DESCRIPTION

# HYDRAULIC STAIN-PROOF COATING COMPOSITION, STAIN-PROOF COATING FILM AND UNDERWATER STRUCTURE

## TECHNICAL FIELD

[0001]

The present invention relates to a water-borne curable antifouling coating composition, a coating film having an antifouling property and an underwater structure.

## BACKGROUND ART

[0002]

Marine lives such as acorn barnacles, mussels and algaes tend to adhere to underwater structures such as marine vessels, fishing nets and the like, thus causing a problem of interfering with efficient navigations to result in a waste of fuel in the marine vessels and a problem of clogging a net or shortening a useful life in the fishing nets. In order to prevent the marine lives from adhering to these underwater structures, a coating film having an antifouling property is formed on surfaces of the underwater structures. As an antifouling coating used for forming such a coating film having an antifouling property, solvent base coating compositions containing an uncurable resin are known (See Patent Documents 1 to 5).

[0003]

In recent years, reduction in usage of organic solvents has been required in various coating areas, and various water-borne coatings has been developed and employed. However, in antifouling coating compositions, the attempts to develop the water-borne coatings were little. The reason for this is as follows. That is, in water-borne coatings, since water is used as a medium, binders contained in the water-borne coatings have higher hydrophilicity than those contained in the solvent

type coatings. Therefore, there are problems that the coating films may be dissolved in water without modifications. On the other hand, if the coating film is cured in order to resolve the problems, water resistance can be secured, but another problem that an antifouling agent cannot be eluted from the cured film and therefore the coating film does not have an antifouling property arises. Thus, it has been technically difficult to make the antifouling coatings water-borne.

[0004]

In Patent Documents 6 and 7, compositions containing a resin containing bivalent metal, water and a basic compound are described. But, such a resin is not curable, and the water resistance of a coating film to be obtained from the resin was not sufficient.

[0005]

Patent Document 1: Japanese Kokai Publication Hei-9-52803

Patent Document 2: Japanese Kokai Publication Hei-10-59810

Patent Document 3: Japanese Kokai Publication Hei-11-172159

Patent Document 4: Japanese Kokai Publication 2000-109729

Patent Document 5: Japanese Kokai Publication 2003-277680

Patent Document 6: Japanese Kokai Publication 2002-371166

Patent Document 7: Japanese Kokai Publication 2003-49123

## DISCLOSURE OF THE INVENTION

### Problems to be Solved by the Invention

[0006]

In view of the above-mentioned state of the art, it is an object of the present disclosure to provide a water-borne curable antifouling coating composition which exerts excellent

functions as an antifouling coating, a coating film having an antifouling property obtained from the water-borne curable antifouling coating composition and an underwater structure having the coating film having an antifouling property.

[0006a]

In a first aspect, there is provided a water-borne curable antifouling coating composition, comprising: a water-borne binder component curable by dehydration condensation, wherein said waterborne binder component has at least one species of a curing system of a carbonyl hydrazide system and an acetoacetoxy amine system; and an antifouling agent.

In a second aspect, there is provided a coating film having an antifouling property, wherein said coating film is prepared from the water-borne curable antifouling coating composition as defined above.

In a third aspect, there is provided an underwater structure, containing the coating film having an antifouling property as defined above.

Means for Solving the Problems

[0007]

The present invention pertains to a water-borne curable antifouling coating composition,

wherein said coating composition is obtained by mixing a water-borne binder component having curability and an antifouling agent and a coating film obtained from said coating composition is used in uses being present in water during use.

The above-mentioned curability is preferably controlled by water or air.

A substance formed by curing the above-mentioned water-borne binder component is preferably decomposed by water.

The above-mentioned water-borne binder component is preferably cured by dehydration-condensation.

The water-borne binder component preferably has at least one species of a curing system of a carbonyl-hydrazide system, an acetoacetoxy-amine system, and an alkoxysilyl condensate system.

The water-borne binder component preferably contains an emulsion resin and a curing agent, and said emulsion resin has a group capable of reacting with a functional group which said curing agent has.

[0008]

A substance formed by curing the water-borne binder component may have a structure in which long chain hydrocarbon groups are crosslinked with each other.

The water-borne binder component is preferably cured by oxidative polymerization.

The oxidative polymerization is preferably polymerization in which a higher unsaturated fatty acid-derived

group is involved.

The water-borne binder component preferably contains an emulsion resin having a higher unsaturated fatty acid-derived group and a drier.

The emulsion resin is preferably a copolymer of ethylenic unsaturated monomers having a higher unsaturated fatty acid-derived group.

[0009]

The present invention also pertains to a water-borne curable antifouling coating composition,

containing an antifouling agent paste obtained by mixing a water-soluble dispersion resin having an acid value of 10 to 300 mg KOH/g and a number average molecular weight of 1000 to 20000 and an antifouling agent, and a water-borne binder component having curability.

A weight ratio of solid content between the water-soluble dispersion resin and the antifouling agent in the antifouling agent paste is preferably 1/99 to 50/50.

A coating film to be obtained from the water-borne curable antifouling coating composition is preferably used in water.

The water-borne binder component is preferably cured by an addition reaction.

[0010]

The water-borne binder component is preferably cured by oxidative polymerization.

The oxidative polymerization is preferably polymerization in which a higher unsaturated fatty acid-derived group is involved.

The water-borne binder component preferably contains an emulsion resin having a higher unsaturated fatty acid-derived group and a drier.

The emulsion resin is preferably a copolymer of ethylenic unsaturated monomers having a higher unsaturated fatty acid-derived group.

[0011]

The water-borne curable antifouling coating composition of the present invention is preferably contains organic polymer particles.

The organic polymer particle preferably has a solubility in the artificial seawater specified in ASTM D1141-98 at 23°C is 15 g/l or less, a water-absorbing amount for the artificial seawater specified in ASTM D1141-98 of 0.01% by weight or more and a particle diameter of 0.05 to 100 μm.

The organic polymer particle is preferably a naturally-derived polymer.

The organic polymer particle preferably has a cationic group.

The organic polymer particle is preferably an organic polymer particle having a particle diameter of 0.05 to 100 μm, which comprises at least one species selected from the group consisting of chitin, chitosan, γ-PGA, pulverized silk and derivatives thereof.

[0012]

The above-mentioned organic polymer particle is preferably a synthetic polymer.

The above-mentioned organic polymer particle is preferably an acrylic resin particle.

[0013]

The organic polymer particle is preferably a composite resin particle comprising at least one species of hydrophilic resin selected from the group consisting of starch, pullulan, gum arabic, κ-carrageenan, gelatin, cellulose, and chitosan and derivatives thereof, polyvinyl alcohol, polyallylamine, polyvinylamine, poly(meth)acrylamide, poly(meth)acrylic acid and copolymer thereof, and an acrylic resin.

An amount of the organic polymer particle to be mixed is preferably 0.01 to 15% by weight with respect to the solid content of a coating.

[0014]

The present invention also pertains to a coating film

having an antifouling property,

wherein said coating film is prepared from the water-borne curable antifouling coating composition described above.

The present invention also pertains to an underwater structure, containing the coating film having an antifouling property described above.

Hereinafter, the present invention will be described in detail.

[0015]

The water-borne curable antifouling coating composition of the present invention can convert a coating to a water-borne coating and simultaneously can form a coating film exerting performance required as an antifouling coating.

The water-borne curable antifouling coating composition of the present invention is obtained by mixing a water-borne binder component having curability and an antifouling agent.

[0016]

The water-borne binder component contained in the water-borne curable antifouling coating composition of the present invention is not particularly limited as long as it has curability, and it may consist of a solution in which a water-soluble resin is dissolved, an emulsion resin formed by dispersing a resin dispersible in water, or a dispersion resin formed by forcing to disperse a resin with an emulsifier and the like. It is particularly preferred from the viewpoint of various performances such as water resistance and a antifouling property that the water-borne binder component comprises the emulsion resin formed by dispersing a resin dispersible in water.

[0017]

The above-mentioned emulsion resin contains a functional group for dispersing in water/emulsifying and a curing functional group. The above-mentioned functional group for dispersing in water/emulsifying is not particularly limited,

and examples of them include acidic groups such as a carboxyl group, and a sulfonic group, and basic groups such as an amino group. When the above-mentioned functional group for dispersing in water/emulsifying is an acidic group, these acidic groups are preferably contained within such a range that an acid value of the emulsion resin is 300 mg KOH/g or less, and more preferably, an acid value is 1 to 20 mg KOH/g. As the above-mentioned acidic group, a carboxyl group is particularly preferred. A basic group can also be set in the same manner as in the acidic group. It is also possible to disperse in water and emulsify by adding a polyethylene oxide unit.

[0018]

It is possible to disperse in water and emulsify by adding a base to the above emulsion resin to neutralize the emulsion resin when the above-mentioned functional group for dispersing in water/emulsifying is an acidic group, and by adding an acid to the above emulsion resin to neutralize the emulsion resin when the above-mentioned functional group for dispersing in water/emulsifying is a basic group.

[0019]

The curability of the above-mentioned water-borne binder component is preferably a substance to cure at ambient temperature in consideration of a usage pattern of a coating. The water-borne binder components to cure at ambient temperature generally proceed in a curing reaction by natural drying or forced drying of about 80°C after applying them, and they are well known to those skilled in the art.

[0020]

In the present invention, the above-mentioned curability at ambient temperature is preferably controlled by water or air. Here, to be controlled by water or air refers to a state in which water is removed by drying and thereby a curing reaction proceeds, or a coating comes into contact with oxygen in air due to drying and thereby a curing reaction proceeds.

[0021]

As for the above-mentioned water-borne binder component, a substance formed by curing it preferably has a property of being decomposed by water. By having such a property, the coating film obtained from the coating composition containing the above-mentioned water-borne binder component is decomposed through immersion in water. Therefore, a self-polishing property can be expressed.

As a curing system having the above-mentioned property of being decomposed by water, a dehydration-condensation reaction can be exemplified. That is, in this case, the above-mentioned water-borne binder component is cured by dehydration-condensation.

Since the above-mentioned dehydration-condensation reaction is an equilibrium reaction, in which water is generated, water is removed by drying and thereby a curing reaction proceeds. Further, when the coating film cured by the dehydration-condensation reaction is immersed in water, decomposition which is a reverse reaction of the curing reaction proceeds because of the presence of a large amount of water.

[0022]

Further, as for the above-mentioned water-borne binder component, a substance formed by curing it may have a structure in which long chain hydrocarbon groups are crosslinked with each other. In this case, it is preferred since an antifouling agent becomes easy to be eluted from a cured film formed in the presence of the antifouling agent. The reason is thought that the structure in which long chain hydrocarbon groups are crosslinked with each other becomes a mild network compared with a crosslinked structure achieved by another curing system. Further, the above-mentioned structure in which long chain hydrocarbon groups are crosslinked with each other is a structure in which an unsaturated bond of the long chain hydrocarbon group is bound directly or indirectly to an unsaturated bond of another long chain hydrocarbon group. As an example of binding indirectly, a bond in an oxidative

polymerization reaction described below, in which an oxygen atom intermediates, can be given.

[0023]

As a curing system from which the above-mentioned structure in which long chain hydrocarbon groups are crosslinked with each other can be obtained, an oxidative polymerization reaction can be exemplified.

The above-mentioned oxidative polymerization reaction is a reaction in which polymerization proceeds by absorption of oxygen in an unsaturated bond and has an advantage that a fast curing property is enhanced by using a drier in combination. Incidentally, if a water-borne binder component not having the above-mentioned advantage, such as a urethane curing system, is used, there may be a possibility that a long-range antifouling property is low.

[0024]

When the above-mentioned water-borne binder component is cured by dehydration-condensation, examples of its curing system include a carbonyl-hydrazide system, an acetoacetoxy-amine system, and an alkoxysilyl condensation system. These are publicly known curing systems, and publicly known combinations of a resin and a curing agent can be used.

[0025]

When the above-mentioned water-borne binder component has a curing system based on the carbonyl-hydrazide system, the above-mentioned water-borne binder component preferably contains a carbonyl-containing resin and a hydrazide compound as a curing agent.

[0026]

The above-mentioned carbonyl-containing resin is not particularly limited as long as it is a resin having at least one aldo group and/or keto group, and examples of the carbonyl-containing resin include an acrylic resin, a polyester resin (including an alkyd resin), a urethane resin, an epoxy resin, and modified products/complexes thereof. Among others,

the acrylic resin is preferred in point of water resistance and coating film properties.

[0027]

When the carbonyl-containing resin is a carbonyl-containing acrylic resin, it is preferred to use emulsion resins obtained by emulsion polymerization of a monomer composition containing an ethylenic unsaturated monomer including an aldo group and/or keto group.

[0028]

The above-mentioned ethylenic unsaturated monomer including an aldo group and/or keto group is not particularly limited, and examples of the ethylenic unsaturated monomers include acrolein, diacetoneacrylamide, diacetonemethacrylamide, formylstyrol, vinyl methyl ketone, vinyl ethyl ketone, vinyl isobutyl ketone, acryloxyalkylpropanals, methacryloxyalkylpropanals, diacetone acrylate, diacetone methacrylate, acetonyl acrylate, 2-hydroxypropyl acrylate acetyl acetate, and butanediol acrylate acetyl acetate.

[0029]

The above-mentioned ethylenic unsaturated monomer including an aldo group and/or keto group is preferably used at a rate in which an amount of an aldo group and/or a keto group in a resin obtained is 0.005 to 20 mmol/1 g of resin solid content. When this amount is 0.005 mmol or less, since a curing reaction becomes insufficient, there is a possibility that the water resistance is not adequately attained, and when it is more than 20 mmol, this may have adverse effect on another performance.

[0030]

The above-mentioned carbonyl-containing acrylic resin preferably has an acid value in the above range, and can be obtained by polymerizing a monomer composition containing in a desired amount an ethylenic unsaturated monomer having a carboxylic acidic group. The above-mentioned ethylenic unsaturated monomers having a carboxylic acidic group is not

particularly limited, and examples of them include unsaturated carboxylic acids such as acrylic acid, methacrylic acid, itaconic acid, fumaric acid and maleic acid; anhydrides of unsaturated carboxylic acid such as maleic anhydride; and semi-esters of unsaturated carboxylic acid such as itaconic acid, fumaric acid and maleic acid.

[0031]

The above-mentioned carbonyl-containing acrylic resin is preferably neutralized with a base such as amine. A ratio of the neutralization of the carbonyl-containing acrylic resin is preferably 300% or less, and more preferably 10 to 100%.

[0032]

The above-mentioned carbonyl-containing acrylic resin preferably has a number average molecular weight of 3000 or more. When the above-mentioned number average molecular weight is less than 3000, it is not preferred since the water resistance may be deteriorated. The above number average molecular weight is more preferably 10000 or more. The above number average molecular weight can be appropriately adjusted to an aimed range by using a chain transfer agent, or by adjusting an amount of polymerization initiator or a polymerization temperature to perform polymerization of the resin.

[0033]

For the above-mentioned carbonyl-containing acrylic resin, other monomers can be used in addition to the above-mentioned monomers. Examples of the above-mentioned other monomers include ethylenic unsaturated monomers, for example, acrylate, methacrylate [hereinafter, these may be referred to as just (meth)acrylate], aromatic monomers such as styrene and vinyltoluene; vinyl esters such as vinyl acetate, vinyl propionate and vinyl ester of versatic acid; vinyl cyanides such as (meth)acrylonitrile; vinyl halides such as vinyl chloride and vinylidene chloride; and butadiene. In addition, examples of the above-mentioned other monomers include various functional monomers such as (meth)acrylamide,

vinylpyrrolidone, 2-hydroxyethyl (meth)acrylate, N-methylolacrylamide, N-butoxymethylacrylamide, acid phosphoxyethyl methacrylate, 3-chloro-2-acid phosphoxypropyl methacrylate, acrylamido methylpropane sulfonate, divinylbenzene, (poly)oxyethylene mono(meth)acrylate, (poly)propylene glycol (meth)acrylate, allyl (meth)acrylate, (poly)oxyethylene di(meth)acrylate, trimethylolpropane tri(meth)acrylate, dimethylaminoethyl (meth)acrylate, diethylaminoethyl (meth)acrylate, and γ-(meth)acryloxypropyltrimethoxysilane.

[0034]

Examples of the above-mentioned acrylate or methacrylate include methyl (meth)acrylate, ethyl (meth)acrylate, butyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, cyclohexyl (meth)acrylate, and dodecyl (meth)acrylate.

[0035]

The above-mentioned carbonyl-containing resin is preferably an emulsion resin as described above. As a means for obtaining the emulsion resin, conventionally publicly known emulsion polymerization is preferred. The reason for this is that it is easy to control an amount of a functional group to be introduced, and a molecular weight of a resin to be obtained by this method is relatively large and therefore an effect of increasing a molecular weight through a curing reaction is large, and this enables an improvement in water resistance and an approach to higher solid content. Examples of the above-mentioned conventionally publicly known emulsion polymerization include, specifically, a method in which for example, the above monomer composition is emulsified in advance in a water-borne medium including water or an organic solvent such as alcohol as required using a reactive emulsifier, and the resulting emulsified monomer composition is dropped together with a polymerization initiator while being heated and stirred.

[0036]

The species of the above-mentioned reactive emulsifier is not particularly limited, and any one of an anionic, a cationic, a nonionic and an amphoteric emulsifiers may be used. As the above-mentioned reactive emulsifier, for example, commercially available products such as ELEMINOL JS series (manufactured by Sanyo Chemical Industries, Ltd.), LATEMUL S & K series (manufactured by KAO Corp.), Aqualon HS series (manufactured by DAI-ICHI KOGYO SEIYAKU Co., Ltd.), ADEKA REASOAP-series (manufactured by ADEKA Corp.), and Antox MS-60 (manufactured by NIPPON NYUKAZAI CO.,LTD.) can be used.

[0037]

The above-mentioned polymerization initiator is not particularly limited, and examples of the initiator include azo oily compounds such as azobis(isobutyronitrile), 2,2'-azobis(2-methylbutyronitrile), and 2,2'-azobis(2,4-dimethylvaleronitrile), and anionic water-borne compounds such as 4,4'-azobis(4-cyanovaleric acid) and 2,2'-azobis(N-(2-carboxyethyl)-2-methylpropionicamidine), and Redox type oily peroxide such as benzoyl peroxide, p-chlorobenzoyl peroxide, lauroyl peroxide and t-butyl perbenzoate, and water-borne peroxides such as potassium persulfate and ammonium persulfate.

[0038]

When the above-mentioned carbonyl-containing resin is an emulsion resin, a resin having an average particle diameter of 50 to 600 nm can be given. When the above-mentioned average particle diameter is out of the above range, the dispersibility may be deteriorated and the stability of the water-borne curable antifouling coating composition may become insufficient.

[0039]

When the above-mentioned water-borne binder component has a curing system based on the above-mentioned carbonyl-hydrazide system, it contains a hydrazide compound as a curing agent. The above-mentioned hydrazide compound is not

particularly limited and include, and compounds having a plurality of hydrazide groups or semicarbazide groups can be used.

[0040]

Examples of the above-mentioned compounds having a plurality of hydrazide groups in a molecule include dicarboxylic acid dihydrazide such as oxalic acid hydrazide, succinic acid hydrazide, adipic acid dihydrazide, sebacic acid dihydrazide, glutaric acid dihydrazide, sebacic acid dihydrazide, maleic acid dihydrazide, fumaric acid dihydrazide and itaconic acid dihydrazide; carbonic acid polyhydrazide such as carbonic acid dihydrazide; and carbodihydrazide, thiocarbodihydrazide, 4,4'-oxybenzenesulfonyl hydrazide, aliphatic, alicyclic, aromatic bissemicarbazide, or aromatic dicarboxylic acid hydrazide, and polymer hydrazide such as polyacrylic acid hydrazide. As the above-mentioned compound, adipic dihydrazide is particularly preferred.

[0041]

The above-mentioned compounds having a plurality of semicarbazide groups in a molecule is not particularly limited, and examples of them include semicarbazides such as 1,6-hexamethylene bis(N,N-dimethylsemicarbazide), 1,1,1',1'-tetramethyl-4,4'-(methylene-di-p-phenylene)disemi carbazide, and biuretly tri(hexamethylene-N,N-dimethylsemicarbazide). These compounds may be used alone or in combination of two or more species.

[0042]

A mole ratio of an amount of a curing functional group contained in the above-mentioned carbonyl-containing resin to an amount of a curing agent functional group contained in the above-mentioned curing agent is preferably in the range of 1/10 to 1/0.05. When the above-mentioned mole ratio is out of the above range, the water resistance may be deteriorated. It is more preferred from the viewpoint of the water resistance that

the above-mentioned mole ratio is in the range of 1/0.6 to 1/0.1.

[0043]

When the above-mentioned water-borne binder component has a curing system based on the acetoacetoxy-amine system, the above-mentioned water-borne binder component preferably comprises an acetoacetoxy group-containing resin and an amine compound as a curing agent. The above-mentioned acetoacetoxy group-containing resin is not particularly limited, but it is preferably an acrylic resin as with the above-mentioned carbonyl-containing resin. The above-mentioned acetoacetoxy group-containing acrylic resin is not particularly limited and includes, for example, resins obtained by emulsion polymerization of a monomer composition containing an ethylenic unsaturated monomer including an acetoacetoxy group.

[0044]

The above-mentioned ethylenic unsaturated monomer including an acetoacetoxy group is not particularly limited, and examples of the ethylenic unsaturated monomer include acrylates and methacrylates, having an acetoacetoxy group. Specific examples of them include acetoacetoxyethyl acrylate and acetoacetoxyethyl methacrylate.

[0045]

The above-mentioned acetoacetoxy group-containing resin is preferably an emulsion resin as with the above-mentioned carbonyl-containing resin. A polymerization method of the acetoacetoxy group-containing resin is not particularly limited, and the acetoacetoxy group-containing resin can be obtained, for example, by the same method as in the above-mentioned carbonyl-containing resin.

[0046]

The above-mentioned amine compound is not particularly limited, and examples of the amine compound include compounds having a diamine group or a polyamine group such as 2-methylpentamethylenediamine, cyclohexanediamine, hexamethylenediamine, ethylenediamine, 1,3-diaminopropane,

1,4-diaminobutane, 1,6-hexanediamine, 1,12-diaminododecane, 1,2-diaminocyclohexane, phenylenediamine, piperazine, 2,6-diaminotoluene, diethyltoluenediamine, N,N-bis(2-aminopropyl)ethylenediamine, N,N-bis(3-aminopropyl)-1,3-propanediamine.

[0047]

A mole ratio of an amount of a curing functional group contained in the above-mentioned acetoacetoxy group-containing resin to an amount of a curing agent functional group contained in the above-mentioned curing agent is preferably in the range of 1/10 to 1/0.05. When the above-mentioned mole ratio is out of the above range, the water resistance may be deteriorated. It is more preferred from the viewpoint of the water resistance that the above-mentioned mole ratio is in the range of 1/0.6 to 1/0.1.

[0048]

When the above-mentioned water-borne binder component has a curing system based on the alkoxysilyl condensate system, the above-mentioned water-borne binder component comprises an alkoxysilyl group-containing resin. The above-mentioned alkoxysilyl group is not particularly limited and include, for example, a methoxysilyl group, an ethoxysilyl group, a propioxysilyl group, and a butoxysilyl group. Incidentally, since a Si atom is tetravalent, the above-mentioned alkoxysilyl group can be regarded as a unit element composing functional groups such as a dialkylmonoalkoxysilyl group, a monoalkyldialkoxysilyl group, and a trialkoxysilyl group. Further, the alkoxysilyl group in the present specification means a Si atom and an alkoxysilyl group bonded to the Si atom. For example, the trialkoxysilyl group has three alkoxysilyl groups.

[0049]

The above-mentioned alkoxysilyl group-containing resin is not particularly limited and include, for example, resins obtained by emulsion polymerization of a monomer composition

containing an ethylenic unsaturated monomer having an alkoxysilyl group. The above-mentioned ethylenic unsaturated monomer having an alkoxysilyl group is not particularly limited, and examples of the ethylenic unsaturated monomer include γ-methacryloxypropyltrimethoxysilane, γ-acryloxypropylmethyldimethoxysilane, γ-methacryloxypropylmethyldimethoxysilane, γ-acryloxypropyldimethylmethoxysilane, γ-methacryloxypropyldimethylmethoxysilane, γ-acryloxypropyltriethoxysilane, γ-methacryloxypropyltriethoxysilane, γ-acryloxypropylmethyldiethoxysilane, γ-methacryloxypropylmethyldiethoxysilane, γ-acryloxypropyldimethylethoxysilane, γ-methacryloxypropyldimethylethoxysilane, vinyltrimethoxysilane, vinylmethyldimethoxysilane, vinyltriethoxysilane, vinylmethyldiethoxysilane, trimethoxysilyl styrene, dimethoxymethylsilyl styrene, triethoxysilyl styrene, and diethoxymethylsilyl styrene.

[0050]

The above-mentioned alkoxysilyl group-containing resin is preferably an emulsion resin as with the above-mentioned carbonyl-containing resin. A polymerization method of a mixture of the above-mentioned unsaturated monomers is not particularly limited, and the alkoxysilyl group-containing resin can be obtained, for example, by the same method as in the above-mentioned carbonyl-containing resin.

[0051]

When the above-mentioned water-borne binder component has a curing system based on the alkoxysilyl condensate system, preferably, the above-mentioned water-borne binder component further contains an acid and/or a base. The above-mentioned acid and base is not particularly limited and include resins having acidic groups such as a carboxyl group, a phosphoric group, and a sulfonic group, and resins having basic groups such

as an amino group. As the above-mentioned resins having acidic groups, a resin having a phosphoric group or a sulfonic group is preferred because of high catalyst activity, and a resin having a phosphoric group is particularly preferred by reason of ease of the introduction of a functional group. The above-mentioned amino group is preferably a tertiary amino group in which two alkyl groups are bound to a nitrogen atom, and the above two alkyl groups may be the same or different, but the alkyl groups having 1 to 8 carbon atoms are particularly preferred. Specific examples of such amino groups include a dimethyl amino group, a diethyl amino group, a methyl ethyl amino group, a dibutyl amino group, and a dioctyl amino group. The above-mentioned resin having an acidic group or a basic group is not particularly limited, and examples of the resin include a substance obtained by polymerization of a monomer composition containing an ethylenic unsaturated monomer having at least one acidic group or basic group.

[0052]

A mole ratio of an amount of an alkoxysilyl group contained in the above-mentioned alkoxysilyl group-containing resin to an amount of the above-mentioned acid and/or base is preferably in the range of 1/10 to 1/0.01. When the above-mentioned mole ratio is more than 1/0.01, the curability becomes insufficient and therefore the water resistance may be deteriorated. When the above-mentioned mole ratio is less than 1/10, an amount of unreacted acid and/or base increases and the water resistance may be deteriorated. It is more preferred from the viewpoint of the water resistance that the above-mentioned mole ratio is in the range of 1/0.6 to 1/0.1.

[0053]

In the above-mentioned curing system based on the dehydration-condensation reaction, a carbonyl-hydrazide system is preferred since a self-polishing property is good because of the proceeding of a reverse reaction of the curing reaction, and among others, a combination of a carbonyl compound

and a semicarbazide compound is particularly preferred because of high curing-reactivity.

[0054]

When the above-mentioned water-borne binder has a curing system based on oxidative polymerization, the oxidative polymerization is preferably a polymerization in which a higher unsaturated fatty acid-derived group is involved. The reason for this is that the previously described structure in which long chain hydrocarbon groups are crosslinked with each other is attained by oxidative polymerization of an unsaturated bond in the higher unsaturated fatty acid-derived group.

[0055]

Examples of a resin having the above-mentioned higher unsaturated fatty acid-derived group include alkyd resins, and the alkyd resins are preferably acrylic emulsion resins. Such acrylic emulsion resins having the higher unsaturated fatty acid-derived group can be obtained by emulsion polymerization of monomer compositions containing an ethylenic unsaturated monomer having the higher unsaturated fatty acid-derived group.

[0056]

The above-mentioned ethylenic unsaturated monomer having the higher unsaturated fatty acid-derived group is not particularly limited, and examples of this monomer include substances obtained by the reaction of higher unsaturated fatty acid with glycidyl group-containing ethylenic unsaturated monomer. The above-mentioned higher unsaturated fatty acid is not particularly limited and includes, for example, myristoleic acid, palmitoleic acid, oleic acid, linoleic acid, linoleic acid, and ricinoleic acid. Furthermore, examples of the higher unsaturated fatty acid also include drying oil fatty acid having a nonconjugated double bond and semi-drying oil fatty acid such as linseed oil fatty acid, safflower seed oil fatty acid, soy bean oil fatty acid, rice polishings oil fatty acid, sesame oil fatty acid, castor oil fatty acid, dehydrated castor oil fatty acid, perilla oil fatty acid, hempseed oil fatty acid, cotton

seed oil fatty acid and tall oil fatty acid. In addition, fatty acids having a conjugated double bond such as tung oil fatty acid can be partially used in combination.

An average number of carbon atoms of a hydrocarbon portion of the above higher unsaturated fatty acid is preferably 13 to 23.

[0057]

The above-mentioned glycidyl group-containing ethylenic unsaturated monomer is not particularly limited and includes, for example, glycidyl acrylate, glycidyl methacrylate, methyl glycidyl acrylate, and methyl glycidyl methacrylate.

[0058]

An iodine number of the above-mentioned ethylenic unsaturated monomer having the higher unsaturated fatty acid-derived group is preferably 60 to 180, and more preferably 70 to 150.

[0059]

A method of polymerizing the above-mentioned emulsion resin having the higher unsaturated fatty acid-derived group is not particularly limited, and for example, the same method as in the above-mentioned carbonyl-containing resin can be employed. Further, an iodine number of the above-mentioned emulsion resin having the higher unsaturated fatty acid-derived group is preferably 5 to 100. When the above-mentioned iodine number is more than 100, adequate effect cannot be achieved since drying of the surface of a coating film is too fast.

[0060]

When the above water-borne binder component has a curing system based on an oxidative polymerization reaction, it preferably further contains a drier. The above-mentioned drier serves a function of crosslinking an unsaturated bond of the above higher unsaturated fatty acid-derived group. The above-mentioned drier is not particularly limited as long as it is one generally used for coatings, and among others, examples of the drier include naphthenate, octylate, and

resinate of cobalt, vanadium, manganese, cerium, lead, iron, calcium, zinc, zirconium, cerium, nickel, and tin. An amount of the above drier to be mixed is generally 0.005 to 5 parts by weight with respect to 100 parts by weight of the resin solid content.

[0061]

The above water-borne binder component is preferably cured at ambient temperature by an addition reaction. Such a curing system is not particularly limited, and examples of the curing system include a urethane-urea system, a Michael addition system, and a carbodiimide-carboxyl system.

[0062]

The above-mentioned urethane-urea system is not particularly limited, and examples of this system include a water-borne binder component including a polyisocyanate compound as a curing agent and a hydroxyl group and/or amino group-containing resin. Examples of the above-mentioned hydroxyl group and/or amino group-containing resin include an acrylic resin, a polyester resin, a urethane resin, a polyether resin, and a polycarbonate resin, and these resins well known to those skilled in the art can be used.

[0063]

The above-mentioned polyisocyanate compound is not particularly limited, and examples of the polyisocyanate compound include aromatic diisocyanate compounds such as trilene diisocyanate (TDI), 4,4'-diphenylmethane diisocyanate (MDI) and xylylene diisocyanate (XDI); aliphatic or alicyclic diisocyanate compounds such as hexamethylene diisocyanate (HMDI), isophorone diisocyanate (IPDI), and 2,5- or 2,6-bis(isocyanatemethyl)bicyclo[2,2,1]heptane(norbornane diisocyanate NBDI); and polyisocyanate compounds such as dimmer, trimer and trimethylolpropane adducts of these diisocyanate compounds. A part of or all of these may be blocked with an active hydrogen compound in order to control reactivity. The above-mentioned blocking agent is not particularly limited, and

examples of the blocking agent include aliphatic alcohols such as methanol, ethanol, isopropanol, n-butanol, 2-ethylhexanol, ethylene glycol monobutyl ether and cyclohexanol; phenols such as phenol, nitrophenol and ethylphenol; oximes such as methyl ethyl ketoxime; and lactams such as ε-caprolactam.

[0064]

A mole ratio of an amount of a curing functional group contained in the above-mentioned hydroxyl group and/or amino group-containing resin to an amount of a curing agent functional group contained in the above-mentioned polyisocyanate compound is preferably in the range of 1/10 to 1/0.05. When the above-mentioned mole ratio is more than 1/0.05, the curability becomes insufficient and therefore the water resistance may be deteriorated. When the above-mentioned mole ratio is less than 1/10, an amount of unreacted polyisocyanate compound increases and the water resistance may be deteriorated. It is more preferred from the viewpoint of the water resistance that the above-mentioned mole ratio is in the range of 1/0.6 to 1/0.1.

[0065]

The above-mentioned carbodiimide-carboxyl system is not particularly limited, and examples of this system include a water-borne binder component including a carboxyl group-containing resin containing a carboxyl group as a curing functional group and a polycarbodiimide compound as a curing agent.

[0066]

The above-mentioned carboxyl group-containing resin is not particularly limited, and examples of the carboxyl group-containing resins include a carboxyl group-containing acrylic resin, a carboxyl group-containing polyester resin, a carboxyl group-containing alkyd resin, and a carboxyl group-containing polyurethane resin. When the above-mentioned carboxyl group-containing resin is an acrylic resin, it is preferred to use emulsion resins obtained by emulsion polymerization of a monomer composition containing an

ethylenic unsaturated monomer including a carboxyl group such as acrylic acid and methacrylic acid.

[0067]

As the above-mentioned polycarbodiimide compounds, commercially available articles such as V-02 manufactured by NISSHINBO INDUSTRIES, INC. can be used. In addition, substances formed by converting the previously described polyisocyanate compounds to carbodiimide compounds by using a phospholene oxide which is well known as a catalyst for conversion to carbodiimide to obtain isocyanate terminal polycarbodiimide, and hydrophilizing this polycarbodiimide can be used.

[0068]

A mole ratio of an amount of a curing functional group contained in the above-mentioned carboxyl group-containing resin to an amount of a curing agent functional group contained in the above-mentioned polycarbodiimide compound is preferably in the range of 1/10 to 1/0.05. When the above-mentioned mole ratio is more than 1/0.05, the water resistance may be deteriorated. When the above-mentioned mole ratio is less than 1/10, the water resistance may be deteriorated. It is more preferred from the viewpoint of the water resistance that the above-mentioned mole ratio is in the range of 1/0.6 to 1/0.1.

[0069]

The above-mentioned Michael addition system is not particularly limited, and examples of this system include a water-borne binder component including a compound having an active methylene group and/or active methyne group, and a compound having a plurality of $\alpha,\beta$-unsaturated carbonyl groups.

[0070]

Examples of compounds having the above-mentioned active methylene group and/or active methyne group include aceto acetic acid, malonic acid, cyanoacetic acid, and derivatives thereof. The above-mentioned derivatives are not particularly limited and includes, for example, products of a reaction of

polyol with the above-mentioned compounds.

[0071]

The above-mentioned compound having a plurality of α,β-unsaturated carbonyl groups is not particularly limited, and examples of this compound include a substance having two or more methacrylate groups and/or acrylate groups per molecule, for example, a substance having two or more methacrylate groups and/or acrylate groups, in which there is a double bond between α,β carbons on a carbonyl group. Specific examples of this compound include (meth)acrylate of polyol, and include ethylene glycol di(meth)acrylate, neopentyl glycol di(meth)acrylate, trimethylolpropane tri(meth)acrylate, pentaerythritol tetra(meth)acrylate, dipentaerythritol hexa(meth)acrylate, 1,4-cyclohexyldimethanol di(meth)acrylate, 4,4'-isopropylidenedicyclohexanol di(meth)acrylate, bis(hydroxymethyl)tricycle[5,2,1,0]decane di(meth)acrylate, and 1,3,5-tris(2-hydroxyethyl)cyanurate tri(meth)acrylate; poly(meth)acrylate resin of acrylic polyol, poly(meth)acrylate resin of polyester polyol, poly(meth)acrylate resin of polyether polyol, poly(meth)acrylate resin of epoxy polyol, poly(meth)acrylate resin of polyurethane polyol and poly(meth)acrylate resin of silicone polyol.

[0072]

A mole ratio of an amount of a curing functional group contained in a compound having the above-mentioned active methylene group and/or active methyne group to an amount of an unsaturated bond contained in a compound having a plurality of α,β-unsaturated carbonyl groups is preferably in the range of 1/10 to 1/0.05. When the above-mentioned mole ratio is more than 1/0.05, the curability becomes insufficient and therefore the water resistance may be deteriorated. When the above-mentioned mole ratio is less than 1/10, an amount of unreacted compound having a plurality of α,β-unsaturated carbonyl groups increases and the water resistance may be

deteriorated. It is more preferred from the viewpoint of the water resistance that the above-mentioned mole ratio is in the range of 1/0.6 to 1/0.1.

[0073]

The water-borne curable antifouling coating composition of the present invention further contains an antifouling agent. The above-mentioned antifouling agent is not particularly limited and publicly known antifouling agents can be used, and examples of them include inorganic compounds, organic compounds containing metal and organic compounds not containing metal.

[0074]

The above-mentioned antifouling agent is not particularly limited, and examples of the antifouling agent include cuprous oxide, manganese ethylenebis(dithiocarbamate), zinc dimethylcarbamate, 2-methylthio-4-t-butylamino-6-cyclopropylamino-s-triazine, 2,4,6-tetrachloroisophthalonitrile, N,N-dimethyldichlorophenylurea, zinc ethylenebis(dithiocarbamate), copper rhodanate, 4,5-dichloro-2-n-octyl-3(2H)isothiazolone, N-(fluorodichloromethylthio)phthalimide, N,N'-dimethyl-N'-phenyl-(N-fluorodichloromethylthio)sulfamide, a zinc salt and a copper salt of 2-pyridinethiol-1-oxide, tetramethylthiuram disulfide, 2,4,6-trichlorophenylmaleimide, 2,3,5,6-tetrachloro-4-(methylsulfonyl)pyridine, 3-iode-2-propylbutylcarbamate, diiodemethyl-p-tolylsulfone, phenyl(bispyridyl)bismuth dichloride, 2-(4-thiazoyl)benzimidazole, pyridine-triphenylborane, stearylamine-triphenylborane, and laurylamine-triphenylborane. These antifouling agents may be used singly or in combination of two or more species. It is preferred to use these antifouling agents in combination in point of adequately developing their capability.

[0075]

In the above-mentioned water-borne curable antifouling

coating composition, an amount of the above antifouling agent to be mixed is preferably in the range from 0.1% by weight of a lower limit to 80% by weight of an upper limit in the solid content of a coating. When this amount is less than 0.1% by weight, an effect of antifouling cannot be expected, and when it is more than 80% by weight, defects such as cracks and peeling may be produced in a coating film. The above amount of the antifouling agent to be mixed more preferably has the lower limit of 1% by weight and the upper limit of 60% by weight.

[0076]

The above-mentioned antifouling agent may be mixed in the water-borne curable antifouling coating composition as a antifouling agent paste including a water-soluble dispersion resin and the above-mentioned antifouling agent. By employing such an antifouling agent paste, the release of the antifouling agent in water becomes easy and an excellent antifouling property can be attained. If a water-borne binder component not having the above-mentioned advantage, such as a urethane curing system, is used, it is preferred to use the above-mentioned antifouling agent paste.

[0077]

In the water-borne curable antifouling coating composition of the present invention, since the above-mentioned antifouling agent paste is used together with the water-borne binder component having curability, a coating film to be obtained becomes a cured film and therefore has excellent water resistance and also an excellent antifouling property. The reason for this is thought that when the coating film is used in water, an antifouling agent becomes easy to be eluted by virtue of a water-soluble dispersion resin contained in the above-mentioned antifouling agent paste.

[0078]

The above-mentioned water-soluble dispersion resin is not particularly limited, and publicly known dispersion resins such as an acrylic resin, a polyester resin, and a urethane resin,

can be used, but the dispersion resin preferably has an acid value of 10 to 300 mg KOH/g and a number average molecular weight of 1000 to 20000.

[0079]

When the above-mentioned acid value is less than 10 mg KOH/g, the solubility in water may be deteriorated to impair the stability. On the other hand, when the above-mentioned acid value is more than 300 mg KOH/g, the hydrophilicity of a resin may become too high to deteriorate the water resistance of a coating film. The above-mentioned upper limit is more preferably 100 mg KOH/g.

[0080]

When the above-mentioned number average molecular weight is less than 1000, the molecular weight is too small and therefore there is a possibility that the antifouling agent cannot be dispersed adequately. Further, when the number average molecular weight is more than 20000, solubility in water cannot be secured, or handling may become difficult because of the too high viscosity. More preferably, the above lower limit is 5000 and the above upper limit is 15000.

[0081]

As the above-mentioned water-soluble dispersion resin, various resins exist, and commercially available articles as pigment dispersants can be used. Examples of specific trade names include SOLSPERS 20000, SOLSPERS 27000, SOLSPERS 41090, (all manufactured by Avecia Inkjet Ltd.), DISPERBYK-180, DISPERBYK-181, DISPERBYK-182, DISPERBYK-183, DISPERBYK-184, DISPERBYK-190, DISPERBYK-191, DISPERBYK-192 (all manufactured by BYK Japan KK), POLYMER 450, POLYMER 451, POLYMER 452, POLYMER 453, EFKA-1501, EFKA-1502, EFKA-4540, EFKA-4550 (all manufactured by EFKA Additives), FLOWLEN G-700, FLOWLEN TG-720, FLOWLEN 730W, FLOWLEN 740W, FLOWLEN 745W (all manufactured by Kyoeisha Chemical Co.,Ltd.),and JONCRYL 678, JONCRYL 679, JONCRYL 62 (all manufactured by JHONSON POLYMER).

[0082]

In the above-mentioned antifouling agent paste, a mixing ratio of the above water-soluble dispersion resin to the above antifouling agent is preferably in the range of 1/99 to 50/50 in terms of solid content. When the above-mentioned mixing ratio is out of the above range, the viscosity of the antifouling agent paste dispersed becomes too high or the dispersibility of the antifouling agent is deteriorated, and therefore the stability may become insufficient.

[0083]

Furhter, common additives such as a pigment and a plasticizer described later may be added to the above-mentioned antifouling agent paste in addition to the components described above.

When the above antifouling agent paste includes a pigment, the content of the pigment is preferably 50% by weight or less.

The above-mentioned antifouling agent paste can be obtained, for example, by a method of mixing the above water-soluble dispersion resin and the above antifouling agent with a pigment dispersing machine such as a sand-grinding mill.

[0084]

The above-mentioned antifouling agent paste is preferably mixed in such a way that an amount of the antifouling agent to be mixed in the water-borne antifouling coating composition is in the range from 0.1% by weight of a lower limit to 80% by weight of an upper limit in the solid content of a coating. When this amount is less than 0.1% by weight, an effect of antifouling cannot be expected, and when it is more than 80% by weight, defects such as cracks and peeling may be produced in a coating film. The amount of the antifouling agent to be mixed more preferably has the lower limit of 1% by weight and the upper limit of 60% by weight.

[0085]

The water-borne curable antifouling coating composition of the present invention preferably further includes organic polymer particles. The above-mentioned organic polymer

particle has an excellent property that a coating film having low friction performance can be readily formed by adding the organic polymer particle to the water-borne curable antifouling coating composition of the present invention as an additive.

[0086]

In the above-mentioned organic polymer particle, it is preferred that the solubility in the artificial seawater specified in ASTM D1141-98 at 23°C is 15 g/l or less, the water-absorbing amount for the artificial seawater specified in ASTM D1141-98 is 0.01% by weight or more and a particle diameter is 0.05 to 100 μm. That is, when the organic polymer particle satisfying the above-mentioned properties is added, desired properties can be attained irrespective of a chemical structure of the polymer.

[0087]

In addition, in the present specification, the artificial seawater specified in ASTM D1141-98 was used as standard water for determining the solubility and the water-absorbing amount. Since a coating film formed from the coating composition of the present invention is predominantly used in seawater, it is necessary to measure the above-mentioned solubility and water-absorbing amount using not pure water but seawater as standard water.

[0088]

In the above-mentioned organic polymer particle, it is preferred that the solubility in the artificial seawater specified in ASTM D1141-98 at 23°C is 15 g/l or less. When the above-mentioned solubility is more than 15 g/l, there is a possibility that adequate low friction performance cannot be exerted. The above solubility is preferably 12 g/l or less. Incidentally, the above solubility is a value obtained by drying the organic polymer particle at room temperature under a reduced pressure, weighing the dried particle, and measuring the solubility of the particle in the artificial seawater prepared according to ASTM D1141-98.

[0089]

In the above organic polymer particle, it is preferred that the water-absorbing amount for the artificial seawater specified in ASTM D1141-98 is 0.01% by weight or more. When the above-mentioned water-absorbing amount is less than 0.01% by weight, compatibility with seawater is low and therefore adequate effect cannot be attained and reduction in friction is suppressed. Since the organic polymer particle used in the present invention has a property of swelling when coming into contact with water and not dissolving in water, it can suitably exert low friction performance. The above water-absorbing amount is preferably 0.1% by weight or more.

[0090]

Incidentally, the water-absorbing amount in the present invention was determined by the operational procedures in which 1 g of organic polymer particles dried at room temperature in a vacuum (under a reduced pressure) were precisely weighed out, and the particles were put in 50 g of artificial seawater prepared according to ASTM D1141-98 and stirred at 23°C for 5 hours, and the particles were separated by filtration and a residue was washed with water to be weighed.

[0091]

Furthermore, the particle diameter of the above organic polymer particle is preferably in the range from 0.05 μm of a lower limit to 100 μm of an upper limit. When the above particle diameter is smaller than 0.05 μm, an adequate friction-reducing effect cannot be attained. When it is larger than 100 μm, a problem that the surface condition is deteriorate may arise. Preferably, the above-mentioned lower limit is 0.1 μm and the above-mentioned upper limit is 40 μm. More preferably, the range of the particle diameter is 1 to 30 μm. In addition, the above-mentioned particle diameter is measured under the following conditions and refers to an average particle diameter outputted on selecting a distribution basis described in an instruction manual of the following apparatus as a volume.

Name of apparatus and a manufacturer: SALD-2200, SHIMADZU CORPORATION
Dispersion medium for measuring: deionized water

[0092]

The above organic polymer particle may be a naturally-derived polymer or a synthetic polymer. The above organic polymer particle preferably has an appropriate amount of a hydrophilic functional group and has a crosslinking chain as required. Example of the above-mentioned hydrophilic functional group include a hydroxyl group, an amino group, a carboxyl group, an amide group, and a polyoxyethylene group. A high water-absorbing amount can be attained by having a hydrophilic group, but when the hydrophilicity becomes too high, the solubility in seawater may become too high. When the hydrophilicity becomes too high, the solubility in artificial seawater can be adjusted by introducing a hydrophobic group or crosslinking.

[0093]

Examples of a naturally-derived polymer which can be used as the organic polymer particle of the present invention include polysaccharides such as chitin, chitosan, gum arabic, alginic acid, carrageenan, agar, xanthan gum, gellan gum, cellulose, xylose, starch, pullulan, pectin, roast bean gum, dextran and curdlan; proteins such as keratin, collagen, silk and γ-polyglutamic acid (hereinafter, referred to as γ-PGA); and nucleic acid. Further, naturally-derived polymers also include derivative compounds such as semi-synthetic polymers formed by making naturally-derived polymers become hydrophilic (for example, hydroalkylated), converting naturally-derived polymers to polyethylene glycol, making naturally-derived polymers become hydrophobic (for example, alkylated), grafting naturally-derived polymers, or making naturally-derived polymers become three-dimensional by hydrolyzing or crosslinking these naturally-derived polymers as required.

[0094]

The above-mentioned naturally-derived polymer preferably has a cationic group. It becomes easier to achieve a friction-reducing effect of the coating film in seawater by having the cationic group. The above-mentioned cationic group is not particularly limited, and examples of the cationic group include an amino group, an amide group and a pyridine group. A natural polymer inherently containing a cationic group may be used, or when a polymer not containing a cationic group is used, this polymer may be modified to a derivative to introduce a cationic group into the derivative.

[0095]

The above-mentioned organic polymer particle is more preferably at least one species of an organic polymer particle selected from the group consisting of chitin, chitosan, γ-PGA, pulverized silk and derivatives thereof.

[0096]

The above-mentioned chitin is polysaccharide and a deacetylation product of the polysaccharide is chitosan. The above-mentioned deacetylation may be perfect deacetylation or may be partial deacetylation. The polysaccharide may be modified or crosslinked with polyoxyethylene or an aldehyde group-containing compound as required.

[0097]

The above-mentioned pulverized silk is formed by pulverizing silk which is a cocoon filament produced by a silkworm into particles. It is assumed that fibroin or sericin of a naturally-derived polymer, contained in silk as a main ingredient, has an effect described above in the present invention.

[0098]

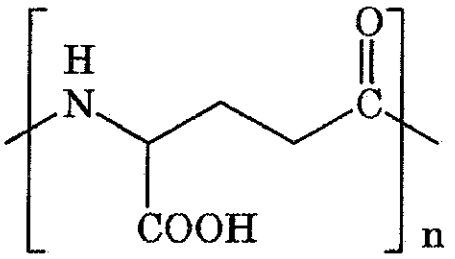
The pulverized silk used in the present invention may be a particle obtained by pulverizing natural silk directly or a particle obtained by removing contaminant components, hydrolyzing, purifying and classifying natural silk as required.

[0099]

A γ-PGA is a polymer expressed by the following formula (1);

[0100]

[Formula. 1]



(1)

[0101]

As a familiar example, a polymer which is a main component of glutinosity produced by bacillus natto and is noted as a polymer absorber material, a biodegradable material, a medical material, a food additive or a cosmetic material is given. A γ-PGA particle used in the present invention is formed by drying naturally-derived substances produced by the above fungus and pulverizing them into particles. The above-mentioned γ-PGA particle may be a particle formed by removing contaminant components, hydrolyzing, purifying and classifying γ-PGA as required.

[0102]

As the above organic polymer particle, a synthetic polymer can also be used. The above-mentioned synthetic polymer is not particularly limited, and examples of the synthetic polymer include an acrylic resin, a polyester resin, an amine resin and a modified polyvinyl alcohol resin. These synthetic polymers are preferably a hydrophilic resin having hydrophilic groups such as a hydroxyl group, an amino group and a carboxyl group, and a part of the synthetic polymer may have a crosslinking structure as required. By adjusting the hydrophilicity/hydrophobicity and a proportion of crosslinking by a publicly known method, the organic polymer particle can be obtained.

[0103]

As the above-mentioned synthetic polymer, particularly, an acrylic resin particle can be suitably employed. The above-mentioned acrylic resin particle can be obtained, for example, by emulsion polymerization of a monomer composition including an acrylic monomer and a crosslinkable monomer.

[0104]

The above-mentioned acrylic monomer is not particularly limited and includes, for example, alkyl esters of acrylic acid or methacrylic acid such as methyl (meth)acrylate, ethyl (meth)acrylate, n-butyl (meth)acrylate, isobutyl (meth)acrylate and 2-ethylhexyl (meth)acrylate; hydroxyl group-containing (meth)acrylate such as 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate and 2-hydroxyethyl (meth)acrylate; and acrylonitrile, methacrylonitrile and dimethylaminoethyl (meth)acrylate.

[0105]

In the above emulsion polymerization, other ethylenic unsaturated monomers may be used. The above-mentioned ethylenic unsaturated monomer is not particularly limited, and examples of the ethylenic unsaturated monomer include styrene, α-methylstyrene, vinyl toluene, t-butylstyrene, vinyl acetate, and vinyl propionate. The above-mentioned acrylic monomers and ethylenic unsaturated monomers may be used singly or in combination of two or more species.

[0106]

The above-mentioned crosslinkable monomer is not particularly limited, and examples of the crosslinkable monomer include a monomer having two or more radically polymerizable ethylenic unsaturated bonds in a molecule.

[0107]

The above-mentioned monomer having two or more radically polymerizable ethylenic unsaturated bonds in a molecule, which can be used for the production of the above acrylic resin particles, is not particularly limited, and examples of the

above-mentioned monomer include polymerizable unsaturated monocarboxylic acid esters of polyhydric alcohol such as ethyleneglycol diacrylate, ethyleneglycol dimethacrylate, triethyleneglycol dimethacrylate, tetraethyleneglycol dimethacrylate, 1,3-butyleneglycol dimethacrylate, trimethylolpropane triacrylate, trimethylolpropane trimethacrylate, 1,4-butanediol diacrylate, neopentylglycol diacrylate, 1,6-hexanediol diacrylate, pentaerythritol diacrylate, pentaerythritol triacrylate, pentaerythritol tetraacrylate, pentaerythritol dimethacrylate, pentaerythritol trimethacrylate, pentaerythritol tetramethacrylate, glycerol dimethacrylate, glycerol diacrylate, glycerol allyloxy dimethacrylate, 1,1,1-tris(hydroxymethylethane) diacrylate, 1,1,1-tris(hydroxymethylethane) triacrylate, 1,1,1-tris(hydroxymethylethane) dimethacrylate, 1,1,1-tris(hydroxymethylethane) trimethacrylate, 1,1,1-tris(hydroxymethylpropane) diacrylate, 1,1,1-tris(hydroxymethylpropane) triacrylate, 1,1-tris(hydroxymethylpropane) dimethacrylate and 1,1,1-tris(hydroxymethylpropane) trimethacrylate; polymerizable unsaturated alcohol esters of polybasic acid such as triallyl cyanurate, triallyl isocyanurate, triallyl trimelitate, diallyl terephthalate and diallyl phthalate; and aromatic compounds substituted by two or more vinyl groups such as divinylbenzene.

[0108]

In the above-mentioned monomer composition, an amount of the above crosslinkable monomer is preferably 1% by weight or more with respect to the total amount of the monomer composition. When the above percentage by weight is out of the above range, there is a possibility that desired acrylic resin particle cannot be obtained. The above percentage by weight is more preferably 5 to 70% by weight.

A method of polymerizing the above-mentioned monomer

composition is not particularly limited and publicly known methods such as emulsion polymerization and suspension polymerization can be employed.

[0109]

The above organic polymer particle may be a composite resin particle including two or more species of polymers. The term a composite resin particle including two or more species of polymers refers to a particle formed by using two or more species of various naturally-derived polymers and synthetic polymers described above, and specific measure for forming a composite particle is not particularly limited and includes any technique such as mixing, grafting, core-shell forming, IPN (interpenetrating polymer network) and surface treating.

[0110]

The above-mentioned two or more species of polymers are not particularly limited, and examples of these polymers include the naturally-derived polymer described above and the above synthetic polymers. Among them, a composite resin particle, in particular, including at least one species of hydrophilic resin selected from the group consisting of starch, pullulan, gum arabic, κ-carrageenan, gelatin, cellulose, chitosan and derivatives thereof, polyvinyl alcohol, polyallylamine, polyvinylamine, poly(meth)acrylamide, and poly(meth)acrylic acid and copolymer thereof, and an acrylic resin is preferable. When such a combination is employed, it is preferred in that hydrophilicity can be attained while changing the properties of a particle at request by the composition of the acrylic resin. The above hydrophilic resin and acrylic resin may be used in the form of combining resins among which a resin alone cannot achieve the object of the present invention. It is more preferred to use at least one resin selected from chitosan, chitosan derivatives, and polyvinyl alcohol as the above hydrophilic resin.

[0111]

The above-mentioned composite resin particle including

the hydrophilic resin and the acrylic resin can be obtained, for example, by emulsion polymerization or suspension polymerization of a raw material monomer of an acrylic resin in the presence of the above hydrophilic resin. As an emulsifier used in polymerization, a publicly known emulsifier can be used, but a reactive emulsifier is preferred from the viewpoint of water resistance. Examples of the above-mentioned reactive emulsifier include substances described above.

[0112]

An amount of the above reactive emulsifier to be added is preferably 15% by weight or less. When this amount is more than 15% by weight, the water resistance of a coating film to be obtained from the coating containing the composite resin particles may be deteriorated.

[0113]

In the synthesis of the above-mentioned composite resin particle, a mixing ratio of a monomer composition being a raw material of acrylic resin and a hydrophilic resin is preferably 40/60 to 97/3 in a weight ratio (solid content).

[0114]

An amount of the above organic polymer particle to be mixed in the coating composition of the present invention is preferably in the range from 0.01% by weight of a lower limit to 15% by weight of an upper limit with respect to the solid content in a coating. When this amount is less than 0.01% by weight, it is not preferred since a desired effect cannot be achieved. When this amount is more than 15% by weight, there may be cases where a friction-reducing effect in water appropriate to the amount of the organic polymer particle to be mixed cannot be achieved. More preferably, the above lower limit is 0.1% by weight and the above upper limit is 12% by weight.

In addition, the water-borne curable antifouling coating composition of the present invention may contain one or two or

more species of the above organic polymer particles.

[0115]

By applying the water-borne curable antifouling coating composition containing the organic polymer particle described above onto the surface of a substance to be coated, it is possible to form a coating film having excellent low friction performance in addition to the water resistance and the antifouling property.

The water-borne curable antifouling coating composition of the present invention, which contains the organic polymer particle described above, can impart good low friction performance, for example, when it is applied to a marine vessel which moves at a speed of about 10 to 30 knot. By applying the above coating composition, it is possible to reduce frictional resistance by 2 to 3% or more compared with the application of the conventional antifouling coating. Thus, the above coating composition of the present invention, which contains with the above organic polymer particle, can contribute to the reduction in navigation fuel economy significantly as a vessel bottom coating.

[0116]

To the water-borne curable antifouling coating composition of the present invention, the common additives such as a plasticizer and a pigment in addition to the above-mentioned components can be added.

Examples of the above-mentioned plasticizer include plasticizers of phthalates such as dioctylphthalate, dimethylphthalate and dicyclohexyl phthalate; plasticizers of aliphatic dibasic acid esters such as isobutyl adipate and dibutyl sebacate; plasticizers of glycol esters such as diethylene glycol dibenzoate and pentaerythritol alkyl ester; plasticizers of phosphorates such as trichlene diphosphate and trichloroethyl phosphate; plasticizers of epoxy such as epoxy soybean oil and octyl epoxystearate; plasticizers of organic tin such as dioctyltin dilaurate and dibutyltin dilaurate; and

trioctyl trimelitate and triacetylene. These plasticizers may be used singly or in combination of two or more species.

[0117]

Examples of the above-mentioned pigment include extenders such as precipitated barium, talc, clay, chalk, silica white, alumina white and bentonite; and color pigments such as titanium oxide, zircon oxide, basic lead sulfate, tin oxide, carbon black, graphite, red iron oxide, chrome yellow, copper phthalocyanine green, copper phthalocyanine blue and quinacridone. These pigments may be used singly or in combination of two or more species.

[0118]

Other additives other than the above additives are not particularly limited, and examples of the other additives include monobasic organic acids such as monobutyl phthalate and monooctyl succinate, and camphor; water binder, and an anti-sagging agent; anti-flooding agent; an antiprecipitation agent; and antifoamer.

[0119]

A method of preparing the water-borne curable antifouling coating composition of the present invention is not particularly limited, but the coating composition can be prepared, for example, by a method in which an antifouling agent, an organic polymer particle, the common additives such as a plasticizer, a compensating agent for coating film attrition and a pigment are added to the water-borne binder component and the resulting mixture is mixed with a stirrer such as a ball mill, a pebble mill, a roll mill, or a sand-grinding mill. In addition, when the antifouling agent is used in the form of antifouling agent paste, the above coating composition can be prepared by mixing the antifouling agent and the water-soluble dispersion resin, and further the pigment, the plasticizer and other additives in advance with a sand-grinding mill, and then mixing the resulting mixture with the water-borne binder component and the organic polymer particle.

[0120]

The above water-borne curable antifouling coating composition preferably has a nonvolatile content of 10 to 90% by weight. When the above-mentioned nonvolatile content is less than 10% by weight, it may become difficult to increase a film thickness. When the above-mentioned nonvolatile content is more than 90% by weight, it may become difficult to adjust the viscosity in coating.

[0121]

The above water-borne curable antifouling coating composition preferably has a PWC of 50 to 90% by weight. When the above-mentioned PWC is less than 50% by weight, a drying property at room temperature may be deteriorated. On the other hand, when the above-mentioned PWC is more than 90% by weight, the formation of a film may become difficult.

[0122]

The above water-borne curable antifouling coating composition can form a dried coating film by applying it onto the surface of a substance to be coated according to a normal method and then vaporizing/removing water at room temperature. The coating film thus obtained has an effect of inhibiting the fouling of underwater structures. A coating film having an antifouling property obtained by applying the above water-borne curable antifouling coating composition also constitutes the present invention, and an underwater structure having the above-mentioned coating film having an antifouling property also constitutes the present invention.

[0123]

The above-mentioned coating film having an antifouling property can be formed by applying the above water-borne curable antifouling coating composition by publicly known methods such as dipping, spraying, brushing, roller application, and electrostatic coating. After application, the applied coating composition may be left standing at room temperature to be dried or may be subjected to forced drying of about 80°C for several

hours or about one day. A dried film thickness of the above coating film having an antifouling property is preferably in the range from 30 μm of a lower limit to 500 μm of an upper limit. If the above-mentioned dried film thickness is in the above-mentioned range, it is preferred since the coating film has a good balance between the water resistance and the antifouling property.

[0124]

A weight ratio of a resin solid content to an antifouling agent in the above coating film having an antifouling property is not particularly limited, but it is preferably from 1:7 to 1:1 from the viewpoint of an antifouling effect. Then, when the above coating film having an antifouling property has a self-polishing property by virtue of the proceeding of a reverse reaction of a curing reaction, an amount of a curing functional group contained in the above coating film having an antifouling property is preferably in the range from 0.00015 to 8 mmol/g with respect to the resin solid content from the viewpoint of the water resistance and the antifouling property. Incidentally, the above-mentioned amount of a curing functional group can be calculated from the coating composition.

[0125]

The above substance to be coated may be pre-treated as required. The above substance to be coated is not particularly limited, but it is preferably an underwater structure because a coating film exhibiting excellent low friction performance is formed.

The above-mentioned underwater structure is not particularly limited, and examples of the underwater structure include a marine vessel, a piping material and a fishing net.

[0126]

The water-borne curable antifouling coating composition of the present invention can attain a coating film having the excellent water resistance and the good antifouling effect.

## EFFECT OF THE INVENTION

[0127]

In accordance with the present invention, the water-borne curable antifouling coating composition, which can form a coating film having the excellent water resistance and the good antifouling effect, could be attained. The coating film having an antifouling property, prepared from the above water-borne curable antifouling coating composition, can be widely applied to the underwater structures since it has the above-mentioned effects.

## BEST MODES FOR CARRYING OUT THE INVENTION

[0128]

Hereinafter, the present invention will be described in more detail by way of examples, but the present invention is not limited to these examples. In addition, "part(s)" refers to "part(s) by weight" in Examples, unless otherwise specified.

[0129]

Production Example 1

Production of carbonyl-containing emulsion resin

A monomer mixture including 10 parts of diacetoneacrylamide, 30 parts of methyl methacrylate, 20 parts of ethyl acrylate, 30 parts of n-butyl acrylate, 9 parts of styrene, and 1 part of methacrylic acid was added to a solution obtained by mixing 60 parts of deionized water and 6 parts of Aqualon HS-10 (anionic reactive emulsifier manufactured by DAI-ICHI KOGYO SEIYAKU Co., Ltd.), and the resulting mixture was emulsified with a stirrer to obtain a pre-emulsion of the monomer mixture. And, 0.3 part of ammonium persulfate was dissolved in 17 parts of deionized water to obtain an aqueous solution of an initiator.

[0130]

Into a reaction vessel equipped with a dropping funnel, a thermometer, a nitrogen inlet tube, a reflux condenser and a stirrer, 70 parts of deionized water and 2 parts of Aqualon

HS-10 were charged, and the mixture was heated to 80°C in an atmosphere of nitrogen. Next, the obtained pre-emulsion and aqueous solution of an initiator were dropped simultaneously over 3 hours from separate dropping funnels. After the completion of dropping, a reaction of the mixture was further continued at the same temperature for 2 hours. After cooling a reactant, it was neutralized with an aqueous solution of a basic neutralizing agent including 7 parts of deionized water and 1 part of dimethyl ethanolamine. The carbonyl group-containing emulsion resin thus obtained had a solid content of 40% by weight and an average particle diameter of 90 nm.

[0131]

Production Example 2

Production of acetoacetoxy group-containing emulsion resin

An acetoacetoxy group-containing emulsion resin was prepared by following the same procedure as in Production Example 1 except for changing 10 parts of diacetoneacrylamide to 10 parts of acetoacetoxyethyl methacrylate. The resulting acetoacetoxy group-containing emulsion resin had a solid content of 40% by weight and an average particle diameter of 90 nm.

[0132]

Production Example 3

Production of alkoxysilyl group-containing emulsion resin

An alkoxysilyl group-containing emulsion resin was prepared by following the same procedure as in Production Example 1 except for changing 10 parts of diacetoneacrylamide to 10 parts of KBM-503 (methacryloxypropyltrimethoxysilane manufactured by Shin-Etsu Chemical Co., Ltd.). The resulting alkoxysilyl group-containing emulsion resin had a solid content of 40% by weight and an average particle diameter of 90 nm.

[0133]

Production Example 4

Production of emulsion resin containing higher unsaturated

fatty acid-derived group

An emulsion resin containing higher unsaturated fatty acid-derived group was prepared by following the same procedure as in Production Example 1 except for changing 10 parts of diacetoneacrylamide to 10 parts of soybean oil fatty acid adduct of glycidyl methacrylate. The resulting emulsion resin containing higher unsaturated fatty acid-derived group had a solid content of 40% by weight and an average particle diameter of 90 nm.

[0134]

Production Example 5

Production of antifouling agent paste

40 parts of cuprous oxide, 5 parts of zinc pyrithione, 5 parts of zinc oxide, 5 parts of red iron oxide, and 5 parts of talc were added to 20 parts of deionized water, and to the mixture, 20 parts of BYK-190 (manufactured by BYK Japan KK) as a pigment dispersant and BYK-019 (manufactured by BYK Japan KK) as an antifoamer were further added, and the resulting mixture was dispersed with a sand-grinding mill to obtain an antifouling agent paste having a solid content of 76.5% by weight, a PWC of 92%, and an particle size of 20 μm.

[0135]

Example 1

A water-borne curable antifouling coating composition was prepared by dispersing 100 parts of the carbonyl group-containing emulsion resin obtained in Production Example 1, 4 parts of Hardener SC (semicarbazide curing agent manufactured by Asahi Kasei Corp., solid content 50% by weight), 200 parts of the antifouling agent paste obtained in Production Example 5, and 3 parts of PUR-2150 (associated urethane thickner manufactured by Akzo Nobel N.V., solid content 35% by weight) with a disper.

[0136]

This coating composition had a PWC of 72%, a solid content of 64% by weight, an amount of a curing functional group/a

carbonyl group: 0.12 mmol/g, a semicarbazide group: 0.047 mmol/g, and an acid value of 1.0 mg KOH/g.

Furthermore, the viscosity of the obtained coating composition was adjusted with deionized water so as to be 90 KU at 25°C in viscosity by a Stomer viscometer.

[0137]

This coating composition was applied to a FRP plate (100 × 300 × 3 mm, gel-coated), which had been roughed with a sand paper (grain size 240), with a brush so as to be 400 μm in a dried film thickness. After application, the coating composition was left standing for one day in an atmosphere of 20°C and 65% in relative humidity to obtain a coated plate for test.

[0138]

Examples 2 to 6

Each water-borne curable antifouling coating composition was prepared by following the same procedure as in Example 1 except for using the acetoacetoxy group-containing emulsion resin, the alkoxysilyl group-containing emulsion resin and the emulsion resin containing higher unsaturated fatty acid-derived group, which were prepared in Production Examples 2, 3, and 4, and WATERSOL 3060 (water-borne alkyd resin manufactured by Dainippon Ink and Chemicals Inc.) and Bayhydrol A145 (polyol for water-borne polyurethane manufactured by Sumika Bayer Urethane Co., Ltd.), and changing the composition to those shown in Table 1. Further, coated plates for test were prepared in the same manner as in Example 1.

[0139]

Comparative example 1

A water-borne noncurable antifouling coating composition for comparison and a coated plate for test were prepared by following the same procedure as in Example 1 except for changing the composition to that shown in Table 1.

[0140]

On each coated plate for test obtained, the water

resistance and the antifouling property were evaluated according to the following criteria.

<Water resistance and antifouling property>

The coated plate for test was suspended/immersed at a depth of 1 meter from a marine-raft in a marine research laboratory of Nippon Paint Marine Coating Co., Ltd. in Tamano city, Okayama Prefecture, Japan, and the surface conditions of the coating film after 1 month, 6 months and 12 months were visually observed. The results are shown in Table 1.

The water resistance was evaluated according the following criteria.

○: There is no abnormal conditions

Δ: There is a little blister.

×: There are blister over the whole area.

[0141]

The antifouling property was evaluated according the following criteria.

◎: There is no lives adhering

○: Only easy-to-remove slime adheres

Δ: An area to which the flora and fauna adhere is less than 10% of a test plate area

×: An area to which the flora and fauna adhere is 10% or more and less than 50% of a test plate area

××: An area to which the flora and fauna adhere is more than 50% of a test plate area

[0142]

On the obtained water-borne curable antifouling coating compositions, a self-polishing property was evaluated according to the following method.

<Self-polishing property>

The obtained water-borne curable antifouling coating composition was applied to a FRP plate (gel-coated), which had been roughed with a sand paper (grain size 240), with an applicator so as to be about 240 μm in a dried film thickness. After application, the coating composition was left standing

for one day in an atmosphere of 20°C and 65% in relative humidity to obtain a coated plate for test. This coated plate for test was attached to a rotational drum installed in the seawater and rotated at a speed of 10 knots and consumed film thickness (μm) was measured every three months. The results of the measurements are shown in Table 1.

[0143]

Table 1

| | | Solid content (%) | Example 1 | Example 2 | Example 3 | Example 4 | Example 5 | Example 6 | Comparative Example 1 |
|---|---|---|---|---|---|---|---|---|---|
| Emulsion resin | Production Example 1 | 40 | 100 | – | – | – | – | – | 100 |
| | Production Example 2 | 40 | – | 100 | – | – | – | – | – |
| | Production Example 3 | 40 | – | – | 100 | – | – | – | – |
| | Production Example 4 | 40 | – | – | – | 100 | – | – | – |
| | WATERSOL 3060*1 | 38 | – | – | – | – | 105 | – | – |
| | Bayhydrol A145*2 | 45 | – | – | – | – | – | 62 | – |
| Curing agent | Hardener SC*3 | 50 | 4 | – | – | – | – | – | – |
| | Hexamethylene diamine | 30 | – | 4 | – | – | – | – | – |
| | Bayhydur 3100*4 | 100 | – | – | – | – | – | 12 | – |
| Curing catalyst | Phosphoric acid | 100 | – | – | 1 | – | – | – | – |
| | Drier*5 | 35 | – | – | – | 1 | 1 | – | – |
| Antifouling agent paste (Production Example 5) | | 76.5 | 200 | 200 | 200 | 200 | 200 | 200 | 200 |
| Thickner | PUR-2150 | 35 | 3 | 3 | 3 | 3 | 3 | 3 | 3 |
| Water resistance | 1 month | | ○ | ○ | ○ | ○ | ○ | ○ | △ |
| | 6 months | | ○ | ○ | ○ | ○ | ○ | ○ | × |
| | 12 months | | ○ | ○ | ○ | ○ | ○ | ○ | × |
| Antifouling property | 1 month | | ◎ | ◎ | ◎ | ◎ | ○ | ○ | ◎ |
| | 6 months | | ◎ | ◎ | ◎ | ○ | ○ | △ | – |
| | 12 months | | ◎ | ○ | ○ | ○ | △ | × | – |
| Self-polishing property ($\mu$m) | 3 months | | 34 | 21 | 15 | 4 | 3 | 5 | unmeasurable |
| | 6 months | | 62 | 44 | 31 | 5 | 5 | 5 | – |
| | 9 months | | 105 | 60 | 48 | 7 | 5 | 5 | – |
| | 12 months | | 136 | 83 | 69 | 7 | 5 | 5 | – |

*1 water-borne alkyd resin manufactured by Dainippon Ink and Chemicals Inc.
*2 polyol for water-borne polyurethane manufactured by Sumika Bayer Urethane Co., Ltd.
*3 semicarbazide curing agent manufactured by Asahi Kasei Corp.
*4 isocyanate for water-borne polyurethane manufactured by Sumika Bayer Urethane Co., Ltd.
*5 cobalt naphthenate

[0144]

It was confirmed from Table 1 that the coating films obtained in Examples have the excellent water resistance and the excellent antifouling property. However, in Example 6 of the urethane cured system, a prolonged antifouling property was low though there was no problem in the water resistance. On the other hand, in Comparative Example 1 in which the coating composition is an uncurable system, it became apparent that there was such a large problem in the water resistance that the coating film is dissolved in seawater. Further, in Examples, it was confirmed that the coating films using the water-borne binder component to be cured by dehydration-condensation have higher antifouling property than those using the water-borne binder component to be cured by oxidative polymerization, and particularly, the coating film of Example 1 using a carbonyl-hydrazide system as a curing system had excellent antifouling property. Incidentally, this expression of an antifouling property is considered to be associated with a self-polishing property.

[0145]

Production Example 6

Production of emulsion resin containing higher unsaturated fatty acid-derived group

A monomer mixture including 10 parts of soybean oil fatty acid adduct of glycidyl methacrylate, 30 parts of methyl methacrylate, 20 parts of ethyl acrylate, 30 parts of n-butyl acrylate, 9 parts of styrene, and 1 part of methacrylic acid was added to a solution obtained by mixing 60 parts of deionized water and 6 parts of Aqualon HS-10 (anionic reactive emulsifier manufactured by DAI-ICHI KOGYO SEIYAKU Co., Ltd.), and the resulting mixture was emulsified with a stirrer to obtain a pre-emulsion of the monomer mixture. And, 0.3 part of ammonium persulfate was dissolved in 17 parts of deionized water to obtain an aqueous solution of an initiator.

[0146]

Into a reaction vessel equipped with a dropping funnel, a thermometer, a nitrogen inlet tube, a reflux condenser and a stirrer, 70 parts of deionized water and 2 parts of Aqualon HS-10 were charged, and the mixture was heated to 80°C in an atmosphere of nitrogen. Next, the obtained pre-emulsion and aqueous solution of an initiator were dropped simultaneously over three hours from separate dropping funnels. After the completion of dropping, a reaction of the mixture was further continued at the same temperature for 2 hours. After cooling a reactant, it was neutralized with an aqueous solution of a basic neutralizing agent including 7 parts of deionized water and 1 part of dimethyl ethanolamine. The obtained emulsion resin containing higher unsaturated fatty acid-derived group had a solid content of 40% by weight and an average particle diameter of 90 nm.

[0147]

Production Example 7

Production of carboxyl group-containing emulsion resin

A monomer mixture including 36 parts of methyl methacrylate, 20 parts of ethyl acrylate, 30 parts of n-butyl acrylate, 10 parts of styrene, and 10 parts of methacrylic acid was added to a solution obtained by mixing 60 parts of deionized water and 6 parts of Aqualon HS-10 (anionic reactive emulsifier manufactured by DAI-ICHI KOGYO SEIYAKU Co., Ltd.), and the resulting mixture was emulsified with a stirrer to obtain a pre-emulsion of the monomer mixture. And, 0.3 part of ammonium persulfate was dissolved in 17 parts of deionized water to obtain an aqueous solution of an initiator.

[0148]

Into a reaction vessel equipped with a dropping funnel, a thermometer, a nitrogen inlet tube, a reflux condenser and a stirrer, 70 parts of deionized water and 2 parts of Aqualon HS-10 were charged, and the mixture was heated to 80°C in an atmosphere of nitrogen. Next, the obtained pre-emulsion and aqueous solution of an initiator were dropped simultaneously

over three hours from separate dropping funnels. After the completion of dropping, a reaction of the mixture was further continued at the same temperature for 2 hours. After cooling a reactant, it was neutralized with an aqueous solution of a basic neutralizing agent including 7 parts of deionized water and 1 part of dimethyl ethanolamine.

The obtained carboxyl group-containing emulsion resin had a solid content of 40% by weight and an average particle diameter of 90 nm.

[0149]

Examples 7 to 10

Water-borne curable antifouling coating compositions were obtained by adding the components of the composition shown in Table 2 and the antifouling agent paste of Production Example 5 in succession. Next, the viscosities of the obtained coating compositions were adjusted with deionized water so as to be 90 KU at 25°C in viscosity by a Stomer viscometer.

[0150]

This coating composition was applied to a FRP plate (100 × 300 × 3 mm, gel-coated), which had been roughed with a sand paper (grain size 240), with a brush so as to be 400 μm in a dried film thickness. After application, the coating composition was left standing for one day in an atmosphere of 20°C and 65% in relative humidity to obtain a coated plate for test.

[0151]

Comparative Examples 2 to 4

By adding the components of the composition shown in Table 2 and an antifouling agent or the antifouling agent paste of Production Example 5 in succession, two kinds of water-borne curable antifouling coating compositions and a water-borne noncurable antifouling coating composition, which were for the purpose of comparison, were obtained. Further, coated plates for test were prepared in the same manner as in Examples.

On each coated plate for test obtained, the water

resistance and the antifouling property were evaluated by following the same methods as those described above except for setting the immersion duration at 1 month and 6 months. The results of evaluations are shown in Table 2.

[0152]

Table 2

| | | Solid content (%) | Example 7 | Example 8 | Example 9 | Example 10 | Comparative Example 2 | Comparative Example 3 | Comparative Example 4 |
|---|---|---|---|---|---|---|---|---|---|
| Emulsion resin | Production Example 6 | 40 | 100 | – | – | – | 100 | – | – |
| | WATERSOL 3060*1 | 38 | – | 105 | – | – | – | – | – |
| | Bayhydrol A145*2 | 45 | – | – | 62 | – | – | 62 | – |
| | Production Example 7 | 40 | – | – | – | 79 | – | – | 100 |
| Curing agent | Bayhydur 3100*3 | 100 | – | – | 12 | – | – | 12 | – |
| | V-02*4 | 40 | – | – | – | 21 | – | – | – |
| Catalyst | Drier*5 | 35 | 1 | 1 | – | – | 1 | – | – |
| Antifouling agent | Paste of Production Example 5 | 76.5 | 200 | 200 | 200 | 200 | – | – | 200 |
| | ZPT water-dispersed content*6 | 50 | – | – | – | – | 300 | 300 | – |
| Thickner | PUR-2150 | 35 | 3 | 3 | 3 | 3 | 3 | 3 | 3 |
| Water resistance | 1 month | | ○ | ○ | ○ | ○ | ○ | ○ | △ |
| | 6 months | | ○ | ○ | ○ | ○ | ○ | ○ | × |
| Antifouling property | 1 month | | ◎ | ○ | ○ | ○ | △ | × | ○ |
| | 6 months | | ○ | ○ | △ | △ | × | ×× | – |

*1 water-borne alkyd resin manufactured by Dainippon Ink and Chemicals Inc.
*2 polyol for water-borne polyurethane manufactured by Sumika Bayer Urethane Co., Ltd.
*3 isocyanate for water-borne polyurethane manufactured by Sumika Bayer Urethane Co., Ltd.
*4 carbazide curing agent manufactured by NISSHINBO INDUSTRIES, INC.
*5 cobalt naphthenate
*6 water-dispersion of zinc pyrithione

[0153]

It was confirmed from Table 2 that the coating films obtained in Examples have the excellent water resistance and the excellent antifouling property. In particular, the coating film of Example 7 of a curing system of oxidative polymerization was superior in the antifouling property to a curing system of other addition polymerization.

On the other hand, in Comparative Examples 2 and 3 in which an antifouling agent paste was not used, the antifouling property was low though there was no problem in the water resistance, and in Comparative Example 4 in which the coating composition is an uncurable system, it became apparent that there was a problem in the water resistance.

[0154]

Production Example 8

Production method of organic polymer particle A

In a four necked flask equipped with a condenser, a thermometer, a stirrer and a nitrogen inlet tube, 500 g of heptane was placed, and the content was heated to 80°C. To this solution, 30 g of methyl methacrylate, 20 g of methoxypolyethyleneglycol methacrylate (n=9), 25 g of N,N-dimethylaminoethyl acrylate, 10 g of ethylene glycol dimethacrylate and 7 g of VPE-0601 (manufactured by Wako Pure Chemical Industries, Ltd.) were added, and the mixture was reacted for 7 hours to obtain a dispersion A of an organic polymer particle having a solid content of 18%. This dispersion was centrifuged to obtain organic polymer particles A. A particle diameter of the obtained organic polymer particle A was measured with a laser diffraction particle size analyzer ("SALD-2200", trade name, manufactured by SHIMADZU CORP.) to yield a particle diameter of 1.8 μm.

[0155]

Production Example 9

Production method of organic polymer particle B

γ-polyglutamic acid was milled with a jet mill to obtain

organic polymer particles B having a particle diameter of 4 μm.

[0156]

Production Examples 10, 11

Production method of organic polymer particles C and D

Chitin (manufactured by Dainichiseika Color & Chemicals Mfg. Co., Ltd.: chitin P), and chitosan (manufactured by KoyoChemical Co., Ltd.: SK-10) each were milled with a jet mill to obtain organic polymer particles C of 7 μm in a particle diameter including chitin and organic polymer particles D of 8 μm in a particle diameter including chitosan.

[0157]

Production Example 12

Production method of organic polymer particle E

An aqueous solution of chitosan was obtained by mixing 7.0 g of chitosan ("DAICHITOSAN VL", NV 100%, manufactured by Dainichiseika Color & Chemicals Mfg. Co., Ltd.), 57.7 g of deionized water and 5.3 g of acrylic acid with a stirrer. To an aqueous solution including 70.0 g of this aqueous solution of chitosan, 30.0 g of ER-20 (nonionic reactive emulsifier manufactured by ADEKA CORPORATION) and 162.6 g of deionized water was added a mixed solution of 28.8 g of methyl methacrylate, 10.1 g of cyclohexyl methacrylate, 40.6 g of 2-ethylhexyl acrylate, 10.0 g of ethylene glycol dimethacrylate and 4.0 g of PEROYL L (peroxide radical initiator manufactured by NOF CORPORATION). Then, the resulting mixture was emulsified using a stirrer to obtain a suspension (a diameter of suspended particle is 10 μm).

Into a reaction vessel equipped with a dropping funnel, a thermometer, a nitrogen inlet tube, a reflux condenser and a stirrer, 0.2 g of hydroquinone, 9.0 g of ER-20 (nonionic reactive emulsifier manufactured by ADEKA CORPORATION), 70.0 g of the above-mentioned aqueous solution of chitosan and 262.2 g of deionized water were charged, and the mixture was heated to 70°C in an atmosphere of nitrogen. Next, to this, 356.1 g of the resulting suspension was added at once and a reaction

of the mixture was continued at the same temperature for 4 hours, and then it was concluded that the polymerization reaction was completed, and the content of the reaction vessel was cooled to obtain a dispersion (solid content 20% by weight) of a organic polymer particle E. It was also possible to obtain the organic polymer particle E alone by removing water from this dispersion. The above organic polymer particle E had a particle diameter of 15 μm.

[0158]

Production Example 13

Production method of organic polymer particle F

An aqueous solution of PEO was obtained by mixing 7.0 g of polyethylene oxide (PEO) ("PEO-1", NV 100%, manufactured by SUMITOMO SEIKA CHEMICALS Co., Ltd.) and 57.7 g of deionized water with a stirrer. To an aqueous solution including 64.7 g of this aqueous solution of PEO, 30.0 g of ER-20 and 162.6 g of deionized water was added a mixed solution of 42.1 g of methyl methacrylate, 21.5 g of n-butyl methacrylate, 26.4 g of 2-ethylhexyl acrylate, 10.0 g of ethylene glycol dimethacrylate and 4.0 g of PEROYL L (peroxide radical initiator manufactured by NOF CORPORATION). Then, the resulting mixture was emulsified using a stirrer to obtain a suspension (a diameter of suspended particle is 34 μm).

Into a reaction vessel equipped with a dropping funnel, a thermometer, a nitrogen inlet tube, a reflux condenser and a stirrer, 0.2 g of hydroquinone, 9.0 g of ER-20, 64.7 g of the same aqueous solution of PEO as that described above and 262.2 g of deionized water were charged, and the mixture was heated to 70°C in an atmosphere of nitrogen. Next, to this, 361.3 g of the suspension obtained above was added at once and a reaction of the mixture was continued at the same temperature for 4 hours, and then it was concluded that the polymerization reaction was completed, and the content of the reaction vessel was cooled to obtain a dispersion (solid content 20% by weight) of a organic polymer particle F. It was also possible to obtain the organic

polymer particle F alone by removing water from this dispersion. The above organic polymer particle F had a particle diameter of 40 μm.

[0159]

On the obtained organic polymer particles A to F, the solubility of the particle in the artificial seawater and the water-absorbing amount of the particle for the artificial seawater were measured according to the following methods.

(Solubility and water-absorbing amount)

1 g of organic polymer particles dried at room temperature in a vacuum (under a reduced pressure) were precisely weighed out, and the particles were put in 50 g of artificial seawater prepared according to ASTM D1141-98 and stirred at 23°C for 5 hours. Then, the particles were separated by filtration, a residue was washed with water, and the particles were weighed to determine the water-absorbing amount.

Next, after drying the organic polymer particles at room temperature under a reduced pressure, the dried particles were weighed to determine the solubility in seawater. The results are shown in Table 3.

[0160]

Examples 11 to 19, Comparative Example 5

Water-borne curable antifouling coating compositions were obtained by adding the components of the composition shown in Table 3, the antifouling agent paste of Production Example 5, and organic polymer particles in succession and dispersing them with a disper. Next, the viscosities of the obtained antifouling coating compositions were adjusted with deionized water so as to be 90 KU at 25°C in viscosity by a Stomer viscometer. In addition, all of units of the amounts to be mixed in Table 3 are "grams". As for the organic polymer particle E and the organic polymer particle F, dispersions of the organic polymer particles E and F were added.

[0161]

This antifouling coating composition was applied to a FRP

plate (100 × 300 × 3 mm, gel-coated), which had been roughed with a sand paper (grain size 240), with a brush so as to be 400 μm in a dried film thickness. After application, the coating composition was left standing for one day in an atmosphere of 20°C and 65% in relative humidity to obtain a coated plate for test.

[0162]

On each coated plate for test obtained, the water resistance and the antifouling property were evaluated by following the same methods as those described above except for setting the immersion duration at 6 months. The results of evaluations are shown in Table 3.

[0163]

On the obtained water-borne curable antifouling coating compositions, a frictional resistance test was evaluated according to the following method.

(Frictional resistance test)

The obtained coating was applied to a vinyl chloride cylindrical drum of 10 cm in diameter and 10 cm in height, and this drum was rotated (Re: 2500000 and 4000000, equivalent to the speeds of about 15 knots and about 25 knots) in seawater and frictional resistance was measured with a torque meter. The respective frictional resistance was measured using the frictional resistance of a smooth vinyl chloride cylindrical drum mirror-finished by buffing as a reference. The respective increases and decreases in frictional resistance are shown in Table 3. The frictional resistance immediately after immersion in seawater and after immersing for 1 month in seawater was measured.

[0164]

Table 3

| | | | | Solid content (%) | Solubility g/l | Water-absorbing amount % by weight | Examples | | | | | | | | | Comparative Example |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 5 |
| Emulsion resin | Production Example 1 | | | 40 | — | — | 100 | 100 | 100 | | | | | | | |
| | Production Example 2 | | | 40 | — | — | | | | 100 | 100 | | | | | |
| | Production Example 3 | | | 40 | — | — | | | | | | 100 | | | | |
| | Production Example 4 | | | 40 | — | — | | | | | | | 100 | 100 | | 100 |
| | Bayhydrol A145*1 | | | 45 | — | — | | | | | | | | | 62 | |
| Curing agent | Hardener SC*2 | | | 50 | — | — | 4 | 4 | 4 | | | | | | | |
| | Hexamethylene diamine | | | 30 | — | — | | | | 4 | 4 | | | | | |
| | Bayhydur 3100*3 | | | 100 | — | — | | | | | | | | | 12 | |
| Curing catalyst | Phosphoric acid | | | 100 | — | — | | | | | | 1 | | | | |
| | Cobalt naphthenate | | | 35 | — | — | | | | | | | 1 | 1 | | 1 |
| Antifouling agent | Production Example 5 | | | 76.5 | — | — | 200 | 200 | 200 | 200 | 200 | 200 | 200 | 200 | 200 | 200 |
| Organic polymer particle | A | | | 100 | <2 | 0.5 | 7 | | | | | | | | 6 | |
| | B | | | 100 | <2 | 0.5 | | | | 8 | | | | | | |
| | C | | | 100 | <2 | 6 | | 6 | | | | | | | | |
| | D | | | 100 | <2 | 8 | | | | | | 4 | 7 | | | |
| | E | | | 20 | <2 | 1.3 | | | 20 | | | | | | | |
| | F | | | 20 | <2 | 3.1 | | | | | 25 | | | 30 | | |
| Thickner*4 | | | | 35 | — | — | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 |
| Water resistance | 6 months | | | | | | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ |
| Antifouling property | 6 months | | | | | | ◎ | ◎ | ◎ | ◎ | ◎ | ◎ | ○ | ○ | △ | ○ |
| Frictional resistance test | Beginning | Re2500000 | equivalent speed | | about 15 knot | | 1.4 | −1.2 | 1.4 | 0.4 | 2.0 | −0.8 | −0.9 | 1.8 | 1.5 | 3.9 |
| | | Re4000000 | | | about 25 knot | | 1.3 | −1.1 | 1.5 | 0.5 | 2.1 | −0.6 | −0.9 | 2.2 | 1.5 | 3.8 |
| | after 1 month of immersion | Re2500000 | | | about 15 knot | | 1.0 | −2.0 | −0.1 | 0.3 | −0.1 | −2.4 | −1.3 | 1.0 | 1.8 | 3.6 |
| | | Re4000000 | | | about 25 knot | | 1.2 | −2.1 | −0.2 | 0.3 | 0.2 | −2.1 | −1.4 | 0.9 | 1.4 | 4.1 |

*1 polyol for water-borne polyurethane manufactured by Sumika Bayer Urethane Co., Ltd.
*2 semicarbazide curing agent manufactured by Asahi Kasei Corp.
*3 isocyanate for water-borne polyurethane manufactured by Sumika Bayer Urethane Co., Ltd.
*4 「PUR-2150」 associated urethane thickner "PUR-2150" manufactured by Akzo Nobel N.V.

[0165]

It was found from Table 3 that a coating film formed by using the coating obtained in Examples exhibits the excellent low friction performance in addition to the excellent water resistance and the excellent antifouling property, and the effect of the coating film is maintained for a long term period. And, the conditions of the surface of the coating film were also excellent.

## INDUSTRIAL APPLICABILITY

[0166]

Since the water-borne curable antifouling coating composition of the present invention comprises a water-borne binder component having curability and an antifouling agent, it can form a coating film having the excellent water resistance and the good antifouling effect, and therefore it can be widely applied to the underwater structures.

CLAIMS

1. A water-borne curable antifouling coating composition, comprising:

a water-borne binder component curable by dehydration condensation, wherein said waterborne binder component has at least one species of a curing system of a carbonyl hydrazide system and an acetoacetoxy amine system; and an antifouling agent

2. The water-borne curable antifouling coating composition according to claim 1,

wherein the water-borne binder component contains an emulsion resin and a curing agent, and said emulsion resin has a group capable of reacting with a functional group which said

curing agent has.

3. The water-borne curable antifouling coating composition according to claim 1 or 2, comprising an antifouling agent paste containing a water-soluble dispersion resin having an acid value of 10 to 300 mg KOH/g and a number average molecular weight of

1000 to 20000 and an antifouling agent in place of the antifouling agent of claim 1.

4. The water-borne curable antifouling coating composition according to claim 3,

wherein a weight ratio of solid content between the water-soluble dispersion resin and the antifouling agent in the antifouling agent paste is 1/99 to 50/50.

5. The water-borne curable antifouling coating composition according to any one of claims 1 to 4, further containing an organic polymer particle.

6. The water-borne curable antifouling coating composition according to claim 5,

wherein the organic polymer particle has a solubility in the artificial seawater specified in ASTM D1141-98 at 23°C is 15 g/l or less, a water-absorbing amount for the artificial seawater specified in ASTM D1141-98 of 0.01% by weight or more and a particle diameter of 0.05 to 100 μm.

7. The water-borne curable antifouling coating composition according to claim 5 or 6,

wherein the organic polymer particle is a naturally-derived polymer.

8. The water-borne curable antifouling coating composition according to claim 7,

wherein the organic polymer particle has a cationic group.

9. The water-borne curable antifouling coating composition according to claim 5 or 6,

wherein the organic polymer particle is an organic polymer particle having a particle diameter of 0.05 to 100 μm, and being composed of at least one species selected from the group consisting of chitin, chitosan, γ-PGA, pulverized silk and derivatives thereof.

10. The water-borne curable antifouling coating composition according to claim 5 or 6,

wherein the organic polymer particle is a synthetic polymer particle.

11. The water-borne curable antifouling coating composition according to claim 10,

wherein the organic polymer particle is an acrylic resin particle.

12. The water-borne curable antifouling coating composition according to claim 5 or 6,

wherein the organic polymer particle is a composite resin particle comprising at least one species of hydrophilic resin selected from the group consisting of starch, pullulan, gum arabic, κ-carrageenan, gelatin, cellulose, and chitosan and derivatives thereof, polyvinyl alcohol, polyallylamine, polyvinylamine, poly(meth)acrylamide, poly(meth)acrylic acid and copolymer thereof, and an acrylic resin.

13. The water-borne curable antifouling coating composition according to any one of claims 5 and 12,

wherein an amount of the organic polymer particle to be mixed is 0.01 to 15% by weight with respect to the solid content of a coating.

14. A coating film having an antifouling property, wherein said coating film is prepared from the water-borne curable antifouling coating composition according to any one of claims 1 to 13.

15. The coating film according to claim 14, wherein said coating film is used in uses being present in water during use.

16. An underwater structure, containing the coating film having an antifouling property according to claim 14.

ABSTRACT

The present invention provides a water-borne curable antifouling coating composition which exerts excellent functions as an antifouling coating, a coating film having an antifouling property obtained from the water-borne curable antifouling coating composition and an underwater structure having the coating film having an antifouling property.

A water-borne curable antifouling coating composition, wherein said coating composition is obtained by mixing a water-borne binder component having curability and an antifouling agent and a coating film obtained from said coating composition is used in uses being present in water during use.