

DESCRIPTION

METHOD FOR REINFORCING FOULING CONTROL COATINGS

TECHNICAL FIELD

[0001]

5 The present invention relates to a reinforcing method which imparts excellent durability to fouling control coatings.

BACKGROUND ART

[0002]

10 In recent years, studies directed to the prevention of the attachment of aquatic organisms to objects such as marine vessels and underwater structures often focus on fouling control coatings which combine an antifouling agent having bioactivity toward marine organisms with an organopolysiloxane
15 coating having the ability to prevent the attachment and settling of marine organisms.

[0003]

 However, organopolysiloxane coatings are prone to external physical damages due to their material
20 characteristics. Further, the addition of antifouling agents results in a decrease in coating strength and the resultant fouling control coatings become more fragile. As a result, the coatings are easily damaged by external physical factors such as impacts during high-pressure washing of docked marine

vessels, and collisions of marine vessels and submarine structures with objects floating in the sea. The consequent damages destroy antifouling properties and cause economic disadvantages such as the need of repair coating application.

5 [0004]

Patent Documents 1 and 2 present fouling control coating compositions including a polysiloxane-based binder, a hydrophilic-modified polysiloxane and a biocide. However, Patent Documents 1 and 2 do not address the problem of damages
10 to coatings obtained from the fouling control coating compositions.

[0005]

Patent Document 3 describes a silicone coating system including an organopolysiloxane and 3-isothiazolones as a
15 biocide. In an aspect, a duplex coating system having a bonding layer and a release layer is described. The bonding layer in the duplex coating system is a reaction product including, on the weight thereof, 10 to 80% organopolysiloxane, 30 to 80% monofunctional monomer, less than 5% free radical initiator,
20 less than 2% polyfunctional monomer, and 0.5 to 25% biocide dispersed therethrough. However, according to the knowledge of the present inventors, the addition of 3-isothiazolones to organopolysiloxane coating compositions sometimes results in, depending on conditions, surface abnormalities and adhesion

failures ascribed to the 3-isothiazolones. Thus, it is difficult to apply the disclosed technique to organopolysiloxane fouling control coatings widely and generally.

5 [0006]

Patent Document 4 describes a structure coated with a first coating layer containing a biocide, and a subsequent coating layer disposed on the first coating layer and containing less biocide than the first coating layer. The first coating layer and/or the subsequent coating layer includes a polyorganosiloxane.

[0007]

Patent Document 5 describes a coating system which includes a first coat and a second coat each including a polysiloxane-based binder matrix including hydrophilic oligomer/polymer moieties or a hydrophilic-modified polysiloxane oil.

[0008]

However, Patent Documents 4 and 5 do not specifically describe methods for preventing coating damages such as separations.

CITATION LIST

PATENT LITERATURE

[0009]

Patent Document 1: JP-A-2013-515122

Patent Document 2: JP-A-2014-524949

Patent Document 3: JP-A-H10-501272

Patent Document 4: JP-A-2004-519978

5 Patent Document 5: WO 2014/117786

SUMMARY OF INVENTION

TECHNICAL PROBLEM

[0010]

The present invention has been made to solve the problems
10 in the art discussed above. It is therefore an object of the
invention to give excellent durability to
organopolysiloxane-based fouling control coatings.

SOLUTION TO PROBLEM

[0011]

15 The present invention pertains to the following items [1]
to [13].

[1] A method for reinforcing a fouling control coating,
comprising:

a step of forming a reinforcing coating (O) by applying
20 and curing a reinforcing coating composition [o], and

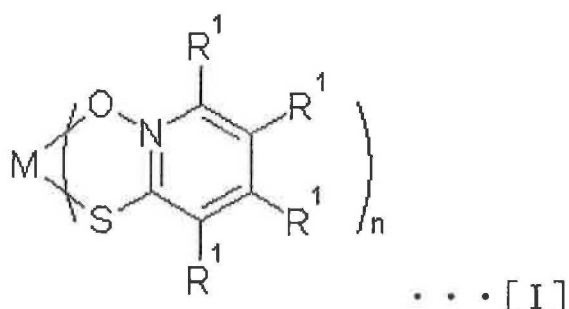
a step of providing a fouling control coating (X) formed
by applying and curing a fouling control coating composition
[x], onto the reinforcing coating (O),

the reinforcing coating composition [o] comprising an

organopolysiloxane (AO) having two or more silanol groups or hydrolyzable groups in the molecule, and a pyrrhione salt compound (BO) represented by the following general formula [I]:

[0012]

5 [Chem. 1]



(in the formula [I], R¹ independently at each occurrence is a hydrogen atom, an alkyl group having 1 to 6 carbon atoms, a cycloalkyl group having 3 to 6 carbon atoms, an alkenyl group having 2 to 6 carbon atoms, an aryl group having 6 carbon atoms, an alkoxy group having 1 to 6 carbon atoms, or a halogenated alkyl group having 1 to 6 carbon atoms,

M is a metal selected from Cu, Zn, Na, Mg, Ca, Ba, Fe and Sr, and

15 n is the valence of the metal M),

the fouling control coating composition [x] comprising an organopolysiloxane (AX) having two or more silanol groups or hydrolyzable groups in the molecule, and an antifouling agent (BX),

20 the content of the pyrrhione salt compound (BO) in the

reinforcing coating (O) being not more than 10 wt%,

the reinforcing coating (O) giving reinforcement to the coating (X) adhering thereto.

[2] The method for reinforcing a fouling control coating
5 described in [1], wherein the content of the pyrithione salt compound (BO) in the reinforcing coating (O) is not more than 5.5 wt%.

[3] The method for reinforcing a fouling control coating described in [1] or [2], wherein M in the general formula [I]
10 is Cu and/or Zn.

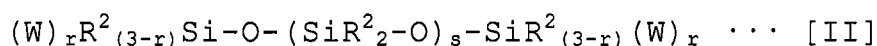
[4] The method for reinforcing a fouling control coating described in any of [1] to [3], wherein the antifouling agent (BX) in the fouling control coating (X) is a pyrithione salt compound represented by the general formula [I] in which M is
15 Cu.

[5] The method for reinforcing a fouling control coating described in any of [1] to [4], wherein the pyrithione salt compound (BO) in the reinforcing coating (O) is a compound represented by the general formula [I] in which M is Zn.

20 [6] The method for reinforcing a fouling control coating described in any of [1] to [5], wherein the content (wt%) of the pyrithione salt compound (BO) in the reinforcing coating (O) is smaller than the content (wt%) of the antifouling agent (BX) in the fouling control coating (X).

[7] The method for reinforcing a fouling control coating described in any of [1] to [6], wherein the organopolysiloxane (AO) and/or the organopolysiloxane (AX) is represented by the following general formula [II]:

5 [0013]



(in the formula [II], W independently at each occurrence is a hydroxyl group or a hydrolyzable group,

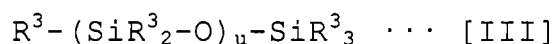
R^2 independently at each occurrence is a hydrogen atom,
 10 an alkyl group having 1 to 10 carbon atoms, an alkenyl group having 2 to 10 carbon atoms, an aryl group having 6 to 10 carbon atoms, an aralkyl group having 7 to 10 carbon atoms, an alkoxy group having 1 to 10 carbon atoms, or a halogenated alkyl group having 1 to 10 carbon atoms,

15 r is an integer of 1 to 3, and

s is an integer of 10 to 10,000).

[8] The method for reinforcing a fouling control coating described in any of [1] to [7], wherein the reinforcing coating composition [o] further comprises one or more
 20 organopolysiloxanes (C) other than the organopolysiloxane (AO), represented by the following general formula [III]:

[0014]



(in the formula [III], u is an integer of 1 to 10,000,

and

R³ independently at each occurrence is an alkyl group having 1 to 30 carbon atoms, an alkenyl group having 2 to 30 carbon atoms, an aryl group having 6 to 30 carbon atoms, an
5 aralkyl group having 7 to 10 carbon atoms, or a halogenated alkyl group having 1 to 30 carbon atoms, and may contain -O-, -S- or -NR- between carbon atoms wherein R is a hydrogen atom or an alkyl group having 1 to 5 carbon atoms).

[9] The method for reinforcing a fouling control coating
10 described in [8], wherein R³s in the general formula [III] are alkyl and/or aryl groups.

[10] The method for reinforcing a fouling control coating described in any of [1] to [9], which is applied to a substrate used in water.

15 [11] A fouling control substrate obtained by applying the method for reinforcing a fouling control coating described in any of [1] to [10] to at least part of a surface of a substrate.

[12] The fouling control substrate described in [11], wherein the substrate is any of a marine vessel, an underwater
20 structure and a fishing gear.

[13] The fouling control substrate described in [11] or [12], which is used in water.

ADVANTAGEOUS EFFECTS OF INVENTION

[0015]

According to the present invention, high impact resistance can be imparted to fouling control coatings. As a result, the peeling, chipping and loss of the coatings by external physical damages which are often encountered in the conventional coatings can be remedied, and stable antifouling performance can be obtained. Other advantages that can be enjoyed include the reduction of the area to be coated at the time of repair coating applications.

DESCRIPTION OF EMBODIMENTS

10 [0016]

The present invention will be described in detail hereinbelow.

[0017]

A method for reinforcing a fouling control coating according to the present invention comprises:

a step of forming a reinforcing coating (O) by applying and curing a reinforcing coating composition [o], and

a step of providing a fouling control coating (X) formed by applying and curing a fouling control coating composition [x], onto the reinforcing coating (O).

The reinforcing coating composition [o] comprises an organopolysiloxane (AO) having two or more silanol groups or hydrolyzable groups in the molecule, and a specific pyrithione salt compound (BO).

The fouling control coating composition [x] comprises an organopolysiloxane (AX) having two or more silanol groups or hydrolyzable groups in the molecule, and an antifouling agent (BX).

5 The content of the pyrithione salt compound (BO) in the reinforcing coating (O) is not more than 10 wt%.

The reinforcing coating (O) gives reinforcement to the fouling control coating (X).

⟨Ingredients⟩

10 Hereinbelow, the ingredients of the reinforcing coating composition [o] and the fouling control coating composition [x] will be described.

[0018]

(AO) and (AX): Organopolysiloxanes having two or more silanol
15 groups or hydrolyzable groups in the molecule

The reinforcing coating composition [o] of the invention contains an organopolysiloxane (AO) having two or more silanol groups or hydrolyzable groups in the molecule. The fouling control coating composition [x] of the invention contains an
20 organopolysiloxane (AX) having two or more silanol groups or hydrolyzable groups in the molecule. These organopolysiloxanes (AO) and (AX) may be of the same type or different types.

[0019]

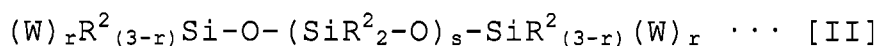
The organopolysiloxanes (AO) and (AX) having two or more silanol groups or hydrolyzable groups in the molecule may be any compounds which include a -Si-O-Si-O- chain structure in the main chain and have two or more silanol groups or

5 hydrolyzable groups in the molecule.

[0020]

Preferably, the organopolysiloxanes (AO) and (AX) used in the invention are each a compound represented by the following general formula [II]:

10 [0021]



(In the formula [II], W independently at each occurrence is a hydroxyl group or a hydrolyzable group,

R² independently at each occurrence is a hydrogen atom,
 15 an alkyl group having 1 to 10 carbon atoms, an alkenyl group having 2 to 10 carbon atoms, an aryl group having 6 to 10 carbon atoms, an aralkyl group having 7 to 10 carbon atoms, an alkoxy group having 1 to 10 carbon atoms, or a halogenated alkyl group having 1 to 10 carbon atoms,

20 r is an integer of 1 to 3, and

s is an integer of 10 to 10,000.)

In the general formula [II], W independently at each occurrence is a hydroxyl group or a hydrolyzable group.

[0022]

Examples of the hydrolyzable groups include alkoxy groups, oxime groups, acetyloxy groups, acyloxy groups, alkenyloxy groups, iminoxy groups, amino groups, amide groups and aminoxy groups, with alkoxy groups and oxime groups being preferable.

5 [0023]

Preferred alkoxy groups are those having a total number of carbon atoms of 1 to 10, and an oxygen atom may be present between one or more pairs of carbon atoms. Examples of such alkoxy groups include methoxy group, ethoxy group, propoxy group, butoxy group, methoxyethoxy group and ethoxyethoxy group.

[0024]

Preferred oxime groups are those having a total number of carbon atoms of 1 to 10, with examples including dimethyl ketoxime, methyl ethyl ketoxime, diethyl ketoxime and methyl isopropyl ketoxime.

[0025]

Preferred acetyloxy groups are aliphatic acetyloxy groups having a total number of carbon atoms of 1 to 10, and aromatic acetyloxy groups having a total number of carbon atoms of 6 to 12, with examples including acetoxy group, propyloxy group, butyloxy group and benzoyloxy group.

[0026]

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 acetoxym group, propionoxym group, butyloxym group and benzoyloxym group.

[0027]

Preferred alkenyloxym groups are those having a total number of carbon atoms of 3 to 10, with examples including isopropenyloxym group, isobutenyloxym group and 1-ethyl-2-methylvinylloxym group.

[0028]

Preferred iminoxym groups ($=\text{N-OH}$, other names are oxyimino groups and ketoxime groups) are those having a total number of carbon atoms of about 3 to 10, with examples including ketoxime group, dimethyl ketoxime group, methyl ethyl ketoxime group, diethyl ketoxime group, cyclopentanoxime group and cyclohexanoxime group.

[0029]

Preferred amino groups are those having a total number of carbon atoms of 1 to 10, with examples including N-methylamino group, N-ethylamino group, N-propylamino group, N-butylamino group, N,N-dimethylamino group, N,N-diethylamino group and cyclohexylamino group.

[0030]

Preferred amide groups are those having a total number of carbon atoms of 2 to 10, with examples including N-methylacetamide group, N-ethylacetamide group and N-methylbenzamide group.

5 [0031]

Preferred aminoxy groups are those having a total number of carbon atoms of 2 to 10, with examples including N,N-dimethylaminoxy group and N,N-diethylaminoxy group.

[0032]

10 In the general formula [II], R^2 independently at each occurrence is a hydrogen atom, an alkyl group having 1 to 10 carbon atoms, an alkenyl group having 2 to 10 carbon atoms, an aryl group having 6 to 10 carbon atoms, an aralkyl group having 7 to 10 carbon atoms, an alkoxy group having 1 to 10
15 carbon atoms, or a halogenated alkyl group having 1 to 10 carbon atoms.

[0033]

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

[0034]

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

group and cyclohexenyl group.

[0035]

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

5 [0036]

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

[0037]

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

[0038]

Examples of the halogenated alkyl groups include groups
resulting from the substitution of the above alkyl groups with
15 halogen atoms such as fluorine atoms, chlorine atoms, bromine
atoms and iodine atoms in place of part or all of the hydrogen
atoms.

[0039]

R^2 s are particularly preferably methyl groups.

20 [0040]

In the general formula [II], r is an integer of 1 to 3.
When W is a hydroxyl group, r is preferably 1. When W is a
hydrolyzable group, r is preferably 2.

[0041]

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

[0042]

In the organopolysiloxanes (AO) and (AX) having two or
5 more silanol groups or hydrolyzable groups in the molecule, the weight average molecular weight measured by gel permeation chromatography (GPC) relative to polystyrene 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 thereof at 23°C is
10 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 are advantageous in that the coating compositions used to form an antifouling coating stack attain excellent production workability,
15 sprayability and coating curability, and form coatings with excellent strength.

[0043]

The organopolysiloxanes (AO) and (AX) having two or more silanol groups or hydrolyzable groups in the molecule are
20 usually present in the reinforcing coating composition [o] and the fouling control coating composition [x], respectively, in an amount of 20 to 90 wt%, and preferably 50 to 70 wt%. The organopolysiloxanes (AO) and (AX) usually each represent 30 to 95 wt%, and preferably 60 to 90 wt% of the weight of the

solids contained in the reinforcing coating composition [o] or the fouling control coating composition [x], namely, the weight of the reinforcing coating (O) or the fouling control coating (X), respectively. When the contents of the organopolysiloxanes (AO) and (AX) are in these ranges, the obtainable antifouling coating stack attains good coating strength and rubber elasticity and exhibits long-term antifouling properties.

[0044]

The organopolysiloxanes (AO) and (AX) may be produced or purchased. Examples of the commercial products include "DMS-S35" (manufactured by GELEST).

[0045]

The organopolysiloxane (AO) present in the reinforcing coating composition [o] and the organopolysiloxane (AX) present in the fouling control coating composition [x] may be of the same type or different types.

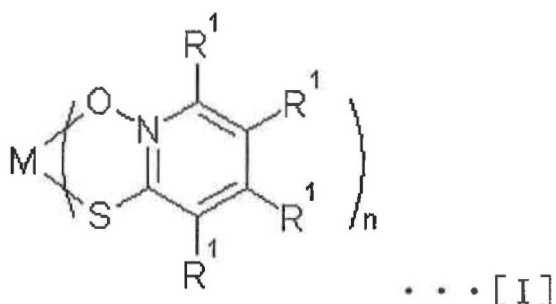
[0046]

(BO): Pyrithione salt compounds

In the invention, the reinforcing coating composition [o] for forming a reinforcing coating (O) contains a pyrithione salt compound (BO) represented by the following general formula [I]:

[0047]

[Chem. 2]



(In the formula [I], R^1 independently at each occurrence is a hydrogen atom, an alkyl group having 1 to 6 carbon atoms, a cycloalkyl group having 3 to 6 carbon atoms, an alkenyl group having 2 to 6 carbon atoms, an aryl group having 6 carbon atoms, an alkoxy group having 1 to 6 carbon atoms, or a halogenated alkyl group having 1 to 6 carbon atoms,

M is a metal selected from Cu, Zn, Na, Mg, Ca, Ba, Fe and Sr, and

n is the valence of the metal M.)

In the general formula [I], M is preferably Cu and/or Zn, and more preferably Zn.

[0048]

The pyrrithione salt compound (BO) is present in an amount of not more than 10 wt% relative to the weight of the solids in the reinforcing coating composition [o], namely, the weight of the reinforcing coating (O) obtained by curing the reinforcing coating composition [o]. The amount is preferably not more than 5.5 wt%, and more preferably 2 to 5 wt%. This

content of the pyrithione salt compound (BO) ensures that the composition will give an excellent reinforcement to the fouling control coating.

[0049]

5 It is preferable that the content (wt%) of the pyrithione compound (BO) in the reinforcing coating (O) be smaller than the content (wt%) of the antifouling agent (BX) in the fouling control coating (X) described later. In this case, the reinforcing coating (O) gives a higher reinforcement to the
10 fouling control coating (X).

[0050]

(BX): Antifouling agents

 In the invention, the fouling control coating composition [x] for forming a fouling control coating (X) contains an
15 antifouling agent (BX).

[0051]

 The antifouling agent (BX) may be organic or inorganic.

[0052]

 Examples of the organic antifouling agents include
20 pyrithione salt compounds represented by the general formula [I], p-isopropylpyridine methyldiphenyl borane, pyridine triphenyl borane, tetramethylthiuram disulfide, carbamate-based compounds (for example: zinc dimethyldithiocarbamate, manganese(II)

ethylenebisdithiocarbamate),

2,4,5,6-tetrachloroisophthalonitrile,

2-(p-chlorophenyl)-3-cyano-4-bromo-5-trifluoromethylpyrrol

e, (RS)-4-[1-(2,3-dimethylphenyl)ethyl]-3H-imidazole and

5 4,5-dichloro-N-octyl-4-isothiazolin-3-one. It is preferable

that the antifouling agent(s) (BX) used include a pyrithione

salt compound represented by the general formula [I], more

preferably include a pyrithione salt compound represented by

the general formula [I] in which M is Cu and/or Zn, and still

10 more preferably be a pyrithione salt compound represented by

the general formula [I] in which M is Cu. It is also preferable

that when the pyrithione salt compound (BO) in the reinforcing

coating (O) is a compound of the general formula [I] in which

M is Zn, the antifouling agent (BX) in the fouling control

15 coating (X) be a compound of the general formula [I] in which

M is Cu.

[0053]

The antifouling agents (BX) may be used singly, or a plurality of different types may be used in combination.

20 [0054]

The antifouling agent (BX) is usually present in an amount of 0.5 to 30 wt%, preferably 2 to 15 wt%, and more preferably 2.5 to 10 wt% relative to the weight of the solids in the fouling control coating composition [x], namely, the weight of the

fouling control coating (X) obtained by applying and curing the fouling control coating composition [x]. It is preferable that the content (wt%) of the antifouling agent (BX) in the fouling control coating (X) be larger than the content (wt%) of the pyrithione compound (BO) in the reinforcing coating (O) described hereinabove. This content of the antifouling agent (BX) ensures that the obtainable fouling control coating will have high antifouling properties and excellent durability.

[0055]

10 Optional ingredients

The reinforcing coating composition [o] and the fouling control coating composition [x] of the invention each may contain optional ingredients other than the organopolysiloxane (AO) or (AX), and the pyrithione salt compound (BO) or the antifouling agent (BX). Examples of such optional ingredients include (C) organopolysiloxanes other than the organopolysiloxanes (AO) or (AX), (D) curing catalysts, (E) organosilanes having two or more hydrolyzable groups in the molecule and/or partial hydrolytic condensates thereof, (F) silane coupling agents, (G) silicas, (H) fillers, (I) organic solvents, (J) anti-sag, anti-settling agents, (K) additional coating ingredients, (L) inorganic dehydrating agents and (M) other additive ingredients.

[0056]

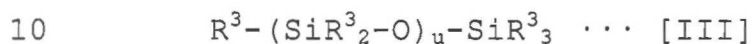
(C): Organopolysiloxanes other than (AO) or (AX)

Where necessary, the reinforcing coating composition [o] and the fouling control coating composition [x] of the invention each may contain an organopolysiloxane (C) other than (AO) or
 5 (AX).

[0057]

A preferred organopolysiloxane (C) other than (AO) or (AX) may be represented by the following general formula [III]:

[0058]



(In the formula [III], u is an integer of 1 to 10,000, and

R^3 independently at each occurrence is an alkyl group having 1 to 30 carbon atoms, an alkenyl group having 2 to 30
 15 carbon atoms, an aryl group having 6 to 30 carbon atoms, an aralkyl group having 7 to 10 carbon atoms, or a halogenated alkyl group having 1 to 30 carbon atoms, and may contain -O-, -S- or -NR- between carbon atoms wherein R is a hydrogen atom or an alkyl group having 1 to 5 carbon atoms.)

20 Such organopolysiloxanes (C) may be produced or purchased. Examples of the commercial organopolysiloxanes (C) include polyorganosiloxanes of the formula [III] in which R^3 's are methyl groups and phenyl groups (such as, in trade names, "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)); and polyorganosiloxanes of the formula [III] in which R³s are alkyl groups and ether-containing alkyl groups (such as, in trade name, "KF-6017" (manufactured by Shin-Etsu Chemical Co., Ltd.)).

[0059]

In the reinforcing coating composition [o] and/or the fouling control coating composition [x], the content of the organopolysiloxane (C) is usually 0 to 20 wt%, and preferably 0 to 7 wt%. This content of the organopolysiloxane (C) ensures that the reinforcing coating composition [o] of the invention attains good adhesion with the substrate and the fouling control coating composition [x] achieves good adhesion with respect to the base and exhibits good antifouling properties.

[0060]

(D): Curing catalysts

Where necessary, the reinforcing coating composition [o] and the fouling control coating composition [x] each may contain a curing catalyst (D).

[0061]

The curing catalyst (D) may be suitably a curable catalyst. For example, those catalysts described in Japanese Patent No. 2522854 may be suitably used. Specific examples include tin

carboxylates such as tin naphthenate and tin oleate; tin
 compounds such as dibutyltin diacetate, dibutyltin
 acetoacetate, dibutyltin dioctoate, dibutyltin dilaurate,
 dibutyltin dioleate, dibutyltin oxide, dibutyltin dimethoxide,
 5 dibutyltin dipentanoate, 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
 10 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,
 15 iron-2-ethylhexoate, cobalt-2-ethylhexoate,
 manganese-2-ethylhexoate, cobalt naphthenate and
 alkoxyaluminum compounds; aminoalkyl group-substituted
 alkoxysilanes such as 3-aminopropyltrimethoxysilane and N- β
 (aminoethyl) γ -aminopropyltrimethoxysilane; amine compounds
 20 and salts thereof such as hexylamine, dodecylamine
 phosphate, dimethylhydroxylamine and diethylhydroxylamine;
 quaternary ammonium salts such as benzyltriethylammonium
 acetate; lower fatty acid salts of alkali metals such as
 potassium acetate, sodium acetate and lithium oxalate; and

guanidyl group-containing silanes or siloxanes such as tetramethylguanidylpropyltrimethoxysilane, tetramethylguanidylpropylmethyldimethoxysilane and tetramethylguanidylpropyltris(trimethylsiloxy)silane.

5 [0062]

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

[0063]

10 The curing catalyst (D) is preferably added to the reinforcing coating composition [o] and/or the fouling control coating composition [x] of the invention in the range of 0.01 to 3 wt%, and more preferably in the range of 0.2 wt% to 1 wt%.

[0064]

15 When added in the above amount, the curing catalyst (D) promotes the formation of coatings and allows dry coatings to be obtained more quickly. When used in the above amount in the reinforcing coating composition [o], the catalyst provides enhanced adhesion with respect to the substrate.

20 [0065]

(E): Organosilanes having two or more hydrolyzable groups in the molecule and/or partial hydrolytic condensates thereof

Where necessary, the reinforcing coating composition [o] and the fouling control coating composition [x] each may contain

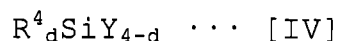
(E) an organosilane having two or more hydrolyzable groups in the molecule and/or a partial hydrolytic condensate thereof.

[0066]

A preferred organosilane having two or more hydrolyzable groups in the molecule and/or partial hydrolytic condensate thereof (E) is one represented by the following general formula

[IV]:

[0067]



In the general formula [IV], R^4 independently at each occurrence is a hydrocarbon group having 1 to 6 carbon atoms.

[0068]

In the general formula [IV], Y independently at each occurrence is a hydrolyzable group. The hydrolyzable groups are similar to those in the general formula [II]. Alkoxy groups and oxime groups are preferable.

[0069]

In the general formula [IV], d is an integer of 0 to 2.

[0070]

The organosilanes and/or partial hydrolytic condensates thereof (E) 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 hydrolyzates 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
5 alkyltrialkoxysilanes include "KBM-13" (manufactured by Shin-Etsu Chemical Co., Ltd.).

[0071]

In the reinforcing coating composition [o] and/or the fouling control coating composition [x] of the invention, the
10 content of the organosilane and/or partial hydrolytic condensate thereof (E) is usually 0.1 to 50 wt%, preferably 1 to 30 wt%, and more preferably 3 to 15 wt%. This content ensures that the reinforcing coating composition [o] and/or the fouling control coating composition [x] of the invention
15 will maintain an appropriate curing rate and the coatings obtained by curing the compositions will attain excellent coating strength and rubber properties.

[0072]

(F): Silane coupling agents

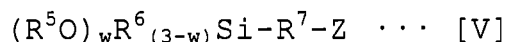
20 Where necessary, the reinforcing coating composition [o] and the fouling control coating composition [x] of the invention each may contain a silane coupling agent (F).

[0073]

A preferred silane coupling agent (F) is one represented

by the following general formula [V]:

[0074]



In the general formula [V], R^5 and R^6 are each

5 independently at each occurrence an alkyl group having 1 to 10 carbon atoms, an alkenyl group having 2 to 10 carbon atoms, an aryl group having 6 to 10 carbon atoms, or a halogenated alkyl group having 1 to 10 carbon atoms. R^5 is preferably a methyl group or an ethyl group.

10 [0075]

The alkyl groups, the alkenyl groups, the aryl groups and the halogenated alkyl groups are similar to those groups in the general formula [II].

[0076]

15 In the general formula [V], R^7 is a bifunctional hydrocarbon group having 1 to 20 carbon atoms which may contain an amino group, an ether group, a thioether group, an ester group or an amide group between carbon atoms, and is preferably an alkylene group having 4 to 11 carbon atoms
20 containing an amino group between carbon atoms.

[0077]

In the general formula [V], Z is a polar group, preferably an amino group, an imino group, a glycidyl group, an isocyanate group, a thiol group, a hydrosilyl group or a (meth)acrylate

group, and more preferably an amino group.

[0078]

In the general formula [V], w is an integer of 2 or 3, and preferably 3.

5 [0079]

Examples of the silane coupling agents (F) include 3-(2-aminoethyl)aminopropyltrimethoxysilane), 3-aminopropyltrimethoxysilane, 3-aminopropyltriethoxysilane, 3-(2-(2-aminoethyl)aminoethyl)aminopropyltrimethoxysilane, 10 3-glycidoxypropyltrimethoxysilane, 3-isocyanatopropyltrimethoxysilane, 3-mercaptopropyltrimethoxysilane and N-phenylpropyltrimethoxysilane.

[0080]

15 The silane coupling agents (F) may be used singly, or a plurality of types may be used in combination.

[0081]

In the reinforcing coating composition [o] and/or the fouling control coating composition [x] of the invention, the 20 content of the silane coupling agent (F) is usually 0.01 to 10 wt%, and preferably 0.05 to 2 wt%.

[0082]

This content of the silane coupling agent (F) ensures that the obtainable coatings will exhibit good adhesion with respect

to the base coating or the substrate and will achieve good damage resistance.

[0083]

(G): Silicas

5 Where necessary, the reinforcing coating composition [o] and the fouling control coating composition [x] of the invention each may contain a silica (G).

[0084]

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

[0085]

20 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 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%,

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]

- 5 The hydrophobic fumed silica is obtained by surface-treating the dry process silica with organosilicon compounds such as methyltrichlorosilane, dimethyldichlorosilane, hexamethyldisilazane, hexamethylcyclotrisiloxane and octamethylcyclotetrasiloxane.
- 10 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
- 15 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 hydrophobic fumed silica is physically reduced or removed by heat treatment
- 20 together with the organopolysiloxane described hereinabove. 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 silica before the heat treatment.

[0089]

The silicas (G) may be purchased in the market. Examples of commercial silicas include "R974" and "RX200" manufactured
5 by NIPPON AEROSIL CO., LTD.

[0090]

The silica (G) may be kneaded with, prior to the use of the coating composition, a component which includes the organopolysiloxane (AO) or (AX) having two or more silanol
10 groups or hydrolyzable groups in the molecule, or a component which includes the organopolysiloxane (C) other than the organopolysiloxanes (A). Alternatively, the silica (G) may be kneaded with the organopolysiloxane before the preparation of a component including any of the above organopolysiloxanes
15 for the reinforcing coating composition [o] and/or the fouling control coating composition [x] of the invention.

[0091]

When the silica (G) is used in the form of a kneadate with the above-described organopolysiloxane, the kneadate is
20 preferably a heat-treated product formed by heat treating the organopolysiloxane and the silica (G) beforehand, or is preferably a mixture of the heat-treated product with another portion of the organopolysiloxane that is not heat treated. Such a manner of use is preferable because the heat treatment

of the silica (G) with part or the whole of the organopolysiloxane enhances the affinity between the two ingredients and thus provides advantageous effects such as the aggregation of the silica being prevented. For example, this
5 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 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.

10 [0092]

The silica (G) is usually added in a ratio of 1 to 100 wt%, preferably 2 to 50 wt%, and more preferably 5 to 30 wt% relative to the weight of the organopolysiloxanes. This content of the silica ensures that the reinforcing coating
15 composition [o] and/or the fouling control coating composition [x] of the invention will exhibit good thixotropic properties and can attain a desired thickness by being applied one time, in particular, by being sprayed one time to form a coating with higher strength and higher hardness. Here, the weight of the
20 organopolysiloxanes means the total weight of the organopolysiloxane (AO) or (AX) and the optional organopolysiloxane (C).

[0093]

The use of the silica (G) described above provides

advantageous effects such as that the stability of the reinforcing coating composition [o] and/or the fouling control coating composition [x] of the invention during their preparation or storage is enhanced, that good fluidity and thixotropic properties are obtained to make it possible to form sufficiently thick coatings by a small number of coating operations even onto vertical surfaces or the like, and that the obtainable coatings attain excellent and well-balanced properties such as hardness, tensile strength and elongation.

10 [0094]

(H): Fillers

Where necessary, the reinforcing coating composition [o] and the fouling control coating composition [x] of the invention each may contain a filler (H).

15 [0095]

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

[0096]

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

[0097]

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; 5 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 10 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.

[0098]

The addition of the filler (H) to the reinforcing coating 15 composition [o] and/or the fouling control coating composition [x] of the invention results in an increase in coating strength. Further, the filler can conceal an undercoating and prevents the undercoating from UV degradation.

[0099]

20 In the reinforcing coating composition [o] and/or the fouling control coating composition [x] of the invention, the content of the filler (H) is preferably 0.1 to 30 wt%.

[0100]

(I): Organic solvents

Where necessary, the reinforcing coating composition [o] and the fouling control coating composition [x] of the invention each may contain an organic solvent (I).

[0101]

5 Examples of the organic solvents (I) include aromatic hydrocarbons, aliphatic hydrocarbons, alicyclic hydrocarbons, ketones and esters. Aromatic hydrocarbons are preferable.

[0102]

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

[0103]

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

[0104]

15 Examples of the alicyclic hydrocarbon organic solvents include cyclohexane, methylcyclohexane and ethylcyclohexane.

[0105]

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

[0106]

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

[0107]

The addition of the organic solvent (I) decreases the viscosity of the reinforcing coating composition [o] and/or the fouling control coating composition [x] of the invention, resulting in an enhancement in coating workability.

5 [0108]

A preferred content of the organic solvent (I) in the reinforcing coating composition [o] or the fouling control coating composition [x] is determined based on the desired viscosity depending on factors such as the manner in which the reinforcing coating composition [o] and/or the fouling control coating composition [x] of the invention is applied. The content in the coating composition is usually 0 to 50 wt%. If the content is excessively high, problems such as poor anti-sagging properties are sometimes caused.

15 [0109]

(J): Anti-sag, anti-settling agents

Where necessary, the reinforcing coating composition [o] and the fouling control coating composition [x] of the invention each may contain an anti-sag, anti-settling agent (J).

20 [0110]

Examples of the anti-sag, anti-settling agents (J) include organic waxes (such as polyethylene wax, oxidized polyethylene wax, amide wax, polyamide wax and hydrogenated castor oil wax), organic clay waxes (such as stearate salts,

lecithin salts and alkylsulfonate salts of Al, Ca and Zn), mixtures of organic clay waxes and organic waxes, and organopolysiloxanes containing polar groups (except hydrolyzable groups).

5 [0111]

The anti-sag, anti-settling agents (J) may be purchased in the market. Examples of such commercial organic waxes include those sold under the trade names of "Disparlon 305" and "Disparlon 4200-20" manufactured by Kusumoto Chemicals, Ltd. Examples of commercial polar group-containing organopolysiloxanes include "FZ-2191" (alkylene glycol-modified silicone oil manufactured by Dow Corning Toray Co., Ltd.) and "BY16-839" (alicyclic epoxy-modified silicone oil manufactured by Dow Corning Toray Co., Ltd.).

15 [0112]

In the reinforcing coating composition [o] and/or the fouling control coating composition [x] of the invention, the content of the anti-sag, anti-settling agent (J) is usually 0.01 to 10 wt%, and preferably 0.1 to 3 wt%. This content of the anti-sag, anti-settling agent (J) ensures that the reinforcing coating composition [o] and/or the fouling control coating composition [x] of the invention will be enhanced in anti-sagging properties and can be applied in a large thickness, and also ensures that good adhesion with respect to the

substrate will be obtained.

[0113]

(K): Additional coating ingredients

While still achieving the objects of the invention, the
5 reinforcing coating composition [o] and/or the fouling control
coating composition [x] of the invention may contain an
additional coating ingredient (K) other than the
organopolysiloxanes which are the main resin ingredients.

[0114]

10 Examples of the additional coating ingredients (K)
include resins that are poorly soluble or insoluble in water
such as acrylic resins, acrylic silicone resins, unsaturated
polyester resins, fluororesins, polybutene resins, silicone
rubbers, urethane resins (rubbers), polyamide resins, vinyl
15 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.

20 [0115]

(L): Inorganic dehydrating agents

Where necessary, the reinforcing coating composition [o]
and the fouling control coating composition [x] of the invention
each may contain an inorganic dehydrating agent (L).

[0116]

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

[0117]

The inorganic dehydrating agent (L) serves also as a
10 stabilizer. In the reinforcing coating composition [o] and/or the fouling control coating composition [x] of the invention, this ingredient prevents a degradation of the composition by water present therein and thus provides a further enhancement in storage stability. In the reinforcing coating composition
15 [o] and/or the fouling control coating composition [x] of the invention, the content of the inorganic dehydrating agent (L) is preferably 0.1 to 10 wt%.

[0118]

(M): Other additives

20 The reinforcing coating composition [o] and the fouling control coating composition [x] of the invention each may contain other additives (M) in amounts that do not make it impossible to achieve the objects of the invention. Such additives (M) may be any known additives used in paints, with

examples including flame retardants, thixotropic agents and thermal conductivity improvers.

[0119]

Examples of the flame retardants include antimony oxide
5 and oxidized paraffin.

[0120]

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

[0121]

10 Examples of the thermal conductivity improvers include boron nitride and aluminum oxide.

[0122]

<Preparation of reinforcing coating composition [o]/fouling control coating composition [x]>

15 The reinforcing coating composition [o] and the fouling control coating composition [x] each may be prepared by mixing the ingredients described hereinabove.

[0123]

The reinforcing coating composition [o] and/or the
20 fouling control coating composition [x] each may be provided as a one-part paint composed of a single component, or as a multi-part paint composed of two or more components. In the case of a two-part or multi-part paint, the reinforcing coating composition [o] and/or the fouling control coating composition

[x] of the invention is prepared by mixing the components together. The reinforcing coating composition [o] and/or the fouling control coating composition [x] may be prepared by mixing the aforementioned raw materials simultaneously or successively by stirring. When the coating composition or the component is prepared by successive addition of the raw materials, the order of addition is not particularly limited. When the coating composition involves the silica (G), it is preferable that the silica (G) be added in the form of a silica-containing organopolysiloxane prepared by mixing the silica (G) with at least part of the organopolysiloxane or by heating such a mixture.

[0124]

Kits for reinforcing coating composition [o]/fouling control coating composition [x]

When the reinforcing coating composition [o] and/or the fouling control coating composition [x] of the invention is provided as a two-part or multi-part paint, 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 coating operation, the contents in the components are mixed together by stirring to give a reinforcing coating composition [o] and/or a fouling control coating composition [x]. That is, in an aspect, the present invention provides a

kit(s) including such components for preparing the reinforcing coating composition [o] and/or the fouling control coating composition [x] of the invention.

[0125]

5 As already described, the reinforcing coating composition [o] and/or the fouling control coating composition [x] of the invention contains the organopolysiloxane (AO) or (AX) having 2 or more silanol groups or hydrolyzable groups in the molecule, and optionally further contains the additional
10 organopolysiloxane (C). A preferred multi-part paint kit(s) for the reinforcing coating composition [o] and/or the fouling control coating composition [x] includes a "base component" which contains the organopolysiloxane that is the main binder resin of the coating composition, and a "curing agent component"
15 which contains a compound that reacts with the polyorganosiloxane to form a crosslinked structure. Additives for the coating composition may be added to the base component or the curing agent component. An additional component such as an "additive component" is preferably added to the paint
20 kit which includes a compound that is reactive with the compounds present in the base component and in the curing agent component and is to be stored separately in order to avoid problems such as deterioration. The use of such an additive component is also preferable when the amount of the additives

needs to be controlled during their addition depending on use application. That is, the reinforcing coating composition [o] and/or the fouling control coating composition [x] of the invention may be provided in the form of, for example, a two-part
5 kit including a base component and a curing agent component, or as a three-part kit including a base component, a curing agent component and an additive component.

[0126]

⟨Fouling control coatings and fouling control substrates⟩

10 A reinforcing coating (O) and a fouling control coating (X) of the invention may be obtained by applying and curing the reinforcing coating composition [o] and the fouling control coating composition [x], respectively.

[0127]

15 The invention involves a step of forming a reinforcing coating (O) by applying and curing the reinforcing coating composition [o], and a step of providing a fouling control coating (X) formed by applying and curing the fouling control coating composition [x], onto the reinforcing coating (O). The
20 fouling control coating (X) may be formed by directly applying the fouling control coating composition [x] onto the reinforcing coating (O) and curing the composition, or the composition may be applied and cured separately and the resultant fouling control coating (X) may be attached onto the

reinforcing coating (O). A binder coating layer may be disposed between the reinforcing coating (O) and the fouling control coating (X). The reinforcing coating (O) of the invention is disposed under the fouling control coating (X).

5 [0128]

In the invention, the coating compositions are applied and cured. In the invention, the term coating operation comprehends general methods which spread the coating compositions, such as application with brushes or rollers, spraying, impregnation and casting.

[0129]

Specifically, the reinforcing coating composition [o] and/or the fouling control coating composition [x] may be applied onto a substrate or may be allowed to impregnate a substrate by a method in which the reinforcing coating composition [o] and/or the fouling control coating composition [x], after being sufficiently agitated, is applied to the substrate or is allowed to impregnate the substrate by spraying or other technique. A specific example method for curing the reinforcing coating composition [o] and/or the fouling control coating composition [x] spread on the substrate by application or impregnation 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. Where necessary,

an undercoating may be applied to the substrate before the application of the reinforcing coating composition [o].

[0130]

A reinforcing coating (O) and/or a fouling control
5 coating (X) of the invention may be formed beforehand and then attached onto a substrate. That is, the reinforcing coating composition [o] and the fouling control coating composition [x] may be applied and cured successively onto such as a film, and the resultant fouling control film may be attached onto
10 a substrate. An example method is such that a fouling control film obtained by curing the reinforcing coating composition [o] and/or the fouling control coating composition [x] is attached onto a substrate using a known technique such as one described in JP-A-2013-129724. Such a method, similarly to the
15 methods described above, results in an antifouling substrate in which a substrate is coated with an antifouling coating.

[0131]

The reinforcing coating (O) and/or the fouling control coating (X) of the invention may be formed in desired thickness
20 in accordance with factors such as use application. Usually, the reinforcing coating composition [o] and/or the fouling control coating composition [x] are each applied one or more times in a thickness of 30 to 400 μm per coating operation, or preferably 50 to 300 μm per coating operation, and are

thereafter cured. Here, a composite coating having excellent coating strength and antifouling performance may be obtained by ensuring that the total film thickness after curing is, for example, 100 to 1000 μm .

5 [0132]

The reinforcing coating composition [o] and/or the fouling control coating composition [x] of the invention can be applied using a wide range of known application techniques such as brushes, rollers, sprayers and dip coaters. The reinforcing coating composition [o] and/or the fouling control coating composition [x] of the invention has characteristics suited for spraying.

[0133]

In a wide range of industrial fields such as power generation, port and civil engineering construction, and marine vessels (building and repairing), the composite coatings including the reinforcing coating (O) and the fouling control coating (X) of the invention may be used to protect the surface 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 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
5 diffusion prevention films in various offshore construction works for building structures such as canals and waterways.
[0134]

The reinforcing coating composition [o] of the invention may be applied directly to the substrate to coat or impregnate
10 the substrate. Even in the case where the reinforcing coating composition [o] of the invention is applied directly to substrates made of such materials as fiber-reinforced plastics (FRPs), steel, wood and aluminum alloys, for example, water supply inlets and drains in nuclear power plants, mega-floats
15 and marine vessels, the composition exhibits good adhesion with respect to the surface of these substrates (materials).
[0135]

Further, the surface of the substrate to which the reinforcing coating composition [o] of the invention will be
20 applied may be already coated with an undercoating. That is, the inventive reinforcing coating composition [o] may be applied to the surface of substrates such as marine vessels or underwater structures already coated with base coatings (undercoatings) such as antirust agents or primers.

Furthermore, the reinforcing coating composition [o] and/or the fouling control coating composition [x] 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 that have been already coated with conventional antifouling coatings or with the fouling control coatings (X) of the invention. The reinforcing coating composition [o] and/or the fouling control coating composition [x] of the invention may be placed in direct contact with any types of coatings without limitation. Similarly to general organopolysiloxane antifouling paints, for example, the inventive coating compositions may be applied to coatings formed from paints based on resins such as epoxy resins, urethane resins and silicone resins. The reinforcing coating composition [o] and/or the fouling control coating composition [x] according to the present invention can be prepared to exhibit good adhesion with respect to the surface of such coatings.

[0136]

The reinforcing coating (O) lies under the fouling control coating (X) of the invention. As long as this requirement is met, the reinforcing coating (O) and the fouling control coating (X) may have a dissimilar coating such as a binder coating therebetween.

EXAMPLES

[0137]

Hereinbelow, the present invention will be described in greater detail based on Examples without limiting the scope of the invention to such Examples.

[0138]

Evaluation methods

In Examples and Comparative Examples below, properties were measured and evaluated by the following methods.

10 [0139]

[Damage resistance test]

A test plate was fixed 50 cm away from a spray nozzle of a high-pressure cleaner (GCT-2015 (manufactured by Komatsu Fork Lift Japan Ltd.)). The spray pattern was focused to the minimum, and the test plate was washed with water at a discharge pressure of 10 MPa and a moving speed of 7 cm/s.

[0140]

After the washing, the proportion (%) of the area of the portion of the fouling control coating (X) as the top coating that had been lost and showed the urethane undercoating or the reinforcing coating (O) was evaluated.

[0141]

[Evaluation of fouling control performance]

Coated test plates fabricated in Examples and Comparative

Examples were immersed in seawater off the Miyajima Bay, Hiroshima, Japan, under static conditions. After 12 months, the areas fouled by organisms on the surface of the test plates were evaluated by visual observation and were rated as follows.

5 [0142]

〈Rating in fouling control performance test〉

0: No aquatic organisms had become attached.

1: Aquatic organisms had become attached locally.

2: Aquatic organisms had become attached to the entire

10 surface.

Reinforcing coating compositions [o] and fouling control
coating compositions [x]

·Ingredients

The ingredients used in the preparation of reinforcing
15 coating compositions [o-1] to [o-13] and fouling control
coating compositions [x-1] to [x-12] are described in Table
1.

[0143]

Silica-containing organopolysiloxanes I, II and III each
20 included the organopolysiloxane and hydrophobized silica or
silica described in Table 1. The content (wt%) of the
hydrophobized silica or the silica is shown, the balance being
the organopolysiloxane.

[0144]

[Table 1]

Table 1

Ingredients	Data including general names and chemical formulae
Silica-containing organopolysiloxane I	HO-[Si(CH ₃) ₂ -O] _n -H, weight average molecular weight 28,500
Silica-containing organopolysiloxane II	Hydrophobized silica (5 wt% in ingredient) (MEKO) ₂ (CH ₂ =CH-)SiO-[Si(CH ₃) ₂ -O] _n -Si(CH=CH ₂)(MEKO) ₂ , weight average molecular weight 35,000 Silica (10 wt% in ingredient)
Silica-containing organopolysiloxane III	(MEKO) ₂ (CH ₂ =CH-)SiO-[Si(CH ₃) ₂ -O] _n -Si(CH=CH ₂)(MEKO) ₂ , weight average molecular weight 35,000 Hydrophobized silica (10 wt% in ingredient)
White pigment	Titanium (IV) oxide
Black pigment	Triiron tetraoxide
Zinc pyrithione (ZnPT)	Zn(-S-C ₅ H ₄ N-O-) ₂
Copper pyrithione (CuPT)	Cu(-S-C ₅ H ₄ N-O-) ₂
Cuprous oxide	Cu ₂ O, average particle size 8 mic., stearic acid-treated surface
Copper rhodanide	CuSCN
KM-2	4-Isopropylpyridine-diphenylmethylborane
Organosilane partial hydrolytic condensate	H ₃ 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 -CH ₃ Phenyl modification rate 5%, 3,000 mPa·s
Ether-modified organopolysiloxane I	H ₃ C-[Si(CH ₃) ₂ -O] _n -[Si(CH ₃)(-R-O-) ₁ -R-] _m -CH ₃ 52.5% methoxypropyl acetate solution, 27.5 mPa·s
Ether-modified organopolysiloxane II	H ₃ C-[Si(CH ₃) ₂ -O] _n -[Si(CH ₃)(-R-O-) ₁ -R-] _m -CH ₃ 250 mPa·s
Epoxy-modified organopolysiloxane	H ₃ C-[Si(CH ₃) ₂ -O] _n -[Si(CH ₃)(-R-C ₆ H ₄ -O-)] _m -CH ₃
Tin catalyst	Dibutyltin dilaurate
Silane coupling agent I	3-(2-Aminoethylamino)propyltrimethoxysilane
Silane coupling agent II	3-(2-(2-Aminoethylamino)ethylamino)propyltrimethoxysilane

*In Table 1, MEKO indicates methyl ketoxime.

- 5 [Production Examples 1 to 13] (Production of reinforcing coating compositions [o-1] to [o-13])

Kits for a reinforcing coating composition (three-part kits) including three components: a base component (1), a curing agent component (2) and an additive component (3) were prepared

10 by mixing the ingredients described in Table 2 together by stirring in the amounts (parts by weight) shown in the table.

[0145]

For coating applications, reinforcing coating compositions ([o-1], [o-2], [o-3], [o-4], [o-5], [o-6], [o-7],

[o-8], [o-10] and [o-11]) were prepared using the kits obtained above. Specifically, the base component (1), the curing agent component (2) and the additive component (3) in the amounts shown in Table 2 were mixed together sufficiently to uniformity
5 by being stirred with use of a disperser.

[0146]

Further, one-part reinforcing coating compositions ([o-9], [o-12] and [o-13]) were prepared by mixing the ingredients described in Table 2 together by stirring in the
10 amounts (parts by weight) shown in the table.

[0147]

Table 2 also describes the content (wt%) of pyrithione salt compound in each of the reinforcing coating compositions obtained, and the content (wt%) of pyrithione salt compound
15 in the solids of the paint (the coating).

[0148]

[Table 2]

Table 2 (Reinforcing coating compositions [o])

	Ingredients	Pro.	Pro.	Pro.	Pro.	Pro.	Pro.	Pro.	Pro.	Pro.	Pro.	Pro.	Pro.	Pro.	Pro.	Pro.	Pro.
		Ex. 1 o-1	Ex. 2 o-2	Ex. 3 o-3	Ex. 4 o-4	Ex. 5 o-5	Ex. 6 o-6	Ex. 7 o-7	Ex. 8 o-8	Ex. 9 o-9	Ex. 10 o-10	Ex. 11 o-11	Ex. 12 o-12	Ex. 13 o-13	Ex. 14 o-14	Ex. 15 o-15	Ex. 16 o-16
Base component (1) or one-part paint	Silica-containing organopolysiloxane I	59.8	59.8	59.8	59.8	59.8	59.8	59.8	59.8		59.8	59.8					
	Silica-containing organopolysiloxane II																
	Silica-containing organopolysiloxane III									42.0				42.0			
	White pigment	7.7	7.7	7.7	7.7	7.7	7.7	7.7	7.7	7.7	7.7	7.7	7.7	7.7	7.7	7.7	7.7
	Black pigment	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
	Copper pyrrhione	2.0	4.0	4.0						4.0		20.0					20.0
	Zinc pyrrhione				4.0	8.0	2.0	2.0	2.0								
	KM-2						2.0										
	Copper rhodanide							2.0									
	Cuprous oxide																
	N-butanol								2.0								
	Organosilane partial hydrolytic condensate									0.5				0.5	0.5	0.5	0.5
	Dimethylpolysiloxane									3.0				3.0	3.0	3.0	3.0
	Phenyl-modified organopolysiloxane									7.0				7.0	7.0	7.0	7.0
	Silane coupling agent I									0.1				0.1	0.1	0.1	0.1
	Xylene	9.5	11.5	11.5	9.5	9.5	9.5	9.5	9.5	26.7	9.5	40.5	26.7	40.7	40.7	40.7	40.7
Curing agent component	Subtotal	79.0	83.0	83.0	81.0	85.0	81.0	81.0	81.0	104.1	77.0	128.0	100.1	134.1	134.1	134.1	134.1
	Organosilane partial hydrolytic condensate	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					
	Tin catalyst	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6		0.6	0.6					
	Acetylacetone	5.4	5.4	5.4	5.4	5.4	5.4	5.4	5.4		5.4	5.4					
	Epoxy-modified organopolysiloxane	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1		0.1	0.1					
	Xylene	2.8	2.8	2.8	2.8	2.8	2.8	2.8	2.8		2.8	2.8					
	Subtotal	18.0	18.0	18.0	18.0	18.0	18.0	18.0	18.0		18.0	18.0					
	Silane coupling agent I	0.1	0.1		0.1	0.1	0.1	0.1	0.1		0.1	0.1					
	Silane coupling agent II			0.1													
Additive component	Xylene	4.9	4.9	4.9	4.9	4.9	4.9	4.9	4.9		4.9	4.9					
	Subtotal	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0		5.0	5.0					
	Total	102.0	106.0	106.0	104.0	108.0	104.0	104.0	104.0	104.1	100.0	151.0	100.1	134.1	134.1	134.1	134.1
Content (wt%) of pyrrhione salt compound in coating composition		2.0	3.8	3.8	3.8	7.4	1.9	1.9	1.9	3.8	0.0	13.2	0.0	14.9	14.9	14.9	14.9
Content (wt%) of pyrrhione salt compound in coating		2.6	5.0	5.0	5.0	9.6	2.5	2.5	2.5	5.2	0.0	21.0	0.0	21.5	21.5	21.5	21.5

[Production Examples 14 to 25] (Production of fouling control coating compositions [x-1] to [x-12])

Kits for a fouling control coating composition (two-part kits) including two components: a base component (1) and a curing agent component (2) were prepared by mixing the ingredients described in Table 3 together by stirring in the amounts (parts by weight) shown in the table.

[0149]

For coating applications, fouling control coating compositions [x-1] to [x-12] were prepared using the kits obtained above. Specifically, the base component (1) and the curing agent component (2) in the amounts shown in Table 3 were mixed together sufficiently to uniformity by being stirred with use of a disperser.

[0150]

Table 3 also describes the content (wt%) of antifouling agent in each of the fouling control coating compositions obtained, and the content (wt%) of antifouling agent in the solids of the paint (the coating).

[0151]

[Table 3]

Table 3 (Fouling control coating compositions [x])

	Ingredients	Pro. Ex. 14	Pro. Ex. 15	Pro. Ex. 16	Pro. Ex. 17	Pro. Ex. 18	Pro. Ex. 19	Pro. Ex. 20	Pro. Ex. 21	Pro. Ex. 22	Pro. Ex. 23	Pro. Ex. 24	Pro. Ex. 25
		x-1	x-2	x-3	x-4	x-5	x-6	x-7	x-8	x-9	x-10	x-11	x-12
(1) Base component	Silica-containing organopolysiloxane I	59.8	59.8	59.8	59.8	59.8	59.8	59.8	59.8	59.8	59.8	59.8	59.8
	White pigment	7.7	7.7	7.7	7.7	7.7	7.7	7.7	7.7	7.7	7.7	7.7	7.7
	Black pigment	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
	Copper pyrrhione	5.0	5.0	5.0				1.0	2.0			1.0	5.0
	Zinc pyrrhione									2.0	5.0		
	Cuprous oxide				10.0	10.0							
	N-butanol				5.0	5.0							
(2) Curing agent component	Xylene	12.5	12.5	12.5	9.5	9.5	4.5	12.5	12.5	12.5	12.5	12.5	12.5
	Subtotal	85.0	85.0	85.0	92.0	92.0	72.0	81.0	82.0	82.0	85.0	81.0	85.0
	Organosilane partial hydrolytic condensate	3.4	3.4	3.4	2.9	2.9	3.4	3.4	3.4	3.4	3.4	3.4	3.4
	Phenyl-modified organopolysiloxane	5.7	5.7	5.7	4.8	4.8	5.7	5.7	5.7	5.7	5.7	5.7	5.7
	Tin catalyst	0.6	0.6	0.6	0.5	0.5	0.6	0.6	0.6	0.6	0.6	0.6	0.6
	Acetylacetone	5.4	5.4	5.4			5.4	5.4	5.4	5.4	5.4	5.4	5.4
	Epoxy-modified organopolysiloxane	0.1	0.1	0.1			0.1	0.1	0.1	0.1	0.1	0.1	0.1
	Ether-modified organopolysiloxane I	10.0	3.0		10.0		10.0	10.0	10.0	10.0	10.0	6.0	20.0
	Ether-modified organopolysiloxane II			10.0		10.0							
	Xylene	2.8	2.8	2.8	1.9	1.9	2.8	2.8	2.8	2.8	2.8	2.8	2.8
	Subtotal	28.0	21.0	28.0	20.0	20.0	28.0	28.0	28.0	28.0	28.0	24.0	38.0
Total		113.0	106.0	113.0	112.0	112.0	100.0	109.0	110.0	110.0	113.0	105.0	123.0
Content (wt%) of antifouling agent in coating composition		4.4	4.7	4.4	8.9	8.9	0.0	0.9	1.8	1.8	4.4	1.0	4.1
Content (wt%) of antifouling agent in coating		5.5	6.0	5.5	10.6	10.6	0.0	1.2	2.3	2.3	5.5	1.2	5.0

[Examples 1 to 20 and Comparative Examples 1 to 7] (Fabrication of test plates)

Sandblasted steel plates were coated with an epoxy anticorrosive paint (trade name: BANNOH 500, manufactured by CHUGOKU MARINE PAINTS, LTD.) as an undercoating paint 1 so that the dry thickness of the cured film would be 100 μm . The wet films were dried, and the resultant coatings were further coated with, as an undercoating paint 2, A: a urethane paint (trade name: CMP BIOCLEAN SG, manufactured by CHUGOKU MARINE PAINTS, LTD., in Examples 1 to 12 and 14 to 20, and Comparative Examples 1 to 3 and 7) or B: an epoxy paint (trade name: CMP BIOCLEAN SG-R, manufactured by CHUGOKU MARINE PAINTS, LTD., in Example 13 and Comparative Examples 4, 5, and 6) so that the dry thickness of the cured film would be 100 μm . The wet films were dried. Anticorrosive coatings were thus formed.

[0152]

Next, onto the anticorrosive coatings, the reinforcing coating compositions [o] described in Table 4 were sprayed with a sprayer at normal temperature so that the dry thickness would be 100 μm . After being allowed to stand at normal temperature for one day, the resultant reinforcing coatings (O) were coated by spraying of the fouling control coating compositions [x] described in Table 4 with use of a sprayer at normal temperature so that the dry thickness would be 200 μm . The wet films were

dried at normal temperature for one week to form fouling control coatings (X). Test plates were thus prepared.

[0153]

The test plates obtained were subjected to the damage
5 resistance test and the evaluation of fouling control
performance. The results are described in Table 4.

[0154]

[Table 4]

Table 4

	Examples																			
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
Reinforcing coating composition [o]	o-1	o-2	o-3	o-4	o-5	o-6	o-7	o-8	o-2	o-2	o-2	o-2	o-9	o-2	o-4	o-4	o-4	o-4	o-4	o-4
Pyrrithione salt M:	Cu	Cu	Cu	Zn	Zn	Zn	Zn	Zn	Cu	Cu	Cu	Cu	Cu	Cu	Zn	Zn	Zn	Zn	Zn	Zn
Content in coating (wt%)	2.6	5.0	5.0	5.0	9.6	2.5	2.5	2.5	5.0	5.0	5.0	5.0	5.2	5.0	5.0	5.0	5.0	5.0	5.0	5.0
Fouling control coating composition [x]	x-1	x-1	x-1	x-1	x-1	x-1	x-1	x-1	x-2	x-3	x-4	x-5	x-1	x-1	x-7	x-8	x-9	x-10	x-11	x-12
Antifouling agent type:	CP	CP	CP	CP	CP	CP	CP	CP	CP	CP	CO	CO	CP	CP	CP	CP	2P	2P	CP	CP
Content in coating (wt%)	5.5	5.5	5.5	5.5	5.5	5.5	5.5	5.5	6.0	5.5	10.6	10.6	5.5	1.2	1.2	2.3	2.3	5.5	1.2	5.0
Damage resistance (% of area of fouling control coating lost)	10	10	5 <	10	5 <	10	10	10	0	0	5 <	0	10	10	10	10	10	10	10	10
Evaluation of antifouling performance	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0

	Comparative Examples						
	1	2	3	4	5	6	7
Reinforcing coating composition [o]	o-10	o-11	o-10	o-12	o-13	o-12	o-11
Pyrrithione salt M:	-	Cu	-	-	Cu	-	Cu
Content in coating (wt%)	0.0	20.0	0.0	0.0	21.5	0.0	20.0
Fouling control coating composition [x]	x-1	x-1	x-4	x-1	x-1	x-6	x-6
Antifouling agent type:	CP	CP	CO	CP	CP	-	-
Content in coating (wt%)	5.5	5.5	10.6	5.5	5.5	0.0	0.0
Damage resistance (% of area of fouling control coating lost)	40	70	60	70	90	50	70
Evaluation of antifouling performance	0	0	1	0	0	2	2

INDUSTRIAL APPLICABILITY

[0155]

In structures and substrates used in water such as marine vessels (such as marine vessel shells), fishery materials (such 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, the invention can impart excellent durability to organopolysiloxane fouling control coatings which protect the surface of these structures and substrates from the attachment of aquatic organisms.

CLAIMS

[Claim 1]

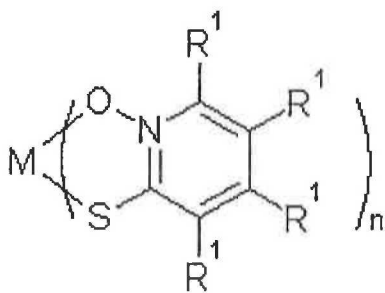
A method for reinforcing a fouling control coating,
comprising:

5 a step of forming a reinforcing coating (O) by applying
and curing a reinforcing coating composition [o], and

a step of providing a fouling control coating (X) formed by applying and curing a fouling control coating composition [x], onto the reinforcing coating (0),

10 the reinforcing coating composition [o] comprising an organopolysiloxane (AO) having two or more silanol groups or hydrolyzable groups in the molecule, and a pyrrithione salt compound (BO) represented by the following general formula [I]:

[Chem. 1]



• • • [I]

(in the formula [I], R¹ independently at each occurrence is a hydrogen atom, an alkyl group having 1 to 6 carbon atoms, a cycloalkyl group having 3 to 6 carbon atoms, an alkenyl group having 2 to 6 carbon atoms, an aryl group having 6 carbon atoms, an alkoxy group having 1 to 6 carbon atoms, or a halogenated

alkyl group having 1 to 6 carbon atoms,

M is a metal selected from Cu, Zn, Na, Mg, Ca, Ba, Fe and Sr, and

n is the valence of the metal M),

5 the fouling control coating composition [x] comprising an organopolysiloxane (AX) having two or more silanol groups or hydrolyzable groups in the molecule, and an antifouling agent (BX),

the content of the pyrithione salt compound (BO) in the reinforcing coating (O) being not more than 10 wt%,

the reinforcing coating (O) giving reinforcement to the fouling control coating (X).

[Claim 2]

The method for reinforcing a fouling control coating according to Claim 1, wherein the content of the pyrithione salt compound (BO) in the reinforcing coating (O) is not more than 5.5 wt%.

[Claim 3]

The method for reinforcing a fouling control coating according to Claim 1 or 2, wherein M in the general formula [I] is Cu and/or Zn.

[Claim 4]

The method for reinforcing a fouling control coating according to any of Claims 1 to 3, wherein the antifouling agent

(BX) in the fouling control coating (X) is a pyrithione salt compound represented by the general formula [I] in which M is Cu.

[Claim 5]

5 The method for reinforcing a fouling control coating according to any of Claims 1 to 4, wherein the pyrithione salt compound (BO) in the reinforcing coating (O) is a compound represented by the general formula [I] in which M is Zn.

[Claim 6]

10 The method for reinforcing a fouling control coating according to any of Claims 1 to 5, wherein the content (wt%) of the pyrithione salt compound (BO) in the reinforcing coating (O) is smaller than the content (wt%) of the antifouling agent (BX) in the fouling control coating (X).

15 [Claim 7]

 The method for reinforcing a fouling control coating according to any of Claims 1 to 6, wherein the organopolysiloxane (AO) and/or the organopolysiloxane (AX) is represented by the following general formula [II]:

20 $(W)_r R^2_{(3-r)} Si-O-(SiR^2_2-O)_s-SiR^2_{(3-r)} (W)_r \cdots$ [II]

 (in the formula [II], W independently at each occurrence is a hydroxyl group or a hydrolyzable group,

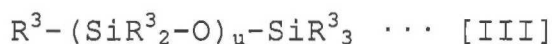
R^2 independently at each occurrence is a hydrogen atom, an alkyl group having 1 to 10 carbon atoms, an alkenyl group

having 2 to 10 carbon atoms, an aryl group having 6 to 10 carbon atoms, an aralkyl group having 7 to 10 carbon atoms, an alkoxy group having 1 to 10 carbon atoms, or a halogenated alkyl group having 1 to 10 carbon atoms,

- 5 r is an integer of 1 to 3, and
 s is an integer of 10 to 10,000).

[Claim 8]

The method for reinforcing a fouling control coating according to any of Claims 1 to 7, wherein the reinforcing
 10 coating composition [o] further comprises one or more organopolysiloxanes (C) other than the organopolysiloxane (AO), represented by the following general formula [III]:



(in the formula [III], u is an integer of 1 to 10,000,
 15 and

R³ independently at each occurrence is an alkyl group having 1 to 30 carbon atoms, an alkenyl group having 2 to 30 carbon atoms, an aryl group having 6 to 30 carbon atoms, an aralkyl group having 7 to 10 carbon atoms, or a halogenated
 20 alkyl group having 1 to 30 carbon atoms, and may contain -O-, -S- or -NR- between carbon atoms wherein R is a hydrogen atom or an alkyl group having 1 to 5 carbon atoms).

[Claim 9]

The method for reinforcing a fouling control coating

according to Claim 8, wherein R³s in the general formula [III] are alkyl and/or aryl groups.

[Claim 10]

The method for reinforcing a fouling control coating
5 according to any of Claims 1 to 9, which is applied to a substrate used in water.