preferred acyloxy groups are aliphatic or aromatic acyloxy groups represented by the formula: RCOO- (wherein R is an alkyl group having 1 to 10 carbon atoms, or an aromatic group having 6 to 12 carbon atoms), with examples including
15 acetoxo group, propionoxo group, butyloxy group and benzoyloxy group.

[0045]

 Preferred alkenyloxy groups are those having 3 to 10 carbon atoms. Examples thereof include isopropenyloxy group,
20 isobutenyloxy group and 1-ethyl-2-methylvinyloxy group.

[0046]

 Preferred amino groups are those having 1 to 10 carbon atoms. Examples thereof include N-methylamino group, N-ethylamino group, N-propylamino group, N-butylamino group,

N,N-dimethylamino group, N,N-diethylamino group and cyclohexylamino group.

[0047]

Preferred amide groups are those having a total of 2 to 10 carbon atoms. Examples thereof include N-methylacetamide group, N-ethylacetamide group and N-methylbenzamide group.

[0048]

Preferred aminoxy groups are those having a total of 2 to 10 carbon atoms. Examples thereof include N,N-dimethylaminoxy group and N,N-diethylaminoxy group.

[0049]

The letter d is an integer of 0 to 2, and is preferably 0.

[0050]

15 The organosilanes may be purchased in the market. Examples of commercial tetraethyl orthosilicates include "Ethyl Silicate 28" (manufactured by COLCOAT CO., LTD.) and "ethyl orthosilicate" (manufactured by TAMA CHEMICALS CO., LTD.). Examples of commercial partial hydrolytic condensates
20 of tetraethyl orthosilicates include "Silicate 40" (manufactured by TAMA CHEMICALS CO., LTD.) and "TES40 WN" (manufactured by WACKER ASAHIKASEI SILICONE CO., LTD.). Example of commercial alkyltrialkoxysilanes include "KBM-13" (manufactured by Shin-Etsu Chemical Co., Ltd.).

[0051]

In the antifouling coating composition, the crosslinking agent (B) is generally present in an amount of 0.1 to 50 wt%, and is usually contained in an amount of 1 to 30 wt%, and
5 preferably 3 to 15 wt%. This content of the crosslinking agent (B) ensures that the antifouling coating composition will maintain an appropriate curing rate and will be cured to give films having excellent film strength and rubber properties.

<(C) Inorganic coppers>

10 The addition of the inorganic copper (C) to the antifouling coating composition makes it possible to reduce the release of spray dust, to enhance the transfer efficiency of the coating gained by the substrate, and to improve the antifouling properties of antifouling films. The present
15 inventors have found that inorganic coppers, which are commonly used as antifouling imparting agents in antifouling coating compositions, have an effect to prevent the release of spray dust. By the use of the inorganic copper (C), the present inventors have realized an enhancement in the antifouling
20 properties of antifouling films and have been also successful in controlling the release of spray dust and in enhancing the transfer efficiency of the coating gained by the substrate.

[0052]

Examples of the inorganic coppers (C) include cuprous

oxide, metallic copper, cupric oxide, copper thiocyanate and copper chloride. In particular, cuprous oxide or metallic copper is preferable. Two or more of these coppers may be used in combination.

5 [0053]

Cuprous oxide and metallic copper may be purchased in the market. Examples of commercial cuprous oxide include "cuprous oxide NC-803" and "cuprous oxide NC-301"

(manufactured by NISSIN CHEMCO Co., Ltd.), and "RED COPP 97N
10 Premium" and "LOLO TINT LM" (American Kemet Corporation).

Examples of commercial metallic copper include "electrolytic copper powder #6" (manufactured by JX Nippon Mining & Metals Corporation).

[0054]

15 In the antifouling coating composition, the content of the inorganic copper (C) is usually 0.5 to 60 wt%, preferably 5 to 40 wt%, and more preferably 10 to 35 wt%. This content ensures that the inorganic copper (C) will provide a high effect in the reduction of the release of spray dust and also will
20 impart high antifouling properties to antifouling films.

(Optional ingredients)

In addition to the organopolysiloxane (A) having two or more silanol groups, the crosslinking agent (B) and the inorganic copper (C), the antifouling coating composition of

the present invention may contain other ingredients such as copper pyrithione, an antifouling imparting agent (D) other than the inorganic copper (C) and copper pyrithione, a silicone oil (E) other than the organopolysiloxane (A), a metallic curing catalyst (F), an organic solvent (G), a silica (H), a filler (I) other than the silica (H), an anti-sag anti-settling agent (J), a silane coupling agent (K), an additional film-forming ingredient (L), an inorganic dehydrating agent (M), a flame retardant (N), a thixotropic agent (O) and a thermal conductivity improver (P).

[Copper pyrithione, and antifouling imparting agents (D) other than inorganic coppers (C) and copper pyrithione]

The antifouling imparting agents other than the inorganic coppers (C) may be organic or inorganic agents.

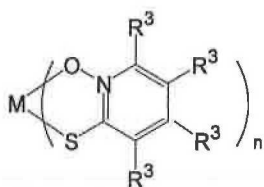
15 [0055]

Examples of the organic antifouling agents include pyrithione salt compounds represented by the general formula [IV] below, tetramethylthiuram disulfide, carbamate compounds (for example, zinc dimethyldithiocarbamate, manganese-2 ethylenebis dithiocarbamate), 2,4,5,6-tetrachloroisophthalonitrile, 2-(p-chlorophenyl)-3-cyano-4-bromo-5-trifluoromethylpyrrole, (RS)-4-[1-(2,3-dimethylphenyl)ethyl]-3H-imidazole, 4,5-dichloro-N-octyl-4-isothiazolin-3-one,

pyridine-triphenylborane and
 p-isopropylpyridinemethyldiphenylborane. It is preferable
 that the agent(s) include a pyrithione salt compound
 represented by the general formula [IV] below:

5 [0056]

[Chem. 4]



[IV]

[0057]

In the general formula [IV] above, R^3 independently at
 10 each occurrence represents a hydrogen atom, or a C_{1-6} alkyl group,
 a cycloalkyl group, an alkenyl group, an aryl group, an alkoxy
 group or a halogenated alkyl group, M represents a metal atom
 selected from Zn, Cu, Na, Mg, Ca, Ba, Fe and Sr, and n is the
 valence of the metal M.

15 [0058]

The antifouling imparting agents other than the inorganic
 coppers (C) may be used singly, or a plurality of the agents
 may be used in combination.

[0059]

20 The incorporation of the antifouling imparting agent
 other than the inorganic copper (C) further enhances the
 antifouling properties in water of films formed from the

antifouling coating composition.

[0060]

Pyrithione salts are preferable as the antifouling imparting agents.

5 [0061]

Of the pyrithione salts, copper pyrithione increases the antifouling properties of the antifouling coating composition and further enhances the effect of the inorganic copper (C) to control the release of spray dust, making it possible to further enhance the transfer efficiency of the coating gained by the substrate. In the antifouling coating composition, the content of the copper pyrithione is preferably 0.1 to 30 wt%, more preferably 0.5 to 15 wt%, and still more preferably 1 to 10 wt%.

15 [0062]

The content of the antifouling imparting agent (D) other than the inorganic copper (C) and copper pyrithione is preferably 0.1 to 30 wt% of the antifouling coating composition.

[0063]

20 Copper pyrithione, and the antifouling imparting agent (D) other than the inorganic copper (C) and copper pyrithione may be used in combination.

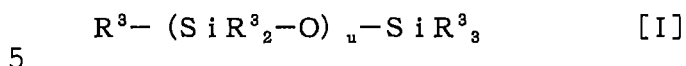
[(E) Silicone oils other than organopolysiloxanes (A)]

Organopolysiloxanes represented by the general formula

[I] below are preferably used as the silicone oils (E) other than the organopolysiloxanes (A).

[0064]

[Chem. 5]



[0065]

In the general formula [I], R^3 independently at each occurrence represents a C_{1-10} alkyl group, an alkenyl group, an aryl group, an aralkyl group, an alkoxy group or a halogenated
 10 alkyl group; or a C_{2-100} polyoxyalkylene group optionally endcapped with a C_{1-10} hydrocarbon group, a hydroxyl group or a silyl group having a condensation reactive group on the silicon atom, and R^3 's preferably represent methyl and phenyl groups, or methyl and polyoxyalkylene groups.

15 [0066]

In the general formula [I], u is an integer of 1 to 10,000.

[0067]

Examples of the silicone oils (E) represented by the general formula [I] in which R^3 's are methyl and phenyl groups
 20 include those commercially available under the tradenames of "KF-54", "KF-56" and "KF-50" (manufactured by Shin-Etsu Chemical Co., Ltd.), "SH510" and "SH550" (manufactured by Dow Corning Toray Co., Ltd.), and "TSF431" (manufactured by Toshiba

silicone).

[0068]

Examples of the silicone oils (E) represented by the general formula [I] in which R³s are methyl and polyoxyalkylene groups include those commercially available under the tradenames of "X-22-6548" (alkylene glycol-modified silicone oil, manufactured by Shin-Etsu Chemical Co., Ltd.), "FZ-2164" (alkylene glycol-modified silicone oil, manufactured by Dow Corning Toray Co., Ltd.), "X-22-4272" (hydroxyl-endcapped/alkylene glycol-modified silicone oil, manufactured by Shin-Etsu Chemical Co., Ltd.), and "BY16-839" (alicyclic epoxy-modified silicone oil, manufactured by Dow Corning Toray Co., Ltd.).

[0069]

In the antifouling coating composition, the content of the silicone oil (E) is usually 0.01 to 30 wt%, and preferably 0.1 to 15 wt%. This content of the silicone oil (E) ensures that the thixotropic properties of the antifouling coating composition will be appropriately enhanced and thereby the anti-sagging properties will be improved to allow the composition to be applied in large thickness, and also ensures that the antifouling performance of antifouling films will be enhanced.

[(F) Metallic curing catalysts]

The metallic curing catalyst (F) serves to accelerate the condensation reaction between homogeneous or heterogeneous molecules of the organopolysiloxane (A) having two or more silanol groups in the molecule and the crosslinking agent (B), and promotes the curing reaction of films to allow for quick formation of cured films after application.

[0070]

The metallic curing catalyst (F) is preferably a tin-containing curing catalyst.

10 [0071]

For example, those catalysts described in JP-A-H04-106156 (Japanese Patent No. 2522854) may be suitably used as the metallic curing catalysts (F). Specific examples include tin carboxylates such as tin naphthenate and tin oleate; tin compounds such as dibutyltin diacetate, dibutyltin acetoacetate, dibutyltin dilaurate, dibutyltin dioleate, dibutyltin oxide, dibutyltin dimethoxide, dibutyltin dipentolate, dibutyltin dioctoate, dibutyltin dineodecanoate, dioctyltin dineodecanoate, bis(dibutyltin laurate) oxide, dibutyl bis(triethoxysiloxy)tin, bis(dibutyltin acetate) oxide, dibutyltin bis(ethyl maleate) and dioctyltin bis(ethyl maleate); titanate esters or titanium chelate compounds such as tetraisopropoxytitanium, tetra-n-butoxytitanium, tetrakis(2-ethylhexoxy)titanium,

dipropoxybis(acetylacetonato)titanium and titanium isopropoxyoctyl glycol; organometallic compounds such as zinc naphthenate, zinc stearate, zinc-2-ethyloctoate, iron-2-ethylhexoate, cobalt-2-ethylhexoate, manganese-2-ethylhexoate, cobalt naphthenate and alkoxyaluminum compounds; and lower fatty acid salts of alkali metals such as potassium acetate, sodium acetate and lithium oxalate.

[0072]

10 The metallic curing catalysts (F) may be purchased in the market. Examples of such commercial products include "NEOSTAN U-100" (manufactured by NITTO KASEI CO., LTD.).

[0073]

15 In the antifouling coating composition, the content of the metallic curing catalyst (F) is usually not more than 10 wt%, and preferably not more than 1 wt%. The lower limit in the use of the catalyst is preferably 0.001 wt%, and particularly preferably 0.01 wt%. This content of the metallic curing catalyst (F) ensures that the coating composition will
20 attain a good balance between the curing rate of films and the serviceable life after the preparation of the coating.

[(G) Organic solvents]

 Examples of the organic solvents (G) include aromatic hydrocarbons, aliphatic hydrocarbons, alicyclic hydrocarbons,

alcohols, ketones and esters. Combined use of aromatic hydrocarbons with alcohols is preferable.

[0074]

The alcohols may be linear, branched or cyclic compounds
5 having an ether group in the molecular chain. Examples include methanol, ethanol, propanol, butanol, pentanol and hexanol.

[0075]

Preferred alcohols are those alcohols having 5 or less carbon atoms, and n-butanol is more preferable. The use of such
10 an alcohol provides a long serviceable time after mixing into the coating.

[0076]

In the antifouling coating composition, the content of the alcohol is usually 1 to 20 wt%, and preferably 3 to 10 wt%.
15 This content of the alcohol ensures that a long serviceable time is obtained after mixing into the coating.

[0077]

Examples of the aromatic hydrocarbon organic solvents include toluene, xylene, styrene and mesitylene.

20 [0078]

Examples of the aliphatic hydrocarbon organic solvents include pentane, hexane, heptane and octane.

[0079]

Examples of the alicyclic hydrocarbon organic solvents

include cyclohexane, methylcyclohexane and ethylcyclohexane.

[0080]

Examples of the ketone organic solvents include acetone, methyl ethyl ketone, methyl isobutyl ketone and dimethyl
5 carbonate.

[0081]

Examples of the ester organic solvents include propylene glycol monomethyl ether acetate.

[0082]

10 The addition of the organic solvent (G) to the antifouling coating composition results in a decrease in the viscosity of the antifouling coating composition and thereby enhances the workability during application.

[0083]

15 A preferred content of the organic solvent (G) is determined based on the viscosity of the antifouling coating composition, but the content in the antifouling coating composition is usually 0 to 50 wt%. If the content is excessively high, problems such as poor anti-sagging
20 properties are caused.

[(H) Silicas]

The silica (H) may be kneaded with the organopolysiloxane beforehand before it is used together with the organopolysiloxane (A) having two or more silanol groups in

the molecule or the silicone oil (E), in particular, before the preparation of an organopolysiloxane-containing component of a multi-part antifouling coating composition.

[0084]

5 Examples of the silicas (H) include hydrophilic silicas (non-surface-treated silicas) such as wet silica (hydrated silica) and dry silica (fumed silica, anhydrous silica), and surface-treated hydrophobic silicas such as hydrophobic wet silica and hydrophobic fumed silica. These silicas may be used
10 singly, or two or more may be used in combination.

[0085]

The wet process silica is not particularly limited. For example, that having an adsorbed water content of about 4 to 8%, a bulk density of 200 to 300 g/L, a primary particle diameter
15 of 10 to 30 μm and a specific surface area (a BET surface area) of not less than 10 m^2/g may be used.

[0086]

The dry process silica is not particularly limited. For example, that having a water content of not more than 1.5%,
20 a bulk density of 50 to 100 g/L, a primary particle diameter of 8 to 20 μm and a specific surface area of not less than 10 m^2/g may be used.

[0087]

The hydrophobic fumed silica is obtained by

surface-treating the dry process silica with organosilicon compounds such as methyltrichlorosilane, dimethyldichlorosilane, hexamethyldisilazane, hexamethylcyclotrisiloxane and octamethylcyclotetrasiloxane.

5 The hydrophobic fumed silica adsorbs little water over time, and the water content is usually not more than 0.3%, and most often 0.1 to 0.2%. The hydrophobic fumed silica is not particularly limited. For example, that having a primary particle diameter of 5 to 50 μm , a bulk density of 50 to 100
10 g/L, and a specific surface area of not less than 10 m^2/g may be used.

[0088]

Water adsorbed to the surface of the silica is physically reduced or removed by heat treatment together with the
15 organopolysiloxane as will be described later. As a result, the water content in the heat-treated hydrophobic fumed silica is usually not more than 0.2%, preferably not more than 0.1%, and still more preferably 0.05 to 0.1%. Other properties such as bulk density are unchanged from the values of the hydrophobic
20 silica before the heat treatment.

[0089]

Commercially available silicas may be used, with examples including "R974" and "RX200" manufactured by NIPPON AEROSIL CO., LTD.

[0090]

When the silica (H) is used in the form of a kneadate with the above-described organopolysiloxane, the kneadate is preferably a heat-treated product formed by heat treating the organopolysiloxane and the silica beforehand, or a mixture of
5 the heat-treated product with another portion of the organopolysiloxane that has not been heat treated. Such a manner of use is preferable because the heat treatment of the silica with part or the whole of the organopolysiloxane enhances
10 the affinity between these two ingredients and consequently provides advantageous effects such as the aggregation of the silica being prevented. For example, this heat treatment may be performed at normal pressure or reduced pressure and at a temperature of not less than 100°C and not more than the
15 decomposition temperatures of the ingredients being mixed, preferably at a temperature of 100 to 300°C, or more preferably 140 to 200°C, usually for about 3 to 30 hours.

[0091]

The silica is usually added in a ratio of 1 to 100 wt%,
20 preferably 2 to 50 wt%, and still more preferably 5 to 30 wt% relative to the organopolysiloxane (A). This content of the silica ensures that the antifouling coating composition will exhibit good thixotropic properties and can attain a desired thickness by being applied, in particular, sprayed one time

to form films having high strength and high hardness.

[0092]

The use of the silica described above provides advantageous effects such as that the stability of the antifouling coating composition during its preparation or storage is enhanced, that good fluidity and thixotropic properties are obtained to make it possible to form sufficiently thick films by a small number of applications even onto vertical surfaces or the like, and that the obtainable films attain excellent and well-balanced properties such as hardness, tensile strength and elongation.

[(I) Fillers other than silicas (H)]

The fillers (I) other than the silicas (H) may be any known organic or inorganic pigments and other fillers.

15 [0093]

Examples of the organic pigments include carbon black, phthalocyanine blue and ultramarine.

[0094]

Examples of the inorganic pigments include neutral and nonreactive pigments such as titanium white (titanium oxide), red oxide, barite powder, talc, chalk and iron oxide powder; and basic pigments (active pigments) reactive with acidic substances in the coating such as white lead, red lead, zinc powder and lead suboxide powder. Examples of the other fillers

include metal oxides such as diatomaceous earth and alumina; metal carbonates such as calcium carbonate, magnesium carbonate and zinc carbonate; and others such as asbestos, glass fibers, quartz powder, aluminum hydroxide, gold powder, silver powder, surface-treated calcium carbonate and glass balloons. The surface of these fillers may be treated with silane compounds. These fillers may be used singly, or two or more may be used in combination. Incidentally, the fillers may include various colorants such as dyes.

10 [0095]

The filler (I) added to the antifouling coating composition enhances the strength of films, and also hides an undercoating film to protect the undercoating film from UV degradation. In the antifouling coating composition, the content of the filler (I) is preferably 0.1 to 30 wt%.

15 [(J) Anti-sag anti-settling agents]

Examples of the anti-sag anti-settling agents (J) include organic clay waxes (such as stearate salts, lecithin salts and alkylsulfonate salts of Al, Ca and Zn), organic waxes (such as polyethylene wax, oxidized polyethylene wax, amide wax, polyamide wax and hydrogenated castor oil wax), mixtures of organic clay waxes and organic waxes, and synthetic fine silica.

20 [0096]

The anti-sag anti-settling agents (J) may be purchased

in the market. Examples of such commercial products include those commercially available under the tradenames of "Disparlon 305", "Disparlon 4200-20" and "Disparlon A630-20X" manufactured by Kusumoto Chemicals, Ltd.

5 [0097]

In the antifouling coating composition, the content of the anti-sag anti-settling agent (J) is usually 0.01 to 10 wt%, and preferably 0.1 to 3 wt%.

[(K) Silane coupling agents]

10 The silane coupling agents (K) are preferably those silane coupling agents that contain one, or two or more kinds of groups such as alkoxysilyl groups, amino groups, imino groups, epoxy groups, hydrosilyl groups, mercapto groups, isocyanate groups and (meth)acrylic groups. Those agents containing an
15 amino group are particularly preferable. Examples of the amino group-containing silane coupling agents include
3-(2-aminoethyl)aminopropyltrimethoxysilane,
3-aminopropyltrimethoxysilane, 3-aminopropyltriethoxysilane
and
20 3-(2-(2-aminoethyl)aminoethyl)aminopropyltrimethoxysilane.
Examples of the silane coupling agents further include
3-glycidoxypropylmethyldimethoxysilane,
vinyltrimethoxysilane, vinyltriethoxysilane,
3-mercaptopropyltrimethoxysilane,

N-phenylpropyltrimethoxysilane and
N-phenylpropyltriethoxysilane. A mixture of these silane
coupling agents may be used.

[0098]

5 By its containing the silane coupling agent (K), the
antifouling coating composition attains stronger adhesion with
respect to an undercoating film or a substrate or the
antifouling coating composition can form films with enhanced
strength. In the antifouling coating composition, the content
10 of the silane coupling agent (K) is preferably 0.01 to 1 wt%.

[(L) Additional film-forming ingredients]

The additional film-forming ingredients (L) may be any
film-forming ingredients other than organopolysiloxanes that
are the main resin ingredients, as long as the object of the
15 invention is not impaired.

[0099]

Examples of the additional film-forming ingredients (L)
include resins that are poorly soluble or insoluble in water
such as acrylic resins, acrylic silicone resins, unsaturated
20 polyester resins, fluororesins, polybutene resins, silicone
rubbers, urethane resins (rubbers), polyamide resins, vinyl
chloride copolymer resins, chlorinated rubbers (resins),
chlorinated olefin resins, styrene-butadiene copolymer resins,
ethylene-vinyl acetate copolymer resins, vinyl chloride resins,

alkyd resins, coumarone resins, trialkylsilyl acrylate (co)polymers (silyl resins) and petroleum resins.

[(M) Inorganic dehydrating agents]

Examples of the inorganic dehydrating agents (M) include
5 anhydrous gypsum (CaSO_4), synthetic zeolite adsorbents (such as Molecular Sieve (tradename)) and silicates. Anhydrous gypsum and Molecular Sieve are preferably used. The inorganic dehydrating agents may be used singly, or two or more may be used in combination.

10 [0100]

The inorganic dehydrating agent (M) serves also as a stabilizer. In the antifouling coating composition, this ingredient prevents a degradation of the antifouling coating composition by water present therein and thus provides a further
15 enhancement in storage stability. In the antifouling coating composition, the content of the inorganic dehydrating agent (M) is preferably 0.1 to 10 wt%.

[(N) Flame retardants]

Examples of the flame retardants (N) include antimony
20 oxide and oxidized paraffin.

[(O) Thixotropic agents]

Examples of the thixotropic agents (O) include polyethylene glycol, polypropylene glycol and derivatives thereof.

[(P) Thermal conductivity improvers]

Examples of the thermal conductivity improvers (P) include boron nitride and aluminum oxide.

-Methods for preparing antifouling coating compositions-

5 The antifouling coating composition of the invention may be prepared by mixing the ingredients described hereinabove.
(Components of antifouling coating composition)

10 The antifouling coating composition of the invention may be provided as a one-part coating composed of a single component, or as a multi-part coating composed of two or more components. In the case of a two-part or multi-part coating, the antifouling coating composition of the invention is prepared by mixing the components together.

15 (Multi-part antifouling coating composition/kit for preparation of antifouling coating composition)

20 When the antifouling coating composition of the invention is provided as a two-part or multi-part coating, each of the components (liquids) contains one or more ingredients and is packed separately and stored in a container such as a can. At the time of application, the contents in the components are mixed together by stirring to give an antifouling coating composition. That is, in an aspect, the present invention provides a kit including such components for preparing an antifouling coating composition according to the invention.

[0101]

In an organopolysiloxane coating composition for fouling prevention, a component which contains the organopolysiloxane as the main binder resin in the antifouling coating composition is generally called the "main agent", whilst a component containing a compound which reacts with the organopolysiloxane to form a crosslinked structure is called the "curing agent". An additional component such as an "additive" is sometimes used which contains a compound that is reactive with the compounds present in the main-agent component and in the curing-agent component and is to be stored separately in order to avoid problems such as deterioration. The antifouling coating composition of the invention (the kit for the preparation of the composition) is sometimes produced as a two-part system including a main-agent component (X) and a curing-agent component (Y), or as a three-part system including a main-agent component (X), a curing-agent component (Y) and an additive component (Z).

[0102]

20 -Antifouling films and antifouling substrates-

An antifouling film is obtained by curing the antifouling coating composition described hereinabove.

[0103]

The antifouling film obtained by curing the antifouling

coating composition attains enhanced resistance to macroorganism fouling and is also resistant to the attachment of microfouling such as slime. Thus, the antifouling films are highly effective for use in applications requiring high antifouling properties such as marine vessels where a strong demand exists for the reduction in resistance caused by hydrodynamic friction.

[0104]

An antifouling substrate is obtained by coating a substrate with the above antifouling film. For example, the antifouling substrate may be produced by a method including a step of applying the antifouling coating composition to a substrate, and a step of curing the antifouling coating composition spread on the substrate by the application step, or by a method including a step of attaching an antifouling film obtained by curing of the antifouling coating composition, onto a substrate.

[0105]

Specifically, the antifouling coating composition may be applied to a substrate by a method in which the antifouling coating composition, after being sufficiently agitated, is applied to the substrate by spraying or other technique. A specific example method for curing the antifouling coating composition spread on the substrate is to allow the composition

to stand in the air at normal temperature for about 0.5 to 3 days or to heat the composition while forcibly blowing air. By these methods, an antifouling substrate in which a substrate is coated with an antifouling film can be manufactured.

5 [0106]

An example method for attaching an antifouling film obtained by curing of the antifouling coating composition, onto a substrate is to attach a film that includes an antifouling film obtained by curing the antifouling coating composition, 10 onto the substrate using a known technique such as one described in JP-A-2013-129724. In this manner, an antifouling substrate in which a substrate is coated with an antifouling film can be manufactured.

[0107]

15 The antifouling films may be formed in desired thickness in accordance with factors such as use applications. Usually, the antifouling coating composition is applied one or more times in a thickness of 30 to 400 μm , or preferably 50 to 300 μm per application, and is thereafter cured. By forming an 20 antifouling film in this manner so that the film thickness after curing will be, for example, 100 to 1000 μm , excellent film strength and antifouling performance can be obtained.

[0108]

The antifouling coating composition can be applied using

a wide range of known application techniques such as brushes, rolls, sprayers and dip coaters. As described hereinabove, the organopolysiloxane antifouling coating composition of the invention has characteristics suited for spraying.

5 Specifically, the antifouling coating composition of the invention can be sprayed to give an antifouling film with enhanced antifouling properties, while realizing a reduction in the release of spray dust and an enhancement in the transfer efficiency of the coating gained by the substrate.

10 [0109]

In a wide range of industrial fields such as power generation, port and civil engineering construction and marine vessels (building and repairing), the antifouling coating compositions of the invention may be used to protect the surface
15 of substrates to be placed in contact with seawater or fresh water from the attachment of marine organisms and thereby to allow the substrates to maintain their normal functions for long periods. Examples of such substrates include marine vessels (such as marine vessel shells), fishery materials (such
20 as ropes, fishing nets, fishing gears, floats and buoys), underwater structures such as water supply inlets and drains in thermal power plants and nuclear power plants, seawater equipment (such as seawater pumps), mega-floats, coast roads, submarine tunnels, port facilities, and sludge diffusion

prevention films in various offshore construction works for building structures such as canals and waterways.

[0110]

The antifouling coating compositions of the invention may
5 be applied directly to substrates to coat or impregnate the
substrates. Even in the case where the antifouling coating
compositions prepared according to the invention are applied
directly to substrates such as water supply inlets and drains
in nuclear power plants, mega-floats and marine vessels made
10 of such materials as fiber-reinforced plastics (FRP), steel,
iron, wood and aluminum alloys, the compositions can exhibit
good adhesion with respect to the surface of these substrates
(bases).

[0111]

15 Further, the antifouling coating compositions of the
invention may be applied to already coated substrates. That
is, the inventive antifouling coating compositions may be
applied to the surface of substrates such as marine vessels
and underwater structures preliminarily coated with base films
20 (primer films) of coatings such as antirust agents and primers.
Furthermore, the antifouling coating compositions of the
invention may be applied as overcoatings to repair the surface
of substrates such as marine vessels, in particular FRP boats,
and underwater structures which have been already coated with

conventional antifouling coatings or with the inventive antifouling coating compositions. The antifouling coating compositions of the invention may be placed in direct contact with any types of underlying coating films without limitation.

5 Similarly to general organopolysiloxane antifouling coatings, for example, the inventive antifouling coating compositions may be applied to coating films formed from coatings based on resins such as epoxy resins, urethane resins and silicone resins. The antifouling coating compositions according to the present
10 invention can be prepared to exhibit good adhesion with respect to the surface of these coating films.

EXAMPLES

[0112]

15 The present invention will be described in greater detail based on Examples given below. The scope of the invention is not limited to such Examples without departing from the spirit of the invention.

⟨Preparation of antifouling coating compositions⟩

20 Table 1 describes data such as the general names and chemical formulas of ingredients for antifouling coating compositions used in Examples and Comparative Examples. The weight average molecular weight Mw described in Table 1 was measured by GPC using a calibration curve recorded based on

polystyrene standards.

[0113]

[Table 1]

Table 1

	Ingredients	Data including general names and chemical formulae*
Main-agent component (X)	Silica-containing organopolysiloxane	HO-[Si(CH ₃) ₂ -O] _n -H, weight average molecular weight 28,500, hydrophobized silica
	Red pigment	Ferric oxide
	Copper pyrithione	Cu(-S-C ₅ H ₄ N-O-) ₂
	Zinc pyrithione	Zn(-S-C ₅ H ₄ N-O-) ₂
	Cuprous oxide 1	Cu ₂ O (LOLO TINT LM, American Kemet Corporation)
	Cuprous oxide 2	Cu ₂ O (NC-803, NISSIN CHEMCO Co., Ltd.)
	Cuprous oxide 3	Cu ₂ O (Red Copp 97N Premium, American Kemet Corporation)
	Cuprous oxide 4	Cu ₂ O (NC-301, NISSIN CHEMCO Co., Ltd.)
	Copper powder	Cu(O) (electrolytic copper powder, NISSIN CHEMCO Co., Ltd.)
	Xylene	Xylene
Curing-agent component (Y)	Organosilane partial hydrolytic condensate	H ₅ C ₂ O[Si(OC ₂ H ₅) ₂ O] _n C ₂ H ₅
	Phenyl-modified organopolysiloxane	H ₃ C[Si(CH ₃) ₂ O] _n [Si(C ₆ H ₅) ₂ O] _m Si(CH ₃) ₃
	Ether-modified organopolysiloxane 1	H ₃ C[Si(CH ₃) ₂ O] _n [Si(CH ₃)(C ₃ H ₆ (OC ₂ H ₄) _p OCH ₃)O] _m Si(CH ₃) ₃
	Ether-modified organopolysiloxane 2	H ₃ C[Si(CH ₃) ₂ O] _n [Si(CH ₃)(C ₃ H ₆ (OC ₂ H ₄) _p (OC ₃ H ₆) _q OH)O] _m Si(CH ₃) ₃
	N-butanol	N-butanol
	Tin catalyst	Dibutyltin dilaurate
	Xylene	Xylene

*The letters m, n, p and q in the formulae are positive integers.

[0114]

The ingredients for a main-agent component (X), and the ingredients for a curing-agent component (Y) described in Table 2 were each mixed together sufficiently in the amounts shown in Table 2 with use of a disperser to uniformity, thus preparing the main-agent component (X) and the curing-agent component (Y). The main-agent component (X) and the curing-agent component (Y) were mixed with each other to give an antifouling coating composition of any of Examples 1 to 10 and Comparative Examples 1 and 2. The values regarding the ingredients for the main-agent component (X) and the curing-agent component (Y)

in Table 2 indicate parts by weight.

[0115]

The antifouling coating compositions of Examples 1 to 10 and Comparative Examples 1 and 2 prepared as described above were tested to measure the dust release ratio during spraying and to test the antifouling properties of antifouling films formed from these antifouling coating compositions. The results are described in Table 2.

[Dust release ratio during spraying]

10 The test to evaluate the dust release ratio during spraying involved a measurement device illustrated in Fig. 1. The measurement device included an inlet duct, a target face F to be coated, a bottom face B and a spray gun G.

[0116]

15 Air was drawn at a wind speed of about 2 m/s through the inlet duct that had been open in the form of a rectangle 900 mm in width and 850 mm in height.

[0117]

20 A plate having the face F to be coated that was 850 mm in height and 700 mm in width was placed so that one side of the face F would be in contact with one side of the inlet duct and the face F would be vertical to the inlet duct. A polyethylene sheet having a known weight was attached to the entirety of the face F.

[0118]

A plate having the bottom face B that was 450 mm in width and 700 mm in width was placed so that two sides of the bottom face B would be in contact with one side of the inlet duct and
5 with one side of the face F. A polyethylene sheet having a known weight was attached to the entirety of the bottom face B.

[0119]

The antifouling coating compositions of Examples 1 to 10 and Comparative Examples 1 and 2 were each loaded into the spray
10 gun G, and the end of the gun (the spraying point S) was set at 700 mm away from the face F and 450 mm above the lower end of the face F. The antifouling coating composition was ejected from the spray gun at a spray pressure of 5 kgf/cm² for 10 seconds toward the center of the face F in a direction perpendicular
15 to the face F.

[0120]

The weight of the spray gun loaded with the antifouling coating composition (the total of the weight of the spray gun and the weight of the antifouling coating composition loaded
20 therein) was measured before and after the application. The weight after the application was subtracted from the weight before the application, and thereby the weight of the antifouling coating composition that had been sprayed was calculated. The sprayed weight was multiplied by the solid

fraction of the antifouling coating composition to give the weight in terms of solids of the antifouling coating composition sprayed.

[0121]

5 After the application, the polyethylene sheet which had been attached to the face F and had gained the antifouling coating composition was dried for 24 hours and thereafter the weight (the total of the weight of the polyethylene sheet and the weight of the antifouling coating composition applied
10 thereto) was measured. The weight of the polyethylene sheet before the application was subtracted from the weight, and thereby the weight of the coating on target was determined.

[0122]

 After the application, the polyethylene sheet which had
15 been attached to the bottom face B and which had gained the antifouling coating composition was dried for 24 hours and thereafter the weight (the total of the weight of the polyethylene sheet and the weight of the antifouling coating composition applied thereto) was measured. The weight of the
20 polyethylene sheet before the application was subtracted from the weight, and thereby the weight of the coating dropped was determined.

[0123]

Assuming that the weight of the airborne spray dust was

the difference obtained by subtracting the weight of the coating gained by the target face and dropped to the bottom face from the weight of solids in the coating sprayed, the dust release ratio was calculated using the following equation.

5 [0124]

[Math. 1]

$$(\text{Dust release ratio (\%)}) = [((\text{Weight of solids in coating sprayed}) - (\text{Weight of coating on target}) - (\text{Weight of coating dropped})) / (\text{Weight of solids in coating sprayed})] \times 100$$

10 [0125]

Each antifouling coating composition was applied two times. Table 2 describes the average and the standard deviation of the dust release ratios obtained.

[0126]

15 The lower the dust release ratio, the less the spray dust is released during the spray application and the higher the transfer efficiency is evaluated.

[Antifouling tests]

(Preparation of test plates)

20 Sandblasted plates were provided which had been coated with an epoxy anticorrosive coating (trade name: BANNOH 500, manufactured by CHUGOKU MARINE PAINTS, LTD.) and further with a silicone binder coating (trade name: CMP BIOCLEAN TIE COAT, manufactured by CHUGOKU MARINE PAINTS, LTD.) in this order each

in a thickness of 100 μm . To the coated plates, each of the compositions of Examples 1 to 10 and Comparative Examples 1 and 2 was applied so that the dry film thickness would be 200 μm . The coatings were cured. Test plates were thus obtained.

5 [0127]

(Method of testing dynamic antifouling properties)

After the test plates were dried at room temperature for 7 days, they were immersed in seawater off the coast in Kure, Hiroshima, Japan, while generating a stream of water with rotors so that the speed was about 15 knots. The stream of water was applied to the surface of the antifouling films of the test plates, and the proportions of the areas fouled by aquatic organisms relative to the surface of the antifouling films of the test plates were evaluated by visual observation every three months. The dynamic antifouling properties were evaluated by giving evaluation points based on the criteria described below.

15 [0128]

(Method of testing static antifouling properties)

After the test plates were dried at room temperature for 7 days, they were immersed in seawater in Miyajima Bay, Hiroshima, Japan, under static conditions. The proportions of the areas fouled by organisms relative to the surface of the antifouling films of the test plates were evaluated by visual observation every three months. The static antifouling

properties were evaluated by giving evaluation points based on the following criteria.

[0129]

(Antifouling tests, evaluation points)

5 0: No aquatic organisms had become attached.

 1: Aquatic organisms had become attached locally.

 2: Aquatic organisms had become attached to the entirety of the surface.

[0130]

10 [Table 2]

Table 2

	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Ex. 6	Ex. 7	Ex. 8	Ex. 9	Ex. 10	Ex. 11	Comp. Ex. 1	Comp. Ex. 2
Main-agent component (X)	Silica-containing organopolysiloxane	59.8	59.8	59.8	59.8	59.8	59.8	59.8	59.8	59.8	59.8	59.8	59.8
	Red pigment	7.7	7.7	7.7	7.7	7.7	7.7	7.7	7.7	7.7	7.7	7.7	30.8
	Xylene	14.1	14.1	20.1	16.7	14.1	14.1	14.1	14.1	14.7	14.1	11.5	14.4
	Cuprous oxide 1	18.4	18.4			18.4							
	Copper pyrrhione		2.0	6.0	6.0								
	Zinc pyrrhione						18.4						
	Cuprous oxide 3			18.4	36.8			18.4					
	Cuprous oxide 4								18.4	36.8			
	Copper powder												
	Total of main-agent component (X)	100.0	102.0	112.0	127.0	106.0	100.0	100.0	100.0	119.0	100.0	79.0	105.0
Curing-agent component (Y)	Organosilane partial hydrolytic condensate	3.4	3.4	3.4	3.4	3.4	3.4	3.4	3.4	3.4	3.4	3.4	3.4
	Phenyl-modified organopolysiloxane	5.7	5.7	5.7	5.7	5.7	5.7	5.7	5.7	5.7	5.7	5.7	5.7
	Tin catalyst	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6
	Ether-modified organopolysiloxane 1	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0
	Ether-modified organopolysiloxane 2					3.0							
	N-butanol	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
	Xylene	2.3	2.3	2.3	2.3	2.3	2.3	2.3	2.3	2.3	2.3	2.3	2.3
	Total of curing-agent component (Y)	20.0	20.0	20.0	20.0	20.0	20.0	20.0	20.0	20.0	20.0	20.0	20.0
	Total of all components	120.0	122.0	132.0	147.0	126.0	120.0	120.0	120.0	139.0	120.0	99.0	125.0
	Solid fraction (wt%)	81.1	81.5	78.3	82.8	82	81.1	81.1	81.1	83.3	81.1	79.8	81.7
Dust release ratio	Average (%)	33.5	31.7	30.5	26.5	34.3	35.6	36.3	36.3	34.6	33.3	41.7	40.6
	Standard deviation (%)	0.9	2	3.8	2.8	0.7	0.4	0.2	2.9	3.0	0.7	0.3	2.3
	3 months	0	0	0	0	0	0	0	0	0	0	0	0
	6 months	0	0	0	0	0	0	0	0	0	0	1	1
	9 months	0	0	0	0	0	0	0	0	0	0	1	1
	12 months	0	0	0	0	0	0	0	0	0	0	2	2
	3 months	0	0	0	0	0	0	0	0	0	0	0	0
	6 months	0	0	0	0	0	0	0	0	0	0	1	1
	9 months	1	0	0	0	0	1	1	1	1	0	2	2
	12 months	2	0	0	0	0	2	2	2	2	1	2	2
Antifouling tests	Dynamic antifouling properties	3 months	0	0	0	0	0	0	0	0	0	0	0
		6 months	0	0	0	0	0	0	0	0	0	1	1
		9 months	0	0	0	0	0	0	0	0	0	1	1
		12 months	0	0	0	0	0	0	0	0	0	2	2
	Static antifouling properties	3 months	0	0	0	0	0	0	0	0	0	0	0
		6 months	0	0	0	0	0	0	0	0	0	1	1
		9 months	1	0	0	0	1	1	1	1	0	2	2
		12 months	2	0	0	0	2	2	2	2	1	2	2

[CLAIMS]

[Claim 1]

An antifouling coating composition comprising:

- (A) an organopolysiloxane having two or more silanol
5 groups in the molecule,
(B) a crosslinking agent,
(C) an inorganic copper, and
copper pyrithione.

[Claim 2]

- 10 The antifouling coating composition according to Claim
1, wherein the inorganic copper (C) is cuprous oxide and/or
metallic copper.

[Claim 3]

- The antifouling coating composition according to any one
15 of Claim 1 or 2, further comprising an antifouling imparting
agent (D) other than the inorganic copper (C) and copper
pyrithione.

[Claim 4]

- The antifouling coating composition according to Claim
20 3, wherein the antifouling imparting agent (D) is a pyrithione
salt other than copper pyrithione.

[Claim 5]

The antifouling coating composition according to any one of Claims 1 to 4, which contains the inorganic copper (C) in an amount of 0.5 to 60 wt%.

5 [Claim 6]

The antifouling coating composition according to any one of Claims 1 to 4, which contains the inorganic copper (C) in an amount of 5 to 40 wt%.

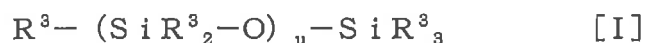
[Claim 7]

10 The antifouling coating composition according to any one of Claims 1 to 6, further comprising a silicone oil (E).

[Claim 8]

The antifouling coating composition according to Claim 7, wherein the silicone oil (E) is an organopolysiloxane represented by the general formula [I] below:

[Chem. 1]



(in the formula, R^3 independently at each occurrence represents a C_{1-10} alkyl group, an alkenyl group, an aryl group, an aralkyl group, an alkoxy group or a halogenated alkyl group; 20 or a C_{2-100} polyoxyalkylene group optionally endcapped with a C_{1-10} hydrocarbon group, a hydroxyl group or a silyl group having a condensation reactive group on the silicon atom, and u is an integer of 1 to 10,000).

[Claim 9]

The antifouling coating composition according to any one of Claims 1 to 8, further comprising a metallic curing catalyst (F) and/or an organic solvent (G).

5 [Claim 10]

The antifouling coating composition according to Claim 9, wherein the organic solvent (G) comprises an aromatic hydrocarbon and an alcohol.

[Claim 11]

10 An antifouling film obtained by curing the antifouling coating composition described in any one of Claims 1 to 10.

[Claim 12]

A method for producing antifouling films, comprising applying the antifouling coating composition described in any
15 one of Claims 1 to 10 to form an antifouling film.

[Claim 13]

An antifouling substrate obtained by coating a substrate with the antifouling film described in Claim 11.

[Claim 14]

20 The antifouling substrate according to Claim 13, wherein the substrate is any of a marine vessel, an underwater structure and fishing equipment.

[Claim 15]

A method for preventing substrates from fouling,
comprising coating a surface of the substrate with the
antifouling film described in Claim 11.

5 [Claim 16]

A method for producing antifouling substrates,
comprising a step of applying the antifouling coating
composition described in any one of Claims 1 to 10 to a substrate,
and a step of curing the antifouling coating composition spread
10 on the substrate by the application step.