

EPOXY RESIN ANTICORROSIVE COATING COMPOSITIONS, EPOXY RESIN ANTICORROSIVE COATING FILMS, LAYERED ANTIFOULING COATING FILMS, ANTIFOULING SUBSTRATES, AND METHODS FOR PRODUCTION THEREOF

5 BACKGROUND OF THE INVENTION

1. Field of the Invention

[0001]

The present invention relates to epoxy resin anticorrosive coating compositions, epoxy resin anticorrosive coating films, layered antifouling coating film including the anticorrosive coating film and an antifouling coating film layered thereon, antifouling substrate having the layered antifouling coating film, and methods for producing these items.

15 2. Description of the Related Art

[0002]

Bottom portions of marine vessels that are submerged in seawater are recoated on a regular basis to repair damages. In general, the coating specification is such that the base surface is treated by treatments such as the removal of rust and film defects, and thereafter an anticorrosive coating and next an antifouling coating are applied to prevent corrosion and the attachment of marine organisms. Requirements in the repair coating operations are that an anticorrosive coating

film and an antifouling coating film adhere strongly and that a layered coating film formed from an anticorrosive coating and an antifouling coating as a top coat exhibits good antifouling properties.

5 [0003]

Epoxy resin anticorrosive coatings are generally used as the anticorrosive coatings.

There is a great number of literature on epoxy resin anticorrosive coatings. For example, Patent Literatures 1 to
10 3 describe epoxy resin anticorrosive coating compositions including components such as a vinyl chloride copolymer, and also describe that an anticorrosive coating film from the coating composition is overcoated with a hydrolyzable antifouling coating.

15 Further, Patent Literatures 2 and 3 evaluate the dynamic antifouling properties and the consumption degree of the layered coating films obtained by overcoating the anticorrosive coating film with the antifouling coating.

CITATION LIST

20 PATENT LITERATURE

[0004]

Patent Literature 1: WO 2006/016625

Patent Literature 2: JP-A-H10-259351

Patent Literature 3: JP-A-H11-333374

SUMMARY OF THE INVENTION

[0005]

In the marine vessel repair coating operations, it is often the case that an anticorrosive coating and an antifouling
5 coating are applied at a short time interval due to reasons such as the scheduling of services or the weather conditions under which the coating operations take place. This shortness of the interval time between the coating operations can cause problems.

10 [0006]

The mechanism by which an epoxy resin anticorrosive coating gives an anticorrosive coating film is such that the epoxy resin is cured by the reaction with a curing agent such as an amine and the resultant film is dried. If an antifouling
15 coating is applied shortly after an epoxy resin anticorrosive coating, the application of the antifouling coating takes place while the reaction of the epoxy resin with the curing agent such as an amine is still insufficient and part of the epoxy resin remains unreacted in the anticorrosive coating film. The
20 present inventors have found that overcoating of such an anticorrosive coating film with an antifouling coating results in the bleeding (migration) of the unreacted epoxy resin into the antifouling coating and consequently the consumption and antifouling properties of the antifouling coating film are

deteriorated. In particular, it has been found that when the coating operations take place at low temperature, the reaction between the epoxy resin and the curing agent is slow and consequently an increased amount of the epoxy resin remains unreacted in the film and comes to exert a greater adverse influence.

[0007]

While the layered coating films of an anticorrosive coating film and an antifouling coating film described in Patent Literatures 2 and 3 have excellent dynamic antifouling properties, the present inventors have revealed that there is room for improvement in terms of static antifouling properties which are evaluated under harsher conditions.

[0008]

Further, an important characteristic to be possessed by repair films on marine vessels is the resistance to plastic deformation or breakage by external pressure (hereinafter, "damage resistance"). In most cases, for reasons such as loading schedules, marine vessels leave the repair facility and are anchored at the pier soon after the coating operations. In view of this, the susceptibility of repair films to deformations and scratches by contact of the marine vessels with the pier ruins the work by the coating operations. Thus,

films that exhibit the damage resistance immediately after the coating operations are highly advantageous.

[0009]

When, however, the coating operations are performed at
5 low temperature such as in winter, the decrease in the reactivity between an epoxy resin and a curing agent decreases the strength of anticorrosive coating films, thus resulting in poor damage resistance of layered coating films.

[0010]

10 A possible approach to solving the above problem is to simply reduce the amount of an epoxy resin in the formulation of an epoxy resin anticorrosive coating. However, a coating with such a formulation is so heavily based on a pigment component that the coating workability is deteriorated,
15 leveling properties are poor and it is impossible to form a continuous film due to the deficiency of resin components. As a result, films that are obtained are poor in appearance, water resistance and corrosion resistance.

[0011]

20 In light of the problems in the art discussed above, an object of the invention is to provide an epoxy resin anticorrosive coating designed to form an epoxy resin anticorrosive coating film which in combination with an antifouling coating film can form a layered antifouling coating

film while ensuring that even when the antifouling coating film is formed on the anticorrosive coating film before sufficient curing of the epoxy resin, the layered antifouling coating film will attain inhibition of antifouling performance (in particular, static antifouling properties) degradation and will attain excellent damage resistance; an epoxy resin anticorrosive coating film used as the anticorrosive coating film in the above layered antifouling coating film; a layered antifouling coating film described above and a method for producing such layered antifouling coating films; and an antifouling substrate having the layered antifouling coating film and a method for producing such antifouling substrates. [0012]

The present inventors carried out extensive studies directed to solving the problems described hereinabove. As a result, the present inventors have found that an epoxy resin anticorrosive coating including an epoxy resin in combination with a relatively large amount of a thermoplastic resin that is solid at room temperature can give a layered antifouling coating film of an anticorrosive coating film with an antifouling coating while ensuring that the decrease in antifouling performance (in particular, static antifouling properties) is small and excellent damage resistance is

obtained. The present invention has been completed based on the finding.

[0013]

The advantageous effects of the invention are obtained
5 probably by the following mechanism.

In an anticorrosive coating film formed from an epoxy resin anticorrosive coating, the epoxy resin that has not reacted with the curing agent such as an amine is in the form of a liquid or a semisolid. When an overcoating is applied onto
10 such a semi-finished anticorrosive coating film, the solvent of the overcoating penetrates into the anticorrosive coating film to soften the anticorrosive coating film and consequently the unreacted epoxy resin bleeds (migrates) into the overcoat. In contrast, in the anticorrosive coating film, a resin that
15 is solid at room temperature is less prone to migrate into the overcoat even if the solvent of the overcoating has penetrated into the anticorrosive coating film. It is considered that the use of such a solid thermoplastic resin with an epoxy resin allows the amount of the epoxy resin to be relatively decreased
20 and thus makes it possible to reduce the amount of bleeding of the unreacted epoxy resin for the reasons described above; and that probably by this mechanism, the anticorrosive coating film allows an antifouling coating film stacked thereon without causing a decrease in antifouling performance (in particular,

static antifouling properties) while ensuring that the resultant layered coating film attains enhanced damage resistance.

[0014]

5 The present invention pertains to the following items [1] to [23].

 [1] An epoxy resin anticorrosive coating composition for forming an anticorrosive coating film in a layered antifouling coating film including the anticorrosive coating film and an
10 antifouling coating film disposed on a surface of a substrate in the order of the anticorrosive coating film and the antifouling coating film from the substrate side,

 the epoxy resin anticorrosive coating composition including an epoxy resin (A), a solid thermoplastic resin (B)
15 and an amine curing agent (C),

 the solid thermoplastic resin (B) being solid at room temperature,

 the content of the solid thermoplastic resin (B) being not less than 50 parts by mass per 100 parts by mass of solids
20 of the epoxy resin (A).

[0015]

 [2] The epoxy resin anticorrosive coating composition described in [1], wherein the epoxy resin (A) is one, or two

or more selected from the group consisting of bisphenol A epoxy resins, bisphenol AD epoxy resins and bisphenol F epoxy resins.

[0016]

[3] The epoxy resin anticorrosive coating composition described in [1] or [2], wherein the composition further includes optionally a silane coupling agent and satisfies a reaction ratio of 0.3 to 0.8 wherein the reaction ratio is represented by the formula (1) below when the composition does not contain a silane coupling agent, the formula (2) below when the composition contains a silane coupling agent reactive to the amine curing agent (C), or the formula (3) below when the composition contains a silane coupling agent reactive to the epoxy resin (A),

[0017]

$$\text{Reaction ratio} = \frac{\frac{\text{Amount of amine curing agent (C)}}{\text{Active hydrogen equivalent weight of amine curing agent (C)}}}{\frac{\text{Amount of epoxy resin (A)}}{\text{Epoxy equivalent of epoxy resin (A)}}} \quad \dots (1)$$

$$\text{Reaction ratio} = \frac{\frac{\text{Amount of amine curing agent (C)}}{\text{Active hydrogen equivalent weight of amine curing agent (C)}}}{\frac{\text{Amount of epoxy resin (A)}}{\text{Epoxy equivalent of epoxy resin (A)}} + \frac{\text{Amount of silane coupling agent reactive to amine curing agent (C)}}{\text{Reactive group equivalent weight of silane coupling agent}}} \quad \dots (2)$$

$$\text{Reaction ratio} = \frac{\frac{\text{Amount of amine curing agent (C)}}{\text{Active hydrogen equivalent weight of amine curing agent (C)}} + \frac{\text{Amount of silane coupling agent reactive to epoxy resin (A)}}{\text{Reactive group equivalent weight of silane coupling agent}}}{\frac{\text{Amount of epoxy resin (A)}}{\text{Epoxy equivalent of epoxy resin (A)}}} \quad \dots (3)$$

(in the formulae (1) to (3), the units of the amount and the equivalent weight are g and g/eq, respectively).

[0018]

[4] The epoxy resin anticorrosive coating composition described in any one of [1] to [3], further including a pigment (E).

[0019]

5 [5] The epoxy resin anticorrosive coating composition described in [4], wherein the pigment volume concentration (PVC) represented by the formula (4) below is 25 to 50%:

Pigment volume concentration (%) = Volume of pigment in anticorrosive coating composition / (Volume of resins in anticorrosive coating composition + Volume of pigment in anticorrosive coating composition) × 100 (4).

[0020]

[6] The epoxy resin anticorrosive coating composition described in any one of [1] to [5], wherein the solid thermoplastic resin (B) includes at least one selected from the group consisting of petroleum resins, chlorinated polyolefins, acrylic resins, butyl acetate resins, styrene resins and vinyl chloride resins.

[0021]

20 [7] The epoxy resin anticorrosive coating composition described in [6], wherein the vinyl chloride resin is a vinyl chloride/vinyl isobutyl ether copolymer.

[0022]

[8] The epoxy resin anticorrosive coating composition described in any one of [1] to [7], further including a tertiary amine as a curing accelerator (D).

[0023]

5 [9] The epoxy resin anticorrosive coating composition described in any one of [1] to [8], further including an adhesion promoter (F).

[0024]

10 [10] The epoxy resin anticorrosive coating composition described in [9], wherein the adhesion promoter (F) is a silane coupling agent.

[0025]

15 [11] The epoxy resin anticorrosive coating composition described in [10], wherein the silane coupling agent is γ -glycidoxypopyl trimethoxysilane.

[0026]

[12] The epoxy resin anticorrosive coating composition described in any one of [1] to [11], wherein the antifouling coating film is a hydrolyzable antifouling coating film.

20 [0027]

[13] An epoxy resin anticorrosive coating film used as an anticorrosive coating film in a layered antifouling coating film including the anticorrosive coating film and an antifouling coating film disposed on a surface of a substrate

in the order of the anticorrosive coating film and the antifouling coating film from the substrate side,

the epoxy resin anticorrosive coating film being a cured product of the epoxy resin anticorrosive coating composition
5 described in any one of [1] to [12].

[0028]

[14] An epoxy resin anticorrosive coating film used as an anticorrosive coating film in a layered antifouling coating film including the anticorrosive coating film and an
10 antifouling coating film disposed on a surface of a substrate in the order of the anticorrosive coating film and the antifouling coating film from the substrate side,

the epoxy resin anticorrosive coating film including a matrix including a cured epoxy resin and a solid thermoplastic
15 resin (B),

the solid thermoplastic resin (B) being solid at room temperature,

the content of the solid thermoplastic resin (B) being
7 to 80 mass%.

20 [0029]

[15] The epoxy resin anticorrosive coating film described in [14], further including an epoxy resin (A).

[0030]

[16] A method for producing an epoxy resin anticorrosive coating film used as an anticorrosive coating film in a layered antifouling coating film including the anticorrosive coating film and an antifouling coating film disposed on a surface of a substrate in the order of the anticorrosive coating film and the antifouling coating film from the substrate side,

the method including a step of curing a film composed of the epoxy resin anticorrosive coating composition described in any one of [1] to [12].

10 [0031]

[17] A layered antifouling coating film including an anticorrosive coating film and an antifouling coating film disposed on a surface of a substrate in the order of the anticorrosive coating film and the antifouling coating film from the substrate side,

the anticorrosive coating film being the epoxy resin anticorrosive coating film described in any one of [13] to [15].

[0032]

[18] The layered antifouling coating film described in [17], wherein the antifouling coating film is a hydrolyzable antifouling coating film.

[0033]

[19] A method for producing a layered antifouling coating film including an anticorrosive coating film and an antifouling

coating film disposed on a surface of a substrate in the order of the anticorrosive coating film and the antifouling coating film from the substrate side,

the method including a step of forming the epoxy resin
5 anticorrosive coating film described in any one of [13] to [15],
and a step of forming the antifouling coating film on the surface of the epoxy resin anticorrosive coating film.

[0034]

[20] An antifouling substrate including a substrate and
10 the layered antifouling coating film described in [17] or [18],
the layered antifouling coating film being disposed on a surface of the substrate in the order of the anticorrosive coating film and the antifouling coating film from the substrate side.

[0035]

15 [21] The antifouling substrate described in [20], which is placed in contact with seawater or fresh water.

[0036]

[22] The antifouling substrate described in [20] or [21], wherein the substrate is at least one selected from the group
20 consisting of marine vessels, offshore structures and onshore structures.

[0037]

[23] A method for producing an antifouling substrate, including a step of forming the layered antifouling coating film described in [17] or [18] on a surface of a substrate. [0038]

5 The epoxy resin anticorrosive coating of the invention can form an anticorrosive coating film while exhibiting excellent curability and, when the coating contains a solvent, drying properties. In a layered antifouling coating film including an anticorrosive coating film and an antifouling
10 coating film disposed on a surface of a substrate in this order from the substrate side, the inventive epoxy resin anticorrosive coating can form the anticorrosive coating film while ensuring that unreacted epoxy resin components present in the anticorrosive coating film will be prevented from
15 bleeding into the antifouling coating film. Consequently, the obtainable layered antifouling coating film attains inhibition of antifouling performance (in particular, static antifouling properties) degradation and attains enhanced damage resistance.

20 DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0039]

Hereinbelow, the present invention will be described in greater detail.

[Epoxy resin anticorrosive coating compositions]

An epoxy resin anticorrosive coating composition of the present invention (hereinafter, also written simply as the "anticorrosive coating composition") is designed to form an anticorrosive coating film in a layered antifouling coating film which includes the anticorrosive coating film and an antifouling coating film disposed on a surface of a substrate in this order from the substrate side. The anticorrosive coating composition includes an epoxy resin (A), a solid thermoplastic resin (B) and an amine curing agent (C).

These components present in the composition will be described below. The layered antifouling coating film will be described later.

[0040]

Epoxy resins (A)

Examples of the epoxy resins (A) include polymers or oligomers containing two or more epoxy groups in the molecule, and polymers or oligomers resulting from the ring-opening reaction of some of the epoxy groups in the above polymers or oligomers.

[0041]

Specific examples of the epoxy resins (A) include bisphenol epoxy resins, for example, bisphenol A epoxy resins such as epichlorohydrin-bisphenol A epoxy resin; bisphenol AD epoxy resins such as epichlorohydrin-bisphenol AD epoxy resin;

bisphenol F epoxy resins such as epoxy novolak resin resulting from the reaction of epichlorohydrin with bisphenol F (4,4'-methylenebisphenol); aromatic epoxy resins such as 3,4-epoxyphenoxy-3',4'-epoxyphenylcarboxymethane;

- 5 brominated epoxy resins resulting from the bromination of epichlorohydrin-bisphenol A epoxy resin in place of at least part of the hydrogen atoms bonded to the benzene rings; aliphatic epoxy resins resulting from the reaction of epichlorohydrin with an aliphatic dihydric alcohol; and
- 10 polyfunctional epoxy resins resulting from the reaction of epichlorohydrin with tri(hydroxyphenyl)methane.

[0042]

Of these, the epoxy resin (A) is preferably at least one selected from the group consisting of bisphenol A epoxy resins, bisphenol AD epoxy resins and bisphenol F epoxy resins.

[0043]

The epoxy resins (A) may be used singly, or two or more may be used in combination.

A preferred weight average molecular weight of the epoxy resin (A) measured by gel permeation chromatography (GPC) (the measurement conditions are the same as or equivalent to those conditions used for the determination of the weight average molecular weight of copolymer (a3) in the section of Examples described later) is 350 to 20,000 though it depends on factors

such as the conditions under which the epoxy resin anticorrosive coating composition will be applied and cured (for example, whether the coating is dried at ambient temperature or the coating is carried out by baking). The viscosity (25°C) of the epoxy resin (A) is preferably not more than 12,000 cPs, and more preferably not more than 10,000 cPs.

[0044]

The epoxy equivalent of the epoxy resin (A) (measured in accordance with JIS K7236) is preferably 150 to 1,000 g/eq.

A preferred epoxy resin (A) is a bisphenol A epoxy resin having an epoxy equivalent of 150 to 700 g/eq.

[0045]

When two or more kinds of epoxy resins are used in combination, the weight average molecular weight and epoxy equivalent of the epoxy resin (A) are the weight average molecular weight and epoxy equivalent of the two or more kinds of epoxy resins as a whole.

[0046]

Typical examples of the bisphenol A epoxy resins which are liquid at room temperature include "jER 828" (manufactured by Mitsubishi Chemical Corporation, epoxy equivalent: 180 to 190 g/eq, viscosity: 12,000 to 15,000 cPs/25°C), "E-028-90X" (manufactured by Ohtake-Meishin Chemical Co., Ltd., 828 type epoxy resin (xylene-cut product NV: 90%), epoxy equivalent:

about 210 g/eq), and "AER260" (bisphenol A epoxy resin, Asahi Kasei Epoxy Co., Ltd., epoxy equivalent: 190 g/eq, NV: 100%).

Typical examples of the bisphenol A epoxy resins which are semi-solid at room temperature include "jER 834-X90"

5 (manufactured by Mitsubishi Chemical Corporation, epoxy equivalent: 230 to 270 g/eq/xylene-cut product NV: 90%), and "E-834-85X" (manufactured by Ohtake-Meishin Chemical Co., Ltd., epoxy equivalent: about 290 to 310 g/eq/xylene-cut product NV: 85%).

10 Typical examples of the bisphenol A epoxy resins which are solid at room temperature include "jER 1001-X75" (manufactured by Mitsubishi Chemical Corporation, epoxy equivalent: 600 to 650 g/eq/xylene-cut product NV: 75%), and "E-001-75X" (manufactured by Ohtake-Meishin Chemical Co., Ltd.,
15 epoxy equivalent: about 610 to 650 g/eq/xylene-cut product NV: 75%).

The content of the epoxy resin (A) is preferably 5 to 80 mass%, and more preferably 10 to 50 mass% of the anticorrosive coating composition.

20 [0047]

Solid thermoplastic resins (B)

The solid thermoplastic resin (B) is a resin that is solid at room temperature (23°C). Being solid at room temperature means that the resin retains the shape after being allowed to

stand at room temperature and ordinary pressure (23°C and 1 atm) for one day.

[0048]

The incorporation of the solid thermoplastic resin (B) in the anticorrosive coating composition reduces the amount of unreacted epoxy resin in the epoxy resin (A) that migrates from the anticorrosive coating film into an antifouling coating film disposed on the anticorrosive coating film, thus making it possible to reduce or prevent the decrease in the antifouling performance (in particular, static antifouling properties) of the antifouling coating film.

[0049]

The weight average molecular weight of the solid thermoplastic resin (B) measured by GPC (the detailed measurement conditions will be described later in the section of Examples) is preferably 5,000 to 100,000, and more preferably 20,000 to 80,000.

[0050]

A more preferred solid thermoplastic resin (B) is one having a glass transition temperature of not less than 30°C.

Examples of the solid thermoplastic resins (B) include chlorinated polyolefins, acrylic resins, butyl acetate resins, styrene resins and vinyl chloride resins.

[0051]

Of these solid thermoplastic resins, examples of commercially available acrylic resins include solid acrylic resins obtained by copolymerizing acrylic acid with an ester or derivative thereof, and solid methacrylic resins obtained by copolymerizing methacrylic acid with an ester or derivative thereof, such as DIANAL BR106 (manufactured by Mitsubishi Rayon Co., Ltd., Mw = 60,000) and PARALOID B66 (manufactured by The Dow Chemical Company, Mw = 70,000).

[0052]

Of the resins described above, vinyl chloride resins are particularly preferable as the solid thermoplastic resin (B) in light of very small impacts on the adhesion with respect to the antifouling coating film, and on the damage resistance and antifouling properties of the film.

Of the vinyl chloride resins, vinyl chloride/vinyl isobutyl ether copolymers are more preferable, and those having a glass transition temperature of not less than 30°C are still more preferable. Examples of commercially available such vinyl chloride/vinyl isobutyl ether copolymers include "Laroflex LR8829", "Laroflex MP-25" (Mw = 28,000 to 30,000), "Laroflex MP-35" and "Laroflex MP-45" manufactured by BASF. Of the above vinyl chloride/vinyl isobutyl ether copolymers, "Laroflex MP-25" is particularly preferable because the use thereof results in a minor increase in the coating viscosity

of the obtainable epoxy resin anticorrosive coating composition and thus provides excellent coating workability.

The solid thermoplastic resins may be used singly, or two or more may be used in combination.

5 [0053]

In order to reduce or prevent the decrease in antifouling performance (in particular, static antifouling properties) by the migration of unreacted epoxy resin in the epoxy resin (A) from the anticorrosive coating film into an antifouling coating
10 film disposed on the anticorrosive coating film, the amount of the solid thermoplastic resin (B) in the anticorrosive coating composition is not less than 50 parts by mass, and preferably not less than 60 parts by mass per 100 parts by mass of the epoxy resin (A). To ensure that the anticorrosive
15 coating film will exhibit excellent anticorrosive properties, over-coatability and drying properties, the upper limit of the amount is preferably 100 parts by mass, and more preferably 80 parts by mass.

[0054]

20 Amine curing agent (C)

The amine curing agent (C) is not particularly limited as long as it contains an active hydrogen and is reactive with the epoxy resin (A). Aliphatic amines, alicyclic amines, aromatic amines and heterocyclic amines are preferable.

[0055]

Specific examples of the aliphatic amines include ethylenediamine, diethylenetriamine, triethylenetetramine, tetrakis(2-aminoethylaminomethyl)methane,

5 1,3-bis(2'-aminoethylamino)propane,

triethylene-bis(trimethylene)hexamine,

bis(3-aminoethyl)amine, bishexamethylenetriamine

$[\text{H}_2\text{N}(\text{CH}_2)_6\text{NH}(\text{CH}_2)_6\text{NH}_2]$ and bis(cyanoethyl)diethylenetriamine.

[0056]

10 Examples of the alicyclic amines include

1,4-cyclohexanediamine, 4,4'-methylenebiscyclohexylamine,

4,4'-isopropylidenebiscyclohexylamine, norbornanediamine

(NBDA/2,5- and 2,6-bis(aminomethyl)-bicyclo[2,2,1]heptane),

bis(aminomethyl)cyclohexane, diaminodicyclohexylmethane,

15 isophoronediamine

(IPDA/3-aminomethyl-3,5,5-trimethylcyclohexylamine) and

menthenediamine.

[0057]

Examples of the aromatic amines include

20 o-xylylenediamine, m-xylylenediamine (MXDA),

p-xylylenediamine, phenylenediamine, naphthylenediamine,

diaminodiphenylmethane, diaminodiethylphenylmethane,

2,2-bis(4-aminophenyl)propane, 4,4'-diaminodiphenyl ether,

4,4'-diaminobenzophenone, 4,4'-diaminodiphenylsulfone,

2,2'-dimethyl-4,4'-diaminodiphenylmethane,
 2,4-diaminobiphenyl, 2,3'-dimethyl-4,4'-diaminobiphenyl,
 3,3'-dimethoxy-4,4'-diaminobiphenyl,
 bis(aminomethyl)naphthalene, bis(aminoethyl)naphthalene and
 5 2,4,6-tris(3-aminomethylphenylmethylaminomethyl)phenol.

[0058]

Examples of the heterocyclic amines include

N-methylpiperazine, morpholine,
 1,4-bis-(3-aminopropyl)-piperazine,
 10 piperazine-1,4-diazacycloheptane,
 1-(2'-aminoethylpiperazine),
 1-[2'-(2"-aminoethylamino)ethyl]piperazine,
 1,11-diazacycloeicosane and 1,15-diazacyclooctacosane.

[0059]

15 Further, polyamides, modified polyamides, epoxy resin
 adducts and Mannich modified products of the above amines may
 be used as the amine curing agents (C).

The active hydrogen equivalent weight (amine equivalent
 weight) of the amine curing agent (C) is preferably 50 to 1,000
 20 g/eq, and more preferably 70 to 500 g/eq.

[0060]

Examples of commercially available amine curing agents
 (C) include LUCKAMIDE TD-966 (manufactured by DIC CORPORATION,
 polyamide, active hydrogen equivalent weight: 377 g/eq), PA-66

(manufactured by Ohtake-Meishin Chemical Co., Ltd., polyamide, active hydrogen equivalent weight: 377 g/eq), PA-290 (A)

(manufactured by Ohtake-Meishin Chemical Co., Ltd., active hydrogen equivalent weight: 277 g/eq), Ancamide 2050

5 (manufactured by Air Products and Chemicals, Inc., polyamide adduct, active hydrogen equivalent weight: 150 g/eq), and NX-4918 (manufactured by Cardolite Corporation, phenalkamine (Mannich reaction product of cardanol and amine) adduct, active hydrogen equivalent weight: 255 g/eq).

10 [0061]

The amount of the amine curing agent (C) in the anticorrosive coating composition is preferably 10 to 100 parts by mass, and more preferably 20 to 100 parts by mass per 100 parts by mass of the epoxy resin (A). This amount of the amine curing agent (C) is preferable from the points of view of the curability of the anticorrosive coating film, drying properties when the coating composition contains a solvent, and the damage resistance of the layered antifouling coating film.

20 [0062]

(Other ingredients)

The epoxy resin anticorrosive coating composition is usually prepared by providing an anticorrosive coating composed of a main agent component including the epoxy resin

(A) and the solid thermoplastic resin (B), and a curing agent component including the amine curing agent (C), and by mixing the main agent component and the curing agent component with each other immediately before the coating operation.

5 [0063]

Where necessary, the main agent component may contain additives such as a curing accelerator (D), a pigment (E), an adhesion promoter (F), a solvent (G), an anti-sagging/anti-settling agent (H), a dehydrator
10 (stabilizer) (I) and any of other film-forming additives (such as dispersants, antifoaming agents and leveling agents) while still achieving the object of the invention. The curing agent component may contain additives such as a curing accelerator (D) and a solvent (G) as required while still achieving the
15 object of the invention.

[0064]

Curing accelerators (D)

Examples of the curing accelerators (D) include tertiary amines. Specific examples of the tertiary amines include
20 triethanolamine ($N(C_2H_5OH)_3$), dialkylaminoethanol ($[CH_3(CH_2)_n]_2NCH_2OH$, n: repeating number), triethylenediamine (1,4-diazabicyclo(2,2,2)octane),
2,4,6-tris(dimethylaminomethyl)phenol ($C_6H_5-CH_2N(CH_3)_2$),
"Versamine EH30" (manufactured by Henkel Hakusui Corp.) and

"Ancamine K-54" (manufactured by Air Products and Chemicals, Inc.).

[0065]

Examples of the curing accelerators (D) further include
5 acrylate ester curing accelerators.

In order to increase the rate of the curing of the epoxy resin (A) by the amine curing agent (C) and to ensure that the obtainable anticorrosive coating film will attain excellent adhesion with respect to an overcoat film, that is, an
10 antifouling coating film and will exhibit excellent flexibility, the amount of the curing accelerator (D) in the anticorrosive coating composition is preferably 0.1 to 5.0 mass% relative to the amount of nonvolatile components in the anticorrosive coating composition taken as 100 mass%.

15 [0066]

In the invention, the amount of "nonvolatile components in the anticorrosive coating composition (or in an antifouling coating composition)" is the amount of residues resulting from heating of the anticorrosive coating composition of the
20 invention (or an antifouling coating composition described later) that is measured in accordance with JIS K5601 1-2 (heating temperature: 125°C, heating time: 60 minutes).

[0067]

Pigments (E)

Examples of the pigments (E) include extender pigments, color pigments and anticorrosive pigments.

Specific examples of the extender pigments include barium sulfate, potassium feldspar, barite powder, silica, calcium carbonate, talc, mica, glass flakes and aluminum stearate.
[0068]

Specific examples of the color pigments include titanium white, red oxide, yellow oxide and carbon black.

Examples of the anticorrosive pigments include aluminum paste, zinc chromate and zinc phosphate. From the point of view of film properties (such as crack resistance), a paste of aluminum scales is preferable.
[0069]

The amount of the extender pigment in the anticorrosive coating composition is preferably 0.1 to 80 mass% relative to the amount of nonvolatile components in the anticorrosive coating composition taken as 100 mass%.

The amount of the color pigment is preferably 0.1 to 50 mass% relative to the amount of nonvolatile components in the anticorrosive coating composition taken as 100 mass%.

The amount of the anticorrosive pigment is preferably 0.1 to 50 mass% relative to the amount of nonvolatile components in the anticorrosive coating composition taken as 100 mass%.
[0070]

Adhesion promoters (F)

Examples of the adhesion promoters (F) include organic acids, chelating agents and silane coupling agents. In particular, silane coupling agents are preferable from the point of view of the storage stability of the anticorrosive coating composition.

[0071]

The silane coupling agent usually has two kinds of functional groups in the molecule and contributes to enhancements such as increasing the adhesion of the anticorrosive coating film with respect to inorganic substrates, and reducing the viscosity of the anticorrosive coating composition. For example, the silane coupling agent is represented by the formula: $X-Si(OR)_3$ [wherein X is a functional group capable of reacting with an organic material (for example, an amino group, a vinyl group, an epoxy group, a mercapto group, a halogen group or a hydrocarbon group containing any of these groups (the hydrocarbon group may contain an ether bond or the like)), and OR is a hydrolyzable group (for example, a methoxy group or an ethoxy group)]. Preferably, the silane coupling agent has reactivity with respect to the epoxy resin (A) or the amine curing agent (C).

[0072]

Specific examples of commercially available silane coupling agents include "KBM403"

(γ -glycidoxypyltrimethoxysilane, manufactured by Shin-Etsu Chemical Co., Ltd.) and "Silane S-510" (manufactured
5 by CHISSO CORPORATION).

[0073]

When the silane coupling agent is used, the amount thereof in the anticorrosive coating composition is preferably 0.1 to 10 mass%, and more preferably 0.5 to 5 mass% relative to the
10 amount of nonvolatile components in the anticorrosive coating composition taken as 100 mass%. This amount of the silane coupling agent ensures that the performance of the obtainable anticorrosive coating film such as adhesion will be enhanced and the anticorrosive coating composition will have low
15 viscosity and attain enhanced coating workability.

[0074]

Solvents (G)

Examples of the solvents (G) include xylene, toluene, methyl isobutyl ketone (MIBK), methoxypropanol, methyl ethyl
20 ketone (MEK), butyl acetate, n-butanol, isobutanol and isopropyl alcohol (IPA).

[0075]

The solvents may be used singly, or two or more may be used in combination.

For example, the content of the solvent (G) in the main agent component is 0.1 to 80 mass% and that in the curing agent component is 0.1 to 80 mass%.

[0076]

5 Anti-sagging/anti-settling agents (H)

Specific examples of the anti-sagging/anti-settling agents (thixotropic agents) (H) include such thixotropic agents as polyamide waxes, polyethylene waxes, bentonite thixotropic agents and OH-containing nanoparticles (AEROSIL
10 and resin beads).

[0077]

Examples of such anti-sagging/anti-settling agents include "DISPARLON 4200-20" and "DISPARLON 6650" manufactured by Kusumoto Chemicals, Ltd., and "ASAT-250F" manufactured by
15 ITOH OIL CHEMICALS CO., LTD.

The amount of nonvolatile components in the anti-sagging/anti-settling agent (H) present in the anticorrosive coating composition is preferably 0.1 to 30 mass% relative to the amount of nonvolatile components in the
20 anticorrosive coating composition taken as 100 mass%.

[0078]

Dehydrators (stabilizers) (I)

The anticorrosive coating composition of the invention may contain a dehydrator (stabilizer) (I) as required, in which

case the composition attains a further enhancement in long-term storage stability.

[0079]

Examples of the dehydrators (I) include inorganic
5 dehydrators and organic dehydrators. Some preferred inorganic dehydrators are synthetic zeolite, gypsum anhydride and gypsum hemihydrate. Some preferred organic dehydrators are alkoxy silanes such as tetramethoxysilane, tetraethoxysilane, tetrabutoxysilane, tetraphenoxysilane,
10 methyltriethoxysilane, dimethyldiethoxysilane and trimethylethoxysilane, condensation products thereof, i.e. polyalkoxy silanes, and alkyl orthoformate esters such as methyl orthoformate and ethyl orthoformate.

The amount of the dehydrator (I) in the anticorrosive
15 coating composition is preferably 0.1 to 50 parts by mass per 100 parts by mass of the epoxy resin (A).

[0080]

(Anticorrosive coating compositions)

The anticorrosive coating composition of the invention
20 includes the epoxy resin (A), the solid thermoplastic resin (B) and the amine curing agent (C) described hereinabove, and may be prepared by mixing these components in accordance with a usual stirring method.

[0081]

(Reaction ratio between epoxy resin (A) and amine curing agent (C))

The epoxy resin (A) reacts with the amine curing agent (C) to form a film.

5 In the anticorrosive coating composition of the invention, the reaction ratio discussed here is represented by the formula (1) below when the composition does not contain a silane coupling agent, the formula (2) below when the composition contains a silane coupling agent reactive to the amine curing agent (C), or the formula (3) below when the composition contains a silane coupling agent reactive to the epoxy resin (A). In any of these cases, the reaction ratio is preferably in the range of 0.3 to 0.8, and more preferably 0.4 to 0.7.

[0082]

$$\text{Reaction ratio} = \frac{\frac{\text{Amount of amine curing agent (C)}}{\text{Active hydrogen equivalent weight of amine curing agent (C)}}}{\frac{\text{Amount of epoxy resin (A)}}{\text{Epoxy equivalent of epoxy resin (A)}}} \quad \dots (1)$$

$$\text{Reaction ratio} = \frac{\frac{\text{Amount of amine curing agent (C)}}{\text{Active hydrogen equivalent weight of amine curing agent (C)}}}{\frac{\text{Amount of epoxy resin (A)}}{\text{Epoxy equivalent of epoxy resin (A)}} + \frac{\text{Amount of silane coupling agent reactive to amine curing agent (C)}}{\text{Reactive group equivalent weight of silane coupling agent}}} \quad \dots (2)$$

$$\text{Reaction ratio} = \frac{\frac{\text{Amount of amine curing agent (C)}}{\text{Active hydrogen equivalent weight of amine curing agent (C)}} + \frac{\text{Amount of silane coupling agent reactive to epoxy resin (A)}}{\text{Reactive group equivalent weight of silane coupling agent}}}{\frac{\text{Amount of epoxy resin (A)}}{\text{Epoxy equivalent of epoxy resin (A)}}} \quad \dots (3)$$

(In the formulae (1) to (3), the units of the amount and the equivalent weight are g and g/eq, respectively.)

20 [0083]

In the above formulae, the "reactive group equivalent weight of silane coupling agent" is the value obtained by dividing the mass (g) of 1 mol of the silane coupling agent (namely, the molecular weight) by the number of functional groups capable of reacting with organic materials (hereinafter, also written as the "reactive groups") in the molecule of the silane coupling agent. As described hereinabove, the silane coupling agent that is used may be one having an amino group or an epoxy group as the reactive group. The calculation of the reaction ratio first involves a determination as to whether or not a silane coupling agent is to be used. When it is decided that a silane coupling agent is used, the type of the reactive groups is examined to determine whether the silane coupling agent is reactive to the epoxy resin (A) or to the amine curing agent (C). Next, an appropriate formula is selected from the formulae (1) to (3), and the reactive group equivalent weight of the silane coupling agent is determined.

[0084]

The above lower limit of the reaction ratio ensures that the epoxy resin (A) will be crosslinked with a large number of crosslinks and little epoxy resin components will remain unreacted, with the result that an anticorrosive coating film can be obtained with excellent curability and drying properties when the composition contains a solvent, and the obtainable

layered antifouling coating film attains inhibition of antifouling performance (in particular, static antifouling properties) degradation and attains excellent damage resistance.

5 [0085]

The above upper limit of the reaction ratio ensures that the amount of the amine curing agent (C) remaining unreacted in the resultant film is negligible so that it is possible to prevent problems such as poor water resistance and
10 discoloration of the film caused by the unreacted amine curing agent (C) attracting water.

[0086]

(PVC)

The nonvolatile components in the inventive
15 anticorrosive coating composition preferably have a pigment volume concentration (hereinafter, also written as the "PVC") defined by the formula (4) below of 25 to 50%, and more preferably 30 to 45%:

Pigment volume concentration (%) = Volume of pigment in
20 anticorrosive coating composition / (Volume of resins in anticorrosive coating composition + Volume of pigment in anticorrosive coating composition) × 100 ... (4)

[0087]

The "volume of resins" described in the denominator in the formula (4) is the total volume of the epoxy resin (A), the solid thermoplastic resin (B), the amine curing agent (C) and the curing accelerator (D).

5 The above lower limit of the PVC ensures that the obtainable film will have excellent drying properties and damage resistance.

 The above upper limit of the PVC ensures that the anticorrosive coating composition will not have a viscosity
10 that is so high that the coating workability of the composition is deteriorated, and also prevents a decrease in corrosion resistance caused by poor leveling properties of the film or the occurrence of pinholes or the like.

[0088]

15 [Epoxy resin anticorrosive coating films]

 An epoxy resin anticorrosive coating film of the invention (hereinafter, also written simply as the "anticorrosive coating film") is an anticorrosive coating film that is used as a anticorrosive coating film in a layered
20 antifouling coating film which includes the anticorrosive coating film and an antifouling coating film disposed on a surface of a substrate in the order of the anticorrosive coating film and the antifouling coating film from the substrate side. The epoxy resin anticorrosive coating film includes a matrix

including a cured epoxy resin and the solid thermoplastic resin (B) (except a cured product of the epoxy resin (A)).

[0089]

In another aspect, an anticorrosive coating film of the invention is a cured product from the inventive anticorrosive coating composition described hereinabove.

The anticorrosive coating film usually contains the solid thermoplastic resin (B) in 7 to 80 mass%, and preferably 7 to 50 mass%, and more preferably 7 to 30 mass%. By virtue of the inventive anticorrosive coating film containing the solid thermoplastic resin (B) in this proportion, it is possible, as described hereinabove, to reduce the amount of unreacted epoxy resin in the epoxy resin (A) that migrates into an antifouling coating film disposed on the anticorrosive coating film and thus to reduce the decrease in the antifouling performance (in particular, static antifouling properties) of the antifouling coating film.

[0090]

A method for producing an anticorrosive coating film of the invention includes a step of curing a film composed of the inventive anticorrosive coating composition. The anticorrosive coating film of the invention may be produced in a manner similar to that for producing conventional epoxy resin anticorrosive coating films except that the production

involves the anticorrosive coating composition of the invention as the anticorrosive paint.

The thickness of the anticorrosive coating film (the dry film thickness) is usually about 50 to 800 μm .

5 [0091]

[Layered antifouling coating films, antifouling substrates and other features]

A layered antifouling coating film of the invention includes an anticorrosive coating film and an antifouling coating film disposed on a surface of a substrate in this order from the substrate side. The anticorrosive coating film is the epoxy resin anticorrosive coating film of the invention described hereinabove.

An antifouling substrate of the invention includes a substrate and the inventive layered antifouling coating film disposed on a surface of the substrate in the order of the anticorrosive coating film and the antifouling coating film from the substrate side.

[0092]

20 (Antifouling coating compositions)

An antifouling coating composition for forming the antifouling coating film as an overcoat on the anticorrosive coating film may be a conventional antifouling coating composition. A hydrolyzable antifouling coating composition

is preferable in view of the fact that an antifouling coating film from such a composition can be particularly effectively prevented from a decrease in antifouling performance by the migration of unreacted epoxy resin in the epoxy resin (A) from the anticorrosive coating film into the antifouling coating film.

[0093]

Some example film-forming resins in the hydrolyzable antifouling coatings are:

10 metal salt-containing copolymers which have a side-chain terminal group represented by the general formula (I):



[in the formula (I), M represents zinc or copper, and R^1 is an organic group],

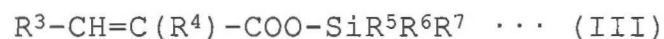
15 metal salt-containing copolymers which include structural units derived from a monomer represented by the general formula (II) below, and structural units derived from an unsaturated monomer that is copolymerizable with the above monomer:



[in the formula (II), M represents zinc or copper, and R^2 is a hydrogen atom or a methyl group], and

silyl ester-containing copolymers which include structural units derived from a monomer represented by the

general formula (III) below, and structural units derived from an unsaturated monomer that is copolymerizable with the above monomer:



5 [in the formula (III), R^4 is a hydrogen atom or a methyl group, R^5 , R^6 and R^7 are each independently a C_{1-20} monovalent organic group optionally having a heteroatom, and R^3 is a hydrogen atom or R^8-O-CO (wherein R^8 is a C_{1-20} monovalent organic group optionally having a heteroatom or is a silyl group
10 represented by $SiR^9R^{10}R^{11}$ wherein R^9 , R^{10} and R^{11} are each independently a C_{1-20} monovalent organic group optionally having a heteroatom)].

The use of these hydrolyzable resins is advantageous in that the obtainable antifouling coating composition attains
15 stable long-term antifouling properties and stable long-term film properties.

[0094]

Examples of the unsaturated monomers that are copolymerizable with the monomers represented by the general
20 formula (II) or the general formula (III) include (meth)acrylate esters, monocarboxylic acids, dicarboxylic acids as well as half esters (monoesters) and diesters thereof, vinyl esters and styrenes.

[0095]

Specific examples of the unsaturated monomers include such (meth)acrylate esters as methyl (meth)acrylate, ethyl (meth)acrylate, butyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, lauryl (meth)acrylate, tridecyl (meth)acrylate, stearyl (meth)acrylate, allyl (meth)acrylate, cyclohexyl (meth)acrylate, benzyl (meth)acrylate, isobornyl (meth)acrylate, methoxy (meth)acrylate, ethoxy (meth)acrylate, glycidyl (meth)acrylate, tetrahydrofurfuryl (meth)acrylate, hydroxyethyl (meth)acrylate, hydroxypropyl (meth)acrylate and hydroxybutyl (meth)acrylate; such monocarboxylic acids as (meth)acrylic acid; such dicarboxylic acids as itaconic acid, maleic acid and succinic acid, and half esters (monoesters) and diesters thereof; such styrenes as styrene and α -methylstyrene; and such vinyl esters as vinyl acetate and vinyl propionate. These monomers may be used singly, or two or more may be used in combination.

[0096]

From the point of view of film properties, the amount of the film-forming resin in the antifouling coating composition is preferably 5 to 50 mass%, and more preferably 5 to 30 mass% relative to the amount of nonvolatile components in the antifouling coating composition taken as 100 mass%.

[0097]

Where necessary, the antifouling coating composition further includes components selected from, among others, rosins and/or monocarboxylic compounds, copper or copper compounds, organic antifouling agents, color pigments, extender pigments, dehydrators, plasticizers, pigment dispersants, anti-sagging agents, anti-settling agents and solvents.

[0098]

Rosins and/or monocarboxylic compounds

Examples of the rosins include such rosins as gum rosin, wood rosin and tall oil rosin, and rosin derivatives such as hydrogenated rosin and disproportionated rosin. Rosin is a residue that remains after the distillation of pine resin, a pine tree sap. This naturally occurring resin is chiefly composed of rosin acids (such as abietic acid, palustric acid and isopimaric acid).

[0099]

Examples of the monocarboxylic compounds include aliphatic or alicyclic monocarboxylic acids, derivatives thereof, and metal salts thereof. Specific examples of the monocarboxylic compounds include naphthenic acid, cycloalkenylcarboxylic acid, bicycloalkenylcarboxylic acid, versatic acid, trimethylisobutenylcyclohexenecarboxylic acid,

stearic acid, hydroxystearic acid, salicylic acid and metal salts of these acids.

[0100]

The mass ratio (W_A/W_B) of the mass (W_A) of the film-forming resin to the mass (W_B) of the rosin and/or the monocarboxylic compound is preferably 99.9/0.1 to 30/70, more preferably 95/5 to 35/65, and still more preferably 90/10 to 40/60. This mass ratio ensures that the antifouling coating film will attain higher self-polishing properties (film consumption properties) and consequently antifouling properties (in particular, static antifouling properties) will be enhanced.

[0101]

Copper or copper compounds

The copper compounds may be any organic or inorganic copper compounds, with examples including powdery copper (copper powder), cuprous oxide, copper thiocyanate, cupronickel and copper pyrithione.

[0102]

From the point of view of long-term antifouling properties, the amount of the copper or the copper compound (the total amount of the copper and the copper compound) in the antifouling coating composition is preferably 0.1 to 90 mass%, and more preferably 0.5 to 80 mass% relative to the amount

of nonvolatile components in the antifouling coating composition taken as 100 mass%.

[0103]

Organic antifouling agents

5 Examples of the organic antifouling agents include metal
pyrithiones (except copper pyrithione) such as zinc pyrithione,
4,5-dichloro-2-n-octyl-4-isothiazolin-3-one,
4-bromo-2-(4-chlorophenyl)-5-(trifluoromethyl)-1H-pyrrole-
3-carbonitrile, pyridinetriphenylborane,
10 4-isopropylpyridinediphenylmethylborane,
N,N-dimethyl-N'-(3,4-dichlorophenyl)urea,
N-(2,4,6-trichlorophenyl)maleimide,
2,4,5,6-tetrachloroisophthalonitrile,
2-methylthio-4-tert-butylamino-6-cyclopropylamino-1,3,5-tri-
15 iadine, medetomidine, bisdimethyldithiocarbamoylzinc
ethylenebisdithiocarbamate, chloromethyl-n-octyl disulfide,
N',N'-dimethyl-N-phenyl-(N-fluorodichloromethylthio)sulfam-
ide, tetraalkylthiuram disulfide, zinc
dimethyldithiocarbamate, zinc ethylenebisdithiocarbamate,
20 2,3-dichloro-N-(2',6'-diethylphenyl)maleimide and
2,3-dichloro-N-(2'-ethyl-6'-methylphenyl)maleimide.

[0104]

From the points of view of long-term antifouling properties and the retention of water resistance of the

antifouling coating film (the retention of mechanical characteristics), the amount of the organic antifouling agent in the antifouling coating composition is preferably 0.1 to 90 mass%, and more preferably 0.5 to 80 mass% relative to the amount of nonvolatile components in the antifouling coating composition taken as 100 mass%.

[0105]

Color pigments

Examples of the color pigments include various known organic and inorganic color pigments. Examples of the organic color pigments include carbon black, naphthol red and phthalocyanine blue. Examples of the inorganic color pigments include red oxide, barite powder, titanium white and yellow iron oxide.

[0106]

The antifouling coating composition may include colorants except the color pigments, such as dyes, together with or instead of the color pigments.

From the points of view of coloring properties, hiding properties, exposure discoloration resistance, antifouling properties and water resistance (mechanical characteristics) of the antifouling coating film, the amount of the color pigment in the antifouling coating composition is preferably 0.01 to 50 mass%, and more preferably 0.1 to 30 mass% relative to the

amount of nonvolatile components in the antifouling coating composition taken as 100 mass%.

[0107]

Extender pigments

5 Examples of the extender pigments include talc, silica, mica, clay, potassium feldspar, zinc oxide, calcium carbonate, kaolin, alumina white, white carbon, aluminum hydroxide, magnesium carbonate, barium carbonate and barium sulfate. Of these, preferred extender pigments are talc, silica, mica, clay,
10 calcium carbonate, kaolin, barium sulfate, potassium feldspar and zinc oxide. Calcium carbonate and white carbon are also used as anti-settling agents described later.

[0108]

 From the points of view of water resistance (mechanical
15 characteristics) of the antifouling coating film, antifouling properties and hydrolyzability (consumption properties) of the antifouling coating film, the amount of the extender pigment in the antifouling coating composition is preferably 0.1 to 80 mass%, and more preferably 0.5 to 70 mass% relative to the
20 amount of nonvolatile components in the antifouling coating composition taken as 100 mass%.

[0109]

Dehydrators

Examples of the dehydrators include known gypsum and tetraethoxysilane.

In order to effectively prevent an increase in viscosity during storage, the amount of the dehydrator in the antifouling coating composition is preferably 0.01 to 30 mass%, and more preferably 0.1 to 20 mass% relative to the amount of nonvolatile components in the antifouling coating composition taken as 100 mass%.

[0110]

10 Plasticizers

Examples of the plasticizers include paraffin chlorides (chlorinated paraffins), petroleum resins, ketone resins, TCP (tricresyl phosphate), polyvinyl ethyl ether and dialkyl phthalates. From the points of view of water resistance (mechanical characteristics) of the antifouling coating film and hydrolyzability (consumption properties) of the antifouling coating film, preferred plasticizers are paraffin chlorides (chlorinated paraffins), petroleum resins and ketone resins.

20 [0111]

Specific examples of the paraffin chlorides include "TOYOPARAX 150" and "TOYOPARAX A-70" (both manufactured by Tosoh Corporation). Examples of the petroleum resins include C5 resins, C9 resins, styrene resins, dichloropentadiene

resins and hydrogenated products of these resins. Specific examples of the petroleum resins include "Quintone 1500" and "Quintone 1700" (both manufactured by ZEON CORPORATION).

[0112]

5 From the points of view of antifouling properties, water resistance (mechanical characteristics) of the antifouling coating film and, when the film-forming resin is hydrolyzable, hydrolyzability (consumption properties) of the antifouling coating film, the amount of the plasticizer in the antifouling
10 coating composition is preferably 0.1 to 80 mass%, and more preferably 0.5 to 70 mass% relative to the amount of nonvolatile components in the antifouling coating composition taken as 100 mass%.

[0113]

15 Pigment dispersants

 Examples of the pigment dispersants include known various organic and inorganic pigment dispersants such as aliphatic amines and organic acids (for example, "Duomeen TDO" (manufactured by Lion Corporation) and "Disperbyk 101" (manufactured by BYK Japan K.K.)).

[0114]

 In order to obtain low coating viscosity and to prevent flooding, the amount of the pigment dispersant in the antifouling coating composition is preferably 0.01 to 20 mass%,

and more preferably 0.1 to 10 mass% relative to the amount of nonvolatile components in the antifouling coating composition taken as 100 mass%.

[0115]

5 Anti-sagging agents

Examples of the anti-sagging agents include amide wax, hydrogenated castor oil wax, polyamide wax, mixtures of these waxes, and synthetic fine powdery silica. From the points of view of storage stability and recoatability or overcoatability
10 with coatings of the same kind or different kinds, particularly preferred anti-sagging agents are amide wax and synthetic fine powdery silica.

[0116]

Some example commercially available anti-sagging agents
15 are "DISPARLON A630-20X" (manufactured by Kusumoto Chemicals, Ltd.) and "ASAT-250F" (manufactured by ITOH OIL CHEMICALS CO., LTD.).

From the points of view of storage stability and recoatability or overcoatability with coatings of the same kind
20 or different kinds, the amount of the anti-sagging agent in the antifouling coating composition is preferably 0.1 to 50 mass%, and more preferably 0.5 to 30 mass% relative to the amount of nonvolatile components in the antifouling coating composition taken as 100 mass%.

[0117]

Anti-settling agents

Examples of the anti-settling agents include amine salts of Al, Ca or Zn, polyethylene wax and polyethylene oxide wax.

- 5 In particular, polyethylene oxide wax is preferable. An example commercially available polyethylene oxide wax is "DISPARLON 4200-20X" (manufactured by Kusumoto Chemicals, Ltd.).

[0118]

- 10 From the points of view of storage stability and recoatability or overcoatability with coatings of the same kind or different kinds, the amount of the anti-settling agent in the antifouling coating composition is preferably 0.1 to 50 mass%, and more preferably 0.5 to 30 mass% relative to the amount
15 of nonvolatile components in the antifouling coating composition taken as 100 mass%.

[0119]

Solvents

- The antifouling coating composition may include a solvent
20 such as water or an organic solvent as required in order to enhance dispersibility and to control the viscosity of the composition.

[0120]

Examples of the organic solvents include aromatic organic solvents such as xylene, toluene and ethylbenzene; ketones such as methyl ethyl ketone, methyl isobutyl ketone and cyclohexanone; aliphatic (having about 1 to 10 carbon atoms, or preferably about 2 to 5 carbon atoms) monohydric alcohols such as ethanol, isopropyl alcohol, n-butanol and isobutanol; and ester solvents such as ethyl acetate and butyl acetate. The amount of the solvent in the antifouling coating composition is usually 5 to 80 mass%, and preferably 10 to 70 mass% relative to the amount of the antifouling coating composition taken as 100 mass%.

[0121]

(Methods for producing layered antifouling coating films, and other features)

A method for producing a layered antifouling coating film of the invention includes a step of forming an epoxy resin anticorrosive coating film of the invention, and a step of forming an antifouling coating film described hereinabove on the surface of the epoxy resin anticorrosive coating film. A method for producing an antifouling substrate of the invention includes a step of forming a layered antifouling coating film of the invention on a surface of a substrate.

[0122]

Thus, layered antifouling coating films and antifouling substrates of the invention may be produced by conventional methods except that the production involves the epoxy resin anticorrosive coating film of the invention as the epoxy resin
5 anticorrosive coating film. Specifically, a layered antifouling coating film or an antifouling substrate of the present invention may be produced by applying the inventive epoxy resin anticorrosive coating composition onto a surface of a substrate by a conventional technique followed by usual
10 curing to form an epoxy resin anticorrosive coating film, and applying the above-described antifouling coating composition onto the surface of the epoxy resin anticorrosive coating film by a conventional technique followed by usual curing.

[0123]

15 The substrate is preferably one which is required to exhibit anticorrosive properties and antifouling properties in water. Examples thereof include underwater structures such as marine vessels (for example, bottom portions of ships), fishing materials, and water inlets and outlets in thermal power
20 plants and nuclear power plants, and sludge diffusion prevention films used in various marine civil engineering works such as coastal roads, undersea tunnels, harbor facilities, canals and waterways. Some exemplary materials of the substrates are steel, aluminum, wood and FRP. The layered

antifouling coating films of the invention disposed on the surface of these substrates exhibit excellent performance (antifouling properties, in particular, static antifouling properties) in preventing the attachment of aquatic organisms such as sea lettuce, barnacles, green laver, serpula, oysters and bryozoans (*Bugula neritina*) over a long term.

[0124]

The thickness of the antifouling coating film (the dry film thickness) is not particularly limited. When, for example, the substrate is a marine vessel or an underwater structure, the thickness is about 50 to 2000 μm .

EXAMPLES

[0125]

Hereinbelow, the present invention will be described in greater detail based on Examples and Comparative Examples. However, the scope of the invention is not limited to such Examples presented below.

(Preparation of metal salt-containing hydrolyzable antifouling coating S1 and silyl ester-containing hydrolyzable antifouling coating S2)

(Production of metal salt-containing copolymer (a2) solution)

[Production Example 1]

A four-necked flask equipped with a condenser, a thermometer, a dropping funnel and a stirrer was loaded with

85.4 parts by mass of propylene glycol methyl ether (PGM) and 40.7 parts by mass of zinc oxide. While performing stirring, the mixture was heated to 75°C.

[0126]

5 To the resultant milky white mixture, a mixture including 50.0 parts by mass of methacrylic acid (MAA), 36.1 parts by mass of acrylic acid (AA) and 5 parts by mass of water was added dropwise through the dropping funnel at a constant rate over a period of 3 hours. The dropwise addition resulted in a
10 transparent reaction solution. Stirring was performed for another 2 hours, and thereafter 36 parts by mass of propylene glycol methyl ether (PGM) was added. Thus, a transparent, metal salt-containing monomer (a1) solution was obtained. The solid content in the metal salt-containing monomer (a1)
15 solution was 44.8 mass%.

[0127]

Table 1 Production of metal salt-containing monomer (a1)

Amounts (parts by mass)				Metal salt-containing monomer (a1) solution		
				Volatile components (mass%)		Nonvolatile components (mass%)
MAA	AA	ZnO	Water	PGM	Water	
50.0	36.1	40.7	5	53.2	2	44.8

[0128]

[Production Example 2]

20 A four-necked flask equipped with a condenser, a thermometer, a dropping funnel and a stirrer was loaded with 15 parts by mass of propylene glycol methyl ether (PGM), 57

parts by mass of xylene and 4 parts by mass of ethyl acrylate. While performing stirring, the mixture was heated to 100°C. [0129]

To the resultant mixture, a transparent mixture including
5 1 part by mass of methyl methacrylate (MMA), 70.2 parts by mass of ethyl acrylate (EA), 5.4 parts by mass of 2-methoxyethyl acrylate (2-MEA), 52 parts by mass of the metal salt-containing monomer (a1) solution obtained in Production Example 1, 10 parts by mass of xylene, 1 part by mass of a chain transfer agent
10 ("NOFMER MSD" manufactured by NOF CORPORATION), 2.5 parts by mass of azoisobutyronitrile (AIBN, JAPAN FINECHEM COMPANY, INC.) and 7 parts by mass of
2,2'-azobis-(2-methylbutyronitrile) (AMBN) was added dropwise through the dropping funnel at a constant rate over a period
15 of 6 hours. (Hereinafter, this dropping step will be also written as the "dropping step 1".)
[0130]

After the dropwise addition, 0.5 parts by mass of t-butyl peroxyoctoate (TBPO) and 7 parts by mass of xylene were added
20 dropwise over a period of 30 minutes, and the mixture was stirred for 1 hour and half. Thereafter, 4.4 parts by mass of xylene was added. Thus, a transparent light yellow, metal salt-containing copolymer (a2) solution was obtained. The

data of the metal salt-containing copolymer (a2) such as raw materials and characteristics are described in Table 2.

[0131]

Table 2

5 Production of metal salt-containing copolymer (a2) (Production Example 2)

Components added in dropping step 1 (parts by mass)		
Metal salt-containing monomer	Metal salt-containing monomer (a1) solution (Production Example 1)	52
Comonomers	Methyl methacrylate	1
	Ethyl acrylate	70.2
	2-Methoxyethyl acrylate	5.4
Initiators	AIBN	2.5
	AMBN	7
Chain transfer agent	NOFMER MSD	1
Solvent	Xylene	10
Characteristics		
Metal salt-containing copolymer (a2) solution	Residue after heating (mass%)	45.6
	Viscosity (mPa·s)	2,120
Metal salt-containing copolymer (a2)	Number average molecular weight (Mn)	5,200

[0132]

(Production of silyl ester-containing copolymer (a3) solution)

[Production Example 3]

A reactor equipped with a stirrer, a reflux condenser,
 10 a thermometer, a nitrogen inlet tube and a dropping funnel was loaded with 53 parts by mass of xylene. In a nitrogen atmosphere and while performing stirring of xylene with the stirrer, heating was performed until the temperature of xylene in the reactor reached 85°C at ordinary pressure. While
 15 keeping the temperature of xylene in the reactor at 85°C, a monomer mixture including 50 parts by mass of TIPSMA (triisopropylsilyl methacrylate), 30 parts by mass of MEMA (2-methoxyethyl methacrylate), 10 parts by mass of MMA (methyl methacrylate), 10 parts by mass of BA (butyl acrylate) and 1

part by mass of 2,2'-azobis-(2-methylbutyronitrile) was added through the dropping funnel to the reactor over a period of 2 hours.

[0133]

5 Next, 0.5 parts by mass of t-butyl peroxyoctoate was added to the reactor. The liquid in the reactor was stirred with the stirrer for 2 hours while keeping its temperature at 85°C under ordinary pressure. The temperature of the liquid in the reactor was then increased from 85°C to 110°C and was held
10 constant for 1 hour. Thereafter, 14 parts by mass of xylene was added to the reactor and thereby the liquid in the reactor was allowed to cool. Stirring was discontinued when the liquid temperature reached 40°C. In this manner, a solution of a silyl ester-containing copolymer (a3) was prepared. The data of the
15 silyl ester-containing copolymer (a3) such as raw materials and characteristics are described in Table 3.

[0134]

Table 3

Production of silyl ester-containing copolymer (a3) (Production Example 3)

Formulation of monomer mixture (parts by mass)	TIPSMA	50
	MEMA	30
	MMA	10
	BA	10
Properties of copolymer (a3)		
Copolymer (a3) solution	Residue after heating (mass%)	59.9
	Viscosity (mPa·s)	3,580
Copolymer (a3)	Weight average molecular weight (Mw)	39,880

[0135]

- 5 (Evaluation of characteristics of metal salt-containing
copolymer (a2) and silyl ester-containing copolymer (a3))

The characteristics described above of the metal
salt-containing copolymer (a2) and the silyl ester-containing
copolymer (a3) were measured by the following methods.

- 10 (1) Content of residue after heating of copolymer solution

The copolymer solution weighing 1.5 g (X_1 (g)) was held
in a thermostatic chamber at 1 atm and 108°C for 3 hours to
remove volatile components, thus obtaining a residue
(nonvolatile components). Next, the weight of the residue
15 after heating (nonvolatile components) (X_2 (g)) was measured.
The content (%) of the residue after heating of the (co)polymer
solution was calculated using the following equation.

$$\text{Content of residue after heating (\%)} = X_2/X_1 \times 100$$

[0136]

- 20 (2) Average molecular weight of copolymer

The average molecular weight (number average molecular
weight (M_n) or weight average molecular weight (M_w)) of the

copolymer was measured by GPC (gel permeation chromatography) under the following conditions:

GPC conditions:

apparatus: HLC-8120GPC (manufactured by TOSOH

5 CORPORATION)

columns: Super H2000 + H4000 (manufactured by TOSOH CORPORATION, 6 mm (inner diameter), each 15 cm (in length))

eluting solution: tetrahydrofuran (THF)

flow rate: 0.500 ml/min

10 detector: RI

temperature of column thermostatic chamber: 40°C

standard: polystyrene

sample preparation method: The copolymer solution was dehydrated by the addition of a small amount of calcium chloride, and was filtered through a membrane filter. The filtrate was used as the GPC sample.

[0137]

(3) Viscosity of copolymer solution

The viscosity (unit: mPa·s) of the copolymer solution at a liquid temperature of 25°C was measured using a Brookfield viscometer (manufactured by TOKYO KEIKI INC.).

[0138]

(Production of metal salt-containing hydrolyzable antifouling coating S1 and silyl ester-containing hydrolyzable antifouling coating S2)

[Production Example 4]

5 A 1000 ml plastic container was loaded with xylene (16 g), the metal salt-containing copolymer (a2) solution (37 g), zinc oxide (20 g), TTK Talc (10 g), red oxide 404 (1.5 g), Novoperm Red F5RK (0.5 g), Zinc Omadine (8 g) and ECONEA (4 g). Further, 200 g of glass beads were added. The mixture
10 was dispersed for 1 hour. Thereafter, DISPARLON A630-20X (3.0 g) was added, and the mixture was dispersed for 15 minutes and was filtered through a 60 mesh net filter to give a metal salt-containing hydrolyzable antifouling coating S1. The list of the raw materials is described in Table 5.

15 [0139]

[Production Example 5]

A silyl ester-containing hydrolyzable antifouling coating S2 was prepared in the same manner as described above, except that the formulation was changed as shown in Table 4.

20 [0140]

Table 4 Formulations of antifouling coatings (unit: g)

		Prod. Ex. 4	Prod. Ex. 5
		Metal salt-containing hydrolyzable antifouling coating S1	Silyl ester-containing hydrolyzable antifouling coating S2
Hydrolyzable resins	Metal salt-containing copolymer (a2) Silyl ester-containing copolymer (a3)	37	22
Rosin	Gum rosin		4.5
Extender pigments	Zinc oxide	20	4
	TTK Talc	10	5
Color pigments	Red oxide 404	1.5	3
	Novoperm Red F5RK	0.5	
Antifouling agents	Zinc Omadine	8	
	ECONEA	4	
	Cuprous oxide NC301		50
	Copper Omadine		2
Thixotropic agent	DISPARLON A630-20X	3	2
Solvent	Xylene	16	7.5
Total		100	100

[0141]

<Preparation of anticorrosive coating compositions>

[Example 1]

5 An anticorrosive coating composition was prepared as described below.

(Main agent component)

A 1000 ml plastic container was loaded with MIBK (3 g), N-butyl alcohol (3 g), xylene (17 g), jER 1001-X75 (16 g),
 10 Laroflex MP-25 (6 g), TTK Talc (25 g), Barico 300W (8 g), mica powder 325 mesh (5 g), red oxide 404 (2 g), DISPARLON 6650 (1.5 g) and KBM 403 (0.5 g). Further, 200 g of glass beads were added. The mixture was dispersed for 1 hour. The list of the raw materials is described in Table 5. The dispersion was filtered
 15 through a 60 mesh net filter to give a main agent component of an anticorrosive coating.

[0142]

(Curing agent component)

A 200 ml plastic container was loaded with xylene (5.7 g), LUCKAMIDE TD-966 (7 g) and Ancamine K-54 (0.3 g). The mixture was dispersed for 10 minutes. The list of the raw materials is described in Table 5. The dispersion was filtered through a 60 mesh net filter to give a curing agent component of an anticorrosive coating.

[0143]

(Anticorrosive coating composition)

10 An anticorrosive coating composition was prepared by mixing the main agent component and the curing agent component with each other by a usual method immediately before the coating operation.

[0144]

15 [Examples 2 to 7 and Comparative Examples 1 to 7]

Anticorrosive coating compositions were prepared in the same manner as in Example 1, except that the formulations of the main agent component and the curing agent component were changed as shown in Table 6.

20 [0145]

Table 5 Raw materials of antifouling coatings and anticorrosive coatings

Names	Manufacturers	Categories	Solid content (mass%)
jER 834-90X	Mitsubishi Chemical Corporation	Epoxy resin	90
jER 1001-75X	Mitsubishi Chemical Corporation	Epoxy resin	75
Laroflex MP-25	BASe Japan	Vinyl chloride/vinyl isobutyl ether copolymer (Tg 50-52°C)	100
PARALOID B66	The Dow Chemical Company	Solid acrylic resin (Tg 50°C)	100
NECIREX EPX-L	Nevcin Polymers	Petroleum resin that is liquid at room temperature	100
Hirenol PL-1000S	Kolon Industries	Petroleum resin that is liquid at room temperature	100
TCP (tricresyl phosphate)	KYOWA HAKKO KOGYO CO., LTD.	Plasticizer that is liquid at room temperature	100
TTK Talc	Fukuoka Talc Co., LTD.	Extender pigment	100
Barico #300W	Hakusui Tech Co., Ltd.	Extender pigment	100
Mica powder 325 mesh	KURARAY CO., LTD.	Mica pigment	100
Alpaste 1900XS	TOYO ALUMINIUM K.K.	Aluminum paste	75
Red oxide 404	MORISHITA BENGARA KOGYO CO., LTD.	Color pigment	100
KBM403	Shin-Etsu Chemical Co., Ltd.	Coupling agent	100
DISPARLON 6650	Kusumoto Chemicals, Ltd.	Polyamide thixotropic agent	100
LUCKAMIDE TD-966	DIC CORPORATION	Polyamide curing agent	60
Ancamine K-54	Air Products and Chemicals, Inc.	Tertiary amine (curing accelerator)	100
Zinc oxide	Kyushu Hakusui Kagaku K.K.	Extender pigment	100
Red oxide 404	TODA KOGYO CORP.	Color pigment	100
Novoperm Red F5RK	Clariant North America	Organic red pigment	100
Gum rosin		Resin (acid value 168, softening point 75°C, Mw 287)	100
Copper Omadine	Arch Chemical, Inc.	2-Pyridinethiol-1-oxide copper salt (copper pyrithione)	100
ECONEA	Janssen Pharmaceutica NV	4-Bromo-2-(4-chlorophenyl)-5-(trifluoromethyl)-1H-pyrrole-3-carbonitrile	100
Zinc Omadine	Arch Chemical, Inc.	2-Pyridinethiol-1-oxide zinc salt (zinc pyrithione)	100
Cuprous oxide NC301	Nissin Chemco Co., Ltd.	Cuprous oxide	100
DISPARLON A630-20X	Kusumoto Chemicals, Ltd.	Anti-sagging agent	20

[0146]

Table 6 Formulations of anticorrosive coatings (unit: g)

		Examples										Comparative Examples						
		1	2	3	4	5	6	7	1	2	3	4	5	6	7			
Main agent component	Epoxy resins																	
	jER 834-X90 jER 1001-X75	16	16	14	13	16	14	13	18	17	16	14	14	14	13			
	Solid thermoplastic resins	6	6	7	8				3	3	4							
	PARALOID B-66					6	7	8										
	Hirenol PL-1000S NECIRES EPX-L TCP											7	7	7	8			
Main agent component	Adhesion promoter	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	
	KBM 403																	
	TTK Talc	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25		
	Barico 300W	8	8	8	8	8	8	8	8	8	8	8	8	8	8	8		
	Mica powder 325 mesh Alpaste 1900XS Red oxide 404	5 2	5 2	5 2	5 2	5 2	5 2	5 2	5 2	5 2	5 2	5 2	5 2	5 2	5 2	5 2		
Main agent component	Anti-sagging agent	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	
	DISPARLON 6650																	
	Solvents	17	17	18	18	17	18	18	17	18	18	18	18	18	18	18		
	Xylene	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3		
	N-butyl alcohol MIBK	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3		
Curing agent component	(Subtotal)	87	87	87	87	87	87	87	86	86	86	87	87	87	87	87	87	
	Amine curing agent	7	7	10	10	7	10	10	8	10	10	10	10	10	10	10	10	
	LUCKAMIDE TD-966																	
	Curing accelerator	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	
	Ancamine K-54																	
Curing agent component	Solvent	5.7	5.7	2.7	2.7	5.7	2.7	2.7	5.7	3.7	3.7	2.7	2.7	2.7	2.7	2.7	2.7	
	Xylene	13	13	13	13	13	13	13	14	14	14	13	13	13	13	13	13	
	(Subtotal)	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	
	[Total]																	
	Amount (parts by mass) of solid thermoplastic resin per 100 parts by mass of epoxy resin (solid content)	50	50	56	68	50	56	68	22	20	28	56	56	56	56	56	68	
Curing agent component	PVC (%)	43	42	39	39	42	38	38	44	40	39	38	37	38	38	38	38	
	Reaction ratio between epoxy resin and amine curing agent	0.68	0.68	0.51	0.55	0.68	0.51	0.55	0.70	0.43	0.45	0.51	0.51	0.51	0.51	0.51	0.55	

[0147]

⟨Fabrication and evaluation of layered antifouling coating films⟩

(1) Consumption properties of layered antifouling coating
5 films

With use of an applicator, the anticorrosive coating compositions prepared in Examples 1 to 7 and Comparative Examples 1 to 7 were each applied to a 50 mm × 50 mm × 1.5 mm hard vinyl chloride plate so that the dry film thickness would
10 be 150 μm. After one day after the coating operation, the metal salt-containing hydrolyzable antifouling coating S1 or the silyl ester-containing hydrolyzable antifouling coating S2 was applied with an applicator so that the dry film thickness would be 100 μm. The coating was dried at 23°C for 7 days. Test
15 plates having a layered antifouling coating film were thus fabricated.

[0148]

The test plates were mounted to the side of a rotary drum disposed in a thermostatic bath containing 25°C seawater. The
20 rotary drum was rotated at a peripheral speed of 15 knots. The cumulative consumption (thickness loss (μm)) of the antifouling coating film was measured on a monthly basis after the mounting.

[0149]

(2) Static antifouling properties of layered antifouling coating films

With use of an air sprayer, the anticorrosive coating compositions prepared in Examples 1 to 7 and Comparative

5 Examples 1 to 7 were each applied to a 100 mm × 300 mm × 3.2 mm sandblasted steel plate so that the dry film thickness would be 150 μ m. After one day after the coating operation, the metal salt-containing hydrolyzable antifouling coating S1 or the silyl ester-containing hydrolyzable antifouling coating S2 was
10 applied with an air sprayer so that the dry film thickness of the antifouling coating film would be 100 μ m. The coating was dried at 23°C for 7 days. Test plates having a layered antifouling coating film were thus fabricated.

[0150]

15 The test plates were immersed in the sea under static conditions at the bay of Nagasaki, Japan. The area fouled by marine organisms (the percentage (%) of the area fouled by marine organisms to the total area of the antifouling coating film of the test plate taken as 100%) was visually measured
20 on a monthly basis during the immersion. The static antifouling properties were evaluated based on the following criteria.

0: No marine organisms were attached.

0.5: The area fouled by marine organisms was above 0% and not more than 10%.

1: The area fouled by marine organisms was above 10% and not more than 20%.

5 2: The area fouled by marine organisms was above 20% and not more than 30%.

3: The area fouled by marine organisms was above 30% and not more than 40%.

10 4: The area fouled by marine organisms was above 40% and not more than 50%.

5: The area fouled by marine organisms was above 50%.
[0151]

(3) Damage resistance of layered antifouling coating films

With use of an air sprayer, the anticorrosive coating
15 compositions prepared in Examples 1 to 7 and Comparative
Examples 1 to 7 were each applied to a 70 mm × 150 mm × 1.6
mm sandblasted steel plate so that the dry film thickness would
be 150 μm. The coating was allowed to stand at 5°C for one day,
thus forming an anticorrosive coating film. After one day
20 after the coating operation, the metal salt-containing
hydrolyzable antifouling coating S1 or the silyl
ester-containing hydrolyzable antifouling coating S2 was
applied onto the surface of the anticorrosive coating film with
an air sprayer so that the dry film thickness of the antifouling

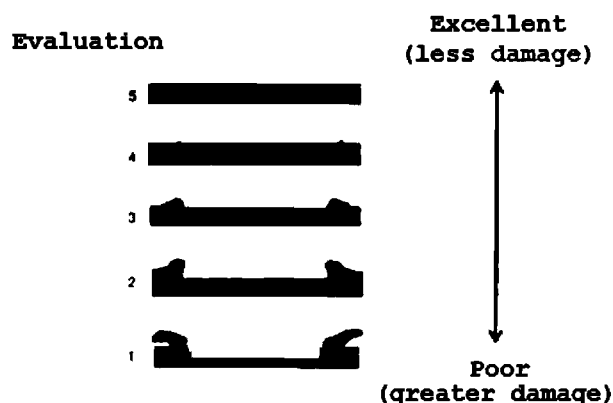
coating film would be 150 μm . The coating was dried at 5°C. Test plates having a layered antifouling coating film were thus fabricated. After one day, two days and three days after the start of the drying of the antifouling coating film, a 30 mm
5 $\times$ 30 mm $\times$ 10 mm wood piece was placed on a central region of the antifouling coating film and a pressure of 40 kgf/cm² (3.9 MPa) was applied in the vertical direction onto the wood piece for 20 minutes. The surface condition of the film was observed (namely, the degree of the deformation of the film was measured),
10 and the damage resistance was evaluated based on the following criteria.

5: The film was free from deformation and the surface condition was excellent.

4: The film had been slightly deformed but the surface
15 condition was good.

3, 2 and 1: The film had been significantly deformed, and the steel plate was partly exposed. The degree of damage (deformation) is greater in the order of 3, 2 and 1.

[0152]



[0153]

[Comparative Reference Examples]

Single antifouling coating films formed from each of the metal salt-containing hydrolyzable antifouling coating S1 and the silyl ester-containing hydrolyzable antifouling coating S2 were tested in the following manner.

[0154]

(1) Consumption properties of antifouling coating films

With use of an applicator, the metal salt-containing hydrolyzable antifouling coating S1 or the silyl ester-containing hydrolyzable antifouling coating S2 was applied to a 50 mm × 50 mm × 1.5 mm hard vinyl chloride plate so that the dry film thickness would be 100 μm. The coating was dried at 23°C for 7 days. Test plates having a single antifouling coating film (without any anticorrosive coating film) were thus fabricated.

[0155]

The test plates were mounted to the side of a rotary drum disposed in a thermostatic bath containing 25°C seawater. The rotary drum was rotated at a peripheral speed of 15 knots. The cumulative consumption (thickness loss (μm)) of the

5 antifouling coating film was measured on a monthly basis.

[0156]

(2) Static antifouling properties of antifouling coating films

With use of an air sprayer, the metal salt-containing hydrolyzable antifouling coating S1 or the silyl

10 ester-containing hydrolyzable antifouling coating S2 was applied to a 100 mm $\times$ 300 mm $\times$ 3.2 mm hard vinyl chloride plate so that the dry film thickness would be 100 μm . The coating was dried at 23°C for 7 days. Test plates having a single antifouling coating film (without any anticorrosive coating
15 film) were thus fabricated.

The test plates having a single antifouling coating film were tested to evaluate static antifouling properties in the same manner as the above-described test plates having a layered antifouling coating film.

20 [0157]

(3) Damage resistance of antifouling coating films

With use of an air sprayer, the metal salt-containing hydrolyzable antifouling coating S1 or the silyl ester-containing hydrolyzable antifouling coating S2 was

applied to a 70 mm × 150 mm × 1.6 mm hard vinyl chloride plate so that the dry film thickness would be 150 μm. The coating was dried at 5°C. Test plates having a single antifouling coating film (without any anticorrosive coating film) were thus
5 fabricated. The test plates having a single antifouling coating film were tested to evaluate their damage resistance in the same manner as the above-described test plates having a layered antifouling coating film.

[0158]

[0159]

Table 9

	Comparative Reference Example 1	Comparative Reference Example 2
	Metal salt-containing hydrolyzable antifouling coating film alone	Silyl ester-containing hydrolyzable antifouling coating film alone
Consumption properties of single film		
1 month	12.3	5.7
2 months	25.6	12.9
3 months	49.8	25.7
4 months	72.3	37.8
5 months	93.4	49.3
6 months	103.5	62.3
Static antifouling properties of single film		
1 month	0	0
2 months	0	0
3 months	0	0
4 months	0	0
5 months	0	0
6 months	0.5	0.5
Damage resistance of single film		
After 1 day of drying at 5°C	4	4
After 2 days of drying at 5°C	5	5
After 3 days of drying at 5°C	5	5

WHAT IS CLAIMED IS:

1. An epoxy resin anticorrosive coating composition for forming an anticorrosive coating film in a layered antifouling coating film including the anticorrosive coating film and an
5 antifouling coating film disposed on a surface of a substrate in the order of the anticorrosive coating film and the antifouling coating film from the substrate side,

the epoxy resin anticorrosive coating composition
10 comprising an epoxy resin (A), a solid thermoplastic resin (B) and an amine curing agent (C),

the solid thermoplastic resin (B) being solid at room temperature,

the content of the solid thermoplastic resin (B) being
15 not less than 50 parts by mass per 100 parts by mass of solids of the epoxy resin (A).

2. The epoxy resin anticorrosive coating composition according to Claim 1, wherein the epoxy resin (A) is one, or
20 two or more selected from the group consisting of bisphenol A epoxy resins, bisphenol AD epoxy resins and bisphenol F epoxy resins.

3. The epoxy resin anticorrosive coating composition according to Claim 1 or 2, wherein the composition further comprises optionally a silane coupling agent, and

the composition satisfies a reaction ratio of 0.3 to 0.8

5 wherein the reaction ratio is represented by the formula (1) below when the composition does not contain a silane coupling agent, the formula (2) below when the composition contains a silane coupling agent reactive to the amine curing agent (C), or the formula (3) below when the composition contains a silane
10 coupling agent reactive to the epoxy resin (A),

$$\text{Reaction ratio} = \frac{\frac{\text{Amount of amine curing agent (C)}}{\text{Active hydrogen equivalent weight of amine curing agent (C)}}}{\frac{\text{Amount of epoxy resin (A)}}{\text{Epoxy equivalent of epoxy resin (A)}}} \quad \dots (1)$$

$$\text{Reaction ratio} = \frac{\frac{\text{Amount of amine curing agent (C)}}{\text{Active hydrogen equivalent weight of amine curing agent (C)}}}{\frac{\text{Amount of epoxy resin (A)}}{\text{Epoxy equivalent of epoxy resin (A)}} + \frac{\text{Amount of silane coupling agent reactive to amine curing agent (C)}}{\text{Reactive group equivalent weight of silane coupling agent}}} \quad \dots (2)$$

$$\text{Reaction ratio} = \frac{\frac{\text{Amount of amine curing agent (C)}}{\text{Active hydrogen equivalent weight of amine curing agent (C)}} + \frac{\text{Amount of silane coupling agent reactive to epoxy resin (A)}}{\text{Reactive group equivalent weight of silane coupling agent}}}{\frac{\text{Amount of epoxy resin (A)}}{\text{Epoxy equivalent of epoxy resin (A)}}} \quad \dots (3)$$

(in the formulae (1) to (3), the units of the amount and
15 the equivalent weight are g and g/eq, respectively).

4. The epoxy resin anticorrosive coating composition according to any one of Claims 1 to 3, further comprising a pigment (E).

5. The epoxy resin anticorrosive coating composition according to Claim 4, wherein the pigment volume concentration (PVC) represented by the formula (4) below is 25 to 50%:

Pigment volume concentration (%) = Volume of pigment in
5 anticorrosive coating composition / (Volume of resins in
anticorrosive coating composition + Volume of pigment in
anticorrosive coating composition) × 100 ... (4).

6. The epoxy resin anticorrosive coating composition
10 according to any one of Claims 1 to 5, wherein the solid
thermoplastic resin (B) includes at least one selected from
the group consisting of petroleum resins, chlorinated
polyolefins, acrylic resins, butyl acetate resins, styrene
resins and vinyl chloride resins.

15

7. The epoxy resin anticorrosive coating composition
according to Claim 6, wherein the vinyl chloride resin is a
vinyl chloride/vinyl isobutyl ether copolymer.

20

8. The epoxy resin anticorrosive coating composition
according to any one of Claims 1 to 7, further comprising a
tertiary amine as a curing accelerator (D).

9. The epoxy resin anticorrosive coating composition according to any one of Claims 1 to 8, further comprising an adhesion promoter (F).

5 10. The epoxy resin anticorrosive coating composition according to Claim 9, wherein the adhesion promoter (F) is a silane coupling agent.

10 11. The epoxy resin anticorrosive coating composition according to Claim 10, wherein the silane coupling agent is γ -glycidoxypopyl trimethoxysilane.

15 12. The epoxy resin anticorrosive coating composition according to any one of Claims 1 to 11, wherein the antifouling coating film is a hydrolyzable antifouling coating film.

20 13. An epoxy resin anticorrosive coating film used as an anticorrosive coating film in a layered antifouling coating film including the anticorrosive coating film and an antifouling coating film disposed on a surface of a substrate in the order of the anticorrosive coating film and the antifouling coating film from the substrate side,

the epoxy resin anticorrosive coating film being a cured product of the epoxy resin anticorrosive coating composition described in any one of Claims 1 to 12.

5 14. An epoxy resin anticorrosive coating film used as an anticorrosive coating film in a layered antifouling coating film including the anticorrosive coating film and an antifouling coating film disposed on a surface of a substrate in the order of the anticorrosive coating film and the
10 antifouling coating film from the substrate side,

the epoxy resin anticorrosive coating film comprising a matrix containing a cured epoxy resin and a solid thermoplastic resin (B),

the solid thermoplastic resin (B) being solid at room
15 temperature,

the content of the solid thermoplastic resin (B) being 7 to 80 mass%.

15. The epoxy resin anticorrosive coating film according
20 to Claim 14, further comprising an epoxy resin (A).

16. A method for producing an epoxy resin anticorrosive coating film used as an anticorrosive coating film in a layered antifouling coating film including the anticorrosive coating

film and an antifouling coating film disposed on a surface of a substrate in the order of the anticorrosive coating film and the antifouling coating film from the substrate side,

the method comprising a step of curing a film composed
5 of the epoxy resin anticorrosive coating composition described in any one of Claims 1 to 12.

17. A layered antifouling coating film comprising an anticorrosive coating film and an antifouling coating film
10 disposed on a surface of a substrate in the order of the anticorrosive coating film and the antifouling coating film from the substrate side,

the anticorrosive coating film being the epoxy resin anticorrosive coating film described in any one of Claims 13
15 to 15.

18. The layered antifouling coating film according to Claim 17, wherein the antifouling coating film is a hydrolyzable antifouling coating film.

20

19. A method for producing a layered antifouling coating film including an anticorrosive coating film and an antifouling coating film disposed on a surface of a substrate in the order

of the anticorrosive coating film and the antifouling coating film from the substrate side,

the method comprising a step of forming the epoxy resin anticorrosive coating film described in any one of Claims 13 to 15, and a step of forming the antifouling coating film on the surface of the epoxy resin anticorrosive coating film.

20. An antifouling substrate comprising a substrate and the layered antifouling coating film described in Claim 17 or 18, the layered antifouling coating film being disposed on a surface of the substrate in the order of the anticorrosive coating film and the antifouling coating film from the substrate side.

21. The antifouling substrate according to Claim 20, which is placed in contact with seawater or fresh water.

22. The antifouling substrate according to Claim 20 or 21, wherein the substrate is at least one selected from the group consisting of marine vessels, offshore structures and onshore structures.

23. A method for producing an antifouling substrate, comprising a step of forming the layered antifouling coating film described in Claim 17 or 18 on a surface of a substrate.