

SPECIFICATION

PAINT COMPOSITION, ANTIFOULING PAINT FILM, SUBMERGED STRUCTURE, AND ANTIFOULING METHOD OF SUBMERGED STRUCTURE

TECHNICAL FIELD

This invention relates to a paint composition, an antifouling paint film, a submerged structure, and an antifouling method of a submerged structure. More particularly, the present invention relates to a paint composition capable of readily forming an antifouling paint film capable of preventing adhesion of aquatic organisms onto the surface of a structure to be contacted with seawater, lake water and the like; an antifouling paint film capable of preventing aquatic organisms from adhering onto a surface of a body to be contacted with seawater, lake water and the like, by being coated with the paint composition; a submerged structure effectively kept from adhesion of aquatic organisms onto the surface of the body to be contacted with seawater, lake water and the like, by being covered with the antifouling paint film; and an antifouling method capable of effectively preventing adhesion of aquatic organisms.

BACKGROUND ART

Conventionally, in order to prevent marine organisms such as barnacles, mussels, polyzoans, ascidians and seaweeds from adhering onto a submerged structure to be contacted with seawater or freshwater, such as a submerged portion of ships, buoys, fixed fish-farming nets, culturing fish-farming nets, various water pipes, fouling prevention films, off-shore drilling wells or the like, there has been widely used a paint composition containing, as main components, an organotin-based hydrolysable resin, and an inorganic compound including copper such as cuprous oxide or cuprous thiocyanate, as a marine-organism-adhesion inhibitor.

Recently, the use of organic compounds has been restricted in view of environmental pollution. Instead, there have been used and proposed paint compositions comprising rosins, various hydrolysable resins, slightly water-soluble resins and the like, and organism-adhesion inhibitors. However, the organism-adhesion inhibiting abilities of those paint compositions have not been considered to be sufficient yet.

The performances required for paint compositions which are to have marine-organism-adhesion inhibiting effects over a long period of time are higher adhesion-inhibiting effects of physiologically active substances to be used as inhibitors, against many kinds of marine organisms; and abilities of the hydrolysable resins, to cause hydrolysis in seawater, thereby gradually dissolving the paint film from its surface.

Furthermore, the affinity of the physiologically active substance with seawater and that of the hydrolysable resin with seawater are required to consume the paint film in a manner to allow the physiologically active substance to effectively show its effect. Thus, such a composite material can be developed, only when the compound as the organism-adhesion inhibitor has a molecular structure with a higher adhesion-inhibiting effect against marine organisms that may adhere to the surface of a submerged structure, and when the compound has an affinity capable of consuming the marine-organism-adhesion inhibitor without causing any defects in the entire paint film where the compound is combined with the hydrolysable resin.

There have been proposed many compositions including only one of a marine-organism-adhesion inhibitor free of metal and a hydrolysable resin. For example is known a submerged-type antifouling paint employing a tetraphenylboron compound represented by the formula of $(C_6H_5)_4B \cdot X$, wherein X represents a potassium atom, an ammonium group, or an organic nitrogen radical brought into a quaternary state. See patent document 1.

Since the submerged-type antifouling paint, described in patent document 1 and containing the tetraphenylboron compound, had an inferior stability and was incapable of sufficiently exhibiting the antifouling property, the paint could never act as a paint composition for inhibiting marine-organism adhesion. In particular, according to the description of patent document 1, marine organisms did start to adhere onto a soft steel plate coated with the submerged-type antifouling paint about nine months from the submergence, when the soft steel plate had been immersed in the sea, thereby failing to exhibit an antifouling property over a long period of time.

[Patent Document 1] JP-B-54-1571 (1571/1979) (Claim 1, Table 1, Table 2)

Meanwhile, hydrolysable type resins are most desirable as resins to cause a marine-organism-adhesion inhibitor to be gradually released into seawater over a long period of time, thereby maintaining the organism-adhesion preventing effect of the inhibitor over a long period of time. A number of paint compositions of such hydrolytic types have also been proposed. (See patent documents 2 and 3.)

The erosive paint for ship-bottom described in patent document 2 comprises a specific polymer binding material comprising "a film-forming polymer without including organotin, the polymer being water-insoluble and erosive by seawater, thereby having a hydrolysis rate of at least 5×10^{-4} milli-equivalents per hour to attain an erosion rate of at least 2 microns per month for the antifouling paint in seawater", and a toxic agent (see claim 1 of patent document 2).

However, patent document 2 describes "tributyl tin fluoride, triphenyl tin hydroxy, triphenyl tin fluoride" and the like as the above-mentioned toxic agents (see col. 10, lines 3 to 8 of patent document 2). These toxic agents described in patent document 2 are substances acting as sex

disruptors, which adversely affect the environment.

The antifouling-paint resin described in patent document 3 is obtained by copolymerizing a specific vinyl monomer with a carboxylic acid (A) in the form where the carboxylic acid is blocked by $-\text{SiR}^{12}\text{R}^{13}\text{R}^{14}$ and a copolymerizable vinyl monomer (B) different from the above monomer at a specific ratio of the former to the latter, and the obtained resin has a specific number-average molecular weight (see claim 1 of patent document 3). According to patent document 3, the antifouling paint is formed by mixing the antifouling-paint resin, an antifouling agent such as an organotin compound, and a metal compound such as zinc suboxide, zinc chromate and the like (see from line 7 of the upper left column to line 3 of the upper right column on page 6 of patent document 3.). The metal compounds such as the above described organotin compound and zinc chromate adversely affect the environment, and also adversely and variously affect human bodies in a long term.

[Patent document 2] JP-B-5-32433 (32433/1993) (claim 1)

[Patent document 3] JP-A-63-215780 (215780/1988) (claim 1)

Meanwhile, there has been proposed a paint composition containing a copolymer of a monomer mixture including monomer (A) where a specific carboxylic acid is blocked by $-\text{SiR}^1\text{R}^2\text{R}^3$ and monomer (B) represented by the formula of $\text{Y}-(\text{CH}_2\text{CH}_2\text{O})_n-\text{R}^4$, and triphenylboronpyridine (see patent document 4).

In patent document 4, triphenylboronpyridine (also called "pyridine-triphenylborane") is mainly used as an organism-adhesion inhibitor, which is incapable of maintaining its antifouling activity over a long period of time. Although pyridine-triphenylborane is effective as a physiologically active substance, it has a higher affinity with seawater and thus has a higher dissolution rate in seawater, resulting in a tendency to be consumed from the

paint film in a short period of time, thereby failing to maintain its effect over a long period of time.

[Patent document 4] JP-A-8-277372 (277372/1996)
(claim 1)

Also known as an antifouling agent is a diaryl type of organic boron compound (see patent document 5 and patent document 6). Specifically, the "organic boron compound as an antifouling agent" described in patent document 5 is a "compound having a specific structure including diphenylalkyl-boronpyridine" (See claim 1 of patent document 5). The harmful-aquatic-organism protectant described in patent document 6 is characterized in that it contains a diaryl(pyridinio or isoquinolinio) boron complex as an active component.

Although the antifouling agents described in patent documents 5 and 6 are recognized to have effects as organism-adhesion inhibitors, these agents have not been yet brought to maintain the antifouling activities over a long period of time (See Table 11 of patent document 5 and Table 4 of patent document 6.).

[Patent document 5] Japanese Patent No. 3034053
(claim 1)

[Patent document 6] JP-A-9-323909 (323909/1997)
(claim 1)

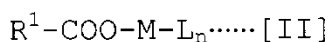
Proposed in patent document 7 is an antifouling agent preventing adhesion of aquatic organisms to a submerged structure, containing, as active components, one kind or two or more kinds of diarylborane-amine complex compounds wherein the primary amine residue is bonded to the boron atom (See claims 1 and 5 of patent document 7.). However, according to the technique described in patent document 7, it is difficult to efficiently release the organic boron compound into water. For example, although the antifouling agent can show the antifouling activity to a certain extent over a certain period of time insofar as it is used in a calm sea area such as in a fishing-net, it is surmised that it will be difficult to efficiently release the organic

boron compound into water in a dynamic environment such as a structural body like a ship which in itself moves over the sea surface and lake surface. The difficulty of release has actually been proven by a result of a long-term antifouling performance obtained by immersing the composition in seawater.

[Patent document 7] JP-A-2001-342192

The invention described in patent document 8 is "an antifouling paint composition characterized in that it contains (a) a copolymer which includes units of a straight-chain aliphatic oxycarbonyl metal-unsaturated carboxylate, and (b) a triphenylboron-amine complex" (See claim 1 of patent document 8.). Further disclosed in its claim 2 is:

"The antifouling paint composition of any one of claims 1 and 2, wherein the copolymer (a) which includes units of a straight-chain aliphatic oxycarbonyl metal-unsaturated carboxylate, is a copolymer containing a component unit derived from the polymerizable compound represented by formula [II]:



[in formula [II],

R^1 represents an organic group containing an unsaturated bond and represented by any one of the formulae $CH_2=C(CH_3)-$, $CH_2=CH-$, $HOOC-CH=CH-$, and $HOOC-CH=C(CH_3)-$,

$-COOH$ in the formulae may form a metal salt or an ester;

M represents a metal atom;

L represents an organic acid residue $-OCOR^2$ (R^2 represents a straight-chain alkyl group, or a straight-chain alkenyl group); and

n represents a numerical value of (the valence number of metal M) minus 1.

However, when pyridine-triphenylborane is employed as a boron-based organism-adhesion inhibitor, it fails to maintain its antifouling activity over a long period of time. This is because, although pyridine-triphenylborane

is effective as a physiologically active substance, it has a higher affinity with seawater and thus has a larger dissolution rate into water, resulting in a tendency to be dissolved from the paint film, thereby failing to maintain its effect over a long period of time. Although it exhibits its effect over a certain period of time insofar as the adhering objects are larger-sized organisms such as mussels, barnacles, serpulas and polyzoans, it has a lower physiological activity against slime, as proven by a recent investigation.

[Patent document 8] JP-A-2001-329228

DISCLOSURE OF THE INVENTION

[Problems to be solved by the Invention]

The present invention is to solve the problems of the above described prior art technologies, and it is an objective of the present invention to provide a paint composition, an antifouling paint film, a submerged structure, and an antifouling method of a submerged structure. The paint film according to the present invention does not have defects such as separation over time after immersed in water, while the paint composition is eroded at a constant rate, which results in an excellent long-term antifouling property. The paint composition can be applied even onto aluminum-made ships. Furthermore, the paint composition has a superior antifouling property also as an antifouling agent for fishing nets, and has an extremely superior environmental safety.

[Means for solving the Problem]

In case of developing a paint composition for inhibiting marine-organism adhesion, the paint film comprising a hydrolysable resin and a marine-organism-adhesion inhibitor should be dealt with as a single composite material as a whole. It can be said that the paint film comprising the hydrolysable resin and the physiologically active substance is made of an interacting-

type of slightly water-soluble composite material. The paint film is of a nature to be made active and to have beneficial effect on marine organisms that can adhere to submerged structures, only after the resin has a mechanism to be slightly dissolved in seawater by hydrolysis of the resin and after the physiologically active substance as the marine-organism-adhesion inhibitor is also slightly dissolved in seawater. Since both of them show the effectiveness thereof when contacted with water molecules and thus the respective substances have affinities with water molecules, the paint film comprising these substances is to perform its function as a slightly water-soluble composite material.

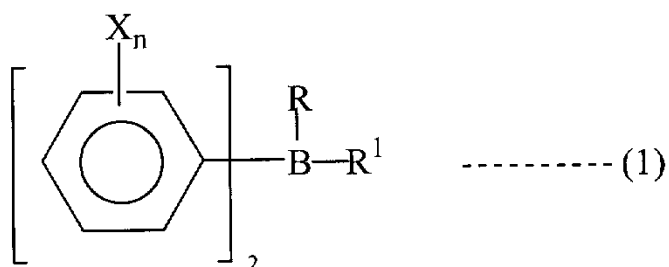
The present inventors have directed attention to a paint composition based on a combination of a specifically useful organo-silyl-based resin and a specific marine-organism-adhesion inhibitor, as a hydrolysable type resin. As a result of intensive research, the present inventors have found that the above problems can be solved by the employment of a specific borane compound together with a specific hydrolysable resin.

The present inventors have also found that a paint composition including, as essential components, a specific resin with organo-silyl groups introduced thereto for the hydrolysable resin, and one or more kinds of borane compounds for the marine-organism-adhesion inhibitor can work as a hydrolytic and self-abrasive type paint composition which are excellent in keeping the environment safe, and provides a paint film excellent in hardness upon the formation of the film, and free from film defects such as exfoliation and/or cracks after immersion in seawater. They have further found that the film can erode at a constant rate and can exhibit an excellent marine-organism-adhesion inhibiting effect for a long time, because it gradually releases the specific borane compound into seawater at a rate effective for inhibiting the adhesion of marine organisms.

The inventions are recited in the following items (1) through (12).

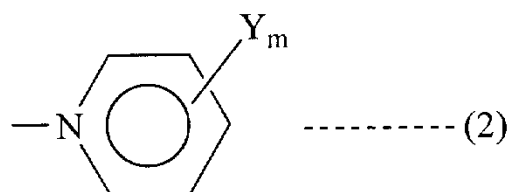
(1) A paint composition comprising:

as component (A), at least one kind of a diphenylborane compound represented by formula (1):



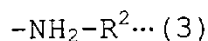
wherein X represents a halogen atom, an alkyl group with 1 to 8 carbon atoms, or an alkoxy group with 1 to 8 carbon atoms; each of two n's is an integer of 0 to 3 independently, and X's may be the same or different from each other when n is 2 or 3; R represents an alkyl group with 1 to 8 carbon atoms, an alkoxy group with 1 to 8 carbon atoms, an alkenyl group with 2 to 8 carbon atoms, an alkynyl group with 2 to 8 carbon atoms, a hydroxyl group, or a halogen atom; and R¹ represents a group represented by the following formula (2), a 5,6,7,8-tetrahydroisoquinoline group or an isoquinoline group which may be substituted by at least one halogen atom, or a group represented by the formula (3) or formula (4);

the formula (2) is:



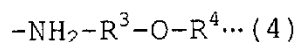
wherein Y represents a halogen atom, an alkyl group with 1 to 8 carbon atoms, a phenyl group, or acetyl group; and m is an integer of 0 to 3 and Y's may be the same or different from each other when m is 2 or 3;

the formula (3) is:



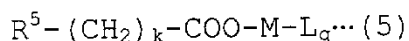
wherein R^2 represents a straight-chain alkyl group with 1 to 24 carbon atoms or a branched alkyl group with 3 to 24 carbon atoms; and

the formula (4) is:



wherein R^3 represents a straight-chain alkylene group with 1 to 24 carbon atoms, a branched alkylene group with 3 to 24 carbon atoms, phenylene group; and R^4 represents a straight-chain alkyl group with 1 to 24 carbon atoms or a branched alkyl group with 3 to 24 carbon atoms; and

as component (B), a copolymer which contains component units derived from a polymeric unsaturated metal-salt compound represented by formula (5):



wherein R^5 represents an organic group including an unsaturated bond, represented by any one of the formulae $\text{CH}_2=\text{C}(\text{CH}_3)-$, $\text{CH}_2=\text{CH}-$, $\text{HOOC}-\text{CH}=\text{CH}-$, and $\text{HOOC}-\text{CH}=\text{C}(\text{CH}_3)-$, wherein $-\text{COOH}$ may be in a form of metal salt or ester; k represents an integer of 0 to 2; M represents a metal atom; L represents $-\text{OCOR}^6$, which is an organic acid residue, wherein R^6 represents an alkyl group or alkenyl group, $-\text{R}^7-\text{CO}-\text{CH}_2-\text{CO}-\text{R}^8$, wherein R^7 represents a divalent group obtained by detaching two hydrogen atoms from a straight-chain or branched alkane or phenyl derivative; and R^8 represents a monovalent group comprising an alkyl group or phenyl derivative), or $-\text{OH}$; and q represents a numerical value of (the valence number of metal M) minus 1.

(2) The paint composition of (1) wherein the paint composition contains at least one kind of rosin-based compound selected from the group consisting of a rosin, a rosin-derivative and a metal rosinate.

(3) The paint composition of (1) or (2), wherein the metal M in the component (B) is a divalent metal.

(4) The paint composition of any one of (1) through (3), wherein the component (A) is a methyl(diphenyl)borane

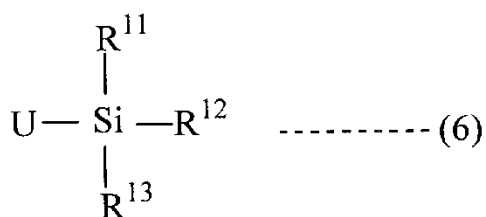
compound.

(5) The paint composition of any one of (1) through (4), wherein the component (A) is at least one kind of methyl(diphenyl)borane compound selected from the group consisting of pyridine-methyl(diphenyl)borane, 3-methylpyridine-methyl(diphenyl)borane, 3-bromopyridine-methyl(diphenyl)borane, 4-isopropylpyridine(N-B)methyl(diphenyl)borane, 4-t-butylpyridine-methyl(diphenyl)borane, 4-phenylpyridine-methyl(diphenyl)borane, n-octadecylamine-methyl(diphenyl)borane, and 3-(2-ethylhexyloxy)-propylamine-methyl(diphenyl)borane.

(6) A paint composition comprising:

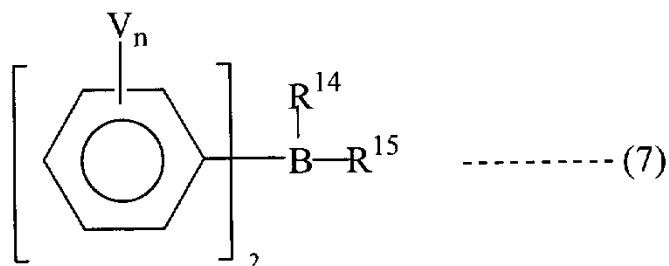
a resin P comprising a polymer (PA) obtained by polymerizing one kind or two or more kinds of monomer(s) (A) represented by formula (6) below; and/or a copolymer (PAB) obtained by polymerizing one kind or two or more kinds of the monomer(s) (A) with one kind or two or more kinds of monomer(s) (B) which is/are copolymerizable with the monomer(s) (A) and is/are different from the monomer(s) (A); and one kind or two or more kinds of borane(s) represented by formula (7), wherein

the formula (6) is:



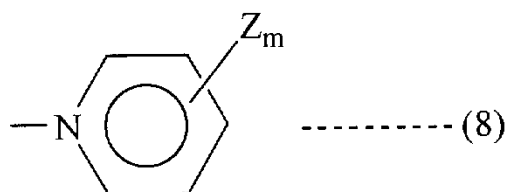
wherein each of R^{11} through R^{13} is a hydrocarbon group with 1 to 20 carbon atoms, and R^{11} , R^{12} and R^{13} may be the same or different from each other; and U is acryloyloxy group, methacryloyloxy group, maleinoyloxy group, fumaroyloxy group, or itaconoyloxy group; and

the formula (7) is:



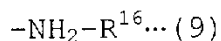
wherein V is an halogen atom, an alkyl group with 1 to 8 carbon atoms, or an alkoxy group with 1 to 8 carbon atoms; n is an integer of 0 to 3 and V's may be the same or different from each other when n is 2 or 3; R¹⁴ represents an alkyl group with 1 to 8 carbon atoms, an alkoxy group with 1 to 8 carbon atoms, an alkenyl group with 2 to 8 carbon atoms, an alkynyl group with 2 to 8 carbon atoms, hydroxyl group, or a halogen atom; and R¹⁵ denotes a group represented by formula (8), a 5,6,7,8-tetrahydroisoquinoline group or an isoquinolinone group which may be substituted by at least one halogen atom, a group represented by formula (9) or formula (10):

wherein the formula (8) is:



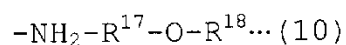
wherein Z is an halogen atom, an alkyl group with 1 to 8 carbon atoms, a phenyl group, or acetyl group; and m is an integer of 0 to 3;

the formula (9) is:



wherein R¹⁶ denotes a straight-chain or branched alkyl group with 3 to 24 carbon atoms; and

the formula (10) is:



wherein R¹⁷ is a straight-chain or branched alkyl group with 3 to 24 carbon atoms; and R¹⁸ is a straight-

chain or branched alkyl group with 3 to 24 carbon atoms.

(7) The paint composition of (6), wherein the paint composition includes a rosin compound in an amount of 0.1 to 90 mass% relative to the resin P.

(8) The paint composition of (6) or (7), wherein the paint composition includes a marine-organism-adhesion inhibitor for inhibiting adhesion of marine organisms.

(9) The paint composition of (8), wherein the marine-organism-adhesion inhibitor is an organic inhibitor free of metal.

(10) An antifouling paint film wherein the antifouling paint film is formed from the paint composition of any one of (1) through (9).

(11) A submerged structure wherein the submerged structure has a surface coated with an antifouling paint film formed from the paint composition of any one of (1) through (9).

(12) An antifouling method of a submerged structure comprising a step of coating a surface of the structure with the paint composition of any one of (1) through (9), thereby forming an antifouling paint film.

[Advantages of the Invention]

The above-mentioned paint composition of the present invention as well as the paint composition acting as a composite material comprising the same can be used for ship bottoms, submerged structures such as fishing nets or cooling-water pipes, for which fouling by organisms in the sea is required to be inhibited. It can also be used as a sludge-diffusion-preventing antifouling paint film in offshore engineering works. The paint film according to the present invention never forms a residual layer on the paint film surface even after immersed over a long period of time, so that defects such as cracks and separations are not caused by virtue of the paint-film properties and so that the paint-film eroding ability is unchanged over time and is kept at more than a certain rate, thereby making it

possible to show an antifouling activity over a long period of time. The paint film exhibits an extremely superior antifouling activity over a long period of time also as a fishing-net antifouling agent. Furthermore, it can be applied onto an aluminum-made ship, since the risk of pitting corrosion into aluminum is absent when other metal-containing antifouling agents are not used together. Moreover, some paint compositions according to this invention are capable of showing an extremely superior antifouling activity even without using cuprous oxide in combination. These paint compositions can be colored in any vivid colors to thereby exhibit a remarkably superior designing flexibility, whereas typical cuprous-oxide containing antifouling paints cannot be colored in vivid colors.

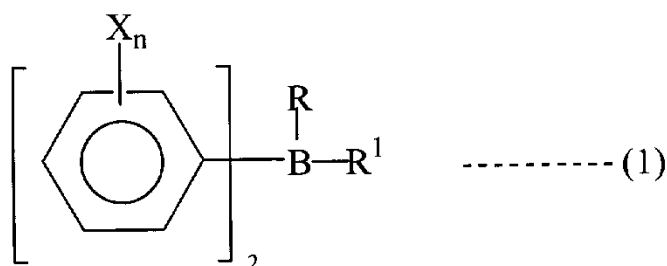
Furthermore, according to other embodiments of the present invention, it is possible to provide a paint composition, an antifouling paint film, a submerged structure, and a method of forming an antifouling paint film on a submerged structure, in a manner that the paint composition and the antifouling paint film derived therefrom never cause paint film defects such as separations and cracks over time even after immersed in seawater or freshwater, with erosion at a constant rate to thereby show superior marine-organism-adhesion inhibiting effects, while assuring environmental safety by virtue of absence of any metal components.

BEST MODE FOR CARRYING OUT THE INVENTION

<Paint Compositions of Inventions (1) through (5)>

Firstly, description of the inventions (1) through (5) noted in the paragraphs of "Means for solving the Problem" is provided.

To obtain the paint composition of the present invention is used at least one kind of diphenylborane compound represented by formula (1):



In formula (1), X represents a halogen atom, an alkyl group with 1 to 8 carbon atoms, or an alkoxyl group with 1 to 8 carbon atoms. Examples of the alkyl group with 1 to 8 carbon atoms include methyl group, ethyl group, a propyl group, a butyl group, a pentyl group, a hexyl group, and an octyl group. The alkoxyl group includes methoxyl group, ethoxyl group, a propoxyl group, a butoxyl group, a pentoxyl group, a hexoxyl group, and an octoxyl group.

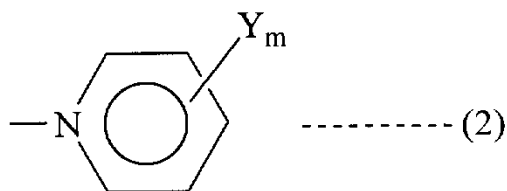
In formula (1), each of two n's is an integer of 0 to 3 independently, and X's may be the same or different from each other when n is 2 or 3.

In formula (1), R represents an alkyl group with 1 to 8 carbon atoms, an alkoxyl group with 1 to 8 carbon atoms, an alkenyl group with 2 to 8 carbon atoms, an alkynyl group with 2 to 8 carbon atoms, hydroxyl group, or a halogen atom. The alkyl group with 1 to 8 carbon atoms includes methyl group, ethyl group, a propyl group, a butyl group, a pentyl group, a hexyl group, and an octyl group. The alkoxy group exemplarily includes methoxyl group, ethoxyl group, a propoxyl group, a butoxyl group, a pentoxyl group, a hexoxyl group, and an octoxyl group. The alkenyl group with 2 to 8 carbon atoms includes an alkenyl group having an end double bond or an alkenyl group having a double bond in its carbon chain, such as vinyl group, a propenyl group, a butenyl group, a pentenyl group, a hexenyl group, and an octenyl group.

In formula (1), R¹ represents a group represented by formula (2), a 5,6,7,8-tetrahydroisoquinoline group or isoquinolinone group which may be substituted by at least one halogen atom, or a group represented by formula (3) or

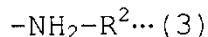
formula (4).

Formula (2) is:



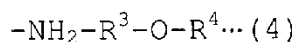
In formula (2), Y denotes a halogen atom, an alkyl group with 1 to 8 carbon atoms, a phenyl group, or acetyl group. "m" is an integer of 0 to 3, and Y's may be the same or different from each other when m is 2 or 3. The alkyl group in formula (2) includes methyl group, ethyl group, n-propyl group, isopropyl group, a butyl group, isobutyl group, tertiary-butyl group, a pentyl group, a hexyl group, and an octyl group. Furthermore, when Y in formula (2) is a phenyl group, this phenyl group may have one or more substituents.

Formula (3) is:



In formula (3), R^2 denotes a straight-chain alkyl group with 1 to 24 carbon atoms or a branched alkyl group with 3 to 24 carbon atoms. Although the straight-chain alkyl group with 1 to 24 carbon atoms or the branched alkyl group with 3 to 24 carbon atoms for R^2 in formula (3) is not particularly limited, it is typically a straight-chain or branched alkyl group with 3 to 24 carbon atoms, preferably with 8 to 24 carbon atoms, more preferably with 8 to 18 carbon atoms, such as n-octyl, n-nonyl, n-decyl, n-dodecyl, n-tetradecyl, n-hexadecyl, n-octadecyl, 2-ethyl-hexyl, 3-ethyl-hexyl, 2,2-dimethyl-hexyl, and 2,3-dimethyl-hexyl.

Formula (4) is:



In formula (4), R^3 denotes a straight alkylene group with 1 to 24 carbon atoms, a branched alkylene group with 3 to 24 carbon atoms, or a phenylene group. R^4 is a

straight-chain alkyl group with 1 to 24 carbon atoms or a branched alkyl group with 3 to 24 carbon atoms.

Examples of the straight-chain alkylene group with 1 to 24 carbon atoms, or the branched alkylene group with 3 to 24 carbon atoms for R^3 in formula (4) include methylene group, ethylene group, trimethylene group, propylene group, tetramethylene group, 2-methyl-trimethylene group, 1,1-dimethyl-ethylene group, 1,2-dimethyl-ethylene group, 1-ethylethylene group, pentamethylene group, hexamethylene group, 1-butyl-ethylene group, octamethylene group, 2-ethyl-hexamethylene group. Examples of the straight-chain alkyl group with 1 to 24 carbon atoms or the branched alkyl group with 3 to 24 carbon atoms for R^4 include methyl group, ethyl group, n-propyl group, isopropyl group, n-butyl group, isobutyl group, sec-butyl group, tert-butyl group, a pentyl group, a hexyl group, a heptyl group, an octyl group, 2-ethylhexyl group, a nonyl group, a decyl group, an undecyl group, a lauryl group, a tridecyl group, a tetradecyl group, a pentadecyl group, a hexadecyl group, a heptadecyl group, and stearyl group.

The amount of the diphenylborane compound represented by formula (1) is suitably set within a range of usually 0.01 to 60 mass%, and preferably 0.1 to 40 mass%, based on the solid content of the paint. When the diphenylborane compound is used in an excessively smaller amount, the paint will not have the antifouling effect. On the other hand, the use of an excessively larger amount of the compound often results in causing defects such as cracks and separations of the paint film, thereby also failing to obtain excellent antifouling effects.

In the paint composition according to the present invention, it is possible to use one kind of the diphenylborane compound represented by formula (1), or to use two or more kinds of the diphenylborane compounds in combination. Among the diphenylborane compounds, 4-isopropylpyridine-methyl(diphenyl)borane is particularly preferable.

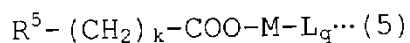
Furthermore, in the paint composition according to this invention, it is possible to use other antifouling agents known in the technical field of paint in combination with the one or more kinds of diphenylborane compounds represented by formula (1).

Examples of those other known antifouling agents include N-trihalomethyl-thiophthalimide, dithiocarbamic acid, N-arylmaleimides, 3-substituted amino-1,3-thiazolidine-2,4-diones, dithiocyano compounds, triazine compounds, cuprous thiocyanate, pyrithione compounds, and others. More particularly, they include 2-methylthio-4-t-butylamino-6-cyclopropylamino-s-triazine, 2,4,5,6-tetrachloro-isophthalonitrile, N,N-dimethyl-N'-dichlorophenylurea, 4,5-dichloro-n-octyl-isothiazoline-3-one, N-(fluorodichloromethylthio)phthalimide, N,N-dimethyl-N'-phenyl-(N-fluorodichloromethylthio)sulfamide, tetramethylthiuram-disulphide, 2,4,6-trichlorophenyl-maleimide, 2,3,5,6-tetrachloro-4-(methylsulfonyl)pyridine, diiodomethylparatolyl sulfone, 2-(4-thiazolyl)benzimidazole, 2-pyridinethiol-1-oxide-zinc salt or copper salt.

The paint composition according to the present invention includes a polymer having a specific structure, together with the diphenylborane compounds represented by formula (1).

The polymer having the specific structure is a copolymer containing component units derived from a polymeric unsaturated metal salt represented by formula (5).

Formula (5) is:



In formula (5), R^5 represents an organic group including an unsaturated bond, represented by any one of the formulae $CH_2=C(CH_3)-$, $CH_2=CH-$, $HOOC-CH=CH-$, and $HOOC-CH=C(CH_3)-$, wherein $-COOH$ may be in a form of a metal salt or ester.

k denotes an integer of 0 to 2. M is a metal atom. L denotes $-OCOR^6$, an organic acid residue, wherein R^6 is an alkyl group or alkenyl group, or $-R^7-CO-CH_2-CO-R^8$ wherein R^7

is a divalent group obtained by detaching two hydrogen atoms from a straight-chain or branched alkane or a phenyl derivative, and R^8 is a monovalent group comprising an alkyl group or a phenyl derivative, or $-OH$. q denotes a numerical value of (the valence number of metal M) minus 1.

When L in formula (5) is the carboxylic acid residue ($-OCOR^6$), the carboxylic acid ($HOCOR^6$) adapted to derive this residue includes those in which R^6 is an alkyl group (saturated hydrocarbon) or an unsaturated hydrocarbon group having one or two or more carbon-carbon double bonds. Another atom may be interposed between carbon atoms in the main chain constituting R^6 to thereby lead to presence of another type of bond, such as an ether bond (e.g. $C-O-C$, or $C-S-C$), or an ester bond ($-COO-$). The number of carboxyl groups may be one (monovalent) or plural (multivalent).

Examples of the carboxylic acid from which the carboxylic acid residue L may be derived include saturated monovalent carboxylic acids such as acetic acid, propionic acid (C_2H_5COOH), butanoic acid ($CH_3(CH_2)_2COOH$), valeric acid ($CH_3(CH_2)_3COOH$), versatic acid, lauric acid ($CH_3(CH_2)_{10}COOH$), palmitic acid ($CH_3(CH_2)_{14}COOH$), and stearic acid ($C_{17}H_{35}COOH$); and unsaturated monovalent carboxylic acids such as acrylic acid, 2-butenic acid ($CH_3CH=CHCOOH$), oleic acid [$CH_3(CH_2)_7CH=CH(CH_2)_7COOH$], linoleic acid [$CH_3(CH_2)_4CH=CHCH_2CH=CH(CH_2)_7COOH$], and linolenic acid [$CH_3CH_2(CH=CHCH_2)_3(CH_2)_5COOH$].

Furthermore, the multivalent carboxylic acid which has two or more carboxylic groups and can provide the carboxylic acid residue L includes fumaric acid ($HOOCCH=CHCOOH$) and azelaic acid ($HOOC(CH_2)_7COOH$). Among these carboxylic acids, those typically with 1 to 25 carbon atoms, and preferably with 1 to 18 carbon atoms are desirable in this invention. One of these carboxylic acids or two or more thereof in combination may be used. When two or more carboxylic acids are used in combination, the number of the carbon atoms in R^5 in formula (5) is represented by the average value. When L in formula (5) is

a group represented by $-R^7-CO-CH_2-CO-R^8$, examples thereof include residues of acetylacetone and 1-phenyl-1,3-butane-diones.

In formula (5), k is preferably 0. When L in formula (5) is $-OH$, any resins such as polyester, polyurethane, natural resin, and vinyl polymer are usable for the resin having a carboxyl group in the molecule. Among them the vinyl polymer is desirable from a standpoint of freedom of compositional variation. Furthermore, although the resin may have one carboxyl group per molecule when the resin has a lower molecular weight, it is necessary to have two or more carboxyl groups per molecule when the resin has a higher molecular weight. The reason is that resins with higher molecular weights preferably have an acid value in the range of 30 to 300.

Although the synthesizing method is not particularly limited, 0.5 to 5 wt.% of water, oxide or hydroxide of a divalent metal which is desired to be added are added to the resin having a carboxyl group within its molecule. The mixture is allowed to react at a temperature of 50 to 200°C for 1 to 20 hours. When the system is apt to be cloudy because of the presence of water, the addition of a minimum amount of a polar solvent is required.

Examples of the polar solvent include alcohol-based solvents such as n-butanol, and isopropyl alcohol; ketone-based solvents such as methyl ethyl ketone, and methyl isobutyl ketone; ester-based solvents such as ethyl acetate, butyl acetate, and isobutyl acetate; and ether-based solvents such as cellosolve, butyl cellosolve, diethylene glycol, diethylene glycol monoethyl ether, and diethylene glycol monobutyl ether. Although the metal compound in a powder form does not dissolve in the solvent initially, the system becomes transparent as the reaction progresses.

The metal in formula (5) includes metals belonging to the Ib, IIa, IIb, IIIa, IIIb, IVa, IVb, Va, Vb, VIb, VIIb and VIII groups in the periodic table, and specifically divalent or multivalent metals such as Cu, Ni, Co, Pb, Al,

Mg, Sn, and Ge. Among them, divalent metals such as Cu, Zn, Mg are desirable, with Cu and Zn being particularly desirable.

The number-average molecular weight of the polymeric unsaturated metal-salt compound represented by formula (5) is typically from 4,000 to 100,000, and its glass transition temperature is typically from -30°C to $+70^{\circ}\text{C}$. Furthermore, although the manufacturing method of the polymeric unsaturated metal-salt compound represented by formula (5) is not particularly limited, the compound may be manufactured, for example, by mixing the above-described polymeric unsaturated metal-salt compound with a different polymeric monomer, which is copolymerizable with the compound, as required, and by reacting the mixture at a reaction temperature of 60 to 180°C for 5 to 14 hours in the presence of a radical initiator. While it is possible to employ emulsion polymerization and suspension polymerization in addition to solution polymerization, which is carried out in an organic solvent, it is advantageous to employ the solution polymerization in a typical organic solvent such as toluene, xylene, methylisobutyl ketone, n-butyl acetate, propylene glycol monomethyl ether, or n-butanol, from a viewpoint of productivity.

The copolymer as component (B) in this invention includes a copolymer obtained by copolymerizing two or more kinds of polymeric unsaturated metal-salt compounds represented by formula (5) with each other, and a copolymer obtained by copolymerizing at least one kind of polymeric unsaturated metal-salt compound represented by formula (5) with a different polymeric monomer which is copolymerizable with the former.

The different polymeric monomer includes aliphatic monomers such as methyl (meth)acrylate, ethyl (meth)acrylate, n-propyl (meth)acrylate, isopropyl (meth)acrylate, n-butyl (meth)acrylate, isobutyl (meth)acrylate, t-butyl (meth)acrylate, 2-ethylhexyl

(meth)acrylate, lauryl (meth)acrylate, stearyl (meth)acrylate, glycidyl (meth)acrylate, 2-methoxyethyl (meth)acrylate, 2-ethoxypropyl (meth)acrylate, 2-propoxyethyl (meth)acrylate, 2-butoxyethyl (meth)acrylate, methoxydiethylene glycol (meth)acrylate, ethoxydiethylene glycol (meth)acrylate, and ethoxyethylene glycol (meth)acrylate; alicyclic monomers such as cyclohexyl (meth)acrylate, and isobornyl (meth)acrylate; aromatic monomers such as phenyl (meth)acrylate, and benzyl (meth)acrylate; monomers such as diethyl maleate, diisopropyl fumarate, and dibutyl itaconate; unsaturated monomers having one hydroxyl group, such as 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, 3-hydroxypropyl (meth)acrylate, 2-hydroxybutyl (meth)acrylate; hydroxyl-group containing unsaturated monomers such as monomers having multiple hydroxyl groups, an example of which is glycerol (meth)acrylate; amino-group or amide-group containing monomers such as (meth)acrylamide, and butylaminoethyl (meth)acrylate; monomers having primary through tertiary amino group or amide group, such as dimethylaminoethyl (meth)acrylate, diethylaminoethyl (meth)acrylate, dimethylaminopropyl (meth)acrylate, dimethylaminobutyl (meth)acrylate, dibutylaminoethyl (meth)acrylate, dimethylaminoethyl (meth)acrylamide, dimethylaminopropyl (meth)acrylamide; and styrene, vinyltoluene, α -methylstyrene, (meth)acrylonitrile, vinyl acetate, vinyl propionate, (meth)acrylic acid, 2-butenic acid, oleic acid, linolenic acid, linoleic acid, maleic acid, fumaric acid, itaconic acid, propionic acid, valeric acid, butanoic acid, palmitic acid, myristic acid, lauric acid, stearic acid and metal salts thereof.

The copolymer as component (B) in this invention can be obtained by polymerizing the polymeric unsaturated metal-salt compound represented by formula (5) with a different polymeric monomer that is copolymerizable with the former. The polymerization reaction may be any one of solution polymerization, bulk polymerization and emulsion

polymerization. The most desirable polymerization reaction is the solution polymerization reaction. When the copolymer as component (B) is produced by the solution polymerization reaction, appropriately usable for the solvent therefor is one which allows dissolution of the polymeric unsaturated metal-salt compound represented by formula (5) as well as the different polymeric monomer copolymerizable with the former.

The solvent is not particularly limited, and includes hydrocarbons such as toluene, xylene, ethylbenzene, cyclopentane, octane, heptane, cyclohexane, and white spirit; ethers such as dioxane, tetrahydrofuran, ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol monobutyl ether, ethylene glycol dibutyl ether, diethylene glycol monoethyl ether; esters such as butyl acetate, propyl acetate, benzyl acetate, and ethylene glycol monomethyl ether acetate; ketones such as methylisobutyl ketone, and ethylisobutyl ketone; and alcohols such as n-butanol, and propanol. These solvents may be used solely, or in combination. To preferably carry out the solution polymerization, it is desirable to use a mixed solvent of ester(s) and alcohol(s).

The polymerization reaction is progressed, by adding a typical polymerization initiator such as a radical polymerization initiator into a mixture of the polymeric unsaturated metal-salt compound represented by formula (5) and the different polymeric monomer copolymerizable with the former, and by heating the resultant mixture to a predetermined temperature.

The paint composition according to this invention contains the diphenylborane compound as component (A) and the copolymer as component (B). The amount of the diphenylborane compound in the paint composition is suitably set within a range of usually 0.01 to 60 mass%, and preferably 0.1 to 40 mass%, in the solid content of paint composition. The diphenylborane compound in an amount less than the lower limit may cause such a

disadvantage that the obtained paint film has an inferior antifouling property, while the compound in an amount exceeding the upper limit may cause disadvantages such as cracks and separations in the paint film. Furthermore, the amount of the copolymer as component (B) in the paint composition is typically 0.1 to 80 mass%, and preferably 1 to 60 mass%, in the solid content of paint composition. The copolymer as component (B) in an amount less than the lower limit may cause disadvantages such as inferior antifouling property of the obtained paint film, while the copolymer in an amount exceeding the upper limit may cause disadvantages such as cracks and separations in the paint film.

The paint composition according to this invention may contain a rosin compound as component (C), if necessary. Examples of the rosin compound include a rosin, a rosin-derivative or a metal rosinate. The rosin includes, for example, tall rosin, gum rosin, and wood rosin. The rosin-derivative includes hydrated rosins, maleic rosins obtained by reacting rosins with maleic anhydride, formylated rosins, and polymerized rosins. The metal rosinate includes calcium rosinate, zinc rosinate, copper rosinate, magnesium rosinate, and reaction products of other metal compounds and rosins.

In this invention, it is possible to select and use one kind or two or more kinds of these rosin compounds, and the amount thereof is generally from 0.1 to 90 mass%, preferably from 0.1 to 80 mass%, in the solids content relative to the amount of the copolymer as component (B). An excessive amount of the rosin compounds tend to make the paint composition deteriorate in a paint-film forming ability so that defects such as cracks and separations are susceptible to be caused in the paint film, thereby possibly failing to obtain an effective antifouling activity.

An oil component such as silicone oil and liquid paraffin may be added to the paint composition of this

invention for the purpose of adjusting the eroding rate. Specifically, the oil component includes, for example, dimethyl silicone oil, methylphenyl silicone oil, polyether-denatured silicone oil, petrolatum, and polybutene.

The paint composition of this invention may be appropriately blended with coloring agents such as pigment and dyes including red ocher, zinc oxide, and talc; water binders; antisagging agents usually used in paints; plasticizers such as chlorinated paraffins, dioctyl phthalates, and tricresyl phosphates; UV absorbers such as benzophenone compounds and benzotriazole compounds; color-separation inhibitors; antisetling agents; antifoaming agents; and various additives such as silanols, polysiloxanes, and alkoxysilanes.

The paint composition according to the present invention can be obtained by mixing the diphenylborane compound as component (A); the product solution of the polymerization in which the copolymer as component (B) has been synthesized, or a copolymer solution prepared by adding a solvent to the copolymer isolated from the product solution; rosin compounds as component (C) to be added as required; and other various additives.

<Paint Compositions of Inventions (6) through (9)>

Next, description of the inventions (6) through (9) summarized in the paragraphs of "Means for solving the Problem" will be provided.

Used as one of the indispensable components of the paint composition of the present invention are the polymer (PA) obtained by polymerizing one kind or two or more kinds of monomer(s) (A) represented by formula (6) shown above; and/or the copolymer (PAB) obtained by polymerizing one kind or two or more kinds of the monomer(s) (A) with one kind or two or more kinds of monomer(s) (B) which is/are copolymerizable with the monomer(s) (A).

As represented by formula (6), monomer (A) has in its

molecule, as an unsaturated group (U), an acryloyloxy group, methacryloyloxy group, maleinoyloxy group [mainly, an ester of maleinoyloxy group with a monoalkyl, which has 1 to 6 carbon atoms], fumaroyloxy group [mainly, an ester of fumaroyloxy group with a monoalkyl, which has 1 to 6 carbon atoms], or itaconoyloxy group [mainly, an ester of itaconoyloxy group with a monoalkyl, which has 1 to 6 carbon atoms]; and a triorganosilyl group.

In the triorganosilyl group, the three hydrocarbon groups (R^{11} to R^{13}) may be the same or different from each other. Specifically, the groups include a straight-chain or branched, unsubstituted or substituted alkyl group with 20 or less carbon atoms, such as methyl, ethyl, propyl, and butyl; a cyclic alkyl group which may have one or more substituents, such as cyclopropyl, and cyclohexyl; an aryl group which may have one or more substituents, such as a phenyl group; and a polycyclic aryl group which may have one or more substituents, such as a naphthyl group.

Furthermore, the substituents of the substituted alkyl group include halogen atoms, aryl groups, acyl groups, alkoxyl groups, aryloxy groups, nitro group and amino group; and the substituents of the substituted aryl group include halogen atoms, alkyl groups, acyl groups, alkoxyl groups, aryloxy groups, nitro group and amino group.

The monomer (A) having a (meth)acryloyloxy group in its molecule includes, for example, trimethylsilyl (meth)acrylate, triethylsilyl (meth)acrylate, tri-n-propylsilyl (meth)acrylate, tri-i-propylsilyl (meth)acrylate, tri-n-butylsilyl (meth)acrylate, tri-i-butylsilyl (meth)acrylate, tri-s-butylsilyl (meth)acrylate, tri-n-amylsilyl (meth)acrylate, tri-i-amylsilyl (meth)acrylate, tri-n-hexylsilyl (meth)acrylate, tri-n-octylsilyl (meth)acrylate, tri-n-dodecylsilyl (meth)acrylate, tri-n-icosylsilyl (meth)acrylate, triphenylsilyl (meth)acrylate, tri-p-methylphenylsilyl (meth)acrylate, tribenzylsilyl (meth)acrylate, and tri-2-methoxyethylsilyl (meth)acrylate.

Other examples of the monomers each having a (meth)acryloyloxy group in the molecule include ethyldimethylsilyl (meth)acrylate, dimethyl-n-propylsilyl (meth)acrylate, dimethyl-i-propylsilyl (meth)acrylate, n-butyldimethylsilyl (meth)acrylate, s-butyldimethylsilyl (meth)acrylate, i-butyldimethylsilyl (meth)acrylate, t-butyldimethylsilyl (meth)acrylate, n-amyldimethylsilyl (meth)acrylate, i-amyldimethylsilyl (meth)acrylate, n-icosyldimethylsilyl (meth)acrylate, n-octyl-di-n-butylsilyl (meth)acrylate, di-i-propylstearylsilyl (meth)acrylate, dicyclohexyl-phenylsilyl (meth)acrylate, lauryl-diphenylsilyl (meth)acrylate, ethyl-di-n-octylsilyl (meth)acrylate, t-butyl-diphenylsilyl (meth)acrylate, cyclohexyl-di-p-tolylsilyl (meth)acrylate, di-t-butylmethylsilyl (meth)acrylate, n-icosa-di-o-nitrophenylsilyl (meth)acrylate, i-amyl-di-m-chlorophenylsilyl (meth)acrylate, ethylmethyl-n-propylsilyl (meth)acrylate, i-amyl-t-butylmethylsilyl (meth)acrylate, and o-cyanophenyl-cyclohexyl-naphthylsilyl (meth)acrylate.

The monomers each having a maleinoyloxy group in the molecule include, for example, trimethylsilylmethyl maleate, triethylsilyl-n-propyl maleate, tri-i-propylsilylmethyl maleate, tri-i-propylsilyl-n-amyl maleate, tri-n-propylsilyl-n-amyl maleate, tri-i-propylsilyl-i-amyl maleate, tri-n-butylsilyl-n-butyl maleate, t-butyl-diphenylsilylmethyl maleate, t-butyl-diphenylsilyl-n-butyl maleate, tri-n-butylsilyl-2-ethylhexyl maleate, tri-s-butylsilyl-n-octyl maleate, tri-n-amylsilylphenyl maleate, tri-i-amylsilylbenzyl maleate, tri-n-dodecylsilyl-o-nitrophenyl maleate, tri-n-icosylsilyl-p-tolyl maleate, triphenylsilyl-2-methoxyethyl maleate, tribenzylsilyl-m-bromophenyl maleate, tri-2-methoxyethyl-silylcyclohexyl maleate, ethyldimethyl-silylmethyl maleate, dimethyl-n-propylsilylmethyl maleate, dimethyl-i-propylsilyl-n-amyl maleate, n-butyldimethylsilyl-i-amyl maleate, s-butyldimethyl-silylphenyl maleate, i-butyldimethyl-silylcyclohexyl maleate, t-butyldimethylsilyl-o-N,N-

dimethylaminophenyl maleate, n-amyldimethylsilyl-t-butyl maleate, i-amyldimethylsilyl-2-methoxyethyl maleate, n-icosadimethylsilyl-2-ethoxyethyl maleate, ethyl-di-n-octylsilyl-p-tolyl maleate, t-butyl-diphenylsilyl-3-methoxycyclohexyl maleate, di-t-butylmethylsilyl-i-propyl maleate, n-icosa-di-o-nitrophenylsilyl-m-fluorophenyl maleate, i-amyl-di-m-chlorophenylsilyl-2-ethylhexyl maleate, ethylmethyl-n-propylsilyl-i-butyl maleate, i-amyl-t-butylmethylsilyl-s-butyl maleate, and o-cyanophenyl-cyclohexylnaphthyl-silylmethyl maleate. Among them, desirable are those organosilanes, each of which is replaced with a monoalkyl-ester of maleinoyloxy group having an alkyl group with 1 to 6 carbon atoms.

The monomers each having a fumaroyloxy group in the molecule include methyl-trimethylsilyl fumarate, tri-i-propylsilylmethyl fumarate, tri-i-propylsilyl-n-amyl fumarate, di-triethylsilyl fumarate, tri-n-propylsilyl-n-amyl fumarate, tri-i-propylsilyl-i-amyl fumarate, tri-n-butylsilyl-2-ethylhexyl fumarate, tri-n-butylsilyl-n-butyl fumarate, t-butyl-diphenylsilylmethyl fumarate, tri-s-butylsilyl-n-octyl fumarate, tri-i-butylsilyl-n-butyl fumarate, t-butyl-diphenylsilyl-n-butyl fumarate, tri-n-amylsilylphenyl fumarate, tri-i-amylsilylbenzyl fumarate, tri-n-dodecylsilyl-o-nitrophenyl fumarate, tri-n-icosasilyl-p-tolyl fumarate, triphenylsilyl-2-methoxyethyl fumarate, tribenzylsilyl-m-bromophenyl fumarate, tri-2-methoxyethyl-silylcyclohexyl fumarate, ethyldimethylsilylmethyl fumarate, ethyldimethyl-n-propylsilyl fumarate, dimethyl-i-propylsilyl-n-amyl fumarate, n-butyldimethylsilyl-i-amyl fumarate, s-butyldimethyl-silylphenyl fumarate, i-butyldimethyl-silylcyclohexyl fumarate, t-butyldimethylsilyl-o-N,N-dimethylaminophenyl fumarate, n-amyldimethylsilyl-t-butyl fumarate, i-amyldimethylsilyl-2-methoxyethyl fumarate, n-icosadimethylsilyl-2-ethoxyethyl fumarate, ethyl-di-n-octylsilyl-p-tolyl fumarate, t-butyl-diphenylsilyl-3-methoxycyclohexyl fumarate, benzylcyclohexyl-di-p-

tolylsilyl fumarate, di-t-butylmethyl-i-propyl fumarate, n-icosa-di-o-nitrophenylsilyl-m-fluorophenyl fumarate, i-amyl-di-m-chlorophenylsilyl-2-ethylhexyl fumarate, ethylmethyl-n-propylsilyl-i-butyl fumarate, i-amyl-t-butylmethylsilyl-s-butyl fumarate, and o-cyanophenyl-cyclohexyl-naphthylsilylmethyl fumarate. Among them, desirable are those organosilanes, each of which is substituted by a monoalkyl-ester fumaroyloxy group having an alkyl group with 1 to 6 carbon atoms.

The monomers each having an itaconoyloxy group in the molecule include trimethylsilylmethyl itaconate, triethylsilyl-n-propyl itaconate, tri-n-propylsilyl-n-amyl itaconate, tri-i-propylsilyl-i-amyl itaconate, tri-n-butylsilyl-2-ethylhexyl itaconate, tri-s-butylsilyl-n-octyl itaconate, tri-n-amylsilylphenyl itaconate, tri-i-amylsilylbenzyl itaconate, tri-n-dodecylsilyl-o-nitrophenyl itaconate, tri-n-icosasilyl-p-tolyl itaconate, triphenylsilyl-2-methoxyethyl itaconate, tribenzylsilyl-m-bromophenyl itaconate, tri-2-methoxyethyl-silylcyclohexyl itaconate, ethyldimethylsilylmethyl itaconate, dimethyl-n-propylsilylmethyl itaconate, dimethyl-i-propylsilyl-n-amyl itaconate, n-butyldimethylsilyl-i-amyl itaconate, s-butyldimethyl-silylphenyl itaconate, i-butyldimethyl-silylcyclohexyl itaconate, t-butyldimethylsilyl-o-N,N-dimethylaminophenyl itaconate, n-amyldimethylsilyl-t-butyl itaconate, i-amyldimethylsilyl-2-methoxyethyl itaconate, n-icosyldimethylsilyl-2-ethoxyethyl itaconate, ethyl-di-n-octylsilyl-p-tolyl itaconate, t-butyl-diphenylsilyl-3-methoxycyclohexyl itaconate, di-t-butylmethyl-i-propyl itaconate, n-icosa-di-o-nitrophenylsilyl-m-fluorophenyl itaconate, i-amyl-di-m-chlorophenylsilyl-2-ethylhexyl itaconate, ethylmethyl-n-propylsilyl-i-butyl itaconate, i-amyl-t-butylmethylsilyl-s-butyl itaconate, and o-cyanophenyl-cyclohexyl-naphthyl-silylmethyl itaconate. Among them, desirable are those organosilanes, each of which is substituted by a monoalkyl-ester itaconoyloxy group having an alkyl group with 1 to 6 carbon atoms.

Examples of the different monomer (B) copolymerizable with these monomers (A) include vinylesters such as acrylic esters, methacrylic esters, styrene, vinyl acetate, vinyl propionate, vinyl butyrate, and vinyl benzoate; and various vinyl monomers such as vinyltoluene, α -methylstyrene, crotonic esters, and itaconic esters.

Resin P in the present invention has various configurations and includes, for example, a homopolymer obtained by polymerizing one kind of monomer (A); a copolymer obtained by copolymerizing two or more kinds of monomers (A) with each other; and a copolymer obtained by polymerizing a monomer mixture of one kind or two or more kinds of monomer(s) (B) which is/are copolymerizable with monomer(s) (A) and is/are different from monomer(s) (A), and one kind or two or more kinds of monomer(s) (A). Mixtures of these polymers may also be employed.

In the copolymer obtained by copolymerizing two or more kinds of monomers (A) with one another, the molar ratio of the monomer (A) to the other monomer(s) (A) is not particularly limited. Furthermore, in the monomer mixture, although the ratio of the amount of the monomer (A) to the amount of the different monomer (B) copolymerizable therewith may be appropriately set in light of the purpose of use of the paint composition, it is typically preferable that the amount of the monomer (A) is 1 to 95 mass% and that of the different monomer (B) copolymerizable with the same is 5 to 99 mass%.

The polymer (PA) or copolymer (PAB) may be obtained by known various polymerizing methods including solution polymerization, bulk polymerization, emulsion polymerization, and suspension polymerization, in the presence of a vinyl polymerization initiator. In using resin P comprising the polymer (PA) and/or the copolymer for a paint, it is convenient to dilute the resin with an organic solvent to thereby prepare a resin solution with an appropriate viscosity, and it is thus desirable to employ the solution polymerization or bulk polymerization method.

As the vinyl polymerization initiator, it is possible to select and use an initiator to be used in typical polymerizations, depending on the intended polymerizing method. Specific examples of the initiator include azobis-based initiators such as 2,2'-azobis-isobutyronitrile, 2,2'-azobis-2-methylbutyronitrile, 2,2'-azobis-2,4-dimethylvaleronitrile, 1,1'-azobis-1-cyclohexane-carbonitrile, dimethyl-2,2'-azobisisobutylate, 4,4'-azobis-4-cyano valeric acid, and 2,2'-azobis-(2-amidinopropane)dihydrochloride; and peroxide-based initiators such as benzoyl peroxide, t-butylperoxy(2-ethylhexanoate), t-butylperoxy-isopropyl carbonate, and t-butylperoxybenzoate.

As the organic solvent mentioned above, it is possible to select, from various organic solvents, one organic solvent or two or more kinds of organic solvents to be mixed, depending on the kind of the monomer(s), the polymerization temperature, etc. Specifically, they include aliphatic hydrocarbon solvents such as pentane, hexane, and heptane; aromatic hydrocarbon solvents such as benzene, toluene, and xylene; ester solvents such as ethyl acetate, butyl acetate, and isobutyl acetate; ketone solvents such as methyl ethyl ketone, methyl isobutyl ketone, and cyclohexanone; and alcohol solvents such as ethanol, isopropanol, and butanol.

Each of the molecular weights of the polymer (PA) and copolymer (PAB) to be obtained by such methods is desirably within a range of 1,000 to 300,000 on the weight average. The employment of the polymer and/or the copolymer with an excessively lower molecular weight makes it difficult to form a normal paint film, while that of the polymer and/or the copolymer with a excessively higher molecular weight requires a lot of thinner when the paint is used, thereby bringing about such a problem that many times of painting operations are required to obtain a necessary film thickness. Also, the viscosity of this resin solution is advantageously 150 poises or less at 25°C, and to that end,

the solid content of the resin solution should advantageously be within a range of 5 to 90 mass%, preferably 15 to 85 mass%.

Although the paint composition of the present invention includes, as indispensable components, the resin components comprising the polymer (PA) and/or copolymer (PAB) obtained by the above-described methods, it is possible to use small amounts of polymers other than the above in combination insofar as they do not disturb the advantages of the present invention.

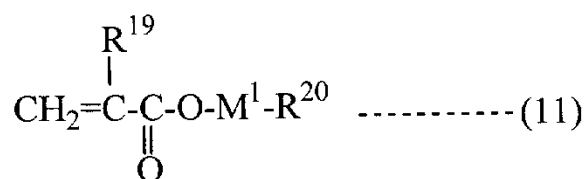
In the paint composition according to the present invention, it is possible to use a rosin compound together with resin P. The rosin compound includes rosins, rosin-derivatives or metal rosinates. The rosins include, for example, tall rosin, gum rosin, and wood rosin. The rosin-derivatives include, for example, hydrated rosins, maleic rosins obtained by reacting rosins with maleic anhydride, formylated rosins, and polymerized rosins. The metal rosinates include zinc rosinates, calcium rosinates, copper rosinates, magnesium rosinates, and reaction products of other metal compounds and rosins.

In the present invention, one kind or two or more kinds are selected from such rosin compounds and used, and the amount of each resin used is advantageously from 0.1 to 90 mass%, preferably from 0.1 to 80 mass%, in the solids content relative to the amount of resin P.

The rosin compound(s) in excessively larger amounts make the paint composition deteriorate in the paint-film forming ability, which leads to causing defects such as cracks and separations in the paint film, thereby failing to obtain an effective marine-organism-adhesion preventing performance. The rosin compound(s) in excessively smaller amounts make the paint fail to exhibit the effectiveness of the rosin compound(s).

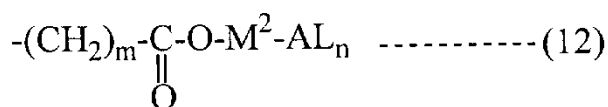
Resin P in the present invention never contains metal therein insofar as resin P consists of the polymer (PA) and/or copolymer (PAB). Resin P is allowed to include

other polymer(s) and/or copolymer(s) as long as they satisfy the condition that they never cause the resin P to include metal therein and they never hinder the achievement of the objectives of the present invention. Furthermore, resin P is allowed to include one kind or two or more kinds of hydrolysable resins that are selected from those known ones including metal therein insofar as such hydrolysable resins never hinder the achievement of the objectives of the present invention, particularly the environmental safety. The hydrolysable resins include, for example, those hydrolysable resins obtained by subjecting a monomer mixture including a metal-containing polymeric monomer to a polymerization reaction, the metal-containing polymeric monomer being represented by formula (11):



In formula (11), R^{19} is a hydrogen atom or methyl group; M^1 is Mg, Zn or Cu; and R^{20} is an organic acid residue having an unsaturated group, selected from oleic acid, elaidic acid, linoleic acid, linolenic acid, stearic acid, ricinoleic acid, ricino-ellagic acid, brassidic acid, and erucic acid).

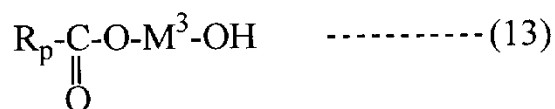
Or, those hydrolysable resins or other known hydrolysable resins, each of which includes, at the end of a side chain, a group represented by formula (12):



In formula (12), m denotes 0, 1 or 2; n denotes (the metal valence number) minus 1; M^2 represents Si, Cu or Zn; and AL is an alkyl group, a group represented by $\text{O}(\text{O}=\text{C})-\text{R}^{21}$, or a group represented by $-\text{R}^{22}-\text{CO}-\text{CH}_2-\text{CO}-\text{R}^{23}$, wherein R^{21} is

a hydrocarbon group with 10 or more carbon atoms, R^{22} is a divalent group comprising an alkylene or a phenyl derivative, and R^{23} is a monovalent group comprising an alkyl group or a phenyl derivative.

Or, those metal-containing hydrolysable resins may be those represented by formula (13):



In formula (13), R_p and M^3 represent a substrate resin and a divalent metal atom, respectively.

In the present invention, the amount of these known hydrolysable resins is desirably from 0.1 to 90 mass%, preferably 0.1 to 80 mass%, in the solids content relative to the silyl-containing copolymer represented by formula (6). When the amounts of the hydrolysable resins used in combination are excessively large, the essential resin and the optional resins do not dissolve in each other, thereby leading to a deterioration in the paint-film forming ability and a possibility of causing defects such as cracks and separations in the paint film. As a result, effective marine-organism-adhesion preventing performances are rarely obtained. The employment of the hydrolysable resin(s) in excessively smaller amounts makes the resin(s) fail to exhibit the effectiveness thereof.

Moreover, the paint composition of the present invention uses, as indispensable components, one or more kinds of borane compounds selected from those represented by formula (7) shown above. Examples of the borane compounds include 4-isopropylpyridine(diphenylmethyl)borane, 4-phenylpyridine(diphenyl)borane, and diphenylborane-n-octadecyl-amine. The amounts of these borane compounds used are typically within a range of 0.01 to 60 mass%, and preferably 0.1 to 40 mass% in the solids content of the paint composition. When the amount is excessively small, a due marine-organism-adhesion inhibiting effect of the

borane compounds cannot be expected. On the other hand, the use of an excessively larger amount of the borane compounds results in causing defects such as cracks and separations in the paint film, thereby also failing to obtain an excellent inhibiting effect.

Note that it is possible in the present invention to use, as required, other marine-organism-adhesion inhibitor(s) known in the field of paint, in addition to the one or more kinds of borane compounds selected from those represented by formula (7). Such other marine-organism-adhesion inhibitors are organic inhibitors that do not include metal, and examples of the additional marine-organism-adhesion inhibitor include N-trihalomethylthiophthalimide, dithiocarbamate, N-arylmaleimide, 3-substituted amino-1,3-thiazolidine-2,4-diones, dithiocyano compounds, triazine-based compounds, cuprous thiocyanate, pyrrithione compounds, and others.

Specific examples are 2-methylthio-4-t-butylamino-6-cyclopropylamino-s-triazine, 2,4,5,6-tetrachloroisophthalonitrile, N,N-dimethyl-N'-dichlorophenylurea, 4,5-dichloro-N-octyl-isothiazoline-3-one, N-(fluorodichloromethylthio)phthalimide, N,N-dimethyl-N'-phenyl-N'-fluorodichloromethylthio-sulfamide, tetramethylthiuram-disulphide, 2,4,6-trichlorophenyl-maleimide, 2,3,5,6-tetrachloro-4-(methylsulfonyl)pyridine, diiodomethylparatolyl sulfone, 2-(4-thiazolyl)benzimidazole, and 2-pyridinethiol-1-oxide-zinc salt or copper salt.

Furthermore, the combination of resin P free of metal and the organic inhibitor(s) free of metal produces a paint composition formed from the hydrolysable resin free of metal and the marine-organism-adhesion inhibitors free of metal, which ensures environmental safety. In this specification, the term "free of metal" means not to contain, as the constituent elements of the organic inhibitors (organic compounds), metal elements such as copper, tin, mercury and the like which are problematic to environmental safety. However, the term never excludes the

presence of extremely small amounts of the above-described metals as impurities originating from the starting materials for synthesizing the organic inhibitors.

An oil component such as silicone oil and liquid paraffin may be added to the paint composition of the present invention. Specifically, the oil component includes dimethyl silicone oil, methylphenyl silicone oil, polyether-denatured silicone oil, petrolatum, and polybutene.

The paint composition of the present invention may additionally be blended with coloring agents such as pigment and dyes including red ocher, titanium dioxide, zinc oxide, talc which are used in typical paints; antisagging agents, color-separation inhibitors, antisetling agents, antifoaming agents which are often used in paints; and plasticizers, other resins and solvents; as required, insofar as they do not obstruct the achievement of the objectives of the present invention. The plasticizers include chlorinated paraffins, dialkylphthalates, tricresyl phosphates, and triphenyl phosphates.

The paint composition of the present invention is characterized in that it contains, as indispensable components, the specific hydrolysable resin having a triorganosilyl group at its side-chain, and one or more kinds of borane compounds selected from those represented by formula (7) shown above. The antifouling paint film as a composite material comprising the paint composition is designed to have an extremely superior affinity with seawater or freshwater as a whole, as compared with the eroding ability of the antifouling paint film, thereby showing an extremely superior adhesion-preventing performance over a long period of time.

Moreover, the paint composition of the present invention makes the film made of it not only free from paint film defects such as separations and cracks, but also eroded at a constant and desirable rate, resulting in a

self-abrasive paint without forming any resin residual layer on the paint film surface, thereby exhibiting an extremely superior re-coating ability as compared with conventional non-hydrolytic paints. In addition, there is no risk of pitting corrosion into aluminum, when other metal-containing marine-organism-adhesion inhibitors are not used in combination.

Since the antifouling paint film according to the present invention has an excellent solubility, the antifouling paint film surface can be always kept flat and smooth. Thus, this advantage can reduce fuel costs of ships and the like, which further results in contributing to preventing the global warming due to carbon dioxide. Moreover, the paint composition according to the present invention is capable of exhibiting an excellent marine-organism-adhesion inhibiting effect even without using cuprous oxide in combination, so that this paint composition can be colored in any vivid colors, which ensures a remarkably superior designing probability, whereas typical paints for inhibiting marine-organism adhesion use cuprous oxide and the like and therefore the paints cannot be colored in vivid colors.

<Antifouling Paint Film and Antifouling Method>

The antifouling paint film of the paint composition according to this invention is formed on at least the surface of the submerged portion of a submerged structure. Coating methods therefor include, for example, spray coating, brush coating, roller coating, and immersion coating. The solvent evaporates, or can be removed at an ordinary temperature or by heating after the coating, so that the dried antifouling paint film can be readily formed on the surface of the submerged portion by this method.

<Antifouled Submerged Structure>

The antifouled submerged structure according to this invention includes submerged structures with the

antifouling paint film according to the present invention on the surfaces thereof.

The submerged structures include ships; fishing materials such as ropes, fishing nets, floats, and buoys; submerged equipment such as the water inlets and outlets of thermal/atomic power plants; coastal roads; undersea tunnels; harbor facilities; canals/watercourses; and various base materials such as sludge-diffusion preventing films for offshore engineering works. The submerged structures further include ships, buoys, various water pipes, offshore drilling wells, bridge piers, pipelines, marine cables, heat exchangers, dams, and water-absorbing screens.

These antifouled submerged structures with the antifouling paint films exhibit superior antifouling properties over a long period of time, and anti-cracking properties even when the paint films are painted in a larger thickness.

Specifically, the antifouling paint film obtained by applying a paint composition of this invention onto the surfaces of various base materials and curing it, is superior in antifouling properties, i.e. continuously preventing adhesion of aquatic organisms, such as mussels, barnacles, serpulas, polyzoans, sea lettuces, green string lettuces, and slimes, over a long period of time. In particular, the paint composition is satisfactorily fixed onto the surfaces of base materials, even when the base materials are made of steel, FRP, wood, aluminum alloy and the like. Furthermore, the paint composition may be applied onto the surface of an existing paint film.

In other words, the paint composition of the present invention has such a feature that marine-organism adhesion can be prevented and the functions of undersea structures can be maintained over a long period of time, when the paint composition is applied onto the surfaces of the undersea structures. In addition, coating fishing materials such as fishing nets or fishing gears with the

paint composition of this invention makes it possible to protect the fishing nets or fishing gears from being fouled, with a lesser risk of environmental pollution. The antifouling paint film of this invention, i.e. the paint film on the water-contacting surface of a ship or submerged structure, is formed from the above described paint composition, so that the paint film has a lesser risk of environmental pollution and exhibits a superior long-term antifouling property against organisms that may adhere onto the ship or submerged structure.

[Examples]

Firstly, the inventions recited in (1) through (5) noted in the paragraphs of "Means for solving the Problem" in the present invention will be described in detail, based on Preparation Examples, Working Examples and Comparative Examples. Note that "parts" in these examples represent parts by weight.

We will explain Preparation Examples of the copolymer containing the component units derived from the polymeric unsaturated metal-salt compound of component (B).

<Preparation Example 1>

Dissolved in a solvent (40 parts by weight of butyl acetate and 20 parts by weight of n-butanol) was 40 parts by weight of a copolymerizable monomer mixture, so that total weight of the reaction mixture was 100 parts by weight. The copolymerizable monomer mixture *per se* consisted of 14 parts by weight of zinc acrylate, 26 parts by weight of zinc oleate acrylate, 15 parts by weight of methyl methacrylate, and 45 parts by weight of ethyl acrylate. The reaction mixture was allowed to copolymerize at 100°C for 6 hours in the presence of AIBN, a polymerization initiator. As a result, solution 1 (including a solids content of 40 mass%) of a polymer having a molecular weight (M_w) of about 8,000 was obtained. Table 1 shows the composition of the reaction monomers for

preparing this polymer solution 1, and the physical properties and the like of the obtained polymer solution 1.

<Preparation Examples 2 through 8>

The polymer solutions listed in Table 1 were obtained in the same manner as polymer solution 1, except that starting materials having the compositions of monomers listed in Table 1 were used, respectively, instead of the monomers for polymer solution 1. The compositions of the monomers and the like are shown in Table 1.

<Preparation Example 9>

8 g of zinc oxide, 5 g of butanol and 1 g of water were added to a 50-mass% butyl acetate solution of a copolymer having a number-average molecular weight of 40,000 and comprising 7.2 parts by weight of acrylic acid, 50 parts by weight of methyl methacrylate and 42.8 parts by weight of ethyl acrylate. The mixture was allowed to react at 120°C for 10 hours, and a transparent polymer solution containing a solids content of 49.2 mass%, which will be called "polymer solution 9", was produced.

<Preparation Example 10>

46 parts of butyl acetate and 42 parts of n-butanol were charged into a reactor provided with a thermometer, a thermostat, a stirrer, a reflux condenser and a dropping pump. Then 7.3 parts of zinc oxide and 5.0 parts of water then the charge was added to the mixed solvent in the reactor with stirring, and the zinc oxide was dispersed in the solvent. The temperature of the mixture was then raised to 100°C with stirring, followed by dropping of 15.3 parts of methacrylic acid, 44.7 parts of ethyl acrylate, 40.0 parts of methoxyethyl acrylate, and 8.0 parts of 2,2'-azobis(2-methylbutyronitrile), which is a polymerization initiator, at a constant rate by means of the dropping pump over 4 hours while the mixture was being kept at 100°C. The resulting mixture was kept stirred at 100°C for 30

minutes after finishing the dropping. Thereafter, dropped into the mixture at a constant rate over 1 hour was a solution obtained by dissolving 1 part of 2,2'-azobis(2,4-dimethylpentylonitrile) as an additional polymerization initiator in 6 parts of butyl acetate and 6 parts of n-butanol. The resultant was kept being stirred for additional 6 hours at 100°C. A uniform and transparent polymer solution including 50 mass% of nonvolatile matter, which will be called "polymer solution 10", was obtained.

[Table 1]

(Working Examples 1 through 26)

One or two of polymer solutions 1 through 10 were mixed with the components shown in Tables 2 to 4 at the compositions listed in the same Tables (the numerical values in Tables are mass%). The components including the polymer solutions were mixed and dispersed with a homo-mixer at 2,000 rpm, whereby 20 kinds of paint compositions were prepared. In the Tables, "Laroflex MP-45", which is the name of a product made by BASF Ltd., is a vinyl chloride resin, "TSF-4445", which is the name of a product made by Toshiba Silicones Co., Ltd., is a polyether-modified silicone oil, and "DISPARLON A630-20XN", which is the name of a product made by Kusumoto Chemicals, Ltd., "DISPARLON 4200-2", which is the name of a product made by Kusumoto Chemicals, Ltd., and "BENTON SD-2", which is the name of a product made by National Red Co., Ltd., are all antisagging additives.

(Comparative Example 1)

15 parts of "Laroflex MP-45" (a product made by BASF Ltd.; vinyl-chloride resin), 10 parts of rosin, 2 parts of chlorinated paraffin, 30 parts of pyridine-methyl(diphenyl)borane, 4 parts of zinc oxide, 6 parts of red ocher, 1 part of "AEROSIL #200" (a product made by Nippon Aerosil Co., Ltd.), 32 parts of xylene, and 5 parts of methyl isobutyl ketone were mixed. The mixture was then mixed and dispersed with a homo-mixer at a rotating speed of 2,000 rpm, so that a paint composition was prepared.

(Comparative Example 2)

15 parts of Acrylic resin (a product made by Hitachi Chemical Co., Ltd.; 50% xylene solution), 7 parts of rosin, 2 parts of tricresyl phosphate, 2 parts of silicone oil TSF-4445 (product name of Toshiba Silicones Co., Ltd.; polyether-denatured silicone oil), 20 parts of n-octadecylamine-triphenylborane, 15 parts of talc, 1 part of zinc oxide, 8 parts of red ocher, and 30 parts of xylene

were mixed. The mixture was then mixed and dispersed with a homo-mixer at a rotating speed of 2,000 rpm, so that a paint composition was prepared.

(Comparative Examples 3 through 7)

The components were mixed with one another at the compositions shown in Table 5 (the numerical values in the Table are mass%). The components were mixed and dispersed with a homo-mixer at a rotating speed of 2,000 rpm, so that paint compositions were prepared.

[Table 2]

[Table 3]

[Table 4]

[Table 5]

For the paint compositions of the Examples 1 through 26 and Comparative Examples 1 through 7 were carried out a paint-film eroding test, an antifouling activity test, an adherence test, a crack resistance test, a re-coating ability test, and a fishing-net antifouling-activity test, based on the following procedures. The results were shown in Table 6 through Table 12.

<Paint-Film Consuming Test>

A steel plate (100 mm × 100 mm × 1 mm) with both surfaces having been coated with a rustproof paint was coated with each paint composition twice with a sprayer, so that the dry-base film thickness by one spraying was 200 μm . The paint composition was dried in a room at a temperature of 20°C for one week, whereby each test piece was prepared.

Each test piece was fixed on an outer surface of a cylindrical drum with a diameter of 50 cm, and then immersed in seawater at a depth of 1 m below the sea surface at Yura Bay in Sumoto, Hyogo, Japan. Then, the drum was rotated with a motor at a circumferential speed of 16 knots, and the eroded thickness of the paint film was measured every 3 months for 24 months. Also, the averaged paint-film-thickness eroding rate ($\mu\text{m}/\text{month}$) was calculated for the period up to 6 months and for the period from 6 months to 24 months. Note that the averaged paint-film-thickness eroding rate correlates with an excellent antifouling activity, if the rate achieves a value of 3 $\mu\text{m}/\text{month}$. Furthermore, it is proven that each paint film was eroded at a constant rate, when the averaged paint-film-thickness eroding rate during the period from 6 months to 24 months is within a range of the "averaged paint-film-thickness eroding rate during the period up to 6 months" ± 1 ($\mu\text{m}/\text{month}$).

<Antifouling Activity Test>

Both surfaces of an FRP plate (100 mm × 200 mm × 1 mm) were coated with each paint composition by spray-

coating twice, so that the dry-base film thickness on each surface was 240 μm . The paint composition was dried in a thermostatic chamber kept at a temperature of 20°C and a humidity of 75% for one week, whereby each test piece was prepared. Each test piece was immersed in seawater at a location of 1.5 m below the sea surface at Osaka Bay in Takaishi, Osaka, Japan for 24 months, and adhesion of aquatic creatures, such as barnacles, ascidians, serpulas, blue mussels, fresh-water mussels, green mussels, and bryozoans; aquatic plants, such as green string lettuces, and sea lettuces; and slimes was measured with the passage of time. Note that the adhesion amounts of the aquatic creatures and aquatic plants in the Tables are indicated by the percentages of the surface areas occupied by the organisms adhering to the tested paint films. Furthermore, the adhesion amounts of slimes were evaluated based on the following evaluation criteria, and indicated by the numerical values.

- 0: no adhesion of slime
- 1: slight amount of adhering slime
- 2: small amount of adhering slime
- 3: medium amount of adhering slime
- 4: medium to large amount of adhering slime
- 5: large amount of adhering slime

<Adherence Test>

An abrasive-blasted steel plate was coated with an epoxy-based rustproof paint twice with a sprayer, so that the dry-base film thickness by one spraying was 125 μm . A sealer coat was further provided thereon so that the dry-base film thickness was 70 μm . Each paint composition was applied thereto twice with a sprayer so that the dry-base film thickness by one spraying was 100 μm , and the paint composition was dried in a thermostatic chamber at a temperature of 20°C and a humidity of 75% for one week, whereby each test piece was prepared.

Each test piece was immersed in artificial seawater,

and a cross-cut adhesion test with a 2 mm spacing was performed for the test pieces taken out of the water at times of 3 months, 6 months, 12 months, 18 months and 24 months from the immersion, respectively. Evaluation of the adherence by this test is indicated by a mark "○" (accepted) when the number of separated pieces in this test was 0 piece/25 pieces and by a mark "No" (rejected) when the number of separated pieces was 1 piece/25 pieces or more.

<Crack Resistance Test>

In the adherence test, the presence/absence of cracks in the paint film was checked by visually observing it upon taking it out of the artificial seawater. Those having no cracks were evaluated as "Yes" (accepted), and those having cracks were evaluated as "No" (rejected).

<Re-Coating Ability Test>

A steel plate (100 mm × 100 mm × 1 mm), both surfaces of which had been coated with a rustproof paint, was coated with each paint composition twice with a sprayer, so that the dry-base film thickness by one spraying was 100 μm . The paint composition was dried in a thermostatic chamber at a temperature of 20°C and a humidity of 75% for one week, whereby two test pieces for each paint composition were prepared.

Each test piece was immersed in artificial seawater, taken out of it at the time of 12 months and that of 24 months from the immersion, then washed with distilled water, and dried in a room at a temperature of 20°C for one week. Thereafter, the surface of each test piece was spray-painted twice with the same paint composition as that already on the test piece such that the new dry-base film thickness by one spraying was 100 μm , and the paint composition thus applied was dried in a room at a temperature of 20°C for one week. Each test piece was then fixed on the outer surface of a cylindrical drum with a

diameter of 50 cm, and then immersed in seawater at a position 1 m below the sea surface at Yura Bay in Sumoto, Hyogo, Japan. The drum was rotated with a motor so that a circumferential speed thereof was 16 knots. Each test piece was taken out of the sea after one week, and the presence/absence of separation between the new paint film and the old one was checked. Test pieces without separation were indicated by "Yes" (accepted), and those with separation by "No" (rejected).

<Fishing-Net Antifouling-Activity Test>

Each paint composition was applied onto a test fishing net having a size of length x width of 50 cm x 25 cm and comprising 24 threads and 10 nodes of polyethylene of 440 dtex, in an amount of 0.4 g for 1 g of the fishing-net weight. Each fishing net was then air-dried for 3 days, and then immersed in seawater at a location 1.5m below the sea surface at Sagami Bay in Odawara, Kanagawa, Japan for 24 months. The amount of attached organisms was measured at predetermined intervals. In the same manner, the adhesion aquatic creatures, such as barnacles, ascidians, serpulas, blue mussels, fresh-water mussels, green mussels, and bryozoans; and aquatic plants, such as green string lettuces, and sea lettuces were checked. Note that the amounts of the adhering aquatic creatures and aquatic plants in the Tables are indicated by the percentages of the surface areas occupied by the organisms adhering to the tested paint films. Furthermore, the adhesion amounts of slimes were evaluated based on the following evaluation criteria, and indicated by the numerical values.

- 0: no adhesion of slime
- 1: slight amount of adhering slime
- 2: small amount of adhering slime
- 3: medium amount of adhering slime
- 4: medium to large amount of adhering slime
- 5: large amount of adhering slime

Table 6

	Paint-film Eroding test							
	Eroded film thickness (μm)							
	3 months	6 months	9 months	12 months	15 months	18 months	21 months	24 months
Working Example 1	15	31	44	61	77	88	103	125
W. Ex. 2	28	60	88	115	151	181	212	243
W. Ex. 3	12	25	36	49	58	74	86	99
W. Ex. 4	8	18	29	38	48	57	65	76
W. Ex. 5	36	72	108	144	180	216	252	288
W. Ex. 6	20	41	66	82	102	128	149	171
W. Ex. 7	26	50	70	95	119	148	172	195
W. Ex. 8	30	65	102	130	168	201	233	267
W. Ex. 9	18	37	56	74	95	112	129	144
W. Ex. 10	39	76	117	150	191	230	269	309
W. Ex. 11	13	29	46	62	71	91	105	121
W. Ex. 12	26	55	81	106	136	165	191	219
W. Ex. 13	27	53	83	102	133	161	189	216
W. Ex. 14	44	89	133	179	222	273	316	362
W. Ex. 15	23	48	71	99	118	142	169	195
W. Ex. 16	46	95	142	193	240	289	338	386
W. Ex. 17	31	59	90	118	152	179	212	235
W. Ex. 18	11	23	38	50	58	70	85	101
W. Ex. 19	35	70	103	142	182	214	250	285
W. Ex. 20	24	47	72	98	121	140	170	189
W. Ex. 21	22	47	75	94	117	141	170	195
W. Ex. 22	26	50	70	95	119	148	172	195
W. Ex. 23	31	65	104	130	170	203	233	267
W. Ex. 24	17	36	55	73	94	111	128	143
W. Ex. 25	40	77	118	151	192	231	270	310
W. Ex. 26	14	29	47	63	72	91	104	122
Comparative Example 1	52	83	83	84	85	85	86	86
Com. Ex. 2	33	83	83	84	85	85	86	86
Com. Ex. 3	90	99	99	100	101	101	102	102
Com. Ex. 4	60	130	170	230	290	347	399	-
Com. Ex. 5	70	147	223	293	370	-	-	-
Com. Ex. 6	77	163	254	342	-	-	-	-
Com. Ex. 7	73	144	231	286	365	-	-	-

Notes:

The mark "-" represents that the rustproof paint film was exposed.

The abbreviations "W. Ex." and "Com. Ex." denote "Working Example" and "Comparative Example", respectively.

Table 7

	Paint-film eroding test Averaged paint-film-thickness eroding rate ($\mu\text{m}/\text{month}$)	
	to 6 months	6 to 24 months
Working Example 1	5.2	5.1
Working Example 2	10.0	10.3
Working Example 3	4.2	4.1
Working Example 4	3.0	3.2
Working Example 5	12.0	12.0
Working Example 6	6.8	7.2
Working Example 7	8.3	8.2
Working Example 8	10.8	11.2
Working Example 9	6.2	6.0
Working Example 10	12.7	12.9
Working Example 11	4.8	5.0
Working Example 12	9.2	9.2
Working Example 13	8.8	9.0
Working Example 14	14.8	15.2
Working Example 15	8.0	8.1
Working Example 16	15.8	16.2
Working Example 17	9.8	9.9
Working Example 18	3.8	4.1
Working Example 19	11.7	12.0
Working Example 20	7.8	7.9
Working Example 21	7.8	8.1
Working Example 22	8.3	8.2
Working Example 23	10.8	11.2
Working Example 24	6.0	6.0
Working Example 25	12.8	12.9
Working Example 26	4.8	5.0
Comparative Example 1	13.8	0.2
Comparative Example 2	13.8	0.2
Comparative Example 3	16.5	0.2
Comparative Example 4	21.7	18.4
Comparative Example 5	24.5	24.6
Comparative Example 6	27.2	29.8
Comparative Example 7	24.0	23.9

Table 8

	Antifouling activity test									
	Occupying area (%) of adhering organisms									
	3 months		6 months		12 months		18 months		24 months	
	A	B	A	B	A	B	A	B	A	B
Working Example 1	0	0	0	0	0	0	0	0	0	0
Working Example 2	0	0	0	0	0	0	0	0	0	0
Working Example 3	0	0	0	0	0	0	0	0	0	0
Working Example 4	0	0	0	0	0	0	0	0	0	0
Working Example 5	0	0	0	0	0	0	0	0	0	0
Working Example 6	0	0	0	0	0	0	0	0	0	0
Working Example 7	0	0	0	0	0	0	0	0	0	0
Working Example 8	0	0	0	0	0	0	0	0	0	0
Working Example 9	0	0	0	0	0	0	0	0	0	0
Working Example 10	0	0	0	0	0	0	0	0	0	0
Working Example 11	0	0	0	0	0	0	0	0	0	0
Working Example 12	0	0	0	0	0	0	0	0	0	0
Working Example 13	0	0	0	0	0	0	0	0	0	0
Working Example 14	0	0	0	0	0	0	0	0	0	0
Working Example 15	0	0	0	0	0	0	0	0	0	0
Working Example 16	0	0	0	0	0	0	0	0	0	0
Working Example 17	0	0	0	0	0	0	0	0	0	0
Working Example 18	0	0	0	0	0	0	0	0	0	0
Working Example 19	0	0	0	0	0	0	0	0	0	0
Working Example 20	0	0	0	0	0	0	0	0	0	0
Working Example 21	0	0	0	0	0	0	0	0	0	0
Working Example 22	0	0	0	0	0	0	0	0	0	0
Working Example 23	0	0	0	0	0	0	0	0	0	0
Working Example 24	0	0	0	0	0	0	0	0	0	0
Working Example 25	0	0	0	0	0	0	0	0	0	0
Working Example 26	0	0	0	0	0	0	0	0	0	0
Comparative Example 1	5	2	30	3	90	5	90	5	90	5
Com. Ex. 2	5	2	40	3	100	5	100	5	100	5
Com. Ex. 3	5	2	30	3	90	5	90	5	90	5
Com. Ex. 4	5	2	30	3	100	5	10	5	100	5
Com. Ex. 5	5	2	40	3	90	5	90	5	90	5
Com. Ex. 6	5	2	30	3	100	5	100	5	100	5
Com. Ex. 7	5	2	30	3	90	5	90	5	90	5

Notes:

"A" represents the percentages of the surface areas to which aquatic creatures and plants adhere.

"B" represents an adhesion amount of slime shown in the numerical values based on the evaluation criteria.

Table 9

	Adherence test				
	3 months	6 months	12 months	18 months	24 months
Working Example 1	Yes	Yes	Yes	Yes	Yes
Working Example 2	Yes	Yes	Yes	Yes	Yes
Working Example 3	Yes	Yes	Yes	Yes	Yes
Working Example 4	Yes	Yes	Yes	Yes	Yes
Working Example 5	Yes	Yes	Yes	Yes	Yes
Working Example 6	Yes	Yes	Yes	Yes	Yes
Working Example 7	Yes	Yes	Yes	Yes	Yes
Working Example 8	Yes	Yes	Yes	Yes	Yes
Working Example 9	Yes	Yes	Yes	Yes	Yes
Working Example 10	Yes	Yes	Yes	Yes	Yes
Working Example 11	Yes	Yes	Yes	Yes	Yes
Working Example 12	Yes	Yes	Yes	Yes	Yes
Working Example 13	Yes	Yes	Yes	Yes	Yes
Working Example 14	Yes	Yes	Yes	Yes	Yes
Working Example 15	Yes	Yes	Yes	Yes	Yes
Working Example 16	Yes	Yes	Yes	Yes	Yes
Working Example 17	Yes	Yes	Yes	Yes	Yes
Working Example 18	Yes	Yes	Yes	Yes	Yes
Working Example 19	Yes	Yes	Yes	Yes	Yes
Working Example 20	Yes	Yes	Yes	Yes	Yes
Working Example 21	Yes	Yes	Yes	Yes	Yes
Working Example 22	Yes	Yes	Yes	Yes	Yes
Working Example 23	Yes	Yes	Yes	Yes	Yes
Working Example 24	Yes	Yes	Yes	Yes	Yes
Working Example 25	Yes	Yes	Yes	Yes	Yes
Working Example 26	Yes	Yes	Yes	Yes	Yes
Comparative Example 1	No	No	No	No	No
Comparative Example 2	No	No	No	No	No
Comparative Example 3	No	No	No	No	No
Comparative Example 4	No	No	No	No	No
Comparative Example 5	No	No	No	No	No
Comparative Example 6	No	No	No	No	No
Comparative Example 7	No	No	No	No	No

Table 10

	Crack resistance test				
	3 months	6 months	12 months	18 months	24 months
Working Example 1	Yes	Yes	Yes	Yes	Yes
Working Example 2	Yes	Yes	Yes	Yes	Yes
Working Example 3	Yes	Yes	Yes	Yes	Yes
Working Example 4	Yes	Yes	Yes	Yes	Yes
Working Example 5	Yes	Yes	Yes	Yes	Yes
Working Example 6	Yes	Yes	Yes	Yes	Yes
Working Example 7	Yes	Yes	Yes	Yes	Yes
Working Example 8	Yes	Yes	Yes	Yes	Yes
Working Example 9	Yes	Yes	Yes	Yes	Yes
Working Example 10	Yes	Yes	Yes	Yes	Yes
Working Example 11	Yes	Yes	Yes	Yes	Yes
Working Example 12	Yes	Yes	Yes	Yes	Yes
Working Example 13	Yes	Yes	Yes	Yes	Yes
Working Example 14	Yes	Yes	Yes	Yes	Yes
Working Example 15	Yes	Yes	Yes	Yes	Yes
Working Example 16	Yes	Yes	Yes	Yes	Yes
Working Example 17	Yes	Yes	Yes	Yes	Yes
Working Example 18	Yes	Yes	Yes	Yes	Yes
Working Example 19	Yes	Yes	Yes	Yes	Yes
Working Example 20	Yes	Yes	Yes	Yes	Yes
Working Example 21	Yes	Yes	Yes	Yes	Yes
Working Example 22	Yes	Yes	Yes	Yes	Yes
Working Example 23	Yes	Yes	Yes	Yes	Yes
Working Example 24	Yes	Yes	Yes	Yes	Yes
Working Example 25	Yes	Yes	Yes	Yes	Yes
Working Example 26	Yes	Yes	Yes	Yes	Yes
Comparative Example 1	No	No	No	No	No
Comparative Example 2	No	No	No	No	No
Comparative Example 3	No	No	No	No	No
Comparative Example 4	No	No	No	No	No
Comparative Example 5	No	No	No	No	No
Comparative Example 6	No	No	No	No	No
Comparative Example 7	No	No	No	No	No

Table 11

	Re-coating ability test	
	Immersed period of old paint film	Immersed period of old paint film
	12 months	24 months
Working Example 1	Yes	Yes
Working Example 2	Yes	Yes
Working Example 3	Yes	Yes
Working Example 4	Yes	Yes
Working Example 5	Yes	Yes
Working Example 6	Yes	Yes
Working Example 7	Yes	Yes
Working Example 8	Yes	Yes
Working Example 9	Yes	Yes
Working Example 10	Yes	Yes
Working Example 11	Yes	Yes
Working Example 12	Yes	Yes
Working Example 13	Yes	Yes
Working Example 14	Yes	Yes
Working Example 15	Yes	Yes
Working Example 16	Yes	Yes
Working Example 17	Yes	Yes
Working Example 18	Yes	Yes
Working Example 19	Yes	Yes
Working Example 20	Yes	Yes
Working Example 21	Yes	Yes
Working Example 22	Yes	Yes
Working Example 23	Yes	Yes
Working Example 24	Yes	Yes
Working Example 25	Yes	Yes
Working Example 26	Yes	Yes
Comparative Example 1	No	No
Comparative Example 2	No	No
Comparative Example 3	No	No
Comparative Example 4	No	No
Comparative Example 5	No	No
Comparative Example 6	No	No
Comparative Example 7	No	No

Table 12

	Fishing-net antifouling-activity test									
	Occupying area (%) of attaching-organisms									
	3 months		6 months		12 months		18 months		24 months	
	A	B	A	B	A	B	A	B	A	B
Working Example 1	0	0	0	0	0	0	0	0	0	0
Working Example 2	0	0	0	0	0	0	0	0	0	0
Working Example 3	0	0	0	0	0	0	0	0	0	0
Working Example 4	0	0	0	0	0	0	0	0	0	0
Working Example 5	0	0	0	0	0	0	0	0	0	0
Working Example 6	0	0	0	0	0	0	0	0	0	0
Working Example 7	0	0	0	0	0	0	0	0	0	0
Working Example 8	0	0	0	0	0	0	0	0	0	0
Working Example 9	0	0	0	0	0	0	0	0	0	0
Working Example 10	0	0	0	0	0	0	0	0	0	0
Working Example 11	0	0	0	0	0	0	0	0	0	0
Working Example 12	0	0	0	0	0	0	0	0	0	0
Working Example 13	0	0	0	0	0	0	0	0	0	0
Working Example 14	0	0	0	0	0	0	0	0	0	0
Working Example 15	0	0	0	0	0	0	0	0	0	0
Working Example 16	0	0	0	0	0	0	0	0	0	0
Working Example 17	0	0	0	0	0	0	0	0	0	0
Working Example 18	0	0	0	0	0	0	0	0	0	0
Working Example 19	0	0	0	0	0	0	0	0	0	0
Working Example 20	0	0	0	0	0	0	0	0	0	0
Working Example 21	0	0	0	0	0	0	0	0	0	0
Working Example 22	0	0	0	0	0	0	0	0	0	0
Working Example 23	0	0	0	0	0	0	0	0	0	0
Working Example 24	0	0	0	0	0	0	0	0	0	0
Working Example 25	0	0	0	0	0	0	0	0	0	0
Working Example 26	0	0	0	0	0	0	0	0	0	0
Comparative Example 1	5	2	30	3	80	5	90	5	90	5
Com. Ex. 2	3	2	30	3	90	5	100	5	100	5
Com. Ex. 3	5	2	30	3	80	5	90	5	90	5
Com. Ex. 4	5	2	30	3	90	4	100	5	100	5
Com. Ex. 5	3	2	40	3	80	4	90	5	90	5
Com. Ex. 6	5	2	40	3	90	4	100	5	100	5
Com. Ex. 7	5	2	30	3	80	4	90	5	90	5

Notes:

"A" represents the percentages of the surface areas to which aquatic creatures and plants adhere.

"B" represents an adhesion amount of slime shown in the numerical values based on the evaluation criteria.

As apparent from the results shown in Table 6 through Table 12 above, the paint composition of Comparative Example 1 (corresponding to the embodiment of JP-A-9-323909 (323909/1997)) adopting a vinyl-chloride resin as a blending polymer, the paint composition of Comparative Example 2 (corresponding to the embodiment of JP-A-2001-342192) adopting a non-hydrolytic acrylic resin, and the paint composition of Comparative Example 3, all exhibited excellent paint-film eroding abilities only for several months after immersion, but they lost paint-film eroding abilities after long-term immersion to thereby show unsatisfactory results in both of the paint-film eroding rates and antifouling activities, while revealing defects in the adherence test, crack resistance test, re-coating ability test and fishing-net antifouling-activity test.

Meanwhile, the paint composition (corresponding to the embodiment of JP-A-2001-329228) of Comparative Example 5 adopting a hydrolysable resin and pyridine-triphenylborane, and the paint compositions of Comparative Examples 4, 6, 7 each adopting a hydrolysable resin and an antifouling agent other than the compound of component (A) described in this invention, though some of them exhibited very excellent paint-film consuming abilities, showed antifouling activities for only a short period of time, while showing defects also in the adherence test, the crack resistance test, the re-coating ability test and the fishing-net antifouling-activity test. Contrary, the paint compositions of Examples 1 through 26 each adopting the compound of component (A) described in this invention and the hydrolysable resin, provided satisfactory results in the respective tests, thereby showing that the paint compositions of this invention possess superior performances based on these results.

Next, the inventions described in (6) through (9) noted in the paragraphs of "Means for solving the Problem" in the present application will be described in detail

based on Preparation Examples, Working Examples and Comparative Examples. Note that "parts" in these examples represent parts by mass, and the molecular weight is a weight-average molecular weight calculated as polystyrene by GPC. Furthermore, monomers (A) ((A1) through (A8)) are those monomers represented by formula (6), and R^{11} through R^{13} and U in formula (6) are as follows.

Table 13

	Organic group in general formula (1)			
	R ¹¹	R ¹²	R ¹³	U
Monomer A ₁	CH ₂	CH ₂	t-C ₄ H ₉	CH ₂ =CHCOO
Monomer A ₂	i-C ₃ H ₇	i-C ₃ H ₇	i-C ₃ H ₇	CH ₂ =CHCOO
Monomer A ₃	n-C ₄ H ₉	n-C ₄ H ₉	n-C ₄ H ₉	CH ₂ =C(CH ₃)COO
Monomer A ₄	C ₅ H ₅	C ₅ H ₅	t-C ₄ H ₉	CH ₂ =C(CH ₃)COO
Monomer A ₅	i-C ₃ H ₇	i-C ₃ H ₇	i-C ₃ H ₇	CH ₂ =C(CH ₃)COO
Monomer A ₆	i-C ₃ H ₇	i-C ₃ H ₇	i-C ₃ H ₇	C ₅ H ₁₁ OOCCH=CHCOO (maleinoyloxy group)
Monomer A ₇	C ₅ H ₅	C ₅ H ₅	t-C ₄ H ₉	C ₅ H ₁₁ OOCCH=CHCOO (fumaroyloxy group)
Monomer A ₈	n-C ₄ H ₉	n-C ₄ H ₉	n-C ₄ H ₉	CH ₂ =C(CH ₂ COOCH ₃)COO (itaconoyloxy group)

[Preparation examples 11 through 15]

Charged into a flask provided with a stirrer was a solvent "a" in conformity with the formula in Table 14 below. Then, the solvent temperature was raised to a predetermined reaction temperature, and thereafter a mixed solution of a monomer (A), a different monomer (B) and polymerization catalyst "a" was dropped into the flask over 3 hours while stirring solvent "a". The resulting mixture after the completion of dropping was kept at the same temperature for 30 minutes. Next, a mixture of solvent "b" and polymerization catalyst "b" was dropped into the flask over 20 minutes, and the polymerization reaction was completed by continuously stirring the contents of the flask for 2 hours at the same temperature. Lastly, the resultant mixture was diluted by adding a diluent solvent thereto, whereby an applicable one of resin solutions S₁ through solution S₅ was obtained. Note that the product named "PERBUTYL I" (a product of NOF CORPORATION), as polymerization catalyst, is t-butylperoxy-isopropyl carbonate, and that named "Veova 9" (a product of Showa Shell Chemicals Ltd.) is a vinylester-based monomer.

[Preparation Example 16]

Charged into a flask provided with a stirrer were a solvent "a", a monomer (A), a different monomer (B) and polymerization catalyst "a" in conformity with the formula in Table 14. Then the mixture temperature was raised to a predetermined reaction temperature while stirring the mixture, and the polymerization reaction was completed by continuously stirring the contents of the flask for 6 hours at the same temperature. Next, the resulting mixture was diluted by adding a diluent solvent thereto, whereby a resin solution S₆ was obtained.

[Preparation Example 17]

Charged into a heat-resistant and pressure-resistant vessel were a monomer (A), a different monomer (B) and polymerization catalyst "a" in conformity with the formula in Table 14. Then the mixture temperature was raised to a predetermined reaction temperature while the vessel, hermetically sealed, was being shaken. The polymerization reaction was completed by continuously shaking the vessel for 8 hours at the same temperature. Next, a diluent solvent was added to the resultant product, and the vessel was shaken for additional 8 hours, which produced resin solution S₇.

Table 14

		Preparation example						
		11	12	13	14	15	16	17
Solvent a	Xylene Butyl acetate	40	40 10	40	30	45		30
Monomer A	Monomer A ₁ Monomer A ₂ Monomer A ₃ Monomer A ₄ Monomer A ₅ Monomer A ₆ Monomer A ₇ Monomer A ₈	10 40	 60 	 30	 40 	 40 40 	 30	 35
Different monomer B	Methoxyethyl acrylate Methoxyethyl methacrylate Ethoxydiethylene glycol acrylate Methoxyethyl-n-butyl maleate Butoxyethylmethyl itaconate Methyl methacrylate n-butyl acrylate Vinyl acetate Veova 9 Dimethyl maleate	 10 10 30 10	10 30	 40 10 20	 20 15 25	 15 5 	 30 10 30	 40 20 5
Polymerization catalyst a	Azobisisobutyronitrile PERBUTYL I	 2	 2	 2	5	 2	 1	 0.5
solvent b	Xylene	10	10	10	10	10		10
Polymerization catalyst b	Azobisisobutyronitrile PERBUTYL I	 1	 1	 1	1	 2		
Diluent solvent	Xylene Butyl acetate	47	37	17 30	54	41	99	59.5
Reaction temperature (°C)		140	135	140	120	80	120	80
Solid content concentration (wt.%)		50	50	50	50	50	50	50
Molecular weight (×1,000) of polymer		30	35	20	3	10	70	100
Mark for polymer solution		S ₁	S ₂	S ₃	S ₄	S ₅	S ₆	S ₇

[Working Examples 27 through 60]

One or two of polymer solutions S₁ through S₇ were mixed with the components shown in Tables 15 to 17 at the

compositions listed in the same Tables (the numerical values in the tables are mass%). The components including the polymer solutions were mixed and dispersed with a homomixer at 2,000 rpm, whereby 20 kinds of paint compositions were prepared. In the Tables, "TSF-4445", which is the name of a product made by Toshiba Silicones Co., Ltd., is a polyether-modified silicone oil, and "DISPARLON A630-20XN", which is the name of a product made by Kusumoto Chemicals, Ltd., and "BENTON SD-2", which is the name of a product made by National Red Co., Ltd., are all antisagging additives. Furthermore, "resin A", "resin B" and "resin C" in Table 17 were prepared in the following ways. The organism-adhesion inhibitors in the Tables relate to those compounds represented by formula (7).

[Preparation Procedure of "Resin A"]

Charged into a four-necked flask provided with a cooler, a thermometer, a dropping funnel and a stirrer, were 20 parts of propylene glycol methyl ether and 40 parts of xylene, and then the temperature of the mixture was raised to 100°C with stirring. Next, dropped over 4 hours at a constant rate into the mixture from the dropping funnel was a mixture of 10 parts of propylene glycol methyl ether, 10 parts of xylene, 30 parts of zinc oleate methacrylate, 5 parts of methyl methacrylate, 60 parts of ethyl acrylate, and 1.5 parts of t-butyl-peroctoate. After the completion of the dropping, 1 part of t-butyl-peroctoate and 10 parts of xylene were further dropped over 1 hour, and 10 parts of xylene was additionally dropped after stirring for 2 hours. Thus a "resin A" was obtained.

[Preparation Procedure of "Resin B"]

Charged into a four-necked flask provided with a cooler, a thermometer, a dropping funnel and a stirrer, were 30 parts of xylene and 15 parts of n-butanol, and the mixture temperature was raised to 110°C with stirring. Next, dropped over 4 hours at equal time intervals, was a

mixture of 7.2 parts of acrylic acid, 4.5 parts of methyl methacrylate, 38.3 parts of ethyl acrylate, and 1 part of azobisisobutyronitrile. After the completion of the dropping, a mixture of 0.3 part of t-butylperoxy-2-ethylhexanoate and 5 parts of xylene was dropped over 1 hour, and the resultant mixture was further stirred for 3 hours, whereby a resin solution was obtained. 10 parts of copper acetate and 5.6 parts of oleic acid were added to 100 parts of this resin solution. Then, the reaction was conducted for 6 hours while removing produced water under reflux. 6.3 parts of xylene was added to the product, and the resultant mixture was cooled. A resin was obtained and named "resin B".

[Preparation Procedure of "Resin C"]

Charged into a four-necked flask provided with a cooler, a thermometer, a dropping funnel and a stirrer, were 23 parts of xylene, 30 parts of butyl acetate, and 30 parts of n-butanol, and the mixture temperature was raised to 105°C with stirring. Next, dropped over 4 hours at a constant rate was a mixture of 15 parts of methacrylic acid, 40 parts of methoxyethyl acrylate, 5 parts of methyl methacrylate, and 8 parts of azobisisobutyronitrile. After the completion of the dropping, a mixture of 6 parts of xylene and 1 part of azobisisobutyronitrile was dropped over 1 hour, and the resultant mixture was further stirred for 1 hour, whereby a resin solution was obtained. 7.5 parts of zinc oxide, 5.3 parts of water, 7.5 parts of butyl acetate, and 7.5 parts of n-butanol were further added to 100 parts of this resin solution, and then the resultant mixture was stirred at 100°C for 20 hours. A resin named "resin C" was obtained.

[Table 15]

[Table 16]

[Table 17]

[Comparative Examples 8 through 14]

One or two of polymer solutions S₁ through S₅ were mixed with the components shown in Table 18 at the compositions listed in the same Table (the numerical values in the table are mass%). The components including the polymer solutions were mixed and dispersed with a homomixer at 2,000 rpm, whereby 3 kinds of paint compositions were prepared. In the table, the products "TSF-4445", "DISPARLON A630-20XN", and "BENTON SD-2" are the same as those in Table 14 and Table 15.

[Table 18]

With the paint compositions of Working Examples 27 through 60 and Comparative Examples 8 through 14 were conducted a paint-film eroding test, marine-organism-adhesion inhibiting test, attaching property test, and crack resistance test based on the following procedures.

[Paint-Film Consuming Test]

Each paint composition, which had been stored in an oven at 50°C for two weeks after the preparation, was spray-applied onto an obverse surface of a steel plate (100 mm × 100 mm × 1 mm) having a reverse surface coated with a rustproof paint, so that the dry-base film thickness was 300 μm , and then dried in a room at a temperature of 20°C for one week, whereby an applicable test piece was prepared. Each test piece was fixed on the outer surface of a cylindrical drum with a diameter of 50 cm, and then immersed in seawater at a position 1 m below the sea surface at Yura Bay in Sumoto, Hyogo, Japan. The drum was rotated by a motor at a circumferential speed of 16 knots, and the eroded paint-film thickness was measured every 3 months for 12 months. In addition was calculated an averaged paint-film-thickness eroding rate ($\mu\text{m}/\text{month}$). Note that the averaged paint-film-thickness eroding rate of 3 $\mu\text{m}/\text{month}$ or more means an excellent antifouling activity.

[Marine-Organism-Adhesion Inhibiting Test]

A Tar-epoxy-based rustproof paint was spray-applied twice onto both surfaces of an abrasive-blasted steel plate (100 mm × 300 mm × 1 mm) so that the dry-base film thickness by one spraying was 125 μm , and a vinyl-based sealer coat was further applied thereon so that the dry-base film thickness was 50 μm . Both surfaces were coated with each paint composition by spray-coating so that the dry-base film thickness on one surface was 150 μm , and the paint composition was dried in a thermostatic chamber at a temperature of 20°C and a humidity of 65% for one week. Each test piece was thus prepared. Each test piece was

immersed in seawater at Osaka Bay in Takaishi, Osaka, Japan for 12 months, to measure the percentages of the surface areas occupied by the organisms adhering to the tested paint films, with the passage of time.

[Attaching Property Test]

A tar-epoxy-based rustproof paint was spray-applied twice onto both surfaces of an abrasive-blasted steel plate (100 mm × 300 mm × 1 mm) so that the dry-base film thickness by one spraying was 125 μm , and a vinyl-based sealer coat was further applied thereon such that the dry-base film thickness was 50 μm . Each paint composition was spray-applied thereto such that the dry-base film thickness on one surface was 150 μm , and the paint composition was dried in a thermostatic chamber at a temperature of 20°C and a humidity of 65% for one week. Each test piece was thus prepared. Each test piece was immersed in artificial seawater, and a cross-cut adhesion test with a 2 mm spacing was performed for the test pieces taken out of the water at times of 3 months, 6 months, 12 months, 18 months and 24 months from the immersion, respectively. Evaluation of the adherence by this test is indicated by a mark "Yes" (accepted) when the number of separated pieces in this test was 25 pieces/25 pieces and by a mark "No" (rejected) when the number of separated pieces was 24 piece/25 pieces or less.

[Crack Resistance Test]

In the adherence test, the presence/absence of cracks in the paint film was checked by visually observing it upon taking it out of the artificial seawater. Those having no cracks were evaluated as "Yes" (accepted), and those having cracks were evaluated as "No" (rejected).

Table 19

	Paint-film eroding test				
	Eroded paint-film thickness (μm)				Averaged paint-film-thickness erosion rate ($\mu\text{m}/\text{month}$)
	3 months	6 months	9 months	12 months	
Working Example 27	54	113	170	230	19.2
28	31	64	99	133	11.1
29	42	87	127	171	14.3
30	36	70	104	143	11.9
31	20	44	68	90	7.5
32	30	61	94	123	10.3
33	62	122	181	246	20.5
34	50	102	155	209	17.4
35	48	92	138	187	15.6
36	52	104	158	211	17.6
37	72	143	212	282	23.5
38	27	56	85	114	9.5
39	32	63	123	158	10.7
40	18	35	51	73	6.1
41	34	69	107	145	12.1
42	60	122	186	256	21.3
43	46	94	144	193	16.1
44	48	100	154	209	17.4
45	65	133	199	265	22.1
46	30	57	86	118	9.8
47	38	73	108	143	11.9
48	26	51	78	107	8.9
49	38	75	115	157	13.0
50	22	47	70	93	8.1
51	30	71	108	142	11.8
52	36	73	115	151	12.6
53	33	66	103	133	11.1
54	42	87	135	181	15.1
55	37	75	110	149	12.4
56	40	85	129	178	14.8
57	45	99	150	204	17.0
58	58	113	173	225	18.8
59	35	75	109	150	12.5
60	30	68	99	135	11.2
Comparative Example 8	26	50	61	separation	
9	21	36	44	46	5.3
10	30	41	49	54	6.0
11	38	68	88	93	7.8
12	42	88	138	190	15.8
13	45	99	142	192	15.1
14	62	128	198	263	21.9

Table 20

	Marine-organism-adhesion inhibiting test			
	Occupying area (%) of adhering-organisms			
	3 months	6 months	9 months	12 months
Working Example 27	0	0	0	0
28	0	0	0	0
29	0	0	0	0
30	0	0	0	0
31	0	0	0	0
32	0	0	0	0
33	0	0	0	0
34	0	0	0	0
35	0	0	0	0
36	0	0	0	0
37	0	0	0	0
38	0	0	0	0
39	0	0	0	0
40	0	0	0	0
41	0	0	0	0
42	0	0	0	0
43	0	0	0	0
44	0	0	0	0
45	0	0	0	0
46	0	0	0	0
47	0	0	0	0
48	0	0	0	0
49	0	0	0	0
50	0	0	0	0
51	0	0	0	0
52	0	0	0	0
53	0	0	0	0
54	0	0	0	0
55	0	0	0	0
56	0	0	0	0
57	0	0	0	0
58	0	0	0	0
59	0	0	0	0
60	0	0	0	0
Comparative Example 8	10	30	60	100
9	3	20	50	90
10	10	40	70	90
11	10	30	50	100
12	1	5	10	30
13	3	15	20	40
14	5	10	30	50

Table 21

		Marine-organism-adhesion inhibiting test
		Adhering-organisms (12 months)
Working Example	27	None
	28	None
	29	None
	30	None
	31	None
	32	None
	33	None
	34	None
	35	None
	36	None
	37	None
	38	None
	39	None
	40	None
	41	None
	42	None
	43	None
	44	None
	45	None
	46	None
	47	None
	48	None
	49	None
	50	None
	51	None
	52	None
	53	None
	54	None
	55	None
	56	None
	57	None
	58	None
	59	None
	60	None
Comparative Example	8	Green string lettuces, barnacles, and serpulas
	9	Green string lettuces, barnacles, and serpulas
	10	Green string lettuces, barnacles, and serpulas
	11	Green string lettuces, barnacles, and serpulas
	12	Green string lettuces
	13	Green string lettuces
	14	Green string lettuces

Table 22

	Attaching property test			
	3 months	6 months	9 months	12 months
Working Example 27	Yes	Yes	Yes	Yes
28	Yes	Yes	Yes	Yes
29	Yes	Yes	Yes	Yes
30	Yes	Yes	Yes	Yes
31	Yes	Yes	Yes	Yes
32	Yes	Yes	Yes	Yes
33	Yes	Yes	Yes	Yes
34	Yes	Yes	Yes	Yes
35	Yes	Yes	Yes	Yes
36	Yes	Yes	Yes	Yes
37	Yes	Yes	Yes	Yes
38	Yes	Yes	Yes	Yes
39	Yes	Yes	Yes	Yes
40	Yes	Yes	Yes	Yes
41	Yes	Yes	Yes	Yes
42	Yes	Yes	Yes	Yes
43	Yes	Yes	Yes	Yes
44	Yes	Yes	Yes	Yes
45	Yes	Yes	Yes	Yes
46	Yes	Yes	Yes	Yes
47	Yes	Yes	Yes	Yes
48	Yes	Yes	Yes	Yes
49	Yes	Yes	Yes	Yes
50	Yes	Yes	Yes	Yes
51	Yes	Yes	Yes	Yes
52	Yes	Yes	Yes	Yes
53	Yes	Yes	Yes	Yes
54	Yes	Yes	Yes	Yes
55	Yes	Yes	Yes	Yes
56	Yes	Yes	Yes	Yes
57	Yes	Yes	Yes	Yes
58	Yes	Yes	Yes	Yes
59	Yes	Yes	Yes	Yes
60	Yes	Yes	Yes	Yes
Comparative Example 8	No	No	No	No
9	No	No	No	No
10	No	No	No	No
11	No	No	No	No
12	Yes	Yes	Yes	Yes
13	Yes	Yes	Yes	Yes
14	Yes	Yes	Yes	Yes

Table 23

	Crack resistance test			
	3 months	6 months	9 months	12 months
Working Example 27	Yes	Yes	Yes	Yes
28	Yes	Yes	Yes	Yes
29	Yes	Yes	Yes	Yes
30	Yes	Yes	Yes	Yes
31	Yes	Yes	Yes	Yes
32	Yes	Yes	Yes	Yes
33	Yes	Yes	Yes	Yes
34	Yes	Yes	Yes	Yes
35	Yes	Yes	Yes	Yes
36	Yes	Yes	Yes	Yes
37	Yes	Yes	Yes	Yes
38	Yes	Yes	Yes	Yes
39	Yes	Yes	Yes	Yes
40	Yes	Yes	Yes	Yes
41	Yes	Yes	Yes	Yes
42	Yes	Yes	Yes	Yes
43	Yes	Yes	Yes	Yes
44	Yes	Yes	Yes	Yes
45	Yes	Yes	Yes	Yes
46	Yes	Yes	Yes	Yes
47	Yes	Yes	Yes	Yes
48	Yes	Yes	Yes	Yes
49	Yes	Yes	Yes	Yes
50	Yes	Yes	Yes	Yes
51	Yes	Yes	Yes	Yes
52	Yes	Yes	Yes	Yes
53	Yes	Yes	Yes	Yes
54	Yes	Yes	Yes	Yes
55	Yes	Yes	Yes	Yes
56	Yes	Yes	Yes	Yes
57	Yes	Yes	Yes	Yes
58	Yes	Yes	Yes	Yes
59	Yes	Yes	Yes	Yes
60	Yes	Yes	Yes	Yes
Comparative Example 8	No	No	No	No
9	No	No	No	No
10	No	No	No	No
11	No	No	No	No
12	Yes	Yes	Yes	Yes
13	Yes	Yes	Yes	Yes
14	Yes	Yes	Yes	Yes

As apparent from the results in Table 18 through Table 23, each of the paint compositions of Examples 27 through 60 of the present invention has showed satisfactory

results in all of the tests whereas the results seen in Comparative Examples 8 through 14 were unsatisfactory concerning the paint-film eroding rate, the marine-organism-adhesion inhibiting performance and the paint-film properties. These results also prove that the paint compositions of the present invention comprising an organosilyl-based hydrolysable resin and a marine-organism-adhesion inhibitor, are extremely superior in environmental safety, and possess excellent performances.

INDUSTRIAL APPLICABILITY

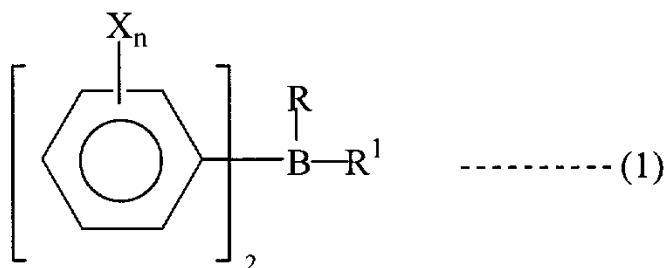
The paint composition of the present invention can be used for ship bottoms, submerged structures such as fishing nets or cooling-water pipes, for which the fouling by organisms in the sea needs to be inhibited, and as a sludge-diffusion-preventing antifouling paint film in offshore engineering works. The paint film of the present invention never forms a residual layer on the paint film surface even after immersed over a long period of time, so that defects such as cracks and separations are not caused by virtue of the paint-film properties and so that the paint-film eroding ability is unchanged over time and is kept higher than a predetermined rate, thereby making it possible to exhibit an antifouling activity over a long period of time, while the paint film exhibits an extremely superior antifouling activity over a long period of time also as a fishing-net antifouling agent. Furthermore, it can be applied onto an aluminum-made ship, since a risk of pitting corrosion into aluminum is absent when other metal-containing antifouling agents are not used together. Moreover, the paint composition of this invention can be colored in any vivid colors to thereby exhibit a remarkably superior designing ability.

In addition, according to other embodiments of the present invention, it is possible to provide a paint composition, an antifouling paint film, a submerged structure, and an antifouling-paint-film forming method of

a submerged structure, in a manner that the paint composition and the antifouling paint film derived therefrom never cause paint film defects, such as separations and cracks, over time even after immersed in seawater or freshwater, with erosion at a constant rate to thereby exhibit superior marine-organism-adhesion inhibiting effects, while ensuring environmental safety.

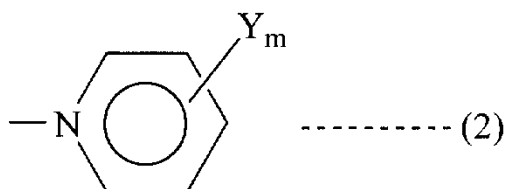
What is claimed is:

1. A paint composition comprising:
as component (A), at least one kind of a
diphenylborane compound represented by formula (1):



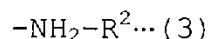
wherein X represents a halogen atom, an alkyl group with 1 to 8 carbon atoms, or an alkoxyl group with 1 to 8 carbon atoms; each of two n's is an integer of 0 to 3 independently, and X's may be the same or different from each other when n is 2 or 3; R represents an alkyl group with 1 to 8 carbon atoms, an alkoxyl group with 1 to 8 carbon atoms, an alkenyl group with 2 to 8 carbon atoms, an alkynyl group with 2 to 8 carbon atoms, a hydroxyl group, or a halogen atom; and R¹ represents a group represented by formula (2), a 5,6,7,8-tetrahydroisoquinoline group or an isoquinoline group which may be substituted by at least one halogen atom, or a group represented by formula (3) or formula (4);

the formula (2) is:



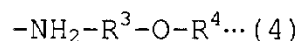
wherein Y represents a halogen atom, an alkyl group with 1 to 8 carbon atoms, a phenyl group, or acetyl group; and m is an integer of 0 to 3 and Y's may be the same or different from each other when m is 2 or 3;

the formula (3) is:



wherein R^2 represents a straight-chain alkyl group with 1 to 24 carbon atoms or a branched alkyl group with 3 to 24 carbon atoms; and

the formula (4) is:



wherein R^3 represents a straight-chain alkylene group with 1 to 24 carbon atoms, a branched alkylene group with 3 to 24 carbon atoms, phenylene group; and R^4 represents a straight-chain alkyl group with 1 to 24 carbon atoms or a branched alkyl group with 3 to 24 carbon atoms; and

as component (B), a copolymer which contains component units derived from a polymeric unsaturated metal-salt compound represented by formula (5):



wherein R^5 represents an organic group including an unsaturated bond, represented by any one of the formulae $\text{CH}_2=\text{C}(\text{CH}_3)-$, $\text{CH}_2=\text{CH}-$, $\text{HOOC}-\text{CH}=\text{CH}-$, and $\text{HOOC}-\text{CH}=\text{C}(\text{CH}_3)-$, wherein $-\text{COOH}$ may be in a form of metal salt or ester; k represents an integer of 0 to 2; M represents a metal atom; L represents $-\text{OCOR}^6$, which is an organic acid residue, wherein R^6 represents an alkyl group or alkenyl group, $-\text{R}^7-\text{CO}-\text{CH}_2-\text{CO}-\text{R}^8$, wherein R^7 represents a divalent group obtained by detaching two hydrogen atoms from a straight-chain or branched alkane or phenyl derivative; and R^8 represents a monovalent group comprising an alkyl group or phenyl derivative), or $-\text{OH}$; and q represents a numerical value of (the valence number of metal M) minus 1.

2. The paint composition according to claim 1, wherein the paint composition contains at least one kind of rosin-based compound selected from the group consisting of a rosin, a rosin-derivative and a metal rosinate.

3. The paint composition according to claim 1 or 2, wherein the metal M in the component (B) is a divalent

metal.

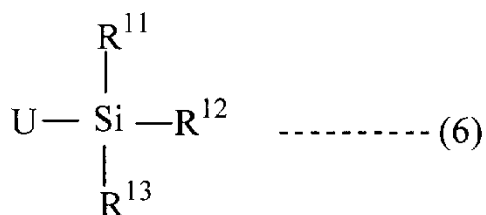
4. The paint composition according to any one of claims 1-3, wherein the component (A) is a methyl(diphenyl)borane compound.

5. The paint composition according to any one of claims 1-4, wherein the component (A) is at least one kind of methyl(diphenyl)borane compound selected from the group consisting of pyridine-methyl(diphenyl)borane, 3-methylpyridine-methyl(diphenyl)borane, 3-bromopyridine-methyl(diphenyl)borane, 4-isopropylpyridine-methyl(diphenyl)borane, 4-t-butylpyridine-methyl(diphenyl)borane, 4-phenylpyridine-methyl(diphenyl)borane, n-octadecylamine-methyl(diphenyl)borane, and 3-(2-ethylhexyloxy)-propylamine-methyl(diphenyl)borane.

6. A paint composition comprising:

a resin P comprising a polymer (PA) obtained by polymerizing one kind or two or more kinds of monomer(s) (A) represented by formula (6); and/or a copolymer (PAB) obtained by polymerizing one kind or two or more kinds of the monomer(s) (A) with one kind or two or more kinds of monomer(s) (B) which is/are copolymerizable with the monomer(s) (A) and is/are different from the monomer(s) (A); and one kind or two or more kinds of borane(s) represented by formula (7), wherein

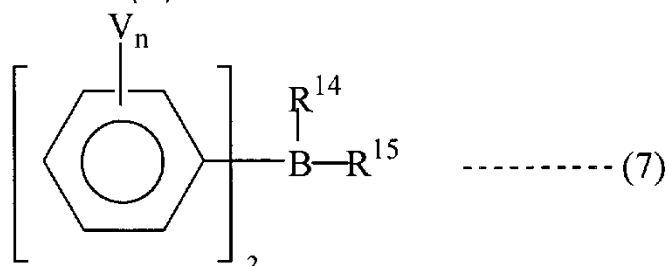
the formula (6) is:



wherein each of R^{11} through R^{13} is a hydrocarbon group

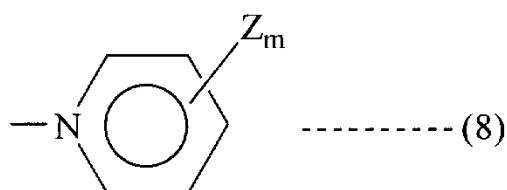
with 1 to 20 carbon atoms, and R^{11} , R^{12} and R^{13} may be the same or different from each other; and U is acryloyloxy group, methacryloyloxy group, maleinoyloxy group, fumaroyloxy group, or itaconoyloxy group; and

the formula (7) is:



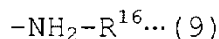
wherein V is an halogen atom, an alkyl group with 1 to 8 carbon atoms, or an alkoxyl group with 1 to 8 carbon atoms; n is an integer of 0 to 3 and V's may be the same or different from each other when n is 2 or 3; R^{14} represents an alkyl group with 1 to 8 carbon atoms, an alkoxyl group with 1 to 8 carbon atoms, an alkenyl group with 2 to 8 carbon atoms, an alkynyl group with 2 to 8 carbon atoms, hydroxyl group, or a halogen atom; and R^{15} denotes a group represented by formula (8), a 5,6,7,8-tetrahydroisoquinoline group or an isoquinolinone group which may be substituted by at least one halogen atom, a group represented by formula (9) or formula (10):

wherein the formula (8) is:



wherein Z is an halogen atom, an alkyl group with 1 to 8 carbon atoms, a phenyl group, or acetyl group; and m is an integer of 0 to 3;

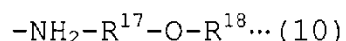
the formula (9) is:



wherein R^{16} denotes a straight-chain or branched

alkyl group with 3 to 24 carbon atoms; and

the formula (10) is:



wherein R^{17} is a straight-chain or branched alkyl group with 3 to 24 carbon atoms; and R^{18} is a straight-chain or branched alkyl group with 3 to 24 carbon atoms.

7. The paint composition according to claim 6, wherein the paint composition includes a rosin compound in an amount of 0.1 to 90 mass% relative to the resin P.

8. The paint composition according to claim 6 or 7, wherein the paint composition includes a marine-organism-adhesion inhibitor for inhibiting adhesion of marine organisms.

9. The paint composition according to claim 8, wherein the marine-organism-adhesion inhibitor is an organic inhibitor free of metal.

10. An antifouling paint film wherein the antifouling paint film is formed from the paint composition of any one of claims 1-9.

11. A submerged structure wherein the submerged structure has a surface coated with an antifouling paint film formed from the paint composition of any one of claims 1-9.

12. An antifouling method of a submerged structure comprising a step of coating a surface of the structure with the paint composition of any one of claims 1-9, thereby forming an antifouling paint film.