

DESCRIPTION

COATING COMPOSITION USED FOR FRICTIONAL RESISTANCE REDUCED SHIP
UTILIZING GAS LUBRICATION FUNCTION IN WATER, COATING FILM FORMED FROM
THE COMPOSITION, SHIP COATED WITH THE COATING FILM, PRODUCTION PROCESS
5 FOR THE SHIP, METHOD FOR PREDICTING EFFECT OF THE FRICTIONAL RESISTANCE
REDUCTION, APPARATUS USED FOR PREDICTION OF THE FRICTIONAL RESISTANCE
REDUCTION EFFECT, AND FRICTIONAL RESISTANCE REDUCTION SYSTEM USED
FOR THE FRICTIONAL RESISTANCE REDUCED SHIP

10 Technical Field

[0001]

The present invention relates to a coating composition mainly
used for a frictional resistance reduced ship utilizing a gas
lubrication function in water, a coating film formed from the
15 composition, a ship coated with the coating film, a production process
for the ship, a method for predicting an effect of the frictional
resistance reduction, an apparatus used for prediction of the
frictional resistance reduction effect, and a frictional resistance
reduction system used for the frictional resistance reduced ship.

20

Background Art

[0002]

On a ship navigating, wave-making resistance due to occurrence
of waves, pressure profile resistance attributable to the profile

of the ship's bottom and frictional resistance (water flow frictional resistance) due to viscosity of water act. The wave-making resistance and the profile resistance have been greatly reduced by the studies having been made so far, but the frictional resistance occupies 60%
5 to 80% of the total resistance of a ship, and for energy saving, reduction of the frictional resistance has been eagerly desired. As methods for reducing the water flow frictional resistance, an air lubrication method of supplying air to a ship's bottom and a method of adding a polymer to a fluid such as sea water (method utilizing Toms effect)
10 have been proposed and studied, and with regard to the former, practical use for ships has been accelerated.

[0003]

For example, in patent literatures 1 to 4, methods for reducing frictional resistance, said methods comprising treating a ship's
15 bottom surface with a coating agent or the like to impart water repellency to the ship's bottom surface and holding air bubbles or an air layer, are disclosed. These methods are each a method wherein air is supplied to a ship's bottom, on which a specific hydrophobic coating film has been formed, to cover the ship's bottom surface with
20 an air layer, whereby frictional resistance is reduced by an air lubrication effect.

[0004]

The hydrophobic coating film is formed from hydrophobic (finely divided) particles contained and a hydrophobic binder resin in a

coating agent, and has a hydrophobic recess-projection rough surface having a high affinity for air. The hydrophobic coating film having a hydrophobic recess-projection rough surface (also referred to as a "hydrophobic recess-projection coating film" hereinafter) exhibits

5 high water repellency attributable to the facts that in air, air adheres to the recess and is held as an air layer and that the surface free energy of the recess is small. In water, however, such a hydrophobic recess-projection coating film changes with time to lose its water repellency, and an affinity for air also disappears. Particularly

10 on a bottom of a ship navigating, this change with time is conspicuous. That is to say, because of a small intermolecular interaction force between air (gas molecule) and the hydrophobic recess-projection coating film (surface constituent molecule), water (molecule) gradually invades this recess to exclude air. This phenomenon is

15 described as "immersional wetting". When there is a water flow on the hydrophobic recess-projection coating film surface, exclusion of air is further accelerated. When water invades a recess of the hydrophobic recess-projection coating film to extrude air (layer), air cannot invade the recess of the hydrophobic recess-projection

20 coating film even if air is newly supplied to the surface, because cohesive energy or mass of water (molecule) is overwhelmingly larger as compared with that of air. That is to say, air (layer) holding performance is not restored. In air, accordingly, the hydrophobic recess-projection coating film exhibits an affinity for air because

an air layer is formed in the recess. In water, however, since the coating film surface is covered with water having invaded the recess, the coating film becomes hydrophilic and loses an affinity for air.

[0005]

5 Further, the hydrophobic recess-projection coating film has small cohesive energy (surface free energy) and also has low mechanical strength. Therefore, such a hydrophobic recess-projection coating film is fragile and has poor adhesion property, and by the action of a water flow, etc. during navigation, the finely divided particles
10 or the hydrophobic recess-projection coating film peels and drops off from the ship's bottom surface, whereby air holding performance of the hydrophobic recess-projection coating film is lowered.

[0006]

 Moreover, the hydrophobic recess-projection coating film has
15 no antifouling performance. From the viewpoint that the increase in frictional resistance attributable to increase in roughness of a ship's bottom surface caused by fouling of the ship's bottom surface due to adhesion of aquatic organisms during anchorage of the ship is prevented, the coating film formed on the ship's bottom is desired
20 to have antifouling property. In a patent literature 5, it is described that in order to allow a recess-projection surface to have antifouling property, an oxidizing gas or an oxidizing liquid is supplied into sea so that such a gas or liquid may flow on the ship's bottom. However, it is difficult to allow the whole of the ship's bottom surface to

be in such an atmosphere at all times, and besides, there is a fear of marine pollution by the oxidizing gas or the oxidizing liquid, so that this technique is of little practicability.

[0007]

5 Thus, these conventional techniques cannot be said to be effective methods for reducing frictional resistance of ships that are used for a long period of time.

 As described in a patent literature 6, a method for judging a frictional resistance reduction effect by a contact angle of a film
10 surface against water is also known, but it is difficult to say that such a method accurately reflects the state or the behavior of a bubble on a coating film surface in water.

Citation List

15 Patent Literature

[0008]

Patent literature 1: Japanese Patent No. 2890340

Patent literature 2: Japanese Patent Laid-Open Publication No.
1996-268380

20 Patent literature 3: Japanese Patent Laid-Open Publication No.
1998-273617

Patent literature 4: Japanese Patent Laid-Open Publication No.
1999-131007

Patent literature 5: Japanese Patent Laid-Open Publication No.

1997-262563

Patent literature 6: Japanese Patent Laid-Open Publication No.

2003-277691

5 Summary of Invention

Technical Problem

[0009]

As described above, the conventional technique is that by injecting air onto a hydrophobic recess-projection coating film having an affinity for air, this coating film holds an air layer and exhibits an frictional resistance reduction effect, but in water, the surface of the hydrophobic recess-projection coating film changes with time and becomes hydrophilic, whereby the affinity for air disappears, and such a frictional resistance reduction effect as above is lowered.

10

Further, since this hydrophobic recess-projection coating film has no antifouling performance, the roughness of the coating film is extremely increased because of fouling by microorganisms, etc., and the frictional resistance tends to be increased.

15

[0010]

20 A method of supplying a large amount of air to a ship's bottom to maintain the frictional resistance reduction effect has been attempted, but the supply of air needs great power, and therefore, energy saving effect due to the frictional resistance reduction is compensated, so that this method is of no practical use.

[0011]

If there are a method for more easily predicting a frictional resistance reduction effect utilizing an air lubrication function of a coating film in water and an apparatus capable of being used for the prediction, they
5 are useful in examination of the above.

[0012]

In the light of the above, the present invention addresses a first problem of providing a coating composition capable of forming a coating film which maintains an affinity for a gas such as air in water over a long
10 period of time, exerts a high frictional resistance reduction effect even by supplying a small amount of gas and has an antifouling function even during navigation or even under static conditions, a coating film formed from the composition, a frictional resistance reduced ship having the coating
15 film formed thereon and a production process for the frictional resistance reduced ship.

[0013]

The present invention further addresses a second problem of providing a coating composition capable of forming a coating film which maintains an affinity for a gas such as air in water over a long period of time, has
20 a high fluid frictional resistance reduction effect even if high power is not introduced for the supply of gas, is economical and has little influence on the environment, a coating film formed from the composition, a frictional resistance reduced ship having the coating film formed thereon, a production process

for the frictional resistance reduced ship, a method for predicting a frictional resistance reduction effect utilizing a gas lubrication function of a coating film in water, and an apparatus used for the prediction.

5 [0014]

The present invention furthermore addresses a third problem of providing a frictional resistance reduction system used for such a frictional resistance reduced ship as above, and a frictional resistance reduced ship utilizing a gas lubrication function in water,
10 said ship having the system.

Solution to Problem

[0015]

In order to solve the above problems, the present inventors
15 have earnestly studied, and as a result, they have found that the first problem can be solved by an antifouling coating composition used for a frictional resistance reduced ship utilizing a gas lubrication function, said composition comprising a specific organopolysiloxane (A), a specific hydrophobic material (C), and if
20 necessary, a specific organosilane and/or its partial condensate (B).

[0016]

Further, the present inventors have found that the second problem can be solved by an antifouling coating composition used for a frictional resistance reduced ship having a coating film with the

specific ranges of the later-described static in-water bubble contact angle and in-water bubble roll (slip) angle and utilizing a gas lubrication function in water, a method for predicting the aforesaid frictional resistance reduction effect utilizing the static in-water bubble contact angle and the in-water bubble roll (slip) angle, and an apparatus having specific constitution capable of measuring the static in-water bubble contact angle and the in-water bubble roll (slip) angle.

[0017]

Furthermore, the present inventors have found that the third problem can be solved by a frictional resistance reduction system having a coating film formed from the composition capable of solving the first problem or the second problem and a gas supply device for supplying gas such as air to the surface of the coating film.

[0018]

The present invention is based on the following findings newly found by the present inventors.

•A coating film formed from an antifouling coating composition comprising a specific organopolysiloxane, a specific hydrophobic material, and if necessary, a specific organosilane and/or its partial condensate exhibits an air lubrication effect efficiently, and a water flow frictional resistance can be efficiently reduced.

•It is presumed that when a compound having a polysiloxane skeleton structure is contained in the antifouling coating composition,

leveling property of the compound has influence on the profile of an antifouling coating film formed from the antifouling coating composition, and a film of the later-described specific profile is formed.

5 •The coating film formed from the above-mentioned antifouling coating composition has a small roughness and a long peak-valley average interval (surface roughness: not more than 50 μm , peak-valley average interval: not less than 700 μm). The coating film profile contributes to exhibition of properties that the static in-water bubble
10 contact angle is less than 90 degrees and the bubble roll (slip) angle is less than 30 degrees. Further, this coating film differs in profile from conventional coating films (e.g., the aforesaid patent literatures 1 to 4) that need conventional fine recesses and projections formed thereon, and is a coating film having a gentle
15 slope as compared with such conventional coating films, and exerts an excellent frictional resistance reduction effect.

 •The hydrophobic component is liquid or greasy at 25°C, and in a ship having a coating film formed from the above coating composition on a submerged surface of a shell plating of the ship, the hydrophobic
20 component bleeds out during navigation to cover the coating film surface, and the coating film formed from the coating composition exhibits antifouling property.

 •When the static in-water bubble contact angle of a coating film is less than 90 degrees and the bubble roll (slip) angle thereof

is less than 30 degrees, bubbles and/or a gas layer smoothly flows while sufficiently contacting the coating film in a ship having the coating film on a submerged surface of the shell plating, so that the air lubrication effect is efficiently exhibited, and water flow
5 frictional resistance is efficiently reduced.

•The coating film can maintain the above characteristics and properties for a long period of time, and besides, the film exerts a high frictional resistance reduction effect even in a small amount of air. On that account, a frictional resistance reduced ship having
10 the coating film on a submerged surface of its shell plating does not need high power for the supply of air, and therefore, the energy saving effect is great.

•In the case of a frictional resistance reduced ship having a coating film formed from the antifouling coating composition
15 containing a hydrophobic material and an antifouling agent on a submerged surface of its shell plating, fouling by aquatic organisms can be further prevented, and an air lubrication effect can be exerted over a longer period of time.

[0019]

20 That is to say, the present invention is as follows.

The antifouling coating composition used for a frictional resistance reduced ship utilizing a gas lubrication function in water according to the present invention is characterized by comprising (A) a reaction-curing type organopolysiloxane having a viscosity at

25°C of 20 to 400000 mm²/s, (C) a hydrophobic material which is liquid or greasy at 25°C (other than the above organopolysiloxane (A) and the following organosilane and/or its partial condensate (B)), and if necessary, (B) an organosilane having, in one molecule, at least
5 two groups each of which is at least one group of a hydroxyl group and a hydrolyzable group and/or its partial condensate (this composition being also referred to as a "first coating composition"). (The "frictional resistance reduced ship utilizing a gas lubrication function in water" is also referred to as a "special frictional
10 resistance reduced ship" hereinafter.)

In the antifouling coating composition according to the present invention, the hydrophobic material (C) preferably contains at least one kind selected from a silicone oil, a fluorine-based oil and paraffins, from the viewpoint that the antifouling property of the
15 antifouling coating composition becomes more excellent.

[0020]

The antifouling coating composition according to the present invention preferably further comprises an antifouling agent (D) in an amount of 5 to 100 parts by weight based on 100 parts by weight
20 of the organopolysiloxane (A), from the viewpoint that the antifouling property of the antifouling coating composition becomes more excellent.

[0021]

The antifouling coating film used for a special frictional

resistance reduced ship according to the present invention is characterized by being formed from the above antifouling coating composition (this film being also referred to as a "first coating film").

5 With regard to the surface profile of the antifouling coating film according to the present invention, it is preferable that the maximum height from the bottom of a recess to the peak of a projection, as measured in accordance with JIS B 0601, is not more than 30 μm , and the peak-valley average interval that is an average of a length
10 of one cycle constituted of one projection and its neighboring one recess, as measured in accordance with JIS B 0601, is not less than 700 μm , from the viewpoint that the frictional resistance can be more effectively reduced.

[0022]

15 In the antifouling coating film according to the present invention, it is preferable that the static in-water bubble contact angle, as measured by the following measuring method for static in-water bubble contact angle, is less than 90 degrees, and the in-water bubble roll (slip) angle, as measured by the following measuring method
20 for in-water bubble roll (slip) angle, is less than 30 degrees, from the viewpoint that the frictional resistance can be more effectively reduced,

<measuring method for static in-water bubble contact angle>

a rigid polyvinyl chloride test panel (maximum height as measured

in accordance with JIS B 0601: not more than 1 μm), which has been coated with a coating composition so that a coating film having a dry film thickness of 150 μm may be formed, is immersed in water at 25°C for 30 days, then the rigid polyvinyl chloride test panel after immersion of 30 days is placed in water in such a manner that the coating film surface becomes horizontal and is on the lower side of the test panel, then 0.1 cc of air is injected into water so that one bubble may be formed on the coating film surface, then a height a of the bubble from the coating film surface, said bubble having been formed on the coating film surface, and a diameter b of a contact portion of the bubble with the coating film surface are measured, and from the following formula (1), a static in-water bubble contact angle (θ_s , unit: degree) that is a contact angle between the coating film surface and the bubble is determined;

[0023]

[Math. 1]

$$\theta_s = 2 \times \frac{180}{\pi} \times \tan^{-1} \frac{2a}{b} \dots (1)$$

[0024]

<measuring method for in-water bubble roll (slip) angle>

in the above measuring method for static in-water bubble contact angle, the coating film surface having the bubble formed thereon is gradually inclined against the horizontal plane, and when the bubble begins to move, an in-water bubble roll (slip) angle (θ_m , unit: degree)

that is an inclination angle of the coating film surface against the horizontal plane is measured.

[0025]

The special frictional resistance reduced ship according to the present invention is characterized in that a submerged surface of a shell plating of the ship has been coated with the antifouling coating film (this ship being also referred to as a "first special frictional resistance reduced ship").

The production process for the first special frictional resistance reduced ship according to the present invention is characterized by comprising forming the above antifouling coating film on a submergence expected surface of a shell plating of a ship to be coated.

[0026]

The frictional resistance reduction system according to the present invention is characterized by having the above coating film (first coating film) and a gas supply device for supplying a gas such as air to the surface of the coating film (this system being also referred to as a "first frictional resistance reduction system").

[0027]

The special frictional resistance reduced ship according to the present invention is characterized by having the first frictional resistance reduction system (this ship being also referred to as a "third special frictional resistance reduced ship").

The coating composition according to the present invention is used for a frictional resistance reduced ship utilizing a gas lubrication function in water, and is characterized by being capable of forming a coating film having a static in-water bubble contact angle, as measured by the following measuring method for static in-water bubble contact angle, of less than 90 degrees, and an in-water bubble roll (slip) angle, as measured by the following measuring method for in-water bubble roll (slip) angle, of less than 30 degrees (this composition being also referred to as a "second coating composition"),

10 [0028]

<measuring method for static in-water bubble contact angle>

a rigid polyvinyl chloride test panel (maximum height as measured in accordance with JIS B 0601: not more than 1 μm), which has been coated with a coating composition so that a coating film having a dry film thickness of 150 μm may be formed, is immersed in water at 25°C for 30 days, then the rigid polyvinyl chloride test panel after immersion of 30 days is placed in water in such a manner that the coating film surface becomes horizontal and is on the lower side of the test panel, then 0.1 cc of air is injected into water so that one bubble may be formed on the coating film surface, then a height a of the bubble from the coating film surface, said bubble having been formed on the coating film surface, and a diameter b of a contact portion of the bubble with the coating film surface are measured, and from the following formula (1), a static in-water bubble contact

angle (θ_s , unit: degree) that is a contact angle between the coating film surface and the bubble is determined;

[0029]

[Math. 2]

$$\theta_s = 2 \times \frac{180}{\pi} \times \tan^{-1} \frac{2a}{b} \dots (1)$$

[0030]

<measuring method for in-water bubble roll (slip) angle>

In the above measuring method for static in-water bubble contact angle, the coating film surface having the bubble formed thereon is gradually inclined against the horizontal plane, and when the bubble begins to move, an in-water bubble roll (slip) angle (θ_m , unit: degree) that is an inclination angle of the coating film surface against the horizontal plane is measured.

[0031]

In the antifouling coating film according to the present invention, it is preferable that the maximum height, as measured in accordance with JIS B 0601, is not more than 30 μm , and the peak-valley average interval, as measured in accordance with JIS B 0601, is not less than 700 μm , from the viewpoint that the frictional resistance can be more effectively reduced.

[0032]

The coating film according to the present invention is characterized by being formed from the coating composition used for

a special frictional resistance reduced ship (this film being also referred to as a "second coating film").

The special frictional resistance reduced ship according to the present invention is characterized by having the above coating film on a submerged surface of its shell plating (this ship being also referred to as a "second special frictional resistance reduced ship").

[0033]

The frictional resistance reduction system according to the present invention is characterized by having the above coating film (second coating film) and a gas supply device for supplying a gas such as air to the surface of the coating film (this system being also referred to as a "second frictional resistance reduction system").

[0034]

The special frictional resistance reduced ship according to the present invention is characterized by having the second frictional resistance reduction system (this ship being also referred to as a "fourth special frictional resistance reduced ship").

The production process for the second special frictional resistance reduced ship according to the present invention is characterized by comprising forming the above coating film on a submergence expected surface of a shell plating of a ship to be coated.

[0035]

The method for predicting a frictional resistance reduction

effect utilizing a gas lubrication function of a coating film in water according to the present invention is characterized by comprising measuring a static in-water bubble contact angle by the following measuring method for static in-water bubble contact angle, measuring an in-water bubble roll (slip) angle by the following measuring method for in-water bubble roll (slip) angle, and predicting a frictional resistance reduction effect utilizing a gas lubrication function of a coating film in water from the static in-water bubble contact angle and the in-water bubble roll (slip) angle,

<measuring method for static in-water bubble contact angle>

a test panel, which has been coated with a coating composition so that a coating film may be formed, is immersed in water, then the test panel after immersion is placed in water in such a manner that the coating film surface becomes horizontal and is on the lower side of the test panel, then air is injected into water so that a bubble may be formed on the coating film surface, then a height a of the bubble from the coating film surface, said bubble having been formed on the coating film surface, and a diameter b of a contact portion of the bubble with the coating film surface are measured, and from the following formula (1), a static in-water bubble contact angle (θ_s , unit: degree) that is a contact angle between the coating film surface and the bubble is determined;

[0036]

[Math. 3]

$$\theta_s = 2 \times \frac{180}{\pi} \times \tan^{-1} \frac{2a}{b} \dots (1)$$

[0037]

<measuring method for in-water bubble roll (slip) angle>

in the above measuring method for static in-water bubble contact
 5 angle, the coating film surface having the bubble formed thereon is
 gradually inclined against the horizontal plane, and when the bubble
 begins to move, an in-water bubble roll (slip) angle (θ_m , unit: degree)
 that is an inclination angle of the coating film surface against the
 horizontal plane is measured.

10 [0038]

The apparatus used for prediction of a frictional resistance
 reduction effect utilizing a gas lubrication function of a coating
 film in water according to the present invention is an apparatus having
 a test board, an inclination angle control device, an immersion
 15 container and an observation device, and is characterized in that
 to the test board, the inclination angle control device is connected;
 on the test board, a test panel having a coating film formed on its
 surface is set in such a manner that a back surface of the test panel
 comes into contact with the lower surface of the test board, and in
 20 the immersion container containing water, the test board is placed
 in such a state that the test panel is immersed in water and that
 a bubble has been formed on the coating film surface of the test panel;
 the observation device is set so as to be able to observe the state

of the test panel and the bubble; when the test panel is horizontal, the state of the bubble formed on the surface of the coating film of the test panel is observed by the observation device to measure a static in-water bubble contact angle; and the test panel is inclined
5 against the horizontal by the inclination angle control device, and the behavior of the bubble is observed by the observation device to measure an in-water bubble roll (slip) angle of the bubble formed on the surface of the coating film of the test panel.

10 Advantageous Effects of Invention

[0039]

Since the antifouling coating composition used for a special frictional resistance reduced ship according to the present invention contains specific components, it can form a coating film capable of
15 efficiently reducing frictional resistance of a submerged surface of a shell plating of a ship (also referred to as "frictional resistance of a hull" simply hereinafter) even by supplying a small amount of a gas, and the energy saving effect is also great. Since a coating film formed from the antifouling coating composition contains a
20 specific hydrophobic material, it can exhibit excellent antifouling property to prevent fouling by aquatic organisms, and an increase in frictional resistance of a hull attributable to fouling by aquatic organisms, etc. can be prevented. Moreover, the coating film formed from the antifouling coating composition can maintain those effects

over a long period of time.

[0040]

When the hydrophobic material (C) added to the antifouling coating composition used for a special frictional resistance reduced ship according to the present invention contains at least one kind selected from a silicone oil, a fluorine-based oil and paraffins, the antifouling coating composition can form a coating film exerting higher antifouling performance, and besides, the frictional resistance reduction effect of the coating film is maintained over a longer period of time. When the antifouling coating composition contains an antifouling agent (D), the effect is further increased.

[0041]

With regard to the surface profile of the antifouling coating film according to the present invention, the maximum height from the bottom of a recess to the peak of a projection, as measured in accordance with JIS B 0601, is not more than 30 μm , and the peak-valley average interval that is an average of a length of one cycle constituted of one projection and its neighboring one recess, as measured in accordance with JIS B 0601, is not less than 700 μm , and therefore, the holding power for bubbles and/or a gas layer is high, and peeling or drop off from a shell plating of a ship or the like hardly occurs, so that the frictional resistance of a hull can be stably reduced over a long period of time.

[0042]

The first special frictional resistance reduced ship of the present invention in which a submerged surface of a shell plating has been coated with an antifouling coating film formed from the antifouling coating composition has an antifouling coating film formed from the antifouling coating composition, and therefore, even if the amount of a gas supplied to the shell plating of the ship is small, a high water flow frictional resistance reduction effect is exerted, and besides, the effect can be stably exerted over a long period of time.

10 [0043]

The production process for the first special frictional resistance reduced ship according to the present invention can produce a specific ship exerting the above effect by a simple method of forming an antifouling coating film from the antifouling coating composition on a submerged surface of a shell plating of the ship.

[0044]

The coating composition used for a special frictional resistance reduced ship according to the present invention can form a coating film having a static in-water bubble contact angle of less than 90 degrees and a bubble roll (slip) angle of less than 30 degrees in water, and therefore, bubbles and/or a gas layer smoothly flows while sufficiently contacting the coating film. On that account, in the (second) special frictional resistance reduced ship having the coating film formed on a submerged surface of its shell plating, an efficient

gas lubrication effect is exerted, the frictional resistance of a hull is efficiently reduced even if the amount of air supplied is small, and the energy saving effect is also great.

[0045]

5 In the production process for the second frictional resistance reduced ship according to the present invention, the above coating film is formed on a submergence expected surface of a shell plating of a ship to be coated, and therefore, there can be produced such a special frictional resistance reduced ship as above in which
10 frictional resistance of a submerged surface of the shell plating is efficiently reduced even if the amount of air supplied is small and which exerts a high energy saving effect.

[0046]

 The method for predicting a frictional resistance reduction
15 effect utilizing a gas lubrication function of a coating film in water according to the present invention can be carried out by measuring a static contact angle and a roll (slip) angle of a bubble formed on a surface of a coating film in water. That is to say, a static contact angle and a roll (slip) angle of a bubble formed on a surface
20 of a coating film in water are measured, and when those angle values are in the specific ranges, it can be predicted that the frictional resistance reduction effect utilizing a gas lubrication function in water is excellent.

[0047]

In the method for predicting a frictional resistance reduction effect according to the present invention, not only can ease of forming a bubble in water be evaluated from the results of the measurement of a static contact angle and a roll (slip) angle of a bubble on a surface of a coating film in water but also the actual state or the behavior of a bubble in water (e.g., fluidity of bubble on coating material) can be observed.

[0048]

The prediction method of the present invention is superior in the above respects to the prior art methods which can evaluate hydrophobicity of a coating film from the contact angle but cannot evaluate the behavior of a bubble in water.

The apparatus used for prediction of a frictional resistance reduction effect utilizing a gas lubrication function of a coating film in water according to the present invention can measure a static in-water bubble contact angle and a bubble roll (slip) angle through simple operations without needing complicated apparatus constitution, and therefore, it can be preferably used for such prediction of a frictional resistance reduction effect as above.

[0049]

The first and the second frictional resistance reduction systems used for frictional resistance reduced ships utilizing a gas lubrication function in water according to the present invention each have such a first or a second coating film as above and a gas supply

device for supplying a gas such as air to the surface of the coating film, and therefore, a frictional resistance reduction system used for a frictional resistance reduced ship utilizing a gas lubrication function in water, said system exerting an excellent frictional resistance reduction effect, can
5 be provided. On that account, affinity for a gas such as air in water is maintained over a long period of time, the fluid frictional resistance reduction effect is great even if high power is not introduced for the supply of a gas, an economical advantage is given, and the influence on the environment is small.

10 [0050]

The third and the fourth special frictional resistance reduced ships of the present invention each have the frictional resistance reduction system, and therefore, they exert an excellent frictional resistance reduction effect. On that account, affinity for a gas such as air in water is maintained over
15 a long period of time, the fluid frictional resistance reduction effect is great even if high power is not introduced for the supply of a gas, an economical advantage is given, and the influence on the environment is small.

20 Brief Description of Drawings

[0051]

[Fig. 1] Fig. 1 is a schematic view of a contact angle measuring apparatus used for prediction of a frictional resistance reduction

effect by measuring a static in-water bubble contact angle and an in-water bubble roll (slip) angle.

[Fig. 2] Fig. 2 is a schematic explanatory view showing how to determine a static in-water bubble contact angle in the measuring
5 method for a static in-water bubble contact angle.

[Fig. 3] Fig. 3 is a schematic explanatory view showing a measuring method for in-water bubble roll (slip) angle.

[Fig. 4] Fig. 4 is a schematic view of a model ship used in measurement of water flow frictional resistance.

10 [Fig. 5] Fig 5 is a view showing a relationship between an equivalent air thickness and a frictional resistance reduction ratio (comparison between before immersion and after immersion of 30 days).

Description of Embodiments

15 [0052]

The present invention is broadly divided into three groups for convenience as described below, and with regard to each group, best modes are specifically described in order hereinafter.

20 First group: an antifouling coating composition used for a special frictional resistance reduced ship (first coating composition), an antifouling coating film formed from the composition (first coating film), a ship coated with the first coating film (first special frictional resistance reduced ship), and a production process for the first ship.

[0053]

Second group: a coating composition used for a special frictional resistance reduced ship (second coating composition), a coating film formed from the composition (second coating film), a ship coated with the coating film (second special frictional resistance reduced ship), a production process for the second ship, a method for predicting a frictional resistance reduction effect utilizing a gas lubrication function of a coating film in water, and an apparatus used for the prediction of a frictional resistance reduction effect.

10 [0054]

Third group: frictional resistance reduction systems each used for a frictional resistance reduced ship utilizing a gas lubrication function in water (first and second frictional resistance reduction systems), and special frictional resistance reduced ships having the systems (third and fourth special frictional resistance reduced ships).

[0055]

The later-described various property measurements are carried out under the pressure conditions of normal pressure (about 0.1013 MPa) and likewise under the temperature conditions of normal temperature (about 25°C), unless otherwise noted.

The following respect is common to the first, the second, the third and the fourth special frictional resistance reduced ships according to the present invention.

[0056]

In order to reduce water flow frictional resistance by a gas lubrication function, it is necessary that bubbles and/or a gas layer sufficiently should come into contact with a surface of a special frictional resistance reduced ship, said surface being in contact with a water flow (submerged surface of a shell plating of a ship).

[0057]

In the present specification, "water" includes not only fresh water but also sea water, river water, lake water, etc.

10 In the present specification, further, "gas" inclusively indicates such gasses as do no damage to ships, such as air, nitrogen gas, carbon dioxide gas, oxygen gas and hydrogen gas. From the viewpoints of influence on the environment, cost, etc., gas particularly preferably indicates air.

[0058]

15 1. First group

In the first special frictional resistance reduced ship of the present invention, for example, an antifouling coating film formed from an antifouling coating composition for a special frictional resistance reduced ship, said composition comprising a specific organopolysiloxane (A), a specific hydrophobic material (C), and if necessary, a specific organosilane and/or its partial condensate (B) in specific amounts, has been formed on a submerged part of its shell plating.

[0059]

By the use of such an antifouling coating composition for a special frictional resistance reduced ship, a coating film having aforesaid various properties, such as frictional resistance reduction property, can be formed.

5 1-1. Antifouling coating composition having specific constitution

In the antifouling coating composition of the present invention, a compound having a polysiloxane skeleton structure is contained, and it is presumed that leveling property peculiar to such a compound has influence on the profile of a coating film formed from the antifouling coating
10 composition. On that account, it is presumed that the antifouling coating composition of the present invention can form such a coating film having a roughness height of not more than 30 μm and a peak-valley average interval of not less than 700 μm as described later. Moreover, it is presumed that the antifouling coating composition of the present invention can form a
15 coating film having such a profile as above and this profile is extremely preferable for exhibition of gas holding property and gas lubrication performance such as gas fluidity on the coating film surface, and therefore, an antifouling coating film usually having a small static in-water bubble contact angle of less than 90 degrees and a small bubble roll (slip) angle
20 of less than 30 degrees can be formed.

[0060]

The hydrophobic material (C) in the antifouling coating composition is present in such a form as that of a filler in a cured coating film, as described later. During navigation of a ship having the cured coating film formed on a submerged surface of its shell plating, the hydrophobic material (C) gradually bleeds out to cover the cured coating film surface. Since this hydrophobic material is liquid or greasy at 25°C, it improves lubrication property of the surface, similarly to, for example, a lubrication agent, to enable prevention of fouling by microorganisms in water, and it imparts antifouling property to the antifouling coating film.

[0061]

The components in the antifouling coating composition are described hereinafter.

1-1-1. Reaction-curing type organopolysiloxane (A)

The reaction-curing type organopolysiloxane (A) has a viscosity at 25°C of 20 to 400000 mm²/s.

[0062]

Here, the reaction-curing type organopolysiloxane is an organopolysiloxane having at least two condensing reactive groups in one molecule, is preferably an organopolysiloxane having at least two condensing reactive groups at both ends, and is an organopolysiloxane which can be cured by curing reaction of only the organopolysiloxane or an organopolysiloxane which does not undergo curing reaction of only the organopolysiloxane but which can be cured

by curing reaction of the organopolysiloxane with a compound such as the later-described organosilane and/or its partial condensate (B).

[0063]

5 The both ends of molecule are two ends of a main chain, and the condensing reactive group is usually a hydroxyl group or a hydrolyzable group, and the two end groups may be the same or different. The organopolysiloxane may have, in addition to hydroxy groups or hydrolyzable groups present at both ends of molecule, a functional
10 group that reacts with the later-described organosilane and/or its partial condensate (B), in the main chain or the side chain. Having at least two condensing reactive groups at both ends is, in other words, having at least one condensing reactive group at each end of the two ends.

15 [0064]

Specific examples of the hydrolyzable groups are the same as the later-described specific examples of X in

$X_{3-b}R_b^3SiO(R^1R^2SiO)_mR_b^3SiX_{3-b}$ that is the organopolysiloxane (A).

From the viewpoint that the hydrolyzable group can be allowed
20 to react with the later-described organosilane and/or its partial condensate (B), the hydrolyzable group of the organopolysiloxane (A) is preferably the same as a hydrolyzable group of the later-described organosilane and/or its partial condensate (B).

[0065]

From the viewpoints of curability, rubber strength of a cured coating film, film thickening property, coating property such as handling property, prevention of sagging in the case of dilution of the resulting composition with a solvent, etc., the viscosity is preferably 25 to 200000 mm²/s, more preferably 500 to 100000 mm²/s.

[0066]

In the present specification, the viscosity is measured by the "JIS Z 8803 liquid viscosity measuring method" using a capillary viscometer (Ubbelohde viscometer).

10 The organopolysiloxane (A) is, for example, an organopolysiloxane represented by $\text{HO}(\text{R}^1\text{R}^2\text{SiO})_m\text{H}$ and having silanol groups at both ends of molecule. R^1 and R^2 are each a monovalent hydrocarbon group of 1 to 10 carbon atoms, such as methyl group, phenyl group or vinyl group, and m is a positive number corresponding to the degree of polymerization and is within the range satisfying the range of the viscosity.

[0067]

In addition, an organopolysiloxane represented by $\text{X}_{3-b}\text{R}^3\text{SiO}(\text{R}^1\text{R}^2\text{SiO})_m\text{R}^3\text{SiX}_{3-b}$ and having a hydrolyzable group at an end of molecule can be mentioned. R^1 and R^2 are the same as those in the aforesaid structural formula, R^3 is the same monovalent hydrocarbon group as R^1 and R^2 , X is the following hydrolyzable group, b is 0, 1 or 2, and m is a positive number corresponding to the degree of polymerization and is within the range satisfying the range of the

viscosity.

[0068]

Examples of the hydrolyzable groups as X include alkoxy group, acyloxy group, alkenyloxy group, iminoxy group, amino group, amide
5 group and aminooxy group, and preferable is alkoxy group.

[0069]

The alkoxy group is desirably that having 1 to 10 carbon atoms in total, and an oxygen atom may be present at one or more positions between carbon atoms. Examples of such alkoxy groups include methoxy
10 group, ethoxy group, propoxy group, butoxy group, methoxyethoxy group and ethoxyethoxy group.

[0070]

The acyloxy group is desirably an aliphatic or aromatic group represented by the formula R^4COO- (wherein R^4 is an alkyl group of
15 1 to 10 carbon atoms or an aromatic group or 6 to 12 carbon atoms), and examples thereof include acetoxym group, propionoxym group, butyloxym group and benzoyloxym group.

[0071]

The alkenyloxy group is desirably that of about 3 to 10 carbon
20 atoms, and examples thereof include isopropenyloxy group, isobutenyloxy group and 1-ethyl-2-methylvinyl group. The iminoxy group (also referred to as " $=N-OH$ ", "oxyimino group" or ketoxime group") is desirably that of about 3 to 10 carbon atoms, and examples thereof include ketoxime group, dimethylketoxime group,

methylethylketoxime group, diethylketoxime group, cyclopentanoxime group and cyclohexanoxime group.

[0072]

The amino group is desirably that of 1 to 10 carbon atoms, and
5 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. The amide group is desirably that having 2 to 10 carbon atoms in total, and examples thereof include N-methylacetamide group, N-ethylacetamide group and
10 N-methylbenzamide group.

[0073]

The aminooxy group is desirably that having 2 to 10 carbon atoms in total, and examples thereof include N,N-dimethylaminooxy group and N,N-diethylaminooxy group.

15 R^1 , R^2 and R^3 are each independently an unsubstituted or substituted monovalent hydrocarbon group of 1 to 12 carbon atoms, more preferably 1 to 10 carbon atoms, particularly preferably 1 to 8 carbon atoms, and examples of such monovalent hydrocarbon groups include alkyl group, alkenyl group, aryl group, cycloalkyl group and
20 aralkyl group.

[0074]

The alkyl group may be any type of straight-chain, branched and alicyclic alkyl groups, and is preferably a straight-chain or branched alkyl group of 1 to 10 carbon atoms, preferably about 1 to

8 carbon atoms, or a cycloalkyl group of 3 to 6 carbon atoms. Examples of such straight-chain or branched alkyl groups include alkyl groups, such as methyl group, ethyl group, propyl group, butyl group, 2-ethylbutyl group and octyl group. Particularly preferable is methyl group. Examples of alicyclic alkyl groups include cyclohexyl group and cyclopentyl group.

[0075]

The alkenyl group is desirably that of 2 to 10 carbon atoms, preferably about 2 to 8 carbon atoms, and examples thereof include vinyl group, hexenyl group and allyl group.

The aryl group is desirably that of 6 to 15 carbon atoms, preferably about 6 to 12 carbon atoms, and examples thereof include phenyl group, tolyl group, xylyl group, naphthyl group and diphenyl group. Particularly preferable is phenyl group.

15 [0076]

The cycloalkyl group is desirably that of 3 to 8 carbon atoms, and examples thereof include cyclohexyl group. The aralkyl group is desirably that having 7 to 10 carbon atoms in total, preferably about 7 to 8 carbon atoms in total, and examples thereof include benzyl group and 2-phenylethyl group.

[0077]

A part or all of hydrogen atoms bonded to carbon atoms of these groups may be replaced with halogen atoms, such as F, Cl, Br and I, cyano group, etc., and examples of halogenated alkyl groups include

chloromethyl group, 3,3,3-trifluoropropyl group and 2-cyanoethyl group.

[0078]

As each of R^1 , R^2 and R^3 , an unsubstituted monovalent hydrocarbon group is preferable among them, and methyl group or phenyl group is particularly preferable. When plural R^3 , plural R^1 , and plural R^2 are present in the organopolysiloxane represented by the above formula and having a hydrolyzable group at an end of molecule, these plural R^3 , plural R^1 , plural R^2 , or R^3 , R^1 and R^2 may be the same as or different from one another.

[0079]

As previously described, the reaction-curing type organopolysiloxane (A) may have, in addition to hydroxyl groups or hydrolyzable silyl groups present at both ends of molecule, a functional group that reacts with the later-described organosilane and/or its partial condensate (B), in the main chain or the side chain. For example, an organopolysiloxane of the aforesaid $HO(R^1R^2SiO)_mH$ or $X_{3-b}R^3_bSiO(R^1R^2SiO)_mR^3_bSiX_{3-b}$ wherein R^1 , R^2 and R^3 are functional groups that react with the organosilane and/or its partial condensate (B) can be also used as the organopolysiloxane (A).

[0080]

As such an organopolysiloxane (A), a dimethylpolysiloxane in which both ends of molecular chain are capped with silanol groups (e.g., trade name "XF3905", manufactured by Momentive Performance

Materials Inc.), a deoxime type organopolysiloxane (e.g., trade name "KE-445", manufactured by Shin-Etsu Chemical Co., Ltd.) , or the like can be mentioned.

[0081]

5 From the viewpoints of cost reduction, handling of the coating composition, etc., the organopolysiloxane (A) is preferably self-condensing and is more preferably self-condensing in the vicinity of normal temperature (usually about 10°C to 30°C, the same shall apply hereinafter).

10 [0082]

Of the organopolysiloxanes (A) previously given as examples, a dimethylpolysiloxane in which both ends of molecular chain are capped with silanol groups (e.g., trade name "XF3905", manufactured by Momentive Performance Materials Inc.), a deoxime type organopolysiloxane (e.g., trade name "KE-445", manufactured by Shin-Etsu Chemical Co., Ltd.), etc. are self-condensing polysiloxanes.

[0083]

20 To the antifouling coating composition used for a frictional resistance reduced ship, these organopolysiloxanes (A) may be added singly or in combination of two or more kinds.

1-1-2. Specific organosilane and/or its partial condensate (B)

The component (B) is an organosilane having, in one molecule, at least two groups each of which is at least one group of a hydroxy

group and a hydrolyzable group, and/or its partial condensate.

[0084]

In the organosilane, two or more groups selected from any one kind of the hydroxy groups and the hydrolyzable groups may be present, or two or more groups selected from both kinds thereof may be present.

From the following viewpoint, the component (B) desirably functions as a crosslinking agent of the organopolysiloxane (A).

[0085]

The organosilane and/or its partial condensate (B) is an arbitrary component, and it is enough just to add this component to the antifouling coating composition, when needed.

When the organopolysiloxane (A) undergoes condensation reaction with an organopolysiloxane (A) (that is, it undergoes self condensation) and is cured, a cured film having excellent hardness is obtained from the antifouling coating composition even if the organosilane and/or its partial condensate (B) is not added. However, if the organosilane and/or its partial condensate (B) is added, there is an advantage that curing rate or hardness of a coating film can be more accurately controlled.

[0086]

In this case, when the organopolysiloxane (A) is an organopolysiloxane that undergoes self condensation in the vicinity of normal temperature by virtue of a catalyst or the like, room temperature vulcanization is possible.

Even when the organopolysiloxane (A) is an organopolysiloxane that does not undergo self condensation in the vicinity of normal temperature, addition of the oragnosilane and/or its partial condensate (B) produces an advantage that condensation reaction of the organopolysiloxane (A) with the oragnosilane and/or its partial condensate (B) is brought about at normal temperature during coating with the antifouling coating material by utilizing hydrolysis reaction with water such as moisture in the atmosphere, and a cured coating film can be obtained even in the vicinity of normal temperature.

10 [0087]

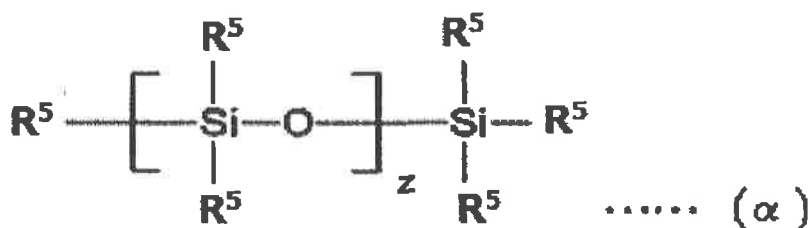
When the organopolysiloxane (A) is an organopolysiloxane that does not undergo self condensation, it is desirable to add (B) the oragnosilane having a functional group undergoing condensation reaction with a condensing reactive functional group of the organopolysiloxane that does not undergo self condensation and/or its partial condensate, from the viewpoints of curing rate, hardness of the resulting coating film, etc.

[0088]

The hydrolyzable group of the oragnosilane and/or its partial condensate (B) for use in the present invention is a functional group capable of undergoing condensation reaction with the condensing reactive group of the reaction-curing type organopolysiloxane (A). As this component (B), an organosilane represented by the following general formula (α) can be used.

[0089]

[Chem. 1]



[0090]

5 In the above general formula (α), plural R^5 may be the same as or different from one another and are each a hydroxyl group, a hydrolyzable group or a monovalent hydrocarbon group of 1 to 8 carbon atoms. However, with regard to R^5 at both ends, at least one of them at each end is a hydroxy group or a hydrolyzable group (at both ends,

10 two or more hydroxy groups and/or hydrolyzable groups in total). At least two or more, desirably three or more, of R^5 including those hydroxy groups and/or hydrolyzable groups at both ends are condensation reactive groups. z is an integer of 0 to 10, preferably an integer of 0 to 8.

15 [0091]

Examples of the monovalent hydrocarbon groups of 1 to 8 carbon atoms in the general formula (α) include substituted or unsubstituted alkyl, alkenyl, aryl, cycloalkyl and aralkyl groups. Examples of the hydrolyzable groups in the general formula (α) include the same

20 groups as described for the hydrolyzable group of X in

$\text{X}_{3-b}\text{R}^3_b\text{SiO}(\text{R}^1\text{R}^2\text{SiO})_m\text{R}^3_b\text{SiX}_{3-b}$ that is given as one example of the

reaction-curing type organopolysiloxane (A), and of these, oxime group, acetyloxy group or alkoxy group is preferable.

[0092]

Further, an organosilane wherein the hydrolyzable groups such
5 as acetyloxy group and alkoxy group have been partially hydrolyzed can be used as the component (B) (that is, a partially hydrolyzed condensate of an organosilane having two or more hydrolyzable groups can be used as the component (B)).

[0093]

10 Furthermore, an organosilane wherein partial dehydrocondensation has been conducted between at least two hydroxyl groups can be also used as the component (B) (that is, a partial condensate of an organosilane having two or more hydrolyzable groups can be used as the component (B)).

15 [0094]

In the present invention, particularly, the organosilane containing an alkoxy group, namely, an alkoxysilane (alkyl silicate), or its partial condensate can be preferably used.

The alkoxysilane is, for example, tetraalkyl orthosilicate
20 (alkyltetraalkoxysilane) such as tetraethyl orthosilicate (TEOS), or alkyltrialkoxysilane, such as methyltrimethoxysilane, ethyltrimethoxysilane or methyltriethoxysilane. As the alkoxysilane, alkyltetraalkoxysilane or alkyltrialkoxysilane is more preferable from the viewpoints of curing property of the resulting

coating film, etc.

[0095]

Particularly when an organopolysiloxane having hydroxyl groups at both ends is used as the component (A), it is preferable to use the alkyl silicate (alkoxysilane) and/or its partial condensate as the component (B) in combination with the component (A). As the organosilane and/or its partial condensate (B), a commercially available one can be used. For example, there can be mentioned, as tetraethyl orthosilicate, "Ethyl Silicate 28" (manufactured by Colcoat Co., Ltd.) or "Ethyl Orthosilicate" (manufactured by Tama Chemicals Co., Ltd.); as partial hydrolyzate of tetraethyl orthosilicate, "Silicate 40" (manufactured by Tama Chemicals Co., Ltd.) or "TES40 WN" (Wacker Asahikasei Silicone Co., Ltd.); and as alkyltrialkoxysilane, "KBM-13" (Shin-Etsu Chemical Co., Ltd.).

15 [0096]

The organosilane and/or its partial condensate (B) can be used in the total amount of 1 to 60 parts by weight based on 100 parts by weight of the organopolysiloxane (A), but from the viewpoints of curability and properties of the cured coating film, it is desirably contained usually in an amount of 1 to 20 parts by weight, preferably 2 to 10 parts by weight, in the antifouling coating composition.

[0097]

With regard to the organosilane and/or its partial condensate (B), any one of the organosilane and its partial condensate may be

added singly, or both of them may be added to an antifouling coating composition used for a frictional resistance reduced ship. Further, the organosilanes or their partial condensates can be added singly or as a mixture of two or more kinds.

5 [0098]

1-1-3. Hydrophobic material (C)

The component (C) is a hydrophobic material which is liquid or greasy at 25°C.

The hydrophobic material (C) may be any of a silicone oil, a
10 fluorine-containing silicone oil, a fluorine-based oil, paraffin and a wax, as long as it is liquid or greasy at ordinary temperature. For example, the hydrophobic material (C) contains at least one kind selected from them.

[0099]

15 However, a hydrophobic material corresponding to the organopolysiloxane (A) and a hydrophobic material corresponding to the organosilane and/or its partial condensate (B) are not included in the hydrophobic materials (C).

[0100]

20 <Silicone oil>

The silicone oil is not specifically restricted provided that it is an unreactive (non-condensing) silicone oil or a silicone oil that bleeds out from a cured product of an antifouling coating composition used for a special frictional resistance reduced ship,

but a silicone oil represented by the following formula [I] or [II] or a silicone oil having a group represented by the following formula [III] is preferable.

[0101]

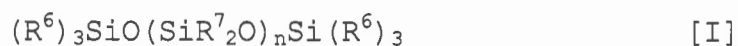
5 Of such silicone oils, the silicone oils [I] and [II] exhibit no reactivity with the organopolysiloxane (A) and no self-condensing property, and it is thought that they have a function to form an antifouling functional layer (film) on a coating film surface (layer) through bleeding-out accompanied by no special chemical change.

10 [0102]

 On the other hand, the silicone oil [III] reacts with the organopolysiloxane (A) that becomes a coating film-forming component or with another compound to form a cured coating film. It is thought that when the coating film is immersed in sea water for a long period
15 of time, the silicone oil is hydrolyzed with time, and the end group becomes a group " $\equiv\text{SiR}^8\text{OH}$ " having an alcoholic hydroxyl group, and the silicone oil bleeds out on the coating film surface, whereby an effect of preventing fouling by marine organisms is exerted.

[0103]

20 [Chem. 2]



[0104]

 In the formula [I], plural R^6 may be the same as or different from one another and are each an alkyl group of 1 to 10 carbon atoms,

an aryl group, an aralkyl group or a fluoroalkyl group, plural R^7 may be the same as or different from one another, each R^7 is an alkyl group of 1 to 10 carbon atoms, an aryl group, an aralkyl group or a fluoroalkyl group, and n is a number of 0 to 150.

5 [0105]

[Chem. 3]

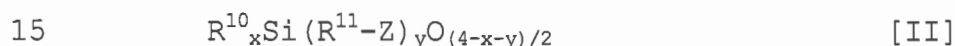


[0106]

In the formula [III], R^8 is an unsubstituted or substituted
10 divalent hydrocarbon group or a divalent hydrocarbon group containing an ether bond, R^9 is an unsubstituted or substituted monovalent hydrocarbon group, Y is a hydrolyzable group, and b is 0, 1 or 2.

[0107]

[Chem. 4]



[0108]

In the formula [II], R^{10} is a hydrogen atom or an alkyl, aryl or aralkyl group of 1 to 10 carbon atoms, R^{11} is a divalent aliphatic hydrocarbon group of 1 to 10 carbon atoms in which an ether group,
20 an ester group or $-\text{NH}-$ may be interposed, Z is an amino group, a carboxyl group, an epoxy group, or a polyethylene glycol or polypropylene glycol group whose end may be capped with an alkyl group of 1 to 6 carbon atoms or an acyl group, and x and y are numbers satisfying the conditions of $0.01 \leq x < 3.99$, $0.01 \leq y < 3.99$ and $0.02 \leq x+y < 4$.

[0109]

As the silicone oil [I] among the above silicone oils, such a silicone oil as described in Japanese Patent Laid-Open Publication No. 1998-316933 can be used, and a silicone oil having a number-average
5 molecular weight, as measured by GPC method, of 180 to 20,000, preferably 1,000 to 10,000, and a viscosity, as measured by the aforesaid Ubbelohde viscometer, of 20 to 30,000 mm²/s, preferably 50 to 3,000 mm²/s, is desirable.

[0110]

10 Examples of such silicone oils [I] include dimethyl silicone oils wherein all of R⁶ and R⁷ are methyl groups and phenylmethyl silicone oils wherein a part of methyl groups in these dimethyl silicone oils are replaced with phenyl groups, and of these, preferable are methylphenyl silicone oils. Specific examples of such methylphenyl
15 silicone oils include those on the market under the trade names 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 and TSF433" (manufactured by Toshiba Silicone Co., Ltd.).

[0111]

20 As the silicone oil (silicone oil [III]) having a group represented by the above formula [III], a silicone oil described in Japanese Patent No. 2522854 proposed by the present applicants can be used, and a silicone oil having a number-average molecular weight, as measured by GPC method, of 250 to 20,000, preferably 1,000 to 10,000,

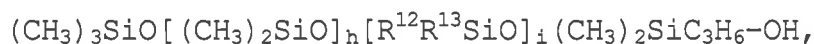
and a viscosity, as measured by the aforesaid method, of 20 to 30,000 mm²/s, preferably 50 to 3,000 mm²/s, is desirable.

[0112]

Specific examples of R⁸ include unsubstituted or substituted
 5 divalent hydrocarbon groups, such as methylene group, ethylene group, propylene group, butylene group and hexamethylene group; and divalent hydrocarbon groups containing an ether bond, which are represented by " $-(CH_2)_p-O-(CH_2)_q-$ " (wherein p and q are each independently an integer of 1 to 6) or the like.

10 [0113]

R⁹ is an unsubstituted or substituted monovalent hydrocarbon group of 1 to 8 carbon atoms. Y is the same group as the hydrolyzable group X of $X_{3-b}R^3_bSiO(R^1R^2SiO)_mR^3_bSiX_{3-b}$ that is given as one example of the reaction-curing type organopolysiloxane (A). Specific
 15 examples of such silicone oils [III] having at least one group represented by the formula [III] include silicone oils wherein hydroxyl groups of silicone oils represented by



20 $(CH_3)_3SiO[(CH_3)_2SiO]_h[R^{12}R^{13}SiO]_i[(CH_3)(C_3H_6-OH)SiO]_j[(CH_3)_2SiCH_3]$ are capped with hydrolyzable groups, such as silicone oils described in the aforesaid Japanese Patent No. 2522854. R¹² and R¹³ in the above formulas are each an aryl group such as phenyl group or tolyl group; an aralkyl group such as benzyl group or β -phenylethyl group; or an

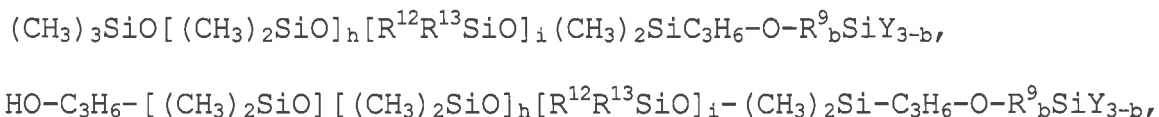
unsubstituted or substituted monovalent hydrocarbon group in the case where at least one of R^{12} and R^{13} is selected from groups other than a methyl group, e.g., a halogenated alkyl group such as a trifluoropropyl group. h , i and j are each a positive number.

5 [0114]

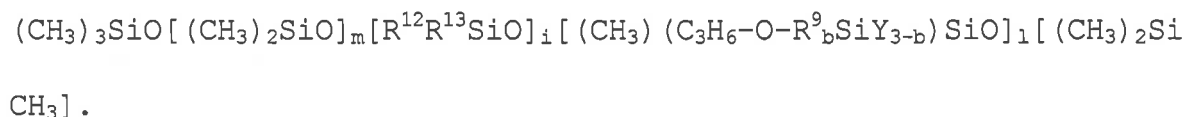
From the viewpoint of storage stability of the resulting composition, silicone oils obtained by allowing the above silicone oils to react with an organosilane represented by the formula " R^9SiY_{3-b} " (R^9 , Y and b are the same as those in the formula [III]) may be used, and examples of such silicone oils are given below, .

[0115]

For example, there can be mentioned



15 and



[0116]

As the silicone oil [II], such a silicone oil as described in Japanese Patent Laid-Open Publication No. 1998-316933 can be specifically used, and a silicone oil having a number-average molecular weight, as measured by GPC method, of 250 to 30,000, preferably 1,000 to 20,000, and a viscosity, as measured by the aforesaid method, of 20 to 30,000 mm^2/s , preferably 50 to 3,000 mm^2/s , is desirable.

[0117]

As such a silicone oil [II], a silicone oil of the above formula [II] wherein R^{10} is a methyl group or a phenyl group and R^{11} is a methylene group, an ethylene group or a propylene group is desirable. When
5 Z is a polyethylene or polypropylene group whose end may be capped with an alkyl group of 6 or less carbon atoms or an acyl group, the number of oxyethylene or oxypropylene repeating units is preferably 10 to 60. Example of the alkyl groups for end capping include methyl group, ethyl group, propyl group and butyl group, and examples of
10 the acyl groups for end capping include ketoxime group, acetyl group and propionyl group.

[0118]

Specific examples of the silicone oils wherein the polar group Z is an amino group include "SF8417" (manufactured by Dow Corning
15 Toray Co., Ltd.), "ISI4700 and ISI4701" (manufactured by Toshiba Silicone Co., Ltd.), and "FZ3712 and AFL-40" (manufactured by Nippon Unicar Co., Ltd.). Examples of the silicone oils wherein the polar group Z is a carboxyl group include "X142-411" (manufactured by Toshiba Silicone Co., Ltd.), "SF8418" (manufactured by Dow Corning Toray Co.,
20 Ltd.) and "FXZ4707" (manufactured by Nippon Unicar Co., Ltd.). Examples of the silicone oils wherein the polar group Z is an epoxy group include "SF8411" (manufactured by Dow Corning Toray Co., Ltd.), "X142-301" (manufactured by Toshiba Silicone Co., Ltd.), and "L-93 and T-29" (manufactured by Nippon Unicar Co., Ltd.). Examples of

the silicone oils wherein the polar group Z is an alkyl group or an acyl group include "ISI4460, ISI4445 and ISI4446" (manufactured by Toshiba Silicone Co., Ltd.), "SH3746, SH8400, SH3749 and SH3700" (manufactured by Dow Corning Toray Co., Ltd.), and "KF6009" (manufactured by Shin-Etsu Chemical Co., Ltd.).

[0119]

<Fluorine-containing silicone oil>

Examples of the fluorine-containing silicone oils include X-22-821 (manufactured by Shin-Etsu Chemical Co., Ltd.) and X-22-822 (manufactured by Shin-Etsu Chemical Co., Ltd., side chain type fluoroalkyl-modified silicone oil).

[0120]

<Fluorine-based oil>

Examples of the fluorine-based oils include Demnum S-65 (manufactured by Daikin Industries, Ltd., perfluoropolyether oil).

[0121]

<Paraffins or wax>

Examples of the paraffins and the waxes include Sumoiru P-350 (manufactured by Matsumura Oil Co., Ltd., liquid paraffin).

[0122]

The amount of the hydrophobic material (C) in the antifouling coating composition used for a special frictional resistance reduced ship according to the present invention is usually 0.1 to 200 parts by weight, preferably 20 to 100 parts by weight, based on 100 parts

by weight of the organopolysiloxane component (A).

[0123]

When the amount of the hydrophobic material (C) is in the above range, an (antifouling) coating film excellent in both of antifouling property and coating film strength is obtained. If the amount of the hydrophobic material (C) is less than the lower limit of the above range, antifouling property is lowered. If the amount thereof exceeds the upper limit of the above range, coating film strength is sometimes lowered.

10 [0124]

To the antifouling coating composition used for a special frictional resistance reduced ship, the hydrophobic materials (C) may be added singly or may be added in combination of two or more kinds.

15 1-2. Production of antifouling coating composition used for special frictional resistance reduced ship

Such an antifouling coating composition used for a special frictional resistance reduced ship according to the present invention can be produced by the following process. First, if necessary, a part or all of the organopolysiloxane (A) and the later-described hydrophilic silica or both of the later-described hydrophilic silica and hydrophobic silica are heat-treated at a temperature of not lower than 100°C but not higher than the decomposition temperature of the components, preferably 100 to 300°C, more preferably about 140 to

20

200°C, usually for 30 minutes to 3 hours at normal pressure or under reduced pressure. In the case where hydrophilic silica or hydrophobic silica is used, the residual organopolysiloxane (A), hydrophilic silica or both of hydrophilic silica and hydrophobic silica, and if
5 necessary, the organosilane and/or its partial condensate (B) are subsequently added, and further, the hydrophobic material (C) is added, whereby the antifouling coating composition can be produced. In the case where hydrophilic silica or hydrophobic silica is not used, the residual organopolysiloxane (A), and if necessary, the organosilane
10 and/or its partial condensate (B) are subsequently added, and further, the hydrophobic material (C) is added, whereby the antifouling coating composition can be produced. In either case, it is also possible that hitherto publicly known organosiloxane curing catalyst, antifouling agent, thixotropic property-imparting agent, plasticizer,
15 inorganic dehydrating agent (stabilizer), anti-sagging/anti-settling agent (thickening agent), pigment/dye, other coating film-forming components, solvent (e.g., xylene), bactericide, mildew proofing agent, anti-aging agent, antioxidant, antistatic agent, flame retardant, heat conduction improver, adhesion
20 imparting agent such as silane coupling agent having a reactive organic group such as amino group, epoxy group or mercapto group, etc. can be added in given ratios at once or in an arbitrary order, then stirred/mixed and dissolved/dispersed in a solvent.

For stirring/mixing such components as above, hithertopublicly known mixing/stirring devices, such as Ross mixer, planetary mixer and universal Shinagawa stirrer, are appropriately used.

<Arbitrary components>

5 (Catalyst)

As the catalyst, for example, a catalyst described in Japanese Patent No. 2522854 can be preferably used. Specific examples thereof include tin carboxylates, such as tin naphthenate and tin oleate; tin compounds, such as dibutyltin diacetate, dibutyltin dioctate, 10 dibutyltin dilaurate, dibutyltin dioleate, dibutyltin oxide, dibutyltin dimethoxide and dibutylbis(triethoxysiloxy)tin; titanitic acid esters or titanium chelate compounds, such as tetraisopropoxytitanium, tetra-n-butoxytitanium, tetrakis(2-ethylhexoxy)titanium, 15 dipropoxybis(acetylacetonato)titanium and titanium isopropoxyoctyl glycol; organometallic compounds, such as zinc naphthenate, zinc stearate, zinc 2-ethyloctate, iron 2-ethylhexoate, cobalt 2-ethylhexoate, manganese 2-ethylhexoate, cobalt naphthenate and alkoxyaluminum compound; aminoalkyl group-substituted alkoxysilanes, 20 such as 3-aminopropyltrimethoxysilane and N- β (aminoethyl)- γ -aminopropyltrimethoxysilane; amine compounds and their salts, such as hexylamine, dodecyl 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 silanes or siloxanes containing guanidyl group, such as tetramethylguanidylpropyltrimethoxysilane, tetramethylguanidylpropylmethyldimethoxysilane and
5 tetramethylguanidylpropyltris(trimethylsiloxy)silane.

[0126]

Such a catalyst is used in an amount of not more than 10 parts by weight, preferably not more than 5 parts by weight, more preferably not more than 1 part by weight, based on 100 parts by weight of the
10 organopolysiloxane (A). When the catalyst is used, a preferred lower limit is 0.001 part by weight, particularly 0.01 part by weight.

[0127]

(Hydrophobic silica, hydrophilic silica)

As silica, hydrophilic silica (surface-untreated silica), such
15 as wet process silica (hydrated silica) or dry process silica (fumed silica, anhydrous silica), or surface-treated hydrophobic silica, such as hydrophobic wet process silica or hydrophobic fumed silica, can be mentioned.

[0128]

20 These silica components can be used singly or in combination of two or more kinds. Use of hydrophobic silica and hydrophilic silica in combination is preferable from the viewpoint that an antifouling coating composition used for a special frictional resistance reduced ship, which is excellent in stability during preparation, storage

and preservation, has sufficient thixotropic property and can form a thick film by one coating, is obtained. Further, a coating film obtained from the antifouling coating composition used for a special frictional resistance reduced ship has a good balance of rubber properties such as hardness, tensile strength and elongation and is excellent also in antifouling property, etc.

[0129]

In the present invention, silica having the following properties may be used as it is, as the silica component, but in its preferred embodiment, it is preferable that at least the hydrophilic silica of the hydrophobic silica and the hydrophilic silica has been heat-treated together with a part or all of the organopolysiloxane (A), and it is more preferable that both of the hydrophilic silica and the hydrophobic silica have been heat-treated together with a part or all of the component (A), as described later in detail, from the viewpoint of improvement in thixotropic property of the coating material and physical properties, strength, etc. of the resulting coating film.

[0130]

Of these silica components, the wet process silica usually has an adsorbed water content (also referred to as a "water content") of about 4 to 8%, a bulk density of 200 to 300 g/L, and a primary particle diameter of 10 to 30 μ m. Although the specific surface area (BET surface area) of the silica has only to be not less than 10 m²/g,

it is preferably 50 to 800 m²/g, more preferably about 100 to 300 m²/g.

[0131]

The dry process silica (fumed silica) usually has a water content of not more than 1.5%. The water content of the dry process silica in the initial stage, e.g., immediately after production, is as low as not more than 0.3%, but if this silica is allowed to stand, it gradually absorbs moisture to increase the water content, and after the lapse of several months after the production, the water content becomes, for example, about 0.5 to 1.0%. The bulk density of such dry process silica varies depending upon the type and is not determined indiscriminately, but it is, for example, 50 to 100 g/L. The primary particle diameter thereof is 8 to 20 μ m. Although the specific surface area (BET surface area) thereof has only to be not less than 10 m²/g, it is preferably 100 to 400 m²/g, more preferably about 180 to 300 m²/g.

[0132]

The hydrophobic fumed silica is silica obtained by surface-treating the dry process silica with an organosilicon compound, such as methyltrichlorosilane, dimethyldichlorosilane, hexamethyldisilazane, hexamethylcyclotrisiloxane or octamethylcyclotetrasiloxane. The water absorption of this silica with time is small, and the water content is usually not more than 0.3%, and in many cases, it is 0.1 to 0.2%. Although the specific

surface area thereof has only to be not less than $10\text{ m}^2/\text{g}$, it is preferably 100 to $300\text{ m}^2/\text{g}$, more preferably about 120 to $230\text{ m}^2/\text{g}$. The primary particle diameter is 5 to $50\text{ }\mu\text{m}$, and the bulk density is 50 to 100 g/L .

5 [0133]

In the hydrophobic fumed silica (heat-treated hydrophobic fumed silica) having been heat-treated together with the organopolysiloxane (A), water adsorbed on the surface of the hydrophobic silica has been reduced or removed, and the water content is usually not more than 0.2% , preferably not more than 0.1% , particularly 0.05 to 0.1% . Other property values, such as bulk density, are the same as those of the aforesaid hydrophobic silica.

[0134]

It is desirable that such a silica component is contained usually in an amount of 1 to 100 parts by weight, preferably 2 to 50 parts by weight, particularly preferably 5 to 30 parts by weight, based on 100 parts by weight of the component (A), in the antifouling coating composition used for a frictional resistance reduced ship according to the present invention. When the silica component is contained in such an amount in the antifouling coating composition used for a frictional resistance reduced ship, the antifouling coating composition is excellent in coating film strength and coating film hardness, has good thixotropic property, has an appropriate viscosity and can be favorably subjected to spray coating in the coating process,

and for example, film thickening of a coating film can be achieved by one coating even on a perpendicularly stand-up base surface, so that such an amount is preferable.

[0135]

5 If the amount of the silica component is less than the lower limit of the above range, sufficient coating film strength and coating film hardness are not obtained, and desired thixotropic property is not obtained, so that film thickening cannot be achieved occasionally by one spray coating in the coating process. If the amount of the
10 silica component is more than the upper limit of the above range, viscosity of the coating material is excessively increased, and it becomes necessary to dilute the antifouling coating composition with a solvent such as thinner to an appropriate viscosity suitable for coating, so that film thickening is not achieved occasionally by one
15 spray coating.

[0136]

 In the present invention, it is desirable to use, as the silica components, the hydrophobic silica (a) such as hydrophobic fumed silica and the hydrophilic silica (b) such as surface-untreated silica in
20 a weight ratio ((a)/(b)) of 1/99 to 99/1, preferably 20/80 to 80/20, particularly preferably 30/70 to 70/30. When the hydrophobic fumed silica (a) and the hydrophilic silica (b) are used in combination in such a quantity ratio, the resulting antifouling coating composition used for a frictional resistance reduced ship is excellent in coating

material stability during preparation, storage and preservation and has sufficient thixotropic property, and a coating film obtained by curing the composition tends to be excellent in coating film strength and coating film hardness.

5 [0137]

<Antifouling agent (D)>

By adding the hydrophobic material (C) to the antifouling coating composition used for a frictional resistance reduced ship according to the present invention, the composition exhibits excellent
10 antifouling property, as described above, but by further adding an antifouling agent (D), the composition can exhibit more excellent antifouling property.

[0138]

The antifouling agent (D) may be any of an inorganic antifouling
15 agent and an organic antifouling agent.

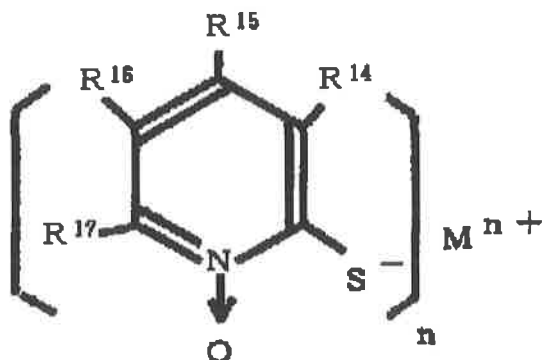
Examples of the inorganic antifouling agents include copper, cuprous oxide, copper rhodanide and an inorganic copper compound. Of these, copper and an inorganic copper compound is preferable.

[0139]

20 Examples of the organic antifouling agents include metal pyrithiones represented by the following formula (β) (wherein R^{14} to R^{17} are each independently hydrogen, an alkyl group, an alkoxy group or a halogenated alkyl group, M is a metal such as Cu, Zn, Na, Mg, Ca, Ba, Pb, Fe or Al, and n represents a valence):

[0140]

[Chem. 5]



. . . . (β)

[0141]

- 5 tetramethylthiuram disulfide, a carbamate-based compound (e.g., zinc dimethyldithiocarbamate, manganese 2-ethylenebisdithiocarbamate, zinc ethylenebisdithiocarbamate),
2,4,5,6-tetrachloroisophthalonitrile,
N,N-dimethyldichlorophenylurea,
- 10 4,5-dichloro-2-n-octyl-3(2H)isothiazoline,
2,4,6-trichlorophenylmaleimide,
2-methylthio-4-t-butylamino-6-cyclopropyl-s-triazine,
N-(fluorodichloromethylthio)phthalimide,
N,N'-dimethyl-N'-phenyl(N-fluorodichloromethylthio)sulfamide,
- 15 N-dichlorofluoromethylthio-N',N'-dimethyl-N-p-tolyl-sulfamide,
2,3,5,6-tetrachloro-4-(methylsulfonyl)pyridine, 3-iodo-2-propynyl butylcarbamate, diiodomethyl p-tolyl sulfone,
bisdimethyldithiocarbamoyl zinc ethylene-bis-dithiocarbamate,

pyridine-triphenylborane (PK) and

4-[1-(2,3-dimethylphenyl)ethyl]-1H-imidazole (medetomidine).

[0142]

Of the above organic antifouling agents, copper pyrithione (M

5 in the formula (β) is Cu), zinc pyrithione (M in the formula (β) is

Zn), N,N-dimethyl-dichlorophenylurea,

2,4,6-trichlorophenylmaleimide,

2-methylthio-4-t-butylamino-6-cyclopropyl-s-triazine,

4,5-dichloro-2-n-octyl-4-isothiazolin-3-one and

10 2,4,5,6-tetrachloroisophthalonitrile are preferable.

[0143]

Of these organic antifouling agents, metal pyrithiones are particularly preferable. The metal pyrithiones and

5-dichloro-2-n-octyl-4-isothiazolin-3-one may be used in combination.

15 These antifouling agents may be used singly or may be used in combination of two or more kinds. The antifouling agent is desirably contained in an amount of 1 to 150 parts by weight, preferably 1 to 100 parts by weight, based on 100 parts by weight of the organopolysiloxane (A).

20 [0144]

It is desirable that in the antifouling coating composition used for a special frictional resistance reduced ship and containing such an antifouling agent, the inorganic copper compound and/or the organic antifouling agent is contained usually in an amount of 0.1

to 50% by weight, preferably 0.5 to 40% by weight, when the amount obtained by subtracting the amount of the solvent from the whole amount of the antifouling coating composition is 100% by weight.

[0145]

5 <Plasticizer (chlorinated paraffin)>

Examples of the plasticizers include TCP (tricresyl phosphate), chlorinated paraffin and polyvinyl ethyl ether. These plasticizers can be used singly or in combination of two or more kinds. These plasticizers contribute to improvement in crack resistance of a coating film formed from the resulting antifouling coating composition used for a special frictional resistance reduced ship (this film being also referred to as an "antifouling coating film" hereinafter).

[0146]

<Anti-sagging/anti-settling agent (thickening agent)>

15 Examples of the anti-sagging/anti-settling agents (thixotropic agents) include organic clay-based agents, salts, such as stearate salts, lecithin salts or alkylsulfonic acid salts of Al, Ca or Zn, polyethylene wax, amide wax, hydrogenated castor oil wax-based agents, polyamide wax-based agents, mixtures of those wax-based agents, 20 synthetic finely divided silica and polyethylene oxide-based waxes. Preferable are polyamide wax, synthetic finely divided silica, polyethylene oxide-based waxes and organic clay-based agents. As such anti-sagging/anti-settling agents, those on the market under the trade names of "Disparlon 305", "Disparlon 4200-20", "Disparlon

A630-20X", etc. manufactured by Kusumoto Chemicals, Ltd. can be mentioned.

[0147]

To the antifouling coating composition used for a special
5 frictional resistance reduced ship, such an
anti-sagging/anti-settling agent is added in an amount of, for example,
0.1 to 10% by weight.

<Pigment/dye>

As the pigments, hitherto publicly known organic or inorganic
10 various pigments can be used. Examples of the organic pigments include
carbon black, phthalocyanine blue and Prussian blue. Examples of
the inorganic pigments include pigments that are neutral and unreactive,
such as titanium white, red iron oxide, barite powder, silica, calcium
carbonate, talc, chalk and iron oxide powder; and pigments (active
15 pigments) that are basic and reactive with an acidic substance in
a coating material, such as zinc white (ZnO, zinc oxide), white lead,
minium, zinc dust and lead suboxide powder.

[0148]

There can be further mentioned metal oxides, such as diatomaceous
20 earth and alumina, pigments obtained by surface-treating surfaces
of these metal oxides with silane compounds; metal carbonates, such
as magnesium carbonate and zinc carbonate; and others, such as asbestos,
glass fiber, quartz powder, aluminum hydroxide, gold powder, silver
powder, surface-treated calcium carbonate and glass balloon.

[0149]

Various colorants such as dyes may be also contained.

These pigments/dyes may be used singly or in combination of two or more kinds.

5 To the antifouling coating composition used for a special frictional resistance reduced ship, such various pigments/dyes are preferably added in the total amount of, for example, about 0.5 to 45% by weight. Such various pigments/dyes are preferably added in the total amount of 1 to 40 parts by weight based on 100 parts by
10 weight of the organopolysiloxane (A).

[0150]

<Other coating film-forming components>

As the coating film-forming components, coating film-forming components other than the aforesaid organopolysiloxane (A), etc. may
15 be contained within limits not detrimental to the object of the present invention. Examples of such "other coating film-forming components" include sparingly water-soluble or water-insoluble resins (also referred to as "sparingly water-soluble/water-insoluble resins" hereinafter), such as acrylic resin, acrylic silicone resin,
20 unsaturated polyester resin, fluoro resin, polybutene resin, silicone rubber, urethane resin (rubber), polyamide resin, vinyl chloride-based copolymer resin, chlorinated rubber (resin), chlorinated olefin resin, styrene/butadiene copolymer resin, ethylene/vinyl acetate copolymer resin, vinyl chloride resin, alkyd

resin, coumarone resin, trialkylsilyl acrylate (co)polymer (silyl-based resin) and petroleum resin.

[0151]

<Other thixotropic property imparting agent, flame retardant,

5 heat conduction improver, adhesion imparting agent, etc.>

Examples of the thixotropic property imparting agents include polyethylene glycol, polypropylene glycol and their derivatives.

Examples of the flame retardants include antimony oxide and paraffin oxide. Examples of the heat conduction improvers include boron

10 nitride and aluminum oxide. Examples of the adhesive components include substances containing one or more kinds of reactive organic groups (e.g., amino group, mercapto group, alkoxysilyl group, epoxy group, hydrosilyl group, acrylic group and hydroxysilyl group), such as silane coupling agent, and mixtures of these substances.

15 [0152]

<Solvent>

In the antifouling coating composition used for a special frictional resistance reduced ship according to the present invention, a solvent may be contained or may not be contained. However, such

20 various components as described above can be used after dissolved or dispersed in solvents. As the solvents used herein, various solvents usually added to antifouling coating materials, such as aliphatic, aromatic, ketone-based, ester-based, ether-based and alcohol-based solvents can be mentioned. Examples of the aromatic

solvents include xylene and toluene. Examples of the ketone-based solvents include MIBK and cyclohexanone. Examples of the ether-based solvents include propylene glycol monomethyl ether and propylene glycol monomethyl ether acetate (PMAC). Examples of the alcohol-based
5 solvents include isopropyl alcohol.

[0153]

Such a solvent can be used in an arbitrary amount, but it is used in an amount of, for example, 0.1 to 9999 parts by weight, preferably 1 to 50 parts by weight, based on 100 parts by weight of the component
10 (A). In the antifouling coating composition of the present invention, the solvent is used in an amount of 1 to 99% by weight, preferably 5 to 50% by weight. The viscosity (25°C, B type viscometer, No. 3 rotor) of the antifouling coating composition used for a special frictional resistance reduced ship, such as an antifouling coating
15 composition used for a special frictional resistance reduced ship and having been diluted with such a solvent as above, is usually 0.001 to 50 Pa·s, preferably about 0.01 to 20 Pa·s, taking into consideration coatability (sagging property), film thickness obtained by one coating, etc.

20 [0154]

<Others>

The antifouling coating composition may be that of one-pack type or multi-pack type such as two-pack type or three-pack type.

[0155]

For example, in the case of blending capable of utilizing hydrolysis reaction of a hydrolyzable group with moisture in air, curing reaction does not occur if a moisture source is removed, so that the composition can be prepared as a one-pack type composition.

5 [0156]

For example, when a component that undergoes curing reaction at normal temperature by the addition of a catalyst is blended, the composition can be prepared as a multi-pack type composition having the catalyst and the component that undergoes reaction by the addition
10 of a catalyst as separate liquids.

A specific example of the one-pack type antifouling coating composition is an antifouling coating composition in which an organopolysiloxane having hydrolyzable groups such as deoxime groups as the condensing reactive groups at both ends of molecule is blended
15 as the organopolysiloxane (A) and an organosilane such as oximesilane is blended as the organosilane and/or its partial condensate (B).
[0157]

As the three-pack type antifouling coating composition, there can be mentioned an antifouling coating composition constituted of
20 three liquids of a main agent containing, as the organopolysiloxane (A), an organopolysiloxane having hydroxyl groups as the condensing reactive groups at both ends of molecule, a curing agent containing, as the organosilane and/or its partial condensate (B), a polyalkoxysilane such as ethyl silicate, and a curing accelerator

containing a catalyst.

[0158]

1-3. Antifouling coating film (first coating film), special
frictional resistance reduced ship (first special frictional
 5 resistance reduced ship)

A coating film formed from the antifouling coating composition used for a special frictional resistance reduced ship according to the present invention has a profile such that the static in-water bubble contact angle in water, as measured by the later-described
 10 method, is usually as small as less than 90 degrees, the in-water bubble roll (slip) angle is as small as less than 30 degrees, the height of roughness is not more than 30 μm , and the peak-valley average interval is not less than 700 μm .

[0159]

15 From the viewpoint that the frictional resistance of a hull is efficiently reduced and the reduction of frictional resistance over a long period of time is realized, the static in-water bubble contact angle in water is preferably not more than 80 degrees, the in-water bubble roll (slip) angle is preferably not more than 20 degrees,
 20 the height of roughness is preferably not more than 25 μm , and the peak-valley average interval is preferably not less than 800 μm .

[0160]

A small static in-water bubble contact angle indicates a property that air is wetted by the coating film (that is, air and the coating

film have affinity for each other), and a small bubble roll (slip) angle or a small roughness and a long peak-valley average interval indicate a property that air easily flows. That is to say, they indicate that the coating film surface has excellent gas lubrication property.

5 These properties can be examined by the use of an in-water bubble contact angle meter, and the gas lubrication effect (water flow frictional resistance reduction effect) can be confirmed by coating a bottom of a model ship with the coating composition and measuring a water flow resistance when air is supplied to the coating film formed
10 on the ship's bottom (circulating water channel test).

[0161]

The coating film having such a profile is obtained by coating a coating object with the antifouling coating composition used for a special frictional resistance reduced ship. Since the antifouling
15 coating composition used for a special frictional resistance reduced ship has specific constitution capable of forming a coating film of the above profile, there is no need to carry out special operations other than general operations of coating the coating object with the antifouling coating composition and drying, and merely by carrying
20 out such simple operations, a coating film having the above profile can be obtained.

[0162]

A special frictional resistance reduced ship in which such an antifouling coating film has been formed on a submerged surface of

the shell plating exerts an excellent frictional resistance reduction effect even by supplying a small amount of a gas, also exhibits an excellent antifouling effect, and can stably exhibit those effects over a long period of time.

5 [0163]

The static in-water bubble contact angle and the in-water bubble roll (slip) angle can be measured by the use of the later-described contact angle measuring apparatus.

<Measuring method for static in-water bubble contact angle>

10 The measuring method for static in-water bubble contact angle is specifically as follows.

[0164]

A rigid polyvinyl chloride test panel (maximum height as measured in accordance with JIS B 0601: not more than 1 μm), which has been
15 coated with a coating composition so that a coating film having a dry film thickness of 150 μm may be formed, is immersed in water at 25°C for 30 days. Specifically, the test panel is fixed to an inner wall of a cylindrical rotary immersion tank, then the center of the panel is rotated (peripheral velocity: 15 knots) in water to produce
20 a water flow, and the panel is immersed in this state for 30 days. After the immersion, the rigid polyvinyl chloride test panel is placed in water in such a manner that the coating film surface becomes horizontal and is on the lower side of the test panel, then 0.1 cc of air is injected into water so that one bubble may be formed on

the coating film surface, then a height a of the bubble from the coating film surface, said bubble having been formed on the coating film surface, and a diameter b of a contact portion of the bubble with the coating film surface are measured, and from the following formula (1), a static in-water bubble contact angle (θ_s , unit: degree) that is a contact angle between the coating film surface and the bubble is determined.

[0165]

[Math. 4]

$$\theta_s = 2 \times \frac{180}{\pi} \times \tan^{-1} \frac{2a}{b} \dots (1)$$

10 [0166]

<Measuring method for in-water bubble roll (slip) angle>

The measuring method for in-water bubble roll (slip) angle is specifically as follows.

In the above measuring method for static in-water bubble contact angle, the coating film surface having the bubble formed thereon is gradually inclined against the horizontal plane, and when the bubble begins to move, an inclination angle (in-water bubble roll (slip) angle) (θ_m , unit: degree) of the coating film surface against the horizontal plane is measured.

20 [0167]

1-4. Production process for special frictional resistance reduced ship

In the production process for a special frictional resistance

reduced ship according to the present invention, the aforesaid antifouling coating film is formed on a submergence expected surface of a shell plating of a ship to be coated. The antifouling coating film can be formed from the aforesaid antifouling coating composition.

5 [0168]

By coating a surface of a submergence portion of a shell plating of a ship with the antifouling coating composition used for a special frictional resistance reduced ship according to the present invention once or plural times in a conventional manner and curing the coated
10 layer, a coating film capable of imparting frictional resistance reduction performance and antifouling performance to the surface can be formed, and besides, those performances can be maintained over a long period of time. For such a coating operation, hitherto publicly known coating means, such as brush, roll, spray and dip coater, are
15 widely used.

[0169]

Such an antifouling coating film obtained by curing the antifouling coating composition used for a special frictional resistance reduced ship according to the present invention has
20 excellent antifouling property such that fouling by aquatic organisms, such as sea lettuce, acorn barnacle, green laver, serpula, oyster and Bugula neritina, can be continuously prevented over a long period of time.

[0170]

It is desirable that the antifouling coating composition used for a special frictional resistance reduced ship according to the present invention is applied onto an anticorrosive coating film having been formed in advance on a shell plating of a ship, from the viewpoints
5 of adhesion property and anticorrosion property.

The surface of a ship having been coated with the antifouling coating composition used for a special frictional resistance reduced ship according to the present invention may be top-coated with the antifouling coating composition used for a special frictional
10 resistance reduced ship according to the present invention for repairing. The thickness of the antifouling coating film formed on a submerged surface of a shell plating of a ship is not specifically restricted, but it is, for example, about 30 to 150 μm /one time.
[0171]

15 The antifouling coating composition used for a special frictional resistance reduced ship according to the present invention is desirably applied to the whole of a submergence surface of a shell plating of a ship, from the viewpoint of frictional resistance reduction performance.

20 2. Second group

2-1. Second coating composition, coating film, special frictional resistance reduced ship

The second coating composition is a coating composition capable of forming a coating film satisfying the static in-water bubble contact

angle and in-water-bubble roll (slip) angle conditions described below.

[0172]

As the coating composition capable of forming a coating film
5 satisfying such conditions, the aforesaid antifouling coating composition (first coating composition) can be mentioned. Details of the first coating composition are as previously described.

<Static in-water bubble contact angle and in-water bubble roll (slip) angle>

10 The static in-water bubble contact angle, as measured by the following measuring method for static in-water bubble contact angle, is less than 90 degrees, and the in-water bubble roll (slip) angle, as measured by the following measuring method for in-water bubble roll (slip) angle, is less than 30 degrees.

15 [0173]

The static in-water bubble contact angle and the in-water bubble roll (slip) angle can be measured by the use of the later-described contact angle measuring apparatus.

The measuring method for static in-water bubble contact angle
20 is specifically as follows.

[0174]

A rigid polyvinyl chloride test panel (maximum height as measured in accordance with JIS B 0601: not more than 1 μm), which has been coated with a coating composition so that a coating film having a

dry film thickness of 150 μm may be formed, is immersed in water at 25°C for 30 days. Specifically, the test panel is fixed to an inner wall of a cylindrical rotary immersion tank, then the center of the panel is rotated (peripheral velocity: 15 knots) in water to produce a water flow, and the panel is immersed in this state for 30 days. After the immersion, the rigid polyvinyl chloride test panel is placed in water in such a manner that the coating film surface becomes horizontal and is on the lower side of the test panel, then 0.1 cc of air is injected into water so that one bubble may be formed on the coating film surface, then a height a of the bubble from the coating film surface, said bubble having been formed on the coating film surface, and a diameter b of a contact portion of the bubble with the coating film surface are measured, and from the following formula (1), a static in-water bubble contact angle (θ_s , unit: degree) that is a contact angle between the coating film surface and the bubble is determined.

[0175]

[Math. 5]

$$\theta_s = 2 \times \frac{180}{\pi} \times \tan^{-1} \frac{2a}{b} \dots (1)$$

[0176]

20 The measuring method for in-water bubble roll (slip) angle is specifically as follows.

In the above measuring method for static in-water bubble contact angle, the coating film surface having the bubble formed thereon is

gradually inclined against the horizontal plane, and when the bubble begins to move, an inclination angle (in-water bubble roll (slip) angle) (θ_m , unit: degree) of the coating film surface against the horizontal plane is measured.

5 [0177]

The static in-water bubble contact angle indicates an extent of wetting of a gas by the coating film (extent of affinity). A small static in-water bubble contact angle indicates that the extent of wetting of a gas by the coating film (extent of affinity of a gas for the coating film) is large, and a large static in-water bubble contact angle indicates that the extent of wetting of a gas by the coating film (extent of affinity of a gas for the coating film) is small.

[0178]

15 The bubble roll (slip) angle indicates ease of flowing of air on the coating film surface. A small bubble roll (slip) angle indicates that air easily flows on the coating film surface, and a large bubble roll (slip) angle indicates that air hardly flows on the coating film surface.

20 [0179]

That is to say, these properties become an indication for judging whether the submerged surface of a shell plating of a ship, on which the above coating film has been formed, has excellent gas lubrication property or not, and a smaller static in-water bubble contact angle

and a smaller bubble roll (slip) angle indicate more excellent gas lubrication property.

[0180]

From the viewpoint that the frictional resistance is reduced
5 and the property of the coating film formed on a shell plating surface of a ship is maintained for a long period of time, the static in-water bubble contact angle is preferably not more than 80 degrees, and from the same viewpoint, the in water bubble roll (slip) angle is preferably not more than 20 degrees.

10 [0181]

In a special frictional resistance reduced ship in which a coating film having an in-water bubble contact angle and an in-water bubble roll (slip) angle in the above ranges has been formed on a submerged surface of a shell plating, the gas lubrication property
15 of the submerged surface of the shell plating is excellent, as described above, and therefore, the frictional resistance of the ship can be reduced even by supplying a small amount of air, and excellent energy saving property is obtained. In the special frictional resistance reduced ship, further, the frictional resistance of the submerged
20 surface of the shell plating is reduced by virtue of the above coating film, and therefore, abrasion of the submerged surface of the shell plating caused by the frictional resistance is greatly suppressed, and an effect that the properties of the coating film are maintained over a long period of time is exerted.

[0182]

<Frictional resistance reduction ratio after immersion in water,
difference in frictional resistance reduction ratio between before
and after immersion in water>

- 5 The gas lubrication effect (water flow frictional resistance reduction effect) can be confirmed by measuring a water flow frictional resistance given when air is supplied to a surface of a coating film that is formed on a ship's bottom of a model ship by coating the ship's bottom with a coating composition (circulating water channel test).
- 10 In the present specification, a case where a test panel having a coating film formed from the coating composition is allowed to stand still in water (preferably sea water) (usually at a temperature of about 25°C) or fixed to an inner wall of a rotary immersion tank to rotate water (preferably sea water) (usually at a temperature of about 25°C)
- 15 and thereby produce a water flow of a peripheral velocity of 15 knots and then a given period of time is allowed to elapse is expressed by "after immersion of X" (X is an elapsed time, and for example, a case of immersion for 30 days is referred to as "after immersion of 30 days"). A case where such operations are not carried out is
- 20 expressed by "before immersion".

[0183]

For example, a test panel is fixed to an inner wall of a cylindrical rotary immersion tank, then the center of the panel is rotated (peripheral velocity: 15 knots) in water to produce a water flow,

then 30 days are allowed to elapse, and thereafter a frictional resistance reduction ratio is measured. In this case, a difference in frictional resistance reduction ratio between before and after immersion is referred to as a "difference in frictional resistance reduction ratio between before immersion and after immersion of 30 days".

[0184]

A specific example of a method for measuring a difference in frictional resistance reduction ratio between before and after immersion is as follows.

As shown in Fig. 4, to a ship's bottom of a model ship having a total length of 2.8 m, a molded breadth of 0.24 m and a molded depth of 0.14 m, a test panel having a length of 2.05 m, a width of 0.24 m and an area of 0.492 m² and having been immersed for 30 days is fixed in such a manner that the coating film surface becomes an external surface (in such a manner that the coating film surface comes into contact with water). The coating film portion of the test panel is referred to as a "test coating film portion 9". Subsequently, in a vertical circulation type circulating water channel having a measuring part size of a length of 8 m, a width of 1.5 m and a water depth of 1.2 m, the model ship is placed, and in the case where air is jetted out (e.g., equivalent air thickness (t_a) = 1.0 mm) to the ship's bottom on which the test panel has been fixed from an air outlet 8 provided in the ship's bottom of the model ship, and in the case

where air is not jetted out, a frictional resistance of a hull is measured under the conditions of a water (12°C) flow velocity of 1.4 m/s. Subsequently, from the following formula (2), a total resistance reduction ratio (η_T) is determined, and from the following formula (3), a frictional resistance reduction ratio (η_F) of the test panel portion is determined. A difference in frictional resistance reduction ratio between before and after immersion can be determined by subtracting the frictional resistance reduction ratio after immersion of 30 days from the frictional resistance reduction ratio before immersion (values of water flow velocity and equivalent air thickness can be appropriately preset).

[0185]

[Math. 6]

$$\eta_T = 100 \times (R_{t0} - R_t) / R_{t0} \quad [\%] \quad (2)$$

15 [0186]

[Math. 7]

$$\eta_F = 100 \times (R_{t0} - R_t) / R_{f0} \quad [\%] \quad (3)$$

[0187]

20 R_{t0} : total resistance of ship in the case where air is not jetted out [Kgf]

R_t : total resistance of ship in the case where air is jetted out [Kgf]

R_{f0} : frictional resistance of test panel represented by the following formula (4) in the case where air is not jetted out [Kgf]

[0188]

[Math. 8]

$$R_{f0}: C_{f0} \times (1/2) \times \rho \times S \times U^2 \quad (4)$$

[0189]

5 ρ : density of water [$\text{kgf} \cdot \text{s}^2/\text{m}^4$] (12°C)

S : area of test panel (m^2)

U : flow velocity of water [m/s]

C_{f0} : coefficient of frictional resistance of test panel

represented by the following formula (5) in the case where air is

10 not jetted out

[0190]

[Math. 9]

$$C_{f0} = 0.463 \log^{10}(R_n) \exp^{-2.6} \quad (5)$$

[0191]

15 R_n : Reynolds number of test panel represented by the following
formula (6)

[0192]

[Math. 10]

$$R_n = U \times L / \nu \quad (6)$$

20 [0193]

U : flow velocity of water [m/s]

L : length of test panel [m]

ν : coefficient of kinematic viscosity of water [m^2/s] (12°C)

[0194]

The aforesaid equivalent air thickness (t_a) [mm] shows an amount of air jetted out, and is represented by the following formula (7).

[0195]

[Math. 11]

$$5 \quad t_a = 1000Q_a / (U \cdot B_a) \quad (7)$$

[0196]

Q_a : amount of air jetted out [m^3/s]

U : flow velocity of water [m/s]

B_a : width of air outlet [m]

10 [0197]

Here, the "total resistance" means a total value of all resistances participating in the above measurement, such as wavemaking resistance, profile resistance and frictional resistance.

The test panel is an aluminum plate (material: A5052P).

15 [0198]

A difference in frictional resistance reduction ratio between before and after immersion indicates how long the reduction of frictional resistance due to the coating film is maintained.

That is to say, a smaller difference in frictional resistance reduction ratio between before and after immersion indicates a smaller change in properties of the coating film with time after a lapse of a given period of time.

[0199]

The special frictional resistance reduced ship in which a coating

film satisfying the above requirements has been formed on a submerged surface of a shell plating has a small difference in frictional resistance reduction ratio between before and after immersion (small change of coating film with time), and therefore, properties of the coating film formed on the shell plating surface of the ship can be maintained for a long period of time. Moreover, even if the amount of air is small (e.g., $t_a=1.0$ mm), a sufficient resistance reduction effect can be exerted, and the energy for supplying air that is necessary for the frictional resistance reduction has only to be low, so that the energy saving effect is also high.

[0200]

2-2. Production process for second special frictional resistance reduced ship

The production process for such a second special frictional resistance reduced ship as above has only to be carried out in accordance with the aforesaid production process for the special frictional resistance reduced ship (first special frictional resistance reduced ship) having been coated with a coating film formed from the antifouling coating composition.

20 [0201]

2-3. Method for predicting frictional resistance reduction effect utilizing gas lubrication function of coating film in water

The method for predicting a frictional resistance reduction effect utilizing a gas lubrication function of a coating film in water

according to the present invention is characterized by comprising measuring a static in-water bubble contact angle by a measuring method for static in-water bubble contact angle, measuring an in-water bubble roll (slip) angle by a measuring method for in-water bubble roll (slip) angle, and predicting a frictional resistance reduction effect utilizing a gas lubrication function of a coating film formed from a coating composition in water from the static in-water bubble contact angle and the in-water bubble roll (slip) angle.

[0202]

The measuring methods for the static in-water bubble contact angle and the in-water bubble roll (slip) angle are each as follows. The static in-water bubble contact angle indicates an extent of wetting of a gas by the coating film (extent of affinity), and the bubble roll (slip) angle indicates ease of flowing of air on the coating film surface.

<Measuring method for static in-water bubble contact angle>

A test panel, which has been coated with a coating composition so that a coating film may be formed, is immersed in water, then the test panel after immersion is placed in water in such a manner that the coating film surface becomes horizontal and is on the lower side of the test panel, then air is injected into water so that a bubble may be formed on the coating film surface, then a height a of the bubble from the coating film surface, said bubble having been formed on the coating film surface, and a diameter b of a contact portion

of the bubble with the coating film surface are measured, and from the following formula (1), a static in-water bubble contact angle (θ_s , unit: degree) that is a contact angle between the coating film surface and the bubble is determined.

5 [0203]

[Math. 12]

$$\theta_s = 2 \times \frac{180}{\pi} \times \tan^{-1} \frac{2a}{b} \dots (1)$$

[0204]

<Measuring method for in-water bubble roll (slip) angle>

10

In the above measuring method for static in-water bubble contact angle, the coating film surface having the bubble formed thereon is gradually inclined against the horizontal plane, and when the bubble begins to move, an in-water bubble roll (slip) angle (θ_m , unit: degree) that is an inclination angle of the coating film surface against the horizontal plane is measured.

15

[0205]

That is to say, these properties become an indication for judging whether the submerged surface of a shell plating of a ship, on which the above coating film has been formed, has excellent gas lubrication property or not, and a smaller static in-water bubble contact angle and a smaller bubble roll (slip) angle indicate more excellent gas lubrication property.

20

[0206]

In the method for evaluating a frictional resistance reduction effect according to the present invention, a coating film having a static in-water bubble contact angle of less than 90 degrees (preferably not more than 80 degrees) and an in-water bubble roll (slip) angle of less than 30 degrees (preferably not more than 20 degrees) as results of the above two kinds of the measuring methods is evaluated as excellent in gas lubrication property and in frictional resistance reduction effect utilizing a gas lubrication function in water.

10 [0207]

As shown by the results of the later-described examples, the coating material highly evaluated in the method for evaluating a frictional resistance reduction effect according to the present invention is highly evaluated also in the evaluation results of water flow frictional resistance using a model ship, and the reverse is also true.

[0208]

The method for predicting a frictional resistance reduction effect utilizing a gas lubrication function of a coating film in water according to the present invention is simple and appropriate, and therefore, it is effective for selecting a coating film.

2-4. Apparatus used for prediction of frictional resistance reduction effect utilizing gas lubrication function of coating film in water

The apparatus (contact angle measuring apparatus) used for prediction of a frictional resistance reduction effect utilizing a gas lubrication function of a coating film in water according to the present invention has a test board, an inclination angle control device,
5 an immersion container and an observation device.

[0209]

To the test board, the inclination angle control device is connected.

On the test board, a test panel having a coating film formed
10 on its surface is set in such a manner that a back surface of the test panel comes into contact with the lower surface of the test board, and in the immersion container containing water, the test board is placed in such a state that the test panel is immersed in water and that a bubble has been formed on the coating film surface of the test
15 panel.

[0210]

The observation device is set so as to be able to observe the state of the test panel and the bubble.

With regard to the static in-water bubble contact angle of the
20 bubble, when the test panel is horizontal, the state of the bubble formed on the surface of the coating film of the test panel is observed by the observation device to measure a static in-water bubble contact angle.

[0211]

With regard to the in-water bubble roll (slip) angle of the bubble, the test panel is inclined against the horizontal by the inclination angle control device, and the behavior of the bubble is observed by the observation device to measure an in-water bubble roll (slip) angle of the bubble formed on the surface of the coating film of the test panel.

[0212]

The contact angle measuring apparatus is specifically described below referring to an apparatus shown in Fig. 1 that is an example of the contact angle measuring apparatus.

In the apparatus shown in Fig. 1, a test board 5 for setting thereon a test panel 6 having a coating film formed on its surface is connected to an inclination angle control mechanism including a rotation drive handle 4, and by rotating the rotation drive handle 4, the inclination angle of the test board 5 against the horizontal is controlled. The angle is measured by an angle meter 3. Owing to an immersion container 7 having been designed so that the test board 5 can be placed in water, the test board 5 is placed in water. In the apparatus shown in Fig. 1, at least a part or all of the immersion container 7 is constituted of a member having transmission property (e.g., acrylic or glass member), and from the outside of the immersion container 7, the test board 5 and a bubble formed on the test panel 6 can be observed. The test panel 6 is set on the lower side of the test board 5 so that the surface on which the coating film has been

formed may face the lower side of the test board 5.

[0213]

Formation of a bubble on the coating film surface of the test panel 6 has only to be carried out using, for example, a syringe 2.

5 Observation of the bubble is carried out by the use of a camera

1. Observation of the bubble can be carried out with the naked eye, but by the use of the camera 1, the behavior of the bubble can be more accurately observed.

[0214]

10 Measurement of the static in-water bubble contact angle and the in-water bubble roll (slip) angle has only to be carried out as previously described, but the type of the test panel, the dry film thickness of the coating film, the immersion time, the volume of the bubble, etc. can be appropriately determined according the purpose.

15 [0215]

In that case, a vinyl chloride plate can be mentioned as one type of the test panel, the dry film thickness of the coating film is usually in the range of 50 to 500 μm , the immersion time is usually in the range of 1 to 180 days, and the volume of the bubble is usually
20 in the range of 0.1 to 3 cc, though they depend upon the purpose. As the test panel, a test panel having a maximum height, as measured in accordance with JIS B 0601, of not more than 1 μm is used.

[0216]

3. Third group

3-1. Frictional resistance reduction systems used for special frictional resistance reduced ships (First and second frictional resistance reduction systems) and special frictional resistance reduced ships having the systems (third and fourth frictional resistance reduced ships)

5 The first and the second frictional resistance reduction systems used for special frictional resistance reduced ships according to the present invention have the first coating film (antifouling coating film) and the second coating film, respectively, and each have a gas supply device for supplying a gas to a surface of the first coating film or the second coating
10 film.

[0217]

 In such a frictional resistance reduction system, a gas such as air is supplied from the gas supply device to the surface of the coating film or the antifouling coating film having excellent frictional resistance
15 reduction performance and having specific properties as described above, and therefore, frictional resistance of the special frictional resistance reduced ship can be greatly reduced.

[0218]

 The gas supply device and the gas used are as previously described.

20 In the third and the fourth special frictional resistance reduced ships having such a first and a second frictional resistance reduction systems, respectively, frictional resistance of the ships in water

is greatly reduced by the systems, and therefore, even if high power is not introduced for the supply of a gas such as air, the fluid frictional resistance reduction effect is great, an economical advantage is obtained, and the influence on the environment is small.

5

Examples

[0219]

The present invention is described in more detail with reference to the following examples, but it should be construed that the present invention is in no way limited to those examples. Unless otherwise noted, the pressure condition is normal pressure (about 0.1013 MPa), and the temperature condition is normal temperature (about 25°C).

[0220]

Details of various tests carried out in the following examples and comparative examples are as follows.

<Measurement of coating film surface roughness>

Surface profile of each coating film was measured using a contact probe profilometer (Handysurf E-35A, manufactured by Tokyo Seimitsu Co., Ltd.) in accordance with JIS B 0601.

20 [0221]

<Measurement of change in contact angle and roll (slip) angle with time>

A coating composition produced in the later-described each example was applied to a rigid polyvinyl chloride plate of 50×50

×2 mm (maximum height as measured in accordance with JIS B 0601: not more than 1 μm) so that the dry film thickness might become 150 μm, and the composition was dried at room temperature for 5 days to prepare a test panel. The test panel was fixed to an inner wall of
5 a cylindrical rotary immersion tank to immerse the coating film formed on the test panel. The center of the test panel was rotated (peripheral velocity: 15 knots) in water to produce a water flow. A static in-water bubble contact angle and an in-water bubble roll (slip) angle of the coating film formed on the test panel were measured in the following
10 manner before immersion, after immersion of 14 days and after immersion of 30 days by the use of a "contact angle measuring apparatus" (see also Fig. 1 to Fig. 4).

[0222]

(Measurement of static in-water bubble contact angle)

15 The test panel before immersion or after immersion of a specific period of time was fixed to a test board 5 in such a manner that the coating film surface became horizontal and was on the lower side of the test board, and then placed in water. Using a syringe 2, 0.1 cc of air was injected into water so that one bubble might be formed
20 on the coating film surface. Using a camera 1 (video microscope), the bubble was observed from the side, and a height a of the bubble from the coating film surface, said bubble having been formed on the coating film surface, and a diameter b of a contact portion of the bubble with the coating film surface were measured, and from the

following formula (1), a contact angle between the coating film surface and the bubble was determined (see Fig. 1 and Fig. 2). This angle is a static in-water bubble contact angle (θ_s), and affinity of the coating film surface for the air bubble can be evaluated. As this

5 θ_s is decreased, the affinity of the coating film surface for air becomes higher.

[0223]

[Math. 13]

$$\theta_s = 2 \times \frac{180}{\pi} \times \tan^{-1} \frac{2a}{b} \dots (1)$$

10 [0224]

(Measurement of in-water bubble roll (slip) angle)

Under the same conditions as in the measurement of a static in-water bubble contact angle, 0.1 cc of air was injected into water so that a bubble might be formed on the coating film surface.

15 Subsequently, a rotation drive handle 4 was rotated to gradually incline the coating film surface against the horizontal plane, and when the bubble began to move, an angle was measured (see Fig. 1 and Fig. 3). This angle is an in-water bubble roll (slip) angle (θ_m), and fluidity of the air bubble on the coating film surface can be

20 evaluated. As this θ_m is decreased, the fluidity becomes better.

[0225]

<Static antifouling property test method>

To a sandblasted steel plate of 100 mm × 300 mm × 2.3 mm, an

epoxy-based zinc rich primer ("Epicon Zinc Rich Primer B-2" manufactured by Chugoku Marine Paints, Ltd.), an epoxy-based anticorrosive coating material ("Bannoh 500" manufactured by Chugoku Marine Paints, Ltd.) and a urethane resin-based anticorrosive coating material ("CMP Bio-Clean SG" manufactured by Chugoku Marine Paints, Ltd.) were applied one after another in this order by the use of an air spray so that the dry film thicknesses might become 20 μm , 150 μm and 100 μm , respectively. The surface of a urethane-based binder coat formed from the urethane resin-based anticorrosive coating material was coated with an antifouling coating composition produced in the later-described example so that the dry film thickness might become 100 μm to 200 μm , whereby a test panel was prepared. The resulting test panel was dried indoors (room temperature: 20°C, relative humidity: 60%) for one week, and thereafter, the test panel was immersed in the water from a raft placed in Hiroshima Bay so that it might be positioned 1 m below the surface of the water, and fouling of the coating film surface of the test panel by organisms for 1, 3, 6 or 12 months was visually observed.

[0226]

Evaluation was carried out by visual observation of an area fouled by marine organisms (%).

Evaluation criteria are as described in Table 3.

<Dynamic antifouling property test method>

A sandblasted steel plate having a size of 170 mm (length) ×

70 mm (width) $\times$ 2.3 mm (thickness) and having been subjected to bending so that it could be fixed to a side surface of a rotary drum placed in sea water in Kure city, Hiroshima Prefecture was prepared. To this sandblasted steel plate, an epoxy-based zinc rich primer ("Epicon
5 Zinc Rich Primer B-2" manufactured by Chugoku Marine Paints, Ltd.), an epoxy-based anticorrosive coating material ("Bannoh 500" manufactured by Chugoku Marine Paints, Ltd.) and a urethane resin-based anticorrosive coating material ("CMP Bio-Clean SG" manufactured by Chugoku Marine Paints, Ltd.) were applied one after another in this
10 order by the use of an air spray so that the dry film thicknesses might become 20 μm , 150 μm and 100 μm , respectively. The surface of a urethane-based binder coat formed from the urethane resin-based anticorrosive coating material was coated with an antifouling coating composition produced in the later-described example so that the dry
15 film thickness might become 100 μm to 200 μm , whereby a test panel was prepared. The resulting test panel was dried indoors (room temperature: 20°C, relative humidity: 60%) for one week, and thereafter, the test panel was fixed to the rotary drum and subjected to rotation immersion at a peripheral velocity of 15 knots, and fouling of the
20 coating film surface of the test panel by organisms in the dynamic environment for 1, 3, 6 or 12 months was visually observed.

[0227]

<Measurement of water flow frictional resistance>

A test panel (length: 2.05 m, width: 0.24 m, area: 0.492 m²,

base material: aluminum plate (A5052P)) coated with an antifouling coating composition produced in the later-described example was fixed to a ship's bottom of a model ship (total length: 2.8 m, molded breath: 0.24 m, molded depth: 0.14 m) shown in Fig. 4 so that the coating film surface might be positioned outside. The coating film portion of the test panel was taken as a test coating film portion 9.

Subsequently, using a vertical circulation type circulating water channel (measuring part size: length: 8 m, width: 1.5 m, water depth: 1.2 m), a frictional resistance of a hull was measured before immersion and after immersion of a specific period of time under the conditions of a specific water (12°C) flow velocity in the case where air of a specific equivalent air thickness (t_a : mm) was jetted out from an air outlet 8 provided in the ship's bottom of the model ship to the ship's bottom on which the test panel had been fixed (test coating film portion 9) and in the case where air was not jetted out. Air was jetted out from an array porous plate (2 mm (diameter) $\times$ 46 holes) provided at the front edge of the test panel while controlling a flow rate of the compressed air from a compressor. Subsequently, a total resistance reduction ratio (η_T) at each water flow velocity and each air flow rate and a frictional resistance reduction ratio (η_F) of the test panel portion were determined in accordance with the following formulas (2) and (3). A difference in frictional resistance reduction ratio between before and after immersion was determined by subtracting the frictional resistance reduction ratio after immersion of 30 days

from the frictional resistance reduction ratio before immersion.

[0228]

[Math. 14]

$$\eta T = 100 \times (R_{t0} - R_t) / R_{t0} \quad [\%] \quad (2)$$

5 [0229]

[Math. 15]

$$\eta F = 100 \times (R_{t0} - R_t) / R_{f0} \quad [\%] \quad (3)$$

[0230]

<Production of antifouling coating composition>

10 [Production Example 1]

90 Parts by weight of dimethylpolysiloxane (manufactured by Momentive Performance Materials Inc., XF3905), both ends of molecular chain of which had been capped with silanol groups and which had a viscosity at 25°C of 700 mm²/s, and 100 parts by weight of fumed silica
15 (manufactured by Nippon Aerosil Co., Ltd., R-972), a surface of which had been subjected to hydrophobic treatment and which had a specific surface area of 200 m²/g, were homogeneously mixed at 150°C for 2 hours by the use of a stirring mixer (manufactured by Dalton Co., 5NDMV) to obtain a base compound 1. The viscosity of the base compound
20 1 was 1530 mm²/s.

[0231]

[Production Examples 2 to 4]

Base compounds 2, 3 and 4 were obtained in the same manner as in Production Example 1, except that YF3057 (viscosity: 3000 mm²/s,

manufactured by Momentive Performance Materials Inc.), YF3807 (viscosity: 20000 mm²/s, manufactured by Momentive Performance Materials Inc.) and YF3802 (viscosity: 80000 mm²/s, manufactured by Momentive Performance Materials Inc.) were used, respectively, as the dimethylpolysiloxane both ends of molecular chain of which had been capped with silanol groups. The viscosities of the base compounds 2 and 3 were 8670 mm²/s and 46000 mm²/s, respectively. Since the base compound 4 was highly viscous, viscosity measurement could not be carried out.

10 [0232]

[Example 1]

In a paint shaker using glass beads as media, 100 parts by weight of the base compound 1 obtained in Production Example 1, 10 parts by weight of a silicone oil KF-50-3000 (trade name: "KF-50-3000", manufactured by Shin-Etsu Chemical Co., Ltd., methylphenyl silicone oil), 12 parts by weight of titanium oxide (trade name: "R-5N", manufactured by Sakai Chemical Industry Co., Ltd.) as a pigment and 1.5 parts by weight of black iron oxide (trade name: "KN320", manufactured by Toda Kogyo Corp.) as a pigment were placed, then they were shaken for 1 hour, and thereafter, the resulting mixture was filtered through a 120-mesh filter to prepare a composition (I liquid).

20 [0233]

Immediately before coating, 123.5 parts by weight of the I liquid and 5 parts by weight of ethyl silicate (trade name: "TES40WN",

manufactured by Wacker Asahikasei Silicone Co., Ltd., ethyl silicate oligomer) as II liquid were sufficiently mixed, and thereafter, 10 parts by weight of a tin catalyst (trade name: "GLECK TL", manufactured by DIC Corporation, dibutyltin dilaurate, 10% xylene solution) as
5 III liquid was added and stirred to obtain an antifouling coating composition.

[0234]

The resulting antifouling coating composition was subjected to the aforesaid various tests under the conditions shown in the
10 following Tables 1 and 3 to 6.

The results are set forth in Tables 1 and 4 to 6.

[0235]

[Examples 2 to 10]

Antifouling coating compositions were prepared in the same
15 manner as in Example 1, except that the type and the amount of each component were changed as shown in Table 1.

[0236]

The resulting antifouling coating compositions were each subjected to the aforesaid various tests under the conditions shown
20 in the following Tables 1 and 3 to 6.

The results are set forth in Tables 1 and 4 to 6.

[0237]

[Example 11]

In a paint shaker using glass beads as media, 100 parts by weight

of a reaction type organopolysiloxane KE-445 (trade name: "KE-445",
manufactured by Shin-Etsu Chemical Co., Ltd, deoxime type
organopolysiloxane, viscosity: 4500 mm²/s), 40 parts by weight of
a silicone oil KF-50-100 (trade name: "KF-50-100", manufactured by
5 Shin-Etsu Chemical Co., Ltd., methylphenyl silicone oil), 22 parts
by weight of KF-50-3000 (trade name: "KF-50-3000", manufactured by
Shin-Etsu Chemical Co., Ltd., methylphenyl silicone oil) and 20 parts
by weight of xylene were placed, then they were shaken for 1 hour,
and thereafter, the resulting mixture was filtered through a 120-mesh
10 filter to prepare an antifouling coating composition.

[0238]

The resulting antifouling coating composition was subjected
to the aforesaid various tests under the conditions shown in the
following Tables 1 and 3 to 6.

15 The results are set forth in Tables 1 and 4 to 6.

[0239]

[Comparative Example 1]

<Super water-repellent coating film 1>

In a paint shaker using glass beads as media, 12.6 parts by
20 weight of a fluororesin LF-200 (trade name: "Lumiflon LF-200",
manufactured by Asahi Glass Co., Ltd., fluorine-based polyol), 24.2
parts by weight of fluorine powder L-2 (trade name: "Lublon L-2",
manufactured by Daikin Industries, Ltd., low-molecular weight
ethylene tetrafluoride-based ultrafine powder), 1.8 parts by weight

of an additive SF-1265-1000 (trade name: "SF-1265-1000", manufactured by Dow Corning Toray Co., Ltd., fluorinated silicone oil), 60.6 parts by weight of butyl acetate and 0.8 part by weight of a tin catalyst (trade name: "GLECK TL", manufactured by DIC Corporation, dibutyltin dilaurate, 0.1% xylene solution) as a curing accelerator were placed, then they were shaken for 1 hour, and thereafter, the resulting mixture was filtered through a 60-mesh filter to prepare a super water-repellent coating composition for a super water-repellent coating film 1.

10 [0240]

Immediately before coating, 100 parts by weight of the super water-repellent coating composition and 1.7 parts by weight of DN-980 (trade name: "Burnock DN-980, manufactured by DIC Corporation, isocyanurate type polyisocyanate) as a curing agent were mixed to prepare a super water-repellent coating composition.

[0241]

The resulting antifouling coating composition was subjected to the aforesaid various tests under the conditions shown in the following Tables 1 and 3 to 6.

20 The results are set forth in Tables 1 and 4 to 6.

[0242]

[Comparative Example 2]

<Super water-repellent coating film 2>

In a paint shaker using glass beads as media, 34.7 parts by

weight of an acrylic resin TZ-343 (trade name: "Acrylic TZ-343",
manufactured by DIC Corporation), 19.6 parts by weight of hydrophobic
finely divided silica (trade name: "Nipsil SS-70", manufactured by
Tosoh Silica Corporation) and 44.3 parts by weight of xylene were
5 placed, then they were shaken for 1 hour, subsequently 1.4 parts by
weight of an additive (trade name: "Disparlon A630-20X", manufactured
by Kusumoto Chemicals, Ltd.) were added and shaken for 15 minutes,
and thereafter, the resulting mixture was filtered through a 60-mesh
filter to prepare a super water-repellent coating composition for
10 a super water-repellent coating film 2.

[0243]

The resulting antifouling coating composition was subjected
to the aforesaid various tests under the conditions shown in the
following Tables 1 and 3 to 6.

15 The results are set forth in Tables 1 and 4 to 6.

[0244]

[Comparative Example 3]

<Aluminum plate>

As a non-coated plate, an anticorrosive aluminum plate
20 (material: A5052P) was used, and the anticorrosive aluminum plate
was subjected to the aforesaid various tests under the conditions
shown in the following Tables 1 and 3 to 6.

[0245]

The results are set forth in Tables 1 and 4 to 6.

In the following Table 1, the amount used is expressed in part (s) by weight.

In the following Tables 4 to 6, R_{t0} (total resistance of ship in the case where air is not jetted out) and R_t (total resistance of ship in the case where air is jetted out) are each expressed in [Kgf], and η_T (total resistance reduction ratio) and η_F (frictional resistance reduction ratio) are each expressed in [%].

[0246]

In Fig. 5, a relationship between an equivalent air thickness t_a and a frictional resistance reduction ratio (comparison between before immersion and after immersion of 30 days) is shown.

[0247]

[Table 1]

Table 1

		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	Comp. Ex. 3
I liquid															
(A) component	Base compound 1 (polymerization degree: 250)	100									100				
	Base compound 2 (polymerization degree: 550)		100	100						100					
	Base compound 3 (polymerization degree: 1000)				100	100	100								
	Base compound 4 (polymerization degree: 1300)							100	100						
	KE-445											100			
Solvent				15	80	110	100	120	125	28	10	20			
(C) component	Xylene														
	Butyl acetate														
	KF-50-100				5							40	*1	*2	*3
	KF-50-3000	10		10			10	10		10	10	22			
	KF-96-10000		5		5	10			10						
(D) antifouling agent	ZnPT									8					
Pigment	CuPT										6				
	R-5N	12	12	12	12	12	12	12	12	12	12				
	KN320	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5				
Subtotal		123.5	118.5	138.5	203.5	233.5	223.5	243.5	248.5	159.5	139.5	182			
II liquid															
(B) component	TES 40WN	5	10	5	5	5	5	5	5	5	5				
III liquid															
Catalyst	GLECK TL	1	1	1	1	1	1	1	1	1	1				
Solvent	Xylene	9	9	9	9	9	9	9	9	9	9				
Total		138.5	138.5	153.5	218.5	248.5	238.5	258.5	263.5	174.5	154.5	182	101.7	100	-

Table 1 (continued)

		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	Comp. Ex. 3
Coating film surface roughness (μm)	Ten point average	1.0	3.1	3.7	4.4	4.0	2.4	3.5	3.9	2.9	3.5	2.8	43.2	40.7	2.5
	Maximum height	1.3	3.5	4.2	4.8	4.4	3.2	4.3	4.5	4.0	4.2	3.3	60.5	54.9	3.5
	Peak-valley interval	1029	1010	1095	1040	948	998	893	872	988	974	1003	650	873	316
In-water bubble contact angle $\theta_b(^{\circ})$	Before immersion	59	62	60	69	68	64	72	77	59	60	60	56.2	47.9	99.1
	After immersion of 14 days	59	65	65	71	72	70	84	86	60	63	62	112.7	125.9	106
	After immersion of 30 days	61	65	63	73	74	70	85	83	68	65	64	115	122.7	107
In-water bubble roll (slip) angle $\theta_a(^{\circ})$	Before immersion	2.9	4.5	5.3	8.9	14.3	9.0	10.1	12.5	5.5	3.2	4.3	34	39.4	13.5
	After immersion of 14 days	5.0	5.1	7.0	10.0	13.1	12.4	21.3	25.4	6.5	4.0	5.6	14.8	0	-
	After immersion of 30 days	6.3	6.7	6.8	9.2	11.4	9.8	18.0	24.8	7.7	5.4	5.2	10.3	0	-
	Immersion of 1 month	5	5	5	5	5	5	5	5	5	5	5	0	5	0
Static antifouling property test	Immersion of 3 months	5	5	5	5	5	5	5	5	5	5	5	0	0	0
	Immersion of 6 months	5	5	5	5	5	5	5	5	5	5	5	0	0	0
	Immersion of 12 months	5	5	5	5	5	5	5	5	5	5	5	0	0	0
	Immersion of 1 month	5	5	5	5	5	5	5	5	5	5	5	3	5	0
Dynamic antifouling property test	Immersion of 3 months	5	5	5	5	5	5	5	5	5	5	5	0	3	0
	Immersion of 6 months	5	5	5	5	5	5	5	5	5	5	5	0	0	0
	Immersion of 12 months	5	5	5	5	5	5	5	5	5	5	5	0	0	0
	Immersion of 1 month	5	5	5	5	5	5	5	5	5	5	5	0	0	0

*1: A super water-repellent coating composition obtained by blending 100 parts by weight of a mixture obtained by shaking 12.6 parts by weight of Lumiflon LF-200, 24.2 parts by weight of Lublon L-2, 1.8 parts by weight of SF-1265-1000, 0.8 part by weight of a 0.1% tin catalyst and 60.6 parts by weight of butyl acetate by a paint shaker, with 1.7 parts by weight of Burnock DN-980 was used.

*2: A super water-repellent coating composition obtained by shaking 34.7 parts by weight of TZ-343, 19.6 parts by weight of Nipsil SS-70 and 44.3 parts by weight of xylene by a paint shaker to obtain a mixture, then adding 1.4 parts by weight of Disparlon A630-20X to the mixture and then shaking the resulting mixture was used.

*3: An anticorrosive aluminum plate (material: A5052P) was used as a non-coated plate.

[0248]

Abbreviations of the raw materials described in Table 1 are as shown in Table 2, and evaluation criteria of the antifouling test are as described in Table 3.

[0249]

[Table 2]

Table 2

Trade name of raw material		Raw material	
	Maker		
KE-445	Shin-Etsu Chemical Co., Ltd.	deoxime type RTV rubber, viscosity (23°C): 5000 mm ² /s	
KF-50-100	Shin-Etsu Chemical Co., Ltd.	methylphenyl silicone oil, viscosity: 100 cSt	
KF-50-3000	Shin-Etsu Chemical Co., Ltd.	methylphenyl silicone oil, viscosity: 3000 cSt	
KF-96-10000	Shin-Etsu Chemical Co., Ltd.	dimethyl silicone oil, viscosity: 10000 cSt	
ZnPT	Olin Corporation	2-pyridinethiol-1-oxide zinc salt	
CuPT	Olin Corporation	2-pyridinethiol-1-oxide copper salt	
R-5N	Sakai Chemical Industry Co., Ltd.	titanium oxide	
KN320	Toda Kogyo Corp.	black iron oxide	
TES 40WN	Wacker Asahikasei Silicone Co., Ltd.	ethyl silicate oligomer	
GLECK TL	DIC Corporation	dibutyltin dilaurate	
Lumiflon LF-200	Asahi Glass Co., Ltd.	fluorine-based polyol	
Lublon L-2	Daikin Industries, Ltd.	low-molecular weight ethylene tetrafluoride ultrafine powder	
Burnock DN-980	Daikin Industries, Ltd.	isocyanurate type polyisocyanate	
Acrylic TZ-343	DIC Corporation	acrylic resin	
Nipsil SS-70	Tosoh Silica Corporation	Hydrophobic finely divided silica	
Disparlon A630-20X	Kusumoto Chemicals, Ltd.	paste type amide wax	

[0250]

[Table 3]

Table 3

Antifouling property test evaluation	
Evaluation	Visual evaluation (state)
5	area fouled by marine organisms: 0%
4	area fouled by marine organisms: not more than 5%
3	area fouled by marine organisms: more than 5% but not more than 10%
2	area fouled by marine organisms: more than 10% but not more than 25%
1	area fouled by marine organisms: more than 25% but not more than 50%
0	area fouled by marine organisms: more than 50%

[0251]

[Table 4-1]

Table 4 Relationship between flow velocity and frictional resistance reduction ratio (equivalent air thickness $t_a=2.0$ mm)

Before immersion		Example											Comparative Example		
		1	2	3	4	5	6	7	8	9	10	11			
Flow velocity 1.4 m/s	R_{t0}	0.461	0.460	0.460	0.461	0.452	0.451	0.456	0.458	0.450	0.463	0.461	0.466	0.463	0.453
	R_t	0.406	0.410	0.413	0.413	0.408	0.408	0.413	0.416	0.406	0.409	0.410	0.413	0.410	0.418
	η_T	12.0	10.9	10.2	10.5	9.8	9.5	9.4	9.2	9.8	11.7	11.1	11.3	11.5	7.7
	η_F	29.9	27.0	25.5	26.2	24.0	23.2	23.2	22.7	23.9	29.2	27.8	28.5	28.8	19.0
Flow velocity 1.8 m/s	R_{t0}	1.131	1.109	1.113	1.126	1.137	1.132	1.136	1.140	1.131	1.138	1.119	1.141	1.144	1.110
	R_t	1.002	0.998	1.012	1.022	0.989	1.033	1.039	1.045	0.964	1.010	1.000	1.029	0.970	1.031
	η_T	11.4	10.0	9.1	9.2	13.0	8.7	8.5	8.3	14.7	11.2	10.6	9.8	15.2	7.1
	η_F	44.1	37.9	34.5	35.3	50.4	33.8	33.2	32.5	56.9	43.7	40.7	38.3	59.6	27.0

[0252]

[Table 4-2]

Table 4 (continued)

After immersion of		Example											Comparative Example		
30 days		1	2	3	4	5	6	7	8	9	10	11	1	2	3
Flow velocity 1.4 m/s	R_{t0}	0.457	0.458	0.458	0.463	0.456	0.453	0.461	0.460	0.455	0.460	0.458	0.462	0.465	0.468
	R_t	0.405	0.409	0.415	0.417	0.414	0.412	0.419	0.417	0.411	0.409	0.409	0.429	0.429	0.441
	η_r	11.4	10.7	9.4	9.9	9.2	9.1	9.1	9.3	9.7	11.1	10.7	7.1	7.7	5.8
	η_F	28.1	26.5	23.2	24.9	22.7	22.2	22.7	23.2	23.8	27.6	26.5	17.8	19.5	14.6
Flow velocity 1.8 m/s	R_{t0}	1.127	1.110	1.109	1.129	1.141	1.134	1.139	1.145	1.133	1.134	1.116	1.137	1.141	1.146
	R_t	1.002	0.990	1.012	1.029	1.002	1.036	1.035	1.048	0.970	1.010	1.002	1.071	1.073	1.085
	η_r	11.1	10.8	8.7	8.9	12.2	8.6	9.1	8.5	14.4	10.9	10.2	5.8	6.0	5.3
	η_F	42.7	41.0	33.2	34.2	47.5	33.5	35.5	33.2	55.7	42.4	39.0	22.6	23.2	20.8

[0253]

[Table 5-1]

Table 5 Relationship between amount of air jetted out t_a and frictional resistance reduction ratio (flow velocity: 1.4 m/s)

Before immersion	Example											Comparative Example		
	1	2	3	4	5	6	7	8	9	10	11	1	2	3
(no air) R_0	0.461	0.460	0.460	0.461	0.452	0.451	0.456	0.458	0.450	0.463	0.461	0.466	0.463	0.453
R_t	0.427	0.452	0.459	0.457	0.448	0.448	0.451	0.452	0.428	0.449	0.455	0.433	0.412	0.448
η_T	7.5	1.8	0.2	0.9	0.9	0.8	1.1	1.3	5.0	3.0	1.4	7.0	11.1	1.1
η_F	18.8	4.4	0.6	2.3	2.2	1.9	2.7	3.2	12.0	7.6	3.4	17.6	27.7	2.6
R_t	0.414	0.428	0.432	0.432	0.421	0.426	0.426	0.426	0.410	0.417	0.417	0.421	0.408	0.433
η_T	10.2	7.0	6.1	6.4	6.8	5.6	6.6	7.0	8.8	10.0	9.6	9.7	11.9	4.3
η_F	25.5	17.3	15.1	15.9	16.6	13.6	16.2	17.3	21.5	24.8	23.7	24.5	29.7	10.6
R_t	0.406	0.410	0.413	0.413	0.408	0.408	0.413	0.416	0.406	0.409	0.410	0.413	0.410	0.418
η_T	12.0	10.9	10.2	10.5	9.8	9.5	9.4	9.2	9.8	11.7	11.1	11.3	11.5	7.7
η_F	29.9	27.0	25.5	26.2	24.0	23.2	23.2	22.7	23.9	29.2	27.8	28.5	28.8	19.0
R_t	0.399	0.398	0.405	0.405	0.404	0.400	0.404	0.402	0.396	0.402	0.407	0.410	0.410	0.406
η_T	13.6	13.5	12.1	12.1	10.5	11.2	11.4	12.2	12.0	13.4	11.8	11.9	11.4	10.4
η_F	34.0	33.6	30.0	30.2	25.7	27.3	28.1	30.3	29.2	33.2	29.4	30.1	28.5	25.4

[0254]

[Table 5-2]

Table 5 (continued)

After immersion of		Example											Comparative Example		
30 days		1	2	3	4	5	6	7	8	9	10	11	1	2	3
ta 1.0mm	(no air) R_{t0}	0.457	0.458	0.458	0.463	0.456	0.453	0.461	0.460	0.455	0.460	0.458	0.462	0.465	0.468
	R_t	0.425	0.452	0.455	0.456	0.451	0.447	0.458	0.452	0.433	0.448	0.448	0.451	0.453	0.471
	η_T	7.0	1.3	0.7	1.5	1.1	1.3	0.7	1.7	4.8	2.6	2.2	2.4	2.6	-0.6
	η_F	17.3	3.2	1.6	3.8	2.7	3.2	1.6	4.3	11.9	6.5	5.4	5.9	6.5	-1.6
ta 1.5mm	R_t	0.412	0.425	0.431	0.433	0.425	0.428	0.430	0.425	0.416	0.416	0.412	0.442	0.444	0.462
	η_T	9.8	7.2	5.9	6.5	6.8	5.5	6.7	7.6	8.6	9.6	10.0	4.3	4.5	1.3
	η_F	24.3	17.8	14.6	16.2	16.8	13.5	16.8	18.9	21.1	23.8	24.9	10.8	11.4	3.2
ta 2.0mm	R_t	0.405	0.409	0.415	0.417	0.414	0.412	0.419	0.417	0.411	0.409	0.409	0.429	0.429	0.441
	η_T	11.4	10.7	9.4	9.9	9.2	9.1	9.1	9.3	9.7	11.1	10.7	7.1	7.7	5.8
	η_F	28.1	26.5	23.2	24.9	22.7	22.2	22.7	23.2	23.8	27.6	26.5	17.8	19.5	14.6
ta 2.5mm	R_t	0.399	0.401	0.405	0.409	0.410	0.402	0.411	0.405	0.403	0.399	0.406	0.427	0.427	0.431
	η_T	12.7	12.4	11.6	11.7	10.1	11.3	10.8	12.0	11.4	13.3	11.4	7.6	8.2	7.9
	η_F	31.4	30.8	28.6	29.2	24.9	27.6	27.0	29.7	28.1	33.0	28.1	18.9	20.5	20.0

[0255]

[Table 6]

Table 6 Amount of air jetted out t_a and difference in frictional resistance reduction ratio between before and after immersion

(flow velocity: 1.4 m/s)

	Example											Comparative Example		
	1	2	3	4	5	6	7	8	9	10	11	1	2	3
t_a 1.0mm	1.5	1.1	-1.0	-1.5	-0.5	-1.4	1.1	-1.1	0.2	1.1	-2.0	21.3	21.3	4.2
t_a 1.5mm	1.2	-0.5	0.5	-0.3	-0.1	0.1	-0.5	-1.6	0.4	1.0	-1.2	13.7	18.3	7.4
t_a 2.0mm	1.8	0.5	2.2	1.3	1.3	1.0	0.5	-0.5	0.2	1.6	1.3	10.6	9.4	4.4
t_a 2.5mm	2.6	2.7	1.4	1.0	0.9	-0.2	1.1	0.5	1.1	0.2	1.3	9.6	8.0	5.4

(unit: %)

[0256]

As shown in Tables 1 and 4 to 6, the coating films obtained from the compositions of Examples 1 to 11 containing an organopolysiloxane as a main component each had a smaller in-water
5 bubble contact angle (less than 90 degrees), a smaller roll or slip angle and smaller changes in these angles with time in immersion in water, as compared with the non-coated aluminum plate (Comparative Example 3). In both of Comparative Examples 1 and 2, the change with time in immersion in water was large, and these coating films were
10 hydrophilized and lost affinity for air. In Examples 1 to 11, the water flow resistance reduction ratio was higher than that in Comparative Examples 1 and 2.

[0257]

As shown in Table 6 and Fig. 5, the coating films obtained from
15 the compositions of the examples each exhibited higher frictional reduction effect even by a small amount of air ($t_a=1.0$ mm) as compared with the non-coated aluminum plate (Comparative Example 3), and therefore, it is possible to reduce energy for generating air, and the coating films are effective for reduction of net energy of a ship.

20 [0258]

As shown in Table 6 and Fig. 5, the coating films obtained from the compositions of the examples each apparently exhibited a smaller change in frictional resistance reduction ratio after immersion, as compared with the super water-repellent coating films 1 and 2

(Comparative Examples 1 and 2).

[0259]

Also in the antifouling property test, as shown in Tables 1 and 3, fouling was not observed after an immersion time of 12 months in the case of the compositions of Examples 1 to 11, but in the case of the compositions of Comparative Examples 1 and 2, fouling was conspicuously observed in spite of the super water-repellent coating films, and those compositions had no sufficient function as antifouling coating materials.

10

Industrial Applicability

[0260]

In the special frictional resistance reduced ship according to the present invention, an efficient gas lubrication effect is exhibited, frictional resistance of a hull is efficiently reduced even if the amount of air supplied is small, and the energy saving effect is also great.

The antifouling coating composition used for a special frictional resistance reduced ship according to the present invention can form a coating film capable of efficiently reducing frictional resistance of a hull even by supplying a small amount of a gas, and the energy saving effect is also great. Further, the coating film formed from the antifouling coating composition exhibits excellent antifouling property and can prevent increase of frictional resistance

of a hull attributable to fouling by aquatic organisms and the like. Furthermore, the antifouling coating composition can maintain those effects over a long period of time.

[0261]

5 In the production process for a special frictional resistance reduced ship according to the present invention, a specific ship exerting the above effects can be produced by a simple method of forming an antifouling coating film from the antifouling coating composition on a submerged surface of a shell plating of a ship.

10 [0262]

 In the method for predicting the above frictional resistance reduction effect according to the present invention, the frictional resistance reduction effect can be predicted by simple and low-cost equipment and means.

15 Accordingly, the special frictional resistance reduced ship, the antifouling coating composition used for a special frictional resistance reduce ship, and the production process for a special frictional resistance reduced ship according to the present invention can be each utilized for various ships requiring frictional resistance
20 reduction, and can be utilized in fields of marine transportation and the like.

Reference Signs List

[0263]

1: camera

2: syringe

3: angle meter

4: rotation drive handle

5 5: test board

6: test panel

7: immersion container

8: air outlet

9: test coating film portion

10

CLAIMS

1. An antifouling coating composition used for a frictional resistance reduced ship utilizing a gas lubrication function in water, comprising:

5 (A) a reaction-curing type organopolysiloxane having a viscosity at 25°C of 20 to 400000 mm²/s,

(C) a hydrophobic material which is liquid or greasy at 25°C (other than the above organopolysiloxane (A) and the following organosilane and/or its partial condensate (B)), and

10 if necessary, (B) an organosilane having, in one molecule, at least two groups each of which is at least one group of a hydroxy group and a hydrolyzable group and/or its partial condensate.

2. The antifouling coating composition as claimed in claim 15 1, wherein the hydrophobic material (C) contains at least one kind selected from a silicone oil, a fluorine-based oil, paraffins and a wax.

3. The antifouling coating composition as claimed in claim 20 1 or 2, which further comprises an antifouling agent (D) in an amount of 1 to 150 parts by weight based on 100 parts by weight of the organopolysiloxane (A).

4. An antifouling coating film used for a frictional

resistance reduced ship utilizing a gas lubrication function in water, said film being formed from the antifouling coating composition as claimed in any one of claims 1 to 3.

5 5. The antifouling coating film as claimed in claim 4, wherein the maximum height from the bottom of a recess to the peak of a projection, as measured in accordance with JIS B 0601, is not more than 30 μm , and the peak-valley average interval that is an average of a length of one cycle constituted of one projection and its
10 neighboring one recess, as measured in accordance with JIS B 0601, is not less than 700 μm .

6. The antifouling coating film as claimed in claim 4 or 5, wherein the static in-water bubble contact angle, as measured by
15 the following measuring method for static in-water bubble contact angle, is less than 90 degrees, and the in-water bubble roll (slip) angle, as measured by the following measuring method for in-water bubble roll (slip) angle, is less than 30 degrees,

 <measuring method for static in-water bubble contact angle>
20 a rigid polyvinyl chloride test panel (maximum height as measured in accordance with JIS B 0601: not more than 1 μm), which has been coated with a coating composition so that a coating film having a dry film thickness of 150 μm may be formed, is immersed in water at 25°C for 30 days, then the rigid polyvinyl chloride test panel after

immersion of 30 days is placed in water in such a manner that the coating film surface becomes horizontal and is on the lower side of the test panel, then 0.1 cc of air is injected into water so that one bubble may be formed on the coating film surface, then a height
 5 a of the bubble from the coating film surface, said bubble having been formed on the coating film surface, and a diameter b of a contact portion of the bubble with the coating film surface are measured, and from the following formula (1), a static in-water bubble contact angle (θ_s , unit: degree) that is a contact angle between the coating
 10 film surface and the bubble is determined;

[Math. 1]

$$\theta_s = 2 \times \frac{180}{\pi} \times \tan^{-1} \frac{2a}{b} \dots (1)$$

<measuring method for in-water bubble roll (slip) angle>

in the above measuring method for static in-water bubble contact
 15 angle, the coating film surface having the bubble formed thereon is gradually inclined against the horizontal plane, and when the bubble begins to move, an in-water bubble roll (slip) angle (θ_m , unit: degree) that is an inclination angle of the coating film surface against the horizontal plane is measured.

20

7. A frictional resistance reduced ship utilizing a gas lubrication function in water, a submerged surface of a shell plating of which has been coated with the antifouling coating film as claimed

in any one of claims 4 to 6.

8. A production process for a frictional resistance reduced ship utilizing a gas lubrication function in water, comprising forming
5 the antifouling coating film as claimed in any one of claims 4 to 6 on a submergence expected surface of a shell plating of a ship to be coated.

9. A frictional resistance reduction system having the
10 antifouling coating film as claimed in any one of claims 4 to 6 and an air supply device for supplying air to the surface of the antifouling coating film.

10. A frictional resistance reduced ship utilizing a gas
15 lubrication function in water, having the frictional resistance reduction system as claimed in claim 9.

11. A coating composition used for a frictional resistance reduced ship utilizing a gas lubrication function in water, said
20 composition being capable of forming a coating film having a static in-water bubble contact angle, as measured by the following measuring method for static in-water bubble contact angle, of less than 90 degrees, and an in-water bubble roll (slip) angle, as measured by the following measuring method for in-water bubble roll (slip) angle, of less than

30 degrees,

<measuring method for static in-water bubble contact angle>

a rigid polyvinyl chloride test panel (maximum height as measured in accordance with JIS B 0601: not more than 1 μm), which has been
 5 coated with a coating composition so that a coating film having a dry film thickness of 150 μm may be formed, is immersed in water at 25°C for 30 days, then the rigid polyvinyl chloride test panel after immersion of 30 days is placed in water in such a manner that the coating film surface becomes horizontal and is on the lower side of
 10 the test panel, then 0.1 cc of air is injected into water so that one bubble may be formed on the coating film surface, then a height a of the bubble from the coating film surface, said bubble having been formed on the coating film surface, and a diameter b of a contact portion of the bubble with the coating film surface are measured,
 15 and from the following formula (1), a static in-water bubble contact angle (θ_s , unit: degree) that is a contact angle between the coating film surface and the bubble is determined;

[Math. 2]

$$\theta_s = 2 \times \frac{180}{\pi} \times \tan^{-1} \frac{2a}{b} \dots (1)$$

20 <measuring method for in-water bubble roll (slip) angle>

in the above measuring method for static in-water bubble contact angle, the coating film surface having the bubble formed thereon is gradually inclined against the horizontal plane, and when the bubble

begins to move, an in-water bubble roll (slip) angle (θ_m , unit: degree) that is an inclination angle of the coating film surface against the horizontal plane is measured.

5 12. A coating film formed from the coating composition used for a frictional resistance reduced ship as claimed in claim 11.

13. A frictional resistance reduced ship utilizing a gas lubrication function in water, having the coating film as claimed
10 in claim 12 on a submerged surface of a shell plating of the ship.

14. A frictional resistance reduction system having the coating film as claimed in claim 12 and an air supply device for supplying air to the surface of the coating film.

15

15. A frictional resistance reduced ship utilizing a gas lubrication function in water, having the frictional resistance reduction system as claimed in claim 14.

20 16. A production process for a frictional resistance reduced ship utilizing a gas lubrication function in water, comprising forming the coating film as claimed in claim 12 on a submergence expected surface of a shell plating of a ship to be coated.

17. A method for predicting a frictional resistance reduction effect utilizing a gas lubrication function of a coating film in water, comprising measuring a static in-water bubble contact angle by the following measuring method for static in-water bubble contact angle,
 5 measuring an in-water bubble roll (slip) angle by the following measuring method for in-water bubble roll (slip) angle, and

predicting a frictional resistance reduction effect utilizing a gas lubrication function of a coating film in water, from the static in-water bubble contact angle and the in-water bubble roll (slip)
 10 angle,

<measuring method for static in-water bubble contact angle>

a test panel, which has been coated with a coating composition so that a coating film may be formed, is immersed in water, then the test panel after immersion is placed in water in such a manner that
 15 the coating film surface becomes horizontal and is on the lower side of the test panel, then air is injected into water so that a bubble may be formed on the coating film surface, then a height a of the bubble from the coating film surface, said bubble having been formed on the coating film surface, and a diameter b of a contact portion
 20 of the bubble with the coating film surface are measured, and from the following formula (1), a static in-water bubble contact angle (θ_s , unit: degree) that is a contact angle between the coating film surface and the bubble is determined;

[Math. 3]

$$\theta_s = 2 \times \frac{180}{\pi} \times \tan^{-1} \frac{2a}{b} \dots (1)$$

<measuring method for in-water bubble roll (slip) angle>

in the above measuring method for static in-water bubble contact angle, the coating film surface having the bubble formed thereon is gradually inclined against the horizontal plane, and when the bubble begins to move, an in-water bubble roll (slip) angle (θ_m , unit: degree) that is an inclination angle of the coating film surface against the horizontal plane is measured.

18. An apparatus used for prediction of a frictional resistance reduction effect utilizing a gas lubrication function of a coating film in water, said apparatus having a test board, an inclination angle control device, an immersion container and an observation device, wherein:

to the test board, the inclination angle control device is connected,

on the test board, a test panel having a coating film formed on its surface is set in such a manner that a back surface of the test panel comes into contact with the lower surface of the test board, and in the immersion container containing water, the test board is placed in such a state that the test panel is immersed in water and that a bubble has been formed on the coating film surface of the test panel,

the observation device is set so as to be able to observe the state of the test panel and the bubble,

when the test panel is horizontal, the state of the bubble formed on the surface of the coating film of the test panel is observed by
5 the observation device to measure a static in-water bubble contact angle, and

the test panel is inclined against the horizontal by the inclination angle control device, and the behavior of the bubble is observed by the observation device to measure an in-water bubble roll
10 (slip) angle of the bubble formed on the surface of the coating film of the test panel.