

Description

Title of Invention: WATER-BASED COATING COMPOSITION AND PROCESS FOR FORMATION OF COATING FILM

Technical Field

[0001] The present invention relates to an aqueous coating composition and a method for forming a coating film.

Background Art

[0002] In general, a solvent-type coating material including an epoxy resin and a polyamine compound is used as an anticorrosive coating material. However, in recent years, from a standpoint of environmental protection, there is a social demand for a shift from the solvent-based coating material to an aqueous coating material. Examples of the aqueous coating material include an aqueous coating material which includes: as a base resin, a mixture obtained by blending a variety of pigments and additives in a water-soluble polyamine resin; an epoxy-resin emulsion; and an acrylic silicon resin emulsion containing a glycidyl group and an alkoxysilyl group (Patent Document 1).

[0003] However, in the case of using a curing reaction of the epoxy resin and the polyamine compound, it is difficult to form a coating film which exerts practical performance at low temperature (e.g., 5°C or less) because the curing reaction hardly proceeds

at low temperature.

Prior Art Document

Patent Document

[0004] [PTL 1] JP 11-166153 A

Summary

[0004a] In a first aspect of the present disclosure, there is provided an aqueous coating composition, comprising:

(A) an aqueous epoxy-based polyamine resin having one or more primary amino groups and/or secondary amino groups in a molecule;

(B) a compound having one or more (meth)acryloyl groups in a molecule; and

(C) an alkoxysilane compound;

wherein an equivalent ratio of an amino group of the aqueous epoxy-based polyamine resin (A) and a (meth)acryloyl group of the compound (B) ((meth)acryloyl group/amino group) is 0.7 to 2.5; and a content of the alkoxysilane compound (C) in a solid content of the aqueous coating composition is 0.2 mass% to 5 mass%;

wherein the aqueous coating composition is a two-component aqueous coating composition comprising a base resin liquid for a coating material and a curing agent,

the base resin liquid for a coating material comprising the aqueous epoxy-based polyamine resin (A) and

the curing agent comprising the compound (B) and the alkoxysilane compound (C);

wherein the aqueous epoxy-based polyamine resin (A) has an amino group equivalent of 100 to 3,000; and

wherein the aqueous epoxy-based polyamine resin (A) is obtained by amine-modification of an epoxy resin, and the epoxy resin has an epoxy equivalent of 180 to 3,800.

[0004b] In a second aspect of the present disclosure, there is provided a method of forming a coating film, comprising applying the aqueous coating composition as defined herein onto a substrate surface to form a coating film.

Problem to be solved by the Invention

[0005] The present invention has been made to solve the conventional problem, and an object of the present invention is to provide an aqueous coating composition which is excellent in low-temperature curability and capable of forming a coating film excellent in corrosion resistance.

Means for solving the Problems

[0006] An aqueous coating composition according to an embodiment of the present invention includes: (A) an aqueous epoxy-based polyamine resin having one or more primary amino groups and/or secondary amino groups in a molecule; (B) a compound having one or more (meth)acryloyl groups in a molecule; and (C) an alkoxysilane compound; wherein: an equivalent ratio of an amino group of the aqueous epoxy-based polyamine resin (A) and a (meth)acryloyl group of the compound (B) ((meth)acryloyl group/amino group) is 0.7 to 2.5; and a content of the alkoxysilane compound (C) in a solid content of the aqueous coating composition is 0.2

mass% to 5 mass%.

In a preferred embodiment of the invention, the aqueous coating composition is a two-component aqueous coating composition comprising a base resin liquid for a coating material and a curing agent, the base resin liquid for a coating material comprising the aqueous epoxy-based polyamine resin (A) and the curing agent comprising the compound (B) and the alkoxysilane compound (C).

In a preferred embodiment of the invention, the aqueous epoxy-based polyamine resin (A) is water-dispersible.

In a preferred embodiment of the invention, the aqueous epoxy-based polyamine resin (A) has an amino group equivalent of 100 to 3,000.

In a preferred embodiment of the invention, the aqueous epoxy-based polyamine resin (A) is obtained by amine-modification of an epoxy resin, and the epoxy resin has an epoxy equivalent of 180 to 3,800.

In a preferred embodiment of the invention, the aqueous epoxy-based polyamine resin (A) includes: an aqueous epoxy-based polyamine resin (A1) obtained by amine-modification of an epoxy resin (a1) having an epoxy equivalent of 400 to 1,500; and an

aqueous epoxy-based polyamine resin (A2) obtained by amine-modification of an epoxy resin (a2) having an epoxy equivalent of 2,000 to 3,200.

In a preferred embodiment of the invention, a mass ratio of the epoxy resin (a1) and the epoxy resin (a2) (a1/a2) is 8/2 to 2/8.

In a preferred embodiment of the invention, the aqueous epoxy-based polyamine resin (A) is obtained by neutralization of an amino group of an epoxy-based polyamine resin with an acid, and a neutralization ratio in the neutralization is 10% to 70%.

In a preferred embodiment of the invention, the compound (B) has a viscosity at 25°C of 3,000 mPa·s or less.

In a preferred embodiment of the invention, the aqueous coating composition further includes a pigment, wherein the pigment has a pigment volume concentration of 20% to 50%.

According to another aspect of the present invention, a method of forming a coating film is provided. The method of forming a coating film includes applying the aqueous coating composition onto a substrate surface to form a coating film.

In a preferred embodiment of the invention, the method of forming a coating film further includes applying a top coating material on the coating film to form a top coating layer.

Effects of the Invention

[0007] The aqueous coating composition of the present invention includes: (A) an aqueous epoxy-based polyamine resin having one or more primary amino groups and/or secondary amino groups in a molecule; (B) a compound having one or more (meth)acryloyl groups in a molecule; and (C) an alkoxysilane compound. Hence, the aqueous coating composition of the present invention exhibits excellent low-temperature curability and is capable of forming a coating film excellent in corrosion resistance.

Description of Embodiments

[0008] A. Outline of aqueous coating composition

An aqueous coating composition of the present invention includes: (A) an aqueous epoxy-based polyamine resin having one or more primary amino groups and/or secondary amino groups in a molecule; (B) a compound having one or more (meth)acryloyl groups in a molecule; and (C) an alkoxysilane compound. In the aqueous coating composition of the present invention, a curing reaction of the aqueous epoxy-based polyamine resin (A) and the compound (B) is caused to proceed by mixing these compounds, to thereby allow a coating film to be formed. The aqueous epoxy-based polyamine resin

(A) and the compound (B) can undergo a curing reaction even at low temperature (e.g., 5°C or less), and hence the aqueous coating composition of the present invention is excellent in low-temperature curability. In addition, the aqueous coating composition of the present invention can form a coating film excellent in adhesive property to a substrate because the composition includes the alkoxysilane compound (C). Such excellent adhesive property can be achieved even in the case where the coating film is formed at low temperature.

[0009] The aqueous coating composition of the present invention is preferably a two-component aqueous coating composition including a base resin liquid for a coating material and a curing agent. It is preferred that the base resin liquid for a coating material include the aqueous epoxy-based polyamine resin (A), and the curing agent include the compound (B) and the alkoxysilane compound (C). When the aqueous coating composition of the present invention is used as the two-component aqueous coating composition, an aqueous coating composition excellent in low-temperature curability can be obtained because it is possible to select a combination of the aqueous epoxy-based polyamine resin (A) and the compound (B) such that both of them exhibit high reactivity to each other.

[0010] Before mixing of the aqueous epoxy-based polyamine resin (A) and the compound (B), the aqueous coating composition of the

present invention may be treated, for example, by (1) diluting the compound (B) with an organic solvent, (2) mixing an emulsifier in the compound (B) or emulsifying or dispersing the compound (B) with a dispersant, an emulsifier, or an aqueous resin, or (3) dispersing the compound (B) in a dispersing element of a resin different from the aqueous epoxy-based polyamine resin (A). When such treatment is carried out, the aqueous epoxy-based polyamine resin (A) and the compound (B) can be mixed without using a special mixing device, to thereby obtain an aqueous coating composition excellent in dispersibility. As a result, the aqueous epoxy-based polyamine resin (A) and the compound (B) can react with each other efficiently. Further, when the treatment (2) of mixing an emulsifier in the compound (B) or emulsifying or dispersing the compound (B) with a dispersant, an emulsifier, or an aqueous resin is carried out, the compound (B) can be treated as a nonhazardous material.

[0011] Examples of the organic solvent to be used when the compound (B) is diluted with the organic solvent include ethylene glycol monobutyl ether and diethylene glycol monobutyl ether.

[0012] A nonionic emulsifier or an anionic emulsifier, for example, is used as the emulsifier to be used when the emulsifier is mixed in the compound (B), or the compound (B) is emulsified or dispersed with a dispersant, an emulsifier, or an aqueous resin. Examples of the nonionic emulsifier include a polyoxyethylene alkyl

phenol ether, polyoxyethylene styrenated phenyl ether, a polyoxyethylene alkyl ether, a polyoxyethylene polyoxypropylene block polymer, and a sorbitan fatty acid ester. Examples of the anionic emulsifier include a dodecylbenzenesulfonic acid salt, a dialkyl succinate sulfonic acid salt, a polyoxyethylene alkyl ether sulfuric acid ester salt, a polyoxyethylene styrenated phenyl ether sulfuric acid ester salt, and an alkyl diphenyl ether disulfonic acid salt. Examples of the dispersant include a polyacrylic acid sodium salt and an ammonium salt of a half ester of a styrene-maleic acid copolymer. Examples of the aqueous resin include a sodium salt of polyacrylic acid ester.

[0013] Examples of the dispersing element used when the compound (B) is dispersed in a dispersing element of a resin different from the aqueous epoxy-based polyamine resin (A) include an emulsion and dispersion of an acrylic resin, and an emulsion and dispersion of a urethane resin.

[0014] The content of the aqueous epoxy-based polyamine resin (A) in terms of a solid content is preferably 5 mass% to 95 mass%, more preferably 10 mass% to 90 mass% with respect to the total solid content of the aqueous coating composition.

[0015] The content of the compound (B) is preferably 2 mass% to 30 mass%, more preferably 5 mass% to 25 mass% with respect to

the total solid content of the aqueous coating composition.

[0016] An equivalent ratio of amino groups in the aqueous epoxy-based polyamine resin (A) and (meth)acryloyl groups in the compound (B) ((meth)acryloyl groups/amino groups) is 0.7 to 2.5, preferably 0.8 to 2.0. When the equivalent ratio is less than 0.7, the low-temperature curability of the aqueous coating composition may reduce. When the equivalent ratio exceeds 2.5, the adhesive property of a coating film to be obtained may reduce.

[0017] The content of the alkoxysilane compound (C) is 0.2 mass% to 5 mass%, preferably 0.3 mass% to 3 mass%, more preferably 0.5 mass% to 2 mass% with respect to the total solid content of the aqueous coating composition. As long as the content of the alkoxysilane compound (C) is in such range, the composition has excellent adhesive property to a substrate, resulting in obtaining an aqueous coating composition capable of forming a coating film which exhibits excellent corrosion resistance. It should be noted that even if the content of the alkoxysilane compound (C) is set to more than 5 mass%, the adhesive property is not further improved, and the curability (in particular, low-temperature curability) of the coating film may reduce.

[0018] The aqueous coating composition of the present invention may further include a pigment. When the pigment is incorporated,

the aqueous coating composition has an increased viscosity and can form a thick coating film by single application. As a result, an aqueous coating composition excellent in application workability can be obtained since the number of application can be reduced, and capable of forming a coating film which exhibits sufficient corrosion resistance can be obtained.

[0019] Specific examples of the pigment include: extender pigments such as precipitated barium sulfate, clay, talc, and mica; color pigments such as titanium dioxide and carbon black; and anti-rust pigments such as zinc phosphate.

[0020] The pigment volume concentration of the pigment in the aqueous coating composition is preferably 20% to 50%, more preferably 25% to 45%, particularly preferably 30% to 40%. When the pigment volume concentration is less than 20%, the effect of the incorporation of the pigment may be insufficient, while when the pigment volume concentration exceeds 50%, the outer appearance of the coating film may deteriorate. The pigment volume concentration can be calculated from the mass of the pigment blended and the specific gravity of each component in the coating material.

[0021] Water, a solvent, an additive, or the like may be blended into the aqueous coating composition of the present invention. Specific examples of the solvent include: glycol-based solvents

such as ethylene glycol, propylene glycol, ethylene glycol monobutyl ether, propylene glycol monobutyl ether, diethylene glycol, dipropylene glycol, diethylene glycol monobutyl ether, dipropylene glycol monobutyl ether, and diethylene glycol dibutyl ether; aromatic solvents such as xylene, Solvesso 100, Solvesso 150, and Solvesso 200; hydrocarbon-based solvents such as mineral spirit; and ester-based solvents such as 2,2,4-trimethyl-1,3-pentanediol monoisobutyrate (manufactured by CHISSO CORPORATION, trade name "CS-12"), 2,2,4-trimethyl-1,3-pentanediol diisobutyrate (manufactured by CHISSO CORPORATION, trade name "CS-16"), diethyl adipate, and diisobutyl adipate. Specific examples of the additive include a dispersant, a viscosity adjuster, a curing catalyst, a surface conditioner, a defoamer, a plasticizer, a film forming aid, a UV absorbing agent, and an antioxidant. When the aqueous coating composition of the present invention is used as a two-component aqueous coating composition, water, the solvent, and/or the additive may be added to a base resin liquid for a coating material or a curing agent before mixing of the base resin liquid for a coating material with the curing agent or may be added after mixing of the base resin liquid for a coating material with the curing agent. Which of the base resin liquid for a coating material and the curing agent water, the solvent, and/or the additive are/is added to may be determined based on the functions and properties expected of them.

[0022] B. Aqueous epoxy-based polyamine resin (A)

The aqueous coating composition of the present invention includes the aqueous epoxy-based polyamine resin (A) having one or more primary amino groups and/or secondary amino groups in a molecule. It should be noted that the concept of "aqueous" as used herein comprehends "water-soluble" and "water-dispersible."

[0023] The aqueous epoxy-based polyamine resin (A) is preferably water-dispersible. When a water-dispersible aqueous epoxy-based polyamine resin (A) is used, an aqueous coating composition capable of forming a coating film excellent in water resistance can be obtained. In addition, in the case where the aqueous epoxy-based polyamine resin (A) is water-dispersible, the resin can be easily mixed with the compound (B). Further, a rapid reaction progress of the aqueous epoxy-based polyamine resin (A) and the compound (B) can be inhibited to appropriately adjust the reactivity, thereby obtaining an aqueous coating composition with a long service life. More specifically, in the case where the aqueous epoxy-based polyamine resin (A) is water-dispersible, in the aqueous coating composition before application, the reaction hardly proceeds even at ordinary temperature, which provides good preservation stability and application property, because the aqueous epoxy-based polyamine resin (A) is hardly brought into contact with the compound (B). On the other hand, after application, a dispersion medium (such as water) volatilizes to facilitate the contact between the aqueous

epoxy-based polyamine resin (A) and the compound (B). Therefore, the curing reaction proceeds even at low temperature, to thereby allow a coating film to be formed.

[0024] The aqueous epoxy-based polyamine resin (A) can be obtained by, for example, amine-modification of an epoxy resin. Further, when the epoxy-based polyamine resin obtained by amine-modification of the epoxy resin is not aqueous, the epoxy-based polyamine resin may be converted into an aqueous resin by neutralization of an amino group with an acid, to thereby obtain the aqueous epoxy-based polyamine resin (A).

[0025] As the epoxy resin, any appropriate epoxy resin may be used. The resin is preferably a bisphenol A-type epoxy resin or a bisphenol F-type epoxy resin, particularly preferably a bisphenol A-type epoxy resin.

[0026] The epoxy equivalent of the epoxy resin may be determined depending on desired coating film physical properties. The epoxy equivalent is preferably 180 to 3,800, more preferably 400 to 3,200, particularly preferably 700 to 3,200. When the epoxy equivalent of the epoxy resin is in such range, a coating film excellent in water resistance, corrosion resistance, and water-resistant adhesive property can be obtained. When the epoxy resin has an epoxy equivalent of less than 180, the initial rain resistance of a coating

film to be obtained may reduce. Meanwhile, when the resin has an epoxy equivalent of more than 3,800, the epoxy-based polyamine resin may not be dispersed in water to cause phase separation, which makes it impossible to convert the coating composition into an aqueous one and to obtain an aqueous coating composition having sufficient water-resistant adhesive property. It should be noted that the epoxy equivalent of the epoxy resin can be determined in accordance with JIS K 7236. In addition, the term "initial rain resistance" as used herein refers to water resistance in an initial stage of the curing of a coating film, specifically, in a stage in which a coating film which has not completely cured but is non-sticky is formed. When the coating film is poor in initial rain resistance, the coating film may break or swell by exposure to rain before the applied coating film cures completely. The aqueous coating composition capable of forming a coating film having high initial rain resistance is particularly effectively used for an outdoor object to be coated which may be exposed to rain before the applied coating film cures completely.

[0027] In one embodiment, the epoxy resin is an epoxy resin (a1) having an epoxy equivalent of 400 to 1,500. When an aqueous epoxy-based polyamine resin (A1) obtained by amine-modification of the epoxy resin (a1) is used, it is possible to obtain an aqueous coating composition capable of forming a coating film excellent in water-resistant adhesive property. The epoxy equivalent of the

epoxy resin (a1) is more preferably 600 to 1,400, particularly preferably 800 to 1,300.

[0028] In another embodiment, the epoxy resin is an epoxy resin (a2) having an epoxy equivalent of 2,000 to 3,200. When an aqueous epoxy-based polyamine resin (A2) obtained by amine-modification of the epoxy resin (a2) is used, it is possible to obtain an aqueous coating composition capable of forming a coating film excellent in initial rain resistance. The epoxy equivalent of the epoxy resin (a2) is more preferably 2,200 to 3,000.

[0029] As the epoxy resin, two or more kinds of epoxy resins may be used in combination.

[0030] As the epoxy resin, there may be used one subjected to chain elongation through utilization of a reaction of an active hydrogen-containing compound capable of reacting with an epoxy group with an epoxy group to increase the molecular weight of the resin or to modify the resin. Examples of the active hydrogen-containing compound include a bifunctional compound such as a dimer acid, diamine, or polyether polyol.

[0031] As the epoxy resin, there may be used one having a fatty acid added before the amine modification. The addition allows a soft component to be introduced into the resin and allows the number

of epoxy groups to be reduced, thereby reducing sites to be amine-modified to lower a reactivity, for example.

[0032] The epoxy-based polyamine resin can be obtained through modification of the epoxy resin by any appropriate modification method. Examples of the modification method include: a method involving adding a primary amino group-containing polyamine to an epoxy resin; and a method involving adding a ketiminated amino group-containing compound to an epoxy resin. The epoxy-based polyamine resin obtained as described above has one or more primary amino groups and/or secondary amino groups, and secondary hydroxyl groups in a molecule. The epoxy-based polyamine resin may be a resin obtained by a reaction of part of the primary amino groups, secondary amino groups, and/or hydroxyl groups in the epoxy-based polyamine resin with a compound having a functional group such as an epoxy group, an acid anhydride group, an acid halogen group, or an isocyanate group. When a product obtained by making an epoxy-based polyamine resin aqueous, the epoxy-based polyamine resin being obtained by a reaction of a compound having such functional group, is incorporated as part of the aqueous epoxy-based polyamine resin (A) to be used, physical properties of the resultant coating film can be adjusted.

[0033] The method involving adding the primary amino group-containing polyamine to the epoxy resin is specifically a method involving reacting a primary amino group in the primary amino

group-containing polyamine with an epoxy group in the epoxy resin to form a secondary amino group, resulting in producing the epoxy-based polyamine resin having the secondary amino group.

[0034] Examples of the primary amino group-containing polyamine include diethylenetriamine, dipropylenetriamine, dibutylenetriamine, and triethylenetetramine. They may be used alone or in combination.

[0035] The method involving adding a ketiminated amino group-containing compound to the epoxy resin is specifically a method involving allowing the ketiminated amino group-containing compound and the epoxy resin to react with each other and then hydrolyzing a ketimine group to form a primary amino group, resulting in producing the epoxy-based polyamine resin having a primary amino group. It should be noted that when the ketiminated amino-group containing compound and the epoxy resin are allowed to react with each other, a secondary amine such as diethanolamine, methylethanolamine, or diethylamine may coexist.

[0036] The ketiminated amino group-containing compound can be obtained by reacting a primary amino group-containing compound with a ketone. Examples of the primary amino group-containing compound include: primary amino group-containing polyamines such as diethylenetriamine, dipropylenetriamine, dibutylenetriamine, and

triethylenetetramine; aminoethylethanolamine; methylaminopropylamine; and ethylaminoethylamine. They may be used alone or in combination. Examples of the ketone include methyl ethyl ketone, acetone, and methyl isobutyl ketone.

[0037] The epoxy-based polyamine resin may further be modified by allowing the resin to react with a compound having a functional group reactive with an amino group, depending on desired coating film physical properties. Examples of the functional group reactive with an amino group include an epoxy group, a (meth)acryloyl group, an isocyanate group, and an acid anhydride group.

[0038] The amount of the amino groups in the epoxy-based polyamine resin may be any appropriate amount depending on desired properties of the aqueous coating composition or desired coating film physical properties. The amount of the amino groups is, as an amino group equivalent, preferably 100 to 3,000, more preferably 500 to 2,000, particularly preferably 800 to 2,000. As long as the amino group equivalent is in such range, the epoxy-based polyamine resin is aqueous, to thereby obtain the aqueous epoxy-based polyamine resin (A). When the aqueous epoxy-based polyamine resin (A) is used, a coating film excellent in low-temperature curability can be obtained. When the amino group equivalent of the epoxy-based polyamine resin is less than 100, water resistance of a coating film to be obtained may reduce. Meanwhile, when the amino group

equivalent exceeds 3,000, the epoxy-based polyamine resin may not be dispersed in water to cause phase separation, which makes it impossible to convert the coating composition into an aqueous composition. It should be noted that the expression "amino group equivalent" as used herein is represented by a molecular weight of a resin solid content per primary amino group in the case where the epoxy-based polyamine resin has the primary amino groups (including the case where the epoxy-based polyamine resin has the primary amino groups and secondary amino groups), or is represented by a molecular weight of a resin solid content per secondary amino group in the case where the epoxy-based polyamine resin has no primary amino group. The amino group equivalent of the epoxy-based polyamine resin can be determined from the blending amounts of raw materials.

[0039] For example, the aqueous epoxy-based polyamine resin (A) may be obtained by converting the epoxy-based polyamine resin (i.e., an epoxy resin obtained by amine-modification) into an aqueous resin by neutralization of the amino groups in the epoxy-based polyamine resin with an acid. The kind of the acid and a neutralization ratio (neutralization ratio with respect to the amino groups in the epoxy-based polyamine resin before conversion into an aqueous resin) may be any appropriate kind of acid and neutralization ratio depending on a desired state of the aqueous epoxy-based polyamine resin (A) (water-soluble to water-dispersible form). Examples of the acid include acetic acid, formic acid, lactic

acid, and phosphoric acid. The neutralization ratio (neutralization ratio with respect to the amino groups in the epoxy-based polyamine resin before conversion into an aqueous resin) is preferably 10% to 100%, more preferably 10% to 70%, particularly preferably 15% to 50%. When the neutralization ratio is less than 10%, the resin may not be dispersed in water to cause phase separation, which makes it impossible to convert the coating composition into an aqueous one. Meanwhile, when the neutralization ratio is adjusted to 70% or less, a water-dispersible aqueous epoxy-based polyamine resin (A) can be obtained.

[0040] The molecular weight (number average) of the aqueous epoxy-based polyamine resin (A) may be any appropriate molecular weight depending on desired properties of the aqueous coating composition or desired coating film physical properties. The molecular weight is preferably 500 to 20,000, more preferably 1,000 to 10,000 in terms of standard polystyrene measured by gel permeation chromatography (GPC). As long as the molecular weight of the aqueous epoxy-based polyamine resin (A) is in such range, the aqueous epoxy-based polyamine resin (A) can react efficiently with the compound (B) because the resin can be mixed easily with the compound. In addition, as long as the molecular weight of the aqueous epoxy-based polyamine resin (A) is in such range, a coating film excellent in corrosion resistance, water resistance, and adhesive property can be obtained.

[0041] The aqueous coating composition of the present invention may include two or more kinds of the aqueous epoxy-based polyamine resins (A).

[0042] The aqueous coating composition of the present invention preferably includes, as the aqueous epoxy-based polyamine resins (A), the aqueous epoxy-based polyamine resin (A1) obtained by amine-modification of the epoxy resin (a1) having an epoxy equivalent of 400 to 1,500 and the aqueous epoxy-based polyamine resin (A2) obtained by amine-modification of the epoxy resin (a2) having an epoxy equivalent of 2,000 to 3,200. A mass ratio of the epoxy resin (a1) having an epoxy equivalent of 400 to 1,500 and the epoxy resin (a2) having an epoxy equivalent of 2,000 to 3,200 (a1/a2) is preferably 8/2 to 2/8, more preferably 7/3 to 3/7. As long as the ratio is in such range, it is possible to obtain an aqueous coating composition capable of forming a coating film excellent in initial rain resistance and water-resistant adhesive property.

[0043] The properties of the aqueous coating composition and coating film physical properties can be controlled by the molecular weight of the aqueous epoxy-based polyamine resin (A) and the amount of the amino groups therein.

[0044] C. Compound (B)

The compound (B) used in the aqueous coating composition of the present invention has one or more (meth)acryloyl groups in a molecule.

[0045] The molecular weight of the compound (B) is preferably 150 or more and 2,000 or less, more preferably 200 or more and 1,700 or less, particularly preferably 250 or more and 1,300 or less. As long as the molecular weight of the compound (B) is in such range, the aqueous epoxy-based polyamine resin (A) and the compound (B) can be easily mixed without using a special mixing device, to thereby obtain an aqueous coating composition excellent in dispersibility. As a result, the aqueous epoxy-based polyamine resin (A) and the compound (B) can react with each other efficiently, to thereby obtain an aqueous coating composition excellent in curability. It should be noted that the molecular weight of the compound (B) can be calculated from its chemical formula.

[0046] The number of the (meth)acryloyl groups in the compound (B) is 1 or more, preferably 2 to 4. The number of the (meth)acryloyl groups in the compound (B) may be determined depending on desired coating film physical properties.

[0047] The viscosity of the compound (B) at 25°C is preferably 3,000 mPa·s or less, more preferably 50 mPa·s to 3,000 mPa·s, particularly preferably 50 mPa·s to 2,200 mPa·s, most preferably

50 mPa·s to 1,100 mPa·s. As long as the viscosity of the compound (B) is in such range, the aqueous epoxy-based polyamine resin (A) and the compound (B) can be easily mixed without using a special mixing device, to thereby obtain an aqueous coating composition excellent in dispersibility. As a result, the aqueous epoxy-based polyamine resin (A) and the compound (B) can react with each other efficiently, to thereby obtain an aqueous coating composition excellent in curability.

[0048] Examples of the compound (B) include: polymerizable unsaturated monocarboxylic acid ester compounds of polyhydric alcohols such as ethylene glycol diacrylate, ethylene glycol dimethacrylate, triethylene glycol diacrylate, triethylene glycol dimethacrylate, tetraethylene glycol diacrylate, tetraethylene glycol dimethacrylate, 1,3-butylene glycol diacrylate, 1,3-butylene glycol dimethacrylate, trimethylolpropane triacrylate, trimethylolpropane trimethacrylate, 1,4-butanediol diacrylate, 1,4-butanediol dimethacrylate, neopentyl glycol diacrylate, neopentyl glycol dimethacrylate, 1,6-hexanediol diacrylate, 1,6-hexanediol dimethacrylate, pentaerythritol diacrylate, pentaerythritol dimethacrylate, pentaerythritol triacrylate, pentaerythritol trimethacrylate, pentaerythritol tetraacrylate, pentaerythritol tetramethacrylate, glycerol diacrylate, glycerol dimethacrylate, glycerol acroxy dimethacrylate, 1,1,1-trishydroxymethylethane diacrylate,

1,1,1-trishydroxymethylethane dimethacrylate,
 1,1,1-trishydroxymethylethane triacrylate,
 1,1,1-trishydroxymethylethane trimethacrylate,
 1,1,1-trishydroxymethylpropane diacrylate, and
 1,1,1-trishydroxymethylpropane dimethacrylate; adducts between
 epoxy group-containing, ethylenically unsaturated monomers and
 carboxyl group-containing, ethylenically unsaturated monomers such
 as a reaction product between glycidyl acrylate or glycidyl
 methacrylate and acrylic acid, methacrylic acid, crotonic acid,
 or maleic acid; and polymerizable unsaturated monocarboxylic acid
 amide compounds of polyamines such as ethylenediamine diacrylate.
 Those compounds may be used alone or in combination.

[0049] As described above, the compound (B) is preferably
 capable of being easily mixed with (capable of reacting with) the
 aqueous epoxy-based polyamine resin (A). It is more preferred that
 the aqueous epoxy-based polyamine resin (A) and the compound (B)
 be used in an inhomogeneous state in such a range that the resin
 and compound can be easily mixed (can react with each other). It
 is particularly preferred that the compound (B) and the aqueous
 epoxy-based polyamine resin (A) be used in different phase states.
 In such states, a rapid reaction progress of the aqueous epoxy-based
 polyamine resin (A) and the compound (B) can be inhibited to
 appropriately adjust the reactivity. More specifically, when the
 aqueous epoxy-based polyamine resin (A) and the compound (B) are

in an inhomogeneous state, the aqueous coating composition before application has good preservation stability and application property because both the components are hardly brought into contact with each other, resulting in inhibiting the reaction at ordinary temperature. On the other hand, after application, a dispersion medium (such as water) volatilizes to make it easy to bring the aqueous epoxy-based polyamine resin (A) into contact with the compound (B), and the curing reaction proceeds even at low temperature, to thereby form a coating film. Examples thereof include: a case where the compound (B) is a water-soluble compound and the aqueous epoxy-based polyamine resin (A) is a water-dispersible resin; a case where the compound (B) is self-emulsifying or is converted into a water-dispersible form with a dispersant; and a case where the compound (B) is emulsified or dispersed with the aqueous epoxy-based polyamine resin (A). It should be noted that a determination of whether the compound (B) is "water-insoluble," "water-soluble," or "self-emulsifying" can be made by: adding 5 g of the compound (B) to 100 g of water at room temperature; stirring the mixture (e.g., for 3 minutes); allowing the mixture to stand still (e.g., for 5 minutes); and then observing its state visually. After allowing the mixture to stand still, if the mixture contains a precipitate, the compound is judged to be "water-insoluble," if the mixture contains no precipitate and is clear, the compound is judged to be "water-soluble," and if the mixture contains no precipitate and is turbid, the compound is judged to be "self-emulsifying." In

addition, if the mixture contains no precipitate and is turbid after the same operation as above has been performed in the co-presence of a dispersant, the compound is judged to be "converted into a water-dispersible form."

[0050] In the case where the compound (B) has been modified by, for example, polyethylene oxide, the compound may be converted into a water-soluble or self-emulsifying compound by increasing the ethylene oxide addition mole number to enhance its hydrophilicity.

[0051] Examples of the compound (B) that is water-soluble include ethoxylated bisphenol A diacrylate (EO 30 mol), ethoxylated trimethylolpropane triacrylate (EO 20 mol), ethoxylated trimethylolpropane triacrylate (EO 30 mol), ethoxylated pentaerythritol tetraacrylate (EO 35 mol), ethoxylated glycerin triacrylate (EO 20 mol), and ethoxylated bisphenol A dimethacrylate (EO 30 mol). They may be used alone or in combination. It should be noted that, for example, the expression "EO 30 mol" as used herein means that 30 ethylene oxide groups are contained in a molecule.

[0052] Examples of the compound (B) that is self-emulsifying or may be converted into a water-dispersible form with a dispersant include polyethylene glycol #400 diacrylate (EO 9 mol), polyethylene glycol #600 diacrylate (EO 14 mol), polyethylene glycol #1000

diacrylate (EO 23 mol), ethoxylated bisphenol A diacrylate (EO 10 mol), ethoxylated bisphenol A diacrylate (EO 20 mol), ethoxylated glycerin triacrylate (EO 9 mol), and polyethylene glycol #1000 dimethacrylate (EO 23 mol). They may be used alone or in combination.

[0053] Examples of the compound (B) that may be emulsified or dispersed with the aqueous epoxy-based polyamine resin (A) include polyethylene glycol #200 glycol diacrylate (EO 4 mol), ethoxylated bisphenol A diacrylate (EO 3 mol), ethoxylated bisphenol A diacrylate (EO 4 mol), propoxylated bisphenol A diacrylate (PO 3 mol), 1,10-decanediol diacrylate, tricyclodecanedimethanol diacrylate, ethoxylated 2-methyl-1,3-propanediol diacrylate (EO 2 mol), neopentyl glycol diacrylate, 1,6-hexanediol diacrylate, 1,9-nonanediol diacrylate, dipropylene glycol diacrylate (PO 2 mol), tripropylene glycol diacrylate (PO 3 mol), polypropylene glycol #400 diacrylate (PO 7 mol), polypropylene glycol #700 diacrylate (PO 12 mol), ethoxylated trimethylolpropane triacrylate (EO 3 mol), ethoxylated trimethylolpropane triacrylate (EO 9 mol), trimethylolpropane triacrylate, propoxylated trimethylolpropane triacrylate (PO 3 mol), pentaerythritol triacrylate, ethoxylated pentaerythritol tetraacrylate (EO 4 mol), ditrimethylolpropane tetraacrylate, propoxylated pentaerythritol tetraacrylate (PO 4 mol), propoxylated bisphenol A diacrylate (PO 4 mol), ethylene glycol dimethacrylate (EO 1 mol), diethylene glycol dimethacrylate (EO 2 mol), triethylene glycol dimethacrylate (EO 3 mol), tetraethylene

glycol dimethacrylate (EO 4 mol), polyethylene glycol #400 dimethacrylate (EO 9 mol), polyethylene glycol #600 dimethacrylate (EO 14 mol), 1,3-butanediol dimethacrylate, 1,4-butanediol dimethacrylate, 1,6-hexanediol dimethacrylate, 1,9-nonanediol dimethacrylate, ethoxylated bisphenol A dimethacrylate (EO 2.6 mol), ethoxylated bisphenol A dimethacrylate (EO 4 mol), ethoxylated bisphenol A dimethacrylate (EO 6 mol), ethoxylated bisphenol A dimethacrylate (EO 10 mol), ethoxylated bisphenol A dimethacrylate (EO 17 mol), neopentyl glycol dimethacrylate, ethoxylated polypropylene glycol #700 dimethacrylate (PO 12 mol, EO 6 mol), glycerin dimethacrylate, tripropylene glycol dimethacrylate (PO 3 mol), polypropylene glycol #400 dimethacrylate (PO 7 mol), trimethylolpropane trimethacrylate, and ethoxylated trimethylolpropane trimethacrylate (EO 9 mol). They may be used alone or in combination.

[0054] The compound (B) may be used as a mixture of two or more kinds of the compounds (B). Through such use of the compounds (B) having different properties in combination, physical properties of the aqueous coating composition and a coating film to be obtained can be controlled. For example, the curability can be controlled by mixing a compound (B) having two (meth)acryloyl groups and a compound (B) having three (meth)acryloyl groups. Further, when a mixture of a water-soluble compound (B) and a water-insoluble compound (B) is used, the water-insoluble compound (B) can be easily

introduced into a reaction system by the water-soluble compound (B). Further, the resultant coating material is excellent in low-temperature curability. Examples of the water-insoluble compound (B) include a compound which is not completely soluble in water, such as propoxylated bisphenol A diacrylate (PO 4 mol). A mixing ratio of the water-soluble compound (B) and the water-insoluble compound (B) (water-soluble/water-insoluble) is preferably 1/9 to 9/1, more preferably 2/8 to 8/2.

[0055] D. Alkoxysilane compound (C)

The aqueous coating composition of the present invention includes the alkoxysilane compound (C). As long as the aqueous coating composition includes the alkoxysilane compound (C), a coating film excellent in adhesive property to a substrate can be obtained. The coating film formed using the aqueous coating composition of the present invention is excellent in adhesive property to a substrate even if the coating film is formed at low temperature. Such coating film which is formed using the aqueous coating composition of the present invention excellent in adhesive property to a substrate exhibits excellent corrosion resistance.

[0056] The alkoxysilane compound (C) has a functional group having reactivity to or affinity for an organic substance and a functional group having reactivity to or affinity for an inorganic substance. Therefore, as the aqueous coating composition of the

present invention includes the alkoxysilane compound (C), it is possible to improve the adhesive property of a formed coating film (organic substance) and a substrate (inorganic substance). Examples of the functional group having reactivity to or affinity for an organic substance include a vinyl group, an epoxy group, a methacryl group, an amino group, and a mercapto group. On the other hand, the functional group having reactivity to or affinity for an inorganic substance is preferably a functional group which can be hydrolyzed, and examples thereof include a methoxysilane group, an ethoxysilane group, and a propoxysilane group.

[0057] Part of the alkoxysilane compound (C) may be subjected to hydrolysis and/or hydrolysis dehydration condensation. Specific examples thereof include: γ -glycidoxyalkyltrialkoxysilanes such as γ -glycidoxypropyltrimethoxysilane, γ -glycidoxypropyltriethoxysilane, and γ -glycidoxypropoxytrimethoxysilane; γ -aminopropyltrialkoxysilanes such as γ -aminopropyltriethoxysilane and γ -aminopropyltripropoxysilane; and N-phenyl- γ -aminoalkyltrialkoxysilanes such as N-phenyl- γ -aminopropyltrimethoxysilane, N-phenyl- γ -aminopropyltriethoxysilane, and N-phenyl- γ -aminopropyltripropoxysilane. Of those, preferred are γ -glycidoxyalkyltrialkoxysilanes, γ -aminopropyltrialkoxysilanes, and N-phenyl- γ -aminoalkyltrialkoxysilanes, more preferred are

γ -glycidoxyalkyltrialkoxysilanes and γ -aminopropyltrialkoxysilanes, and particularly preferred are γ -glycidoxyalkyltrialkoxysilanes. They may be used alone or in combination.

[0058] E. Method of forming coating film

The aqueous coating composition of the present invention can be suitably used in an inner or outer plate part of a ship and a submerged structure in seawater or freshwater. Specifically, an inner or outer plate part of a ship such as deck, hatch coaming, upper structure part, hull part, engine room, living quarter, or car hold; and a submerged structure in seawater or freshwater, such as a piping material can be used as an object to be coated (substrate). As a material for the substrate, there may be given, for example, a metal material such as an iron-based, zinc-based, or aluminum-based material.

[0059] As a method of applying the aqueous coating composition of the present invention, any appropriate application method may be employed. Examples of the application method include airless application, air spray, brush application, trowel application, and roller application. Of those, airless application is preferred. When the composition is applied by the airless application, a thick coating film can be obtained. In addition, the coating film may be formed by applying the composition several times (e.g., two or

three times). When the composition is applied several times, a thick coating film having a good outer appearance can be formed.

[0060] In application of the aqueous coating composition of the present invention, the thickness of the coating film is preferably 50 μm to 250 μm , more preferably 50 μm to 200 μm , in terms of dried coating film. When the thickness of the dried coating film is more than 250 μm , a problem such as dripping may occur in formation of the coating film.

[0061] A method of drying the aqueous coating composition of the present invention may be any appropriate drying method. The method is preferably natural drying or heat drying. In the case of natural drying, the drying time is preferably 24 hours or more, more preferably 1 week or more.

[0062] After formation of the coating film using the aqueous coating composition of the present invention, a top coating layer may be formed on the coating film by further applying a top coating material. According to the present invention, it is possible to provide such method of forming a multilayer coating film. When the top coating layer is formed, a coating film having improved corrosion resistance and outer appearance can be obtained.

[0063] Any appropriate coating material may be adopted as the

top coating material. Examples of the top coating material include an epoxy/amine-based coating material, a two-component urethane-curable coating material, a one-component urethane-curable coating material, and a coating material containing a carbodiimide curing agent. The top coating material may be solvent-based or aqueous. The top coating material is preferably aqueous. When the top coating material is aqueous, a load on the environment can be reduced in formation of the coating film.

[0064] The thickness of the top coating layer may be set to any appropriate thickness depending on the kind of the coating material and the purpose of coating. Typically, the thickness is 10 μm to 300 μm in terms of thickness of a dried coating film.

[0065] An intermediate coating layer may be formed between the coating film formed using the aqueous coating composition and the top coating layer. The intermediate coating layer may be formed by applying an intermediate coating material on the coating film formed using the aqueous coating composition. When the intermediate coating layer is formed, a coating film having further improved corrosion resistance can be obtained.

[0066] Any appropriate coating material may be adopted as the intermediate coating material. Examples of the intermediate coating material include an epoxy/amine-based coating material,

a two-component urethane-curable coating material, and a one-component urethane-curable coating material. The intermediate coating material may be solvent-based or aqueous. The intermediate coating material is preferably aqueous. When the intermediate coating material is aqueous, a load on the environment can be reduced in formation of the coating film.

[0067] The thickness of the intermediate coating layer may be set to any appropriate thickness depending on the kind of the coating material and the purpose of coating. Typically, the thickness is 10 μm to 50 μm in terms of thickness of a dried coating film.

[0068] Before formation of the coating film using the aqueous coating composition, an undercoat layer may be formed by applying an undercoating material on a substrate. When the undercoat layer is formed, a coating film having improved corrosion resistance can be obtained.

[0069] Any appropriate coating material may be adopted as the undercoating material. Examples of the undercoating material include an organic or inorganic zinc-rich coating material. The undercoating material may be solvent-based or aqueous. The undercoating material is preferably aqueous. When the undercoating material is aqueous, a load on the environment can be reduced in formation of the coating film.

[0070] The thickness of the undercoating layer may be set to any appropriate thickness depending on the kind of the coating material and the purpose of coating. Typically, the thickness is 20 μm to 300 μm in terms of thickness of a dried coating film.

[0071] The top coating material, the intermediate coating material, and the undercoating material may each contain a pigment, an additive, and the like. Examples of the pigment and the additive include the pigments and additives described in the above-mentioned section A. The number, kinds, and amounts of pigments and additives to be added may be selected as appropriate depending on purposes.

[0072] As an application method and drying method for each of the top coating material, the intermediate coating material, and the undercoating material, any appropriate methods may be adopted depending on the kind of the coating material to be used. Examples of the application method and drying method for each of the top coating material, the intermediate coating material, and the undercoating material include the same methods described above for the application method and drying method for the aqueous coating composition.

Examples

[0073] Hereinafter, the present invention is described in more

detail by way of examples. However, the present invention is not limited to the examples. It should be noted that, unless otherwise specified, "part(s)" and "%" in the examples are on a mass basis.

[0074] (Production Example 1) Production of aqueous epoxy-based polyamine resin (A)I

702 parts of a raw material resin having an epoxy equivalent of 188 g/equivalent, which was synthesized from bisphenol A and epichlorohydrin, 269 parts of bisphenol A, 108 parts of a dimer acid, and 190 parts of methyl isobutyl ketone (hereinafter, referred to as "MIBK") were fed to a reactor equipped with a stirrer, a cooler, a nitrogen injection tube, and a thermometer, and the mixture was allowed to react at 117°C in the presence of 1 part of benzyldimethylamine until the epoxy equivalent reached 1,079 g/equivalent, to thereby obtain an epoxy resin. After that, 255 parts of a ketimine compound of aminoethylethanolamine (73 mass% MIBK solution) were added thereto, and the mixture was allowed to react at 117°C for 1 hour. Subsequently, the mixture was diluted with MIBK until a nonvolatile content of 75% was achieved, to thereby obtain an epoxy-based polyamine resin having an amino group equivalent of 1,184.

Acetic acid was added thereto so that a neutralization ratio (neutralization ratio of the resin based on amino groups) of 35.0% was achieved, and the mixture was diluted with ion-exchange water.

After that, a mixture of MIBK and water was removed under reduced pressure until a solid content of 40 mass% was achieved, to thereby prepare a milky white aqueous (water-dispersible) epoxy-based polyamine resin (A)I (specific gravity (solid content) 1.2 g/cm³).

[0075] (Production Example 2) Production of aqueous epoxy-based polyamine resin (A)II

742 parts of the raw material resin having an epoxy equivalent of 188 g/equivalent, which was synthesized from bisphenol A and epichlorohydrin, 336 parts of bisphenol A, and 190 parts of MIBK were fed to a reactor equipped with a stirrer, a cooler, a nitrogen injection tube, and a thermometer, and the mixture was allowed to react at 117°C in the presence of 1 part of benzyldimethylamine until the epoxy equivalent reached 1,079 g/equivalent, to thereby obtain an epoxy resin. After that, 350 parts of a ketimine compound of diethylenetriamine (73 mass% MIBK solution) were added thereto, and the mixture was allowed to react at 117°C for 1 hour. Subsequently, 27 parts of ion-exchange water and 188 parts of glycidyl neodecanoate (manufactured by Hexion Specialty Chemicals, Inc., trade name "Cardura E10-P") were fed thereto, and the mixture was allowed to react at 100°C for 2 hours. After that, the mixture was diluted with MIBK until a nonvolatile content of 75% was achieved, to thereby obtain an epoxy-based polyamine resin having an amino group equivalent of 1,093.

Acetic acid was added thereto so that a neutralization ratio (neutralization ratio of the resin based on amino groups) of 35.0% was achieved, and the mixture was diluted with ion-exchange water. After that, a mixture of MIBK and water was removed under reduced pressure until a solid content of 40 mass% was achieved, to thereby prepare a milky white aqueous (water-dispersible) epoxy-based polyamine resin (A)II (specific gravity (solid content) 1.2 g/cm³).

[0076] (Production Example 3) Production of aqueous epoxy-based polyamine resin (A)III

525 parts of the raw material resin having an epoxy equivalent of 188 g/equivalent, which was synthesized from bisphenol A and epichlorohydrin, 205 parts of bisphenol A, and 110 parts of MIBK were fed to a reactor equipped with a stirrer, a cooler, a nitrogen injection tube, and a thermometer, and the mixture was allowed to react at 117°C in the presence of 1 part of benzyldimethylamine until the epoxy equivalent reached 730 g/equivalent, to thereby obtain an epoxy resin. After that, 350 parts of a ketimine compound of diethylenetriamine (73 mass% MIBK solution) were added thereto, and the mixture was allowed to react at 117°C for 1 hour. Subsequently, 27 parts of ion-exchange water and 188 parts of glycidyl neodecanoate (manufactured by Hexion Specialty Chemicals, Inc., trade name "Cardura E10-P") were fed thereto, and the mixture was allowed to react at 100°C for 2 hours. After that, the mixture was diluted with MIBK until a nonvolatile content of 75% was achieved, to thereby

obtain an epoxy-based polyamine resin having an amino group equivalent of 810.

Acetic acid was added thereto so that a neutralization ratio (neutralization ratio of the resin based on amino groups) of 20.0% was achieved, and the mixture was diluted with ion-exchange water. After that, a mixture of MIBK and water was removed under reduced pressure until a solid content of 40 mass% was achieved, to thereby prepare a milky white aqueous (water-dispersible) epoxy-based polyamine resin (A) III (specific gravity (solid content) 1.2 g/cm³).

[0077] (Production Example 4) Production of aqueous epoxy-based polyamine resin (A) IV

1,940 parts of the raw material resin having an epoxy equivalent of 188 g/equivalent, which was synthesized from bisphenol A and epichlorohydrin, 1,060 parts of bisphenol A, and 550 parts of MIBK were fed to a reactor equipped with a stirrer, a cooler, a nitrogen injection tube, and a thermometer, and the mixture was allowed to react at 117°C in the presence of 8 parts of benzyldimethylamine until the epoxy equivalent reached 3,000 g/equivalent, to thereby obtain an epoxy resin. After that, 350 parts of a ketimine compound of diethylenetriamine (73 mass% MIBK solution) were added thereto, and the mixture was allowed to react at 117°C for 1 hour. Subsequently, 1,060 parts of dipropylene glycol monobutyl ether (hereinafter, referred to as "DPnB") were fed thereto, and the mixture was allowed

to react at 100°C for 2 hours. After that, the mixture was diluted with MIBK until a nonvolatile content of 75% was achieved, to thereby obtain an epoxy-based polyamine resin having an amino group equivalent of 1,550.

Acetic acid was added thereto so that a neutralization ratio (neutralization ratio of the resin based on amino groups) of 40.0% was achieved, and the mixture was diluted with ion-exchange water. After that, a mixture of MIBK and water was removed under reduced pressure until a solid content of 40 mass% was achieved, to thereby prepare a milky white aqueous (water-dispersible) epoxy-based polyamine resin (A) IV (specific gravity (solid content) 1.2 g/cm³).

[0078] (Production Examples 5 to 7) Production of aqueous epoxy-based polyamine resins (A) V to VII

Aqueous epoxy-based polyamine resins (A) V to VII were prepared in the same manner as in Production Example 2 except that the neutralization ratio was changed as shown in Table 1 below. The aqueous epoxy-based polyamine resins (A) V to VII were each found to have a specific gravity (solid content) of 1.2 g/cm³.

[0079] (Production Example 8) Production of aqueous epoxy-based polyamine resin (A) VIII

1,440 parts of the raw material resin having an epoxy equivalent of 188 g/equivalent, which was synthesized from bisphenol A and

epichlorohydrin, 760 parts of bisphenol A, and 388 parts of MIBK were fed to a reactor equipped with a stirrer, a cooler, a nitrogen injection tube, and a thermometer, and the mixture was allowed to react at 117°C in the presence of 3 parts of benzyldimethylamine until the epoxy equivalent reached 2,200 g/equivalent, to thereby obtain an epoxy resin. After that, 350 parts of a ketimine compound of diethylenetriamine (73 mass% MIBK solution) were added thereto, and the mixture was allowed to react at 117°C for 1 hour. After having been allowed to react at 100°C for an additional 2 hours, the mixture was diluted with MIBK until a nonvolatile content of 75% was achieved, to thereby obtain an epoxy-based polyamine resin having an amino group equivalent of 1,150.

Acetic acid was added thereto so that a neutralization ratio (neutralization ratio of the resin based on amino groups) of 40.0% was achieved, and the mixture was diluted with ion-exchange water. After that, a mixture of MIBK and water was removed under reduced pressure until a solid content of 40 mass% was achieved, to thereby prepare a milky white aqueous (water-dispersible) epoxy-based polyamine resin (A)VIII (specific gravity (solid content) 1.2 g/cm³).

[0080] [Table 1]

			Production Example 1	Production Example 2	Production Example 3	Production Example 4	Production Example 5	Production Example 6	Production Example 7	Production Example 8
Aqueous epoxy-based polyamine resin (A) No.			I	II	III	IV	V	VI	VII	VIII
Blending amount (part(s))										
Epoxy-based polyamine resin	Epoxy resin	Amount of raw material resin	702	742	525	1,940	742	742	742	1,440
		Bisphenol A	269	336	205	1,060	336	336	336	760
		Dimer acid	108	—	—	—	—	—	—	—
		MIBK	190	190	110	550	190	190	190	388
		Benzyltrimethylamine	1	1	1	8	1	1	1	3
		Ketimine compound of aminoethylethanolamine	255	—	—	—	—	—	—	—
		Ketimine compound of diethylenetriamine	—	350	350	350	350	350	350	350
		Ion-exchange water	—	27	27	—	27	27	27	—
		Glycidyl neodecanoate	—	188	188	—	188	188	188	—
		DPnB	—	—	—	1,060	—	—	—	—
Neutralization ratio (%)		35	35	20	40	100	65	20	40	
Solid content (mass%)		40	40	40	40	40	40	40	40	
Epoxy equivalent of epoxy resin		1,079	1,079	730	3,000	1,079	1,079	1,079	2,200	
Amino group equivalent of aqueous epoxy-based polyamine resin		1,184	1,093	810	1,550	1,093	1,093	1,093	1,150	
State		Water-disper sible	Water-disper sible	Water-disper sible	Water-disper sible	Water-solubl e	Water-disper sible	Water-disper sible	Water-disper sible	
Outer appearance		Milky white	Milky white	Milky white	Milky white	Clear	Milky white	Milky white	Milky white	

[0081] (Production Example 9) Production of epoxy-based polyamine resin

An epoxy-based polyamine resin was prepared in the same manner as in Production Example 2 except that the neutralization ratio was changed to 5%. The epoxy-based polyamine resin was not converted into an aqueous resin and caused phase separation in water.

[0082] (Production Example 10) Production of epoxy-based polyamine resin

2,560 parts of the raw material resin having an epoxy equivalent of 188 g/equivalent, which was synthesized from bisphenol A and epichlorohydrin, 1,439 parts of bisphenol A, and 706 parts of MIBK were fed to a reactor equipped with a stirrer, a cooler, a nitrogen injection tube, and a thermometer, and the mixture was allowed to react at 117°C in the presence of 5 parts of benzyldimethylamine until the epoxy equivalent reached 4,000 g/equivalent, to thereby obtain an epoxy resin. After that, 350 parts of a ketimine compound of diethylenetriamine (73 mass% MIBK solution) were added thereto, and the mixture was allowed to react at 117°C for 1 hour. After having been allowed to react at 100°C for an additional 2 hours, the mixture was diluted with MIBK until a nonvolatile content of 75% was achieved, to thereby obtain an epoxy-based polyamine resin having an amino group equivalent of 2,050.

Acetic acid was added thereto so that a neutralization ratio

(neutralization ratio of the resin based on amino groups) of 40.0% was achieved, and the mixture was diluted with ion-exchange water. After that, a mixture of MIBK and water was removed under reduced pressure until a solid content of 40 mass% was achieved, to thereby prepare an epoxy-based polyamine resin. The epoxy-based polyamine resin was not converted into an aqueous resin and caused phase separation in water.

[0083] (Example 1)

(Production of base resin liquid for coating material)

89.5 parts of talc (manufactured by FUJI TALC INDUSTRIAL CO., LTD., trade name "TALC SP 42," specific gravity: 2.7 g/cm³), 89.5 parts of calcium carbonate (manufactured by MARUO CALCIUM CO., LTD, tradename "NGroundCalciumCarbonate," specific gravity: 2.7 g/cm³), 172 parts of titanium oxide (manufactured by Du Pont, trade name "TI-PUR R706," specific gravity: 4.3 g/cm³), 25 parts of an anti-rust pigment (manufactured by Toho Ganryo Kogyo Co., Ltd., trade name "EXPERT NP1055C," specific gravity: 2.3 g/cm³), 4 parts of a defoamer (manufactured by SAN NOPCO LIMITED, trade name "SN Defoamer 154," specific gravity: 1.0 g/cm³), and 32 parts of a pigment dispersant (manufactured by BYK, trade name "BYK-190," specific gravity: 1.0 g/cm³) were added to 110 parts of water, and the mixture was stirred with a disper for 30 minutes, to thereby produce a pigment-dispersed paste. 400 parts of the aqueous epoxy-based polyamine resin (A)I obtained in Production Example 1, 24 parts of DPnB, and 1 part of

an associated thickener (manufactured by ADECA CORPORATION, trade name "Adecanol UH-420" were added to 500 parts of the pigment paste, and the resultant was mixed, to thereby obtain a base resin liquid for a coating material I.

(Production of curing agent)

40 parts of water, 10 parts of DPnB, and 50 parts of polyethylene glycol #400 dimethacrylate (EO 9 mol) (viscosity (25°C): 58 mPa·s, molecular weight: 508, number of functional groups: 2, acryloyl group equivalent: 254) used as the compound (B) were mixed, and the mixture was stirred using a homogenizer for 10 minutes, to thereby obtain a curing agent I. It should be noted that the specific gravity of the solid content in the curing agent I was found to be 1.2 g/cm³.

(Production of aqueous coating composition)

4.8 parts of an epoxy silane coupling agent (3-glycidoxypropyltrimethoxysilane; manufactured by Shin-Etsu Chemical Co., Ltd., trade name "KBM-403") used as the alkoxysilane compound (C) were added to 40 parts of the curing agent I, and the curing agent was then homogeneously mixed with 500 parts of the base resin liquid for a coating material I, to thereby obtain an aqueous coating composition 1.

[0084] (Examples 2 to 22)

Aqueous coating compositions were obtained in the same manner

as in Example 1 except that the kinds and blending amounts of the base resin liquid for a coating material I, curing agent I, and alkoxysilane compound (C) were changed as shown in Table 2 or Table 3.

It should be noted that base resin liquid for a coating materials II to VIII were obtained in the same manner as in Example 1 except that aqueous epoxy-based polyamine resins (A) shown in Table 4 were used instead of the aqueous epoxy-based polyamine resin (A)I.

Curing agents II to IX containing compounds (B) were obtained according to the curing agent production method of Example 1 using the compounds (B) shown in Table 5 at blending ratios shown in Table 5 by mixing methods shown in Table 5. It should be noted that a nonionic emulsifier (manufactured by Nippon Nyukazai Co., Ltd., trade name "Newcol 740") was used as an emulsifier in each of the curing agents II, IV, V, VIII, and IX. Table 5 shows the viscosity at 25°C, molecular weight, number of functional groups, acryloyl group equivalent, and properties (self-emulsifying, water-insoluble, or water-soluble) of the compound (B) used in each of Examples. The properties of the compound (B) were evaluated as follows. At room temperature, 5 g of the compound (B) were added to 100 g of water, and the mixture was stirred and allowed to stand still, followed by visual observation. If the mixture contained a precipitate, the compound was evaluated to be "water-insoluble,"

if the mixture contained no precipitate and was clear, the compound was evaluated to be "water-soluble," and if the mixture contained no precipitate and was turbid, the compound was evaluated to be "self-emulsifying." It should be noted that the specific gravity of the solid content in each of the curing agents II to IX was found to be 1.2 g/cm³.

As an aminosilane coupling agent used as the alkoxysilane compound (C), N-aminoethyl- γ -aminopropyltrimethoxysilane (manufactured by Shin-Etsu Chemical Co., Ltd., trade name "KBM-603") was used.

[0085] (Comparative Examples 1 to 3)

Aqueous coating compositions were obtained in the same manner as in Example 1 except that the curing agent II was used in blending amounts shown in Table 3 instead of 40 parts of the curing agent I, and the blending amount of the epoxy silane coupling agent (4.8 parts) was changed as shown in Table 3.

[0086] [Table 2]

		Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Example 7	Example 8	Example 9	Example 10	Example 11	Example 12
Base resin liquid for coating material	No.	Blending amount (parts)											
	I	500		500		500		500		500			
	II		500		500		500		500		500		350
	III											500	
	IV												150
	V												
	VI												
	VII												
Curing agent	No.	Blending amount (parts)											
	I	40											
	II		20										
	III			10									
	IV				85							75	
	V					45					60		
	VI						65						
	VII							40					
Alkoxysilane compound (C)	No.	Blending amount (parts)											
	Epoxysilane coupling agent	4.8	4.6	4.6	5.1	4.8	5.0	4.8	4.9	4.6	4.9	5.0	4.7
	Aminosilane coupling agent												
Mass ratio of epoxy resin (a1) having epoxy equivalent of 400 to 1,500 and epoxy resin (a2) having epoxy equivalent of 2,000 to 3,000: a1/a2		10/0	10/0	10/0	10/0	10/0	10/0	10/0	10/0	10/0	10/0	10/0	7/3
Equivalent ratio of amino groups in aqueous epoxy-based polyamine resin (A) and (meth)acryloyl groups in compound (B) ((meth)acryloyl groups/amino groups)		1.1	1.3	0.7	1.9	1.5	1.1	1.3	1.5	0.9	1.8	1.2	1.1
Content ratio of alkoxysilane compound (C) in solid content of aqueous coating composition (%)		1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Pigment volume concentration (%)		41	42	43	38	41	39	41	40	42	40	39	42
Low-temperature curability		A	A	B	A	A	A	A	A	A	A	A	A

Pencil hardness		HB	H	2B	2H	H	HB	HB	H	HB	2H	HB	HB
Initial rain resistance		A	A	A	A	A	A	A	A	A	A	A	AA
Corrosion resistance evaluation A	Grit blasted steel sheet	A	A	A	A	A	A	A	A	A	A	A	A
	Shop primer steel sheet	A	A	A	A	A	A	A	A	A	A	A	A
	Aluminum steel sheet	A	A	A	A	A	A	A	A	A	A	A	A
	Zinc-plated steel sheet	A	A	A	A	A	A	A	A	A	A	A	A
Corrosion resistance evaluation B	Grit blasted steel sheet	A	A	A	A	A	A	A	A	A	A	A	A
	Shop primer steel sheet	A	A	A	A	A	A	A	A	A	A	A	A
	Aluminum steel sheet	A	A	A	A	A	A	A	A	A	A	A	A
	Zinc-plated steel sheet	A	A	A	A	A	A	A	A	A	A	A	A
Top coating property evaluation	Top coating with oil-based coating material	A	A	A	A	A	A	A	A	A	A	A	A
	Top coating with urethane-based coating material	A	A	A	A	A	A	A	A	A	A	A	A
	Top coating with epoxy-based coating material	A	A	A	A	A	A	A	A	A	A	A	A
	Top coating with aqueous epoxy-based coating material	A	A	A	A	A	A	A	A	A	A	A	A
	Top coating with aqueous urethane-based coating material	A	A	A	A	A	A	A	A	A	A	A	A

[0087] [Table 3]

		Example 13	Example 14	Example 15	Example 16	Example 17	Example 18	Example 19	Example 20	Example 21	Example 22	Compara tive Example 1	Compara tive Example 2	Compara tive Example 3
Base resin liquid for coating material	No.	Blending amount (parts)												
	I											500	500	500
	II	150												
	III													
	IV	350	500	250					250	250	250			
	V							500						
	VI			250	200	500			250	250	250			
	VII						500							
	VIII				300									
Curing agent	No.	Blending amount (parts)												
	I											20	20	9
	II													
	III													
	IV													
	V													
	VI													
	VII													
	VIII			35	75				35	35	35			
	IX	30	30			35	35	35						
Alkoxysilane compound (C)	No.	Blending amount (parts)												
	Epoxysilane coupling agent	4.7	4.7	4.7	5.0	4.7	4.7	4.7	0.7	16.0		0.0	20	4.6
	Aminosilane coupling agent										4.7			
Mass ratio between epoxy resin (a1) having epoxy equivalent of 400 to 1,500 and epoxy resin (a2) having epoxy equivalent of 2,000 to 3,000: a1/a2		3/7	0/10	5/5	4/6	10/0	10/0	10/0	5/5	5/5	5/5	10/0	10/0	10/0
Equivalent ratio of amino groups in aqueous epoxy-based polyamine resin (A) and (meth)acryloyl groups in compound (B) ((meth)acryloyl groups/amino groups)		1.5	1.7	1.0	1.9	1.4	1.4	1.4	1.0	1.0	1.0	1.1	1.1	0.5
Content ratio of alkoxysilane compound (C) in solid content of aqueous coating composition (%)		1.5	1.5	1.5	1.5	1.5	1.5	1.5	0.2	4.9	1.5	0.0	6.3	1.5
Pigment volume concentration		42	42	41	39	41	41	41	42	40	41	43	40	43

(%)		A	A	A	A	A	A	A	A	A	A	D	D
Low-temperature curability		A	A	A	A	A	A	A	A	A	A	D	D
Pencil hardness		H	2H	HB	2H	H	H	H	HB	HB	HB	6B	6B
Initial rain resistance		AA	AA	AA	AA	A	A	A	AA	AA	AA	A	C
Corrosion resistance evaluation A	Grit blasted steel sheet	A	A	A	A	A	A	A	A	A	A	B	C
	Shop primer steel sheet	A	A	A	A	A	A	A	A	A	A	B	C
	Aluminum steel sheet	A	A	A	A	A	A	A	A	A	A	B	C
	Zinc-plated steel sheet	A	A	A	A	A	A	A	A	A	A	B	C
Corrosion resistance evaluation B	Grit blasted steel sheet	A	A	A	A	A	A	A	A	A	A	B	C
	Shop primer steel sheet	A	A	A	A	A	A	A	A	A	A	B	C
	Aluminum steel sheet	A	A	A	A	A	A	A	A	A	A	B	C
	Zinc-plated steel sheet	A	A	A	A	A	A	A	A	A	A	B	C
Top coating property evaluation	Top coating with oil-based coating material	A	A	A	A	A	A	A	A	A	A	A	C
	Top coating with urethane-based coating material	A	A	A	A	A	A	A	A	A	A	A	C
	Top coating with epoxy-based coating material	A	A	A	A	A	A	A	A	A	A	A	C
	Top coating with aqueous epoxy-based coating material	A	A	A	A	A	A	A	A	A	A	A	A
	Top coating with aqueous urethane-based coating material	A	A	A	A	A	A	A	A	A	A	A	A

[0088] [Table 4]

Base resin liquid for coating material	Aqueous epoxy-based polyamine resin (A)		
		Epoxy equivalent of epoxy resin	Amino group equivalent of aqueous epoxy-based polyamine resins
I	I (Production Example 1)	1,079	1,184
II	II (Production Example 2)	1,079	1,093
III	III (Production Example 3)	730	810
IV	IV (Production Example 4)	3,000	1,550
V	V (Production Example 5)	1,079	1,093
VI	VI (Production Example 6)	1,079	1,093
VII	VII (Production Example 7)	1,079	1,093
VIII	VIII (Production Example 8)	2,200	1,150

[0089] [Table 5]

Curing agent No.		I	II	III	IV	V	
Compound B	Kind	Polyethylene glycol #400 dimethacrylate (EO 9 mol)	Pentaerythritol acrylate	Trimethylolpropane acrylate	Propoxylated bisphenol A diacrylate (PO 04 mol)	Ethoxylated bisphenol A diacrylate (EO 04 mol)	Propoxylated trimethylolpropane acrylate (PO 03 mol)
	Viscosity (mPa·s)	58	700	95	2,200	1,100	85
	Molecular weight	508	298	296	568	512	470
	Number of functional groups	2	3	3	2	2	3
	Acryloyl group equivalent	254	99	99	284	256	157
	Property	Self-emulsifying	Water-insoluble	Water-insoluble	Water-insoluble	Water-insoluble	Water-insoluble
	Blending amount (parts)	50	50	50	50	25	25
DPnB (parts)		10	10	50	10	10	
Water (parts)		40	35	-	35	35	
Emulsifier (parts)		-	5	-	5	5	
Mixing method		Homogenizer	Homogenizer	Disper	Homogenizer	Homogenizer	

Curing agent No.		VI	VII	VIII	IX
Compound B	Kind	Ethoxylated bisphenol A diacrylate (EO 10 mol)	Ethoxylated glycerin triacrylate (EO 09 mol)	Ethoxylated bisphenol A diacrylate (EO 04 mol)	Propoxylated trimethylolpropane acrylate (PO 03 mol)
	Viscosity (mPa·s)	620	95	1,100	85
	Molecular weight	776	650	512	470
	Number of functional groups	2	3	2	3
	Acryloyl group equivalent	388	217	256	157
	Property	Self-emulsifying	Water-insoluble	Water-insoluble	Water-insoluble
	Blending amount (parts)	50	50	50	50
DPnB (parts)		10	50	10	10
Water (parts)		40	-	35	35
Emulsifier (parts)		-	-	5	5
Mixing method		Homogenizer	Disper	Homogenizer	Homogenizer

[0090] <Evaluations>

The aqueous coating compositions obtained in the foregoing were evaluated by the following methods. Tables 2 and 3 show the results.

(Low-temperature curability)

The aqueous coating compositions obtained in the foregoing were each applied using an applicator onto a 20 cm×30 cm grit blasted steel sheet so that a film thickness of a dried coating film of 100 μ m was achieved, and then allowed to stand at 5°C in an atmosphere of a relative humidity of 50% for 16 hours, to thereby obtain a test sheet having formed thereon a coating film.

A worker with a body weight of 65 kg heeled on the surface of the resultant coating film with his safety shoe for 30 seconds, and the condition of the coating film was then evaluated visually based on the following criteria.

- A: No peeled part
- B: Almost no peeled part
- C: Small peeled part
- D: Large peeled part

(Pencil hardness)

A test sheet was obtained in the same manner as in the evaluation

of the low-temperature curability. The pencil hardness of a coating film formed on the test sheet was measured in accordance with JIS K 5600-5-4.

(Initial rain resistance)

The aqueous coating compositions obtained in the foregoing were each applied onto a polished steel sheet using a brush in an application amount of 200 g/m², and dried in an environment of 5°C for 24 hours, to thereby obtain a test sheet. The test sheet was immersed in water at 5°C, lifted up after a lapse of 24 hours, and allowed to stand still at 5°C for 24 hours. After that, the outer appearance of the coating film was visually observed and evaluated based on the following criteria.

AA: No defect in outer appearance observed

A: Slight changes in luster and color but no mark of cracking or swelling observed

C: Mark of cracking or swelling observed

(Corrosion resistance evaluation A)

The aqueous coating compositions obtained in the foregoing were each spray-applied onto each of a grit blasted steel sheet, a zinc-plated steel sheet, an aluminum steel sheet, and a shop primer steel sheet, each of which had a size of 7 cm×15 cm, so that a dried film thickness of 100 μm was achieved, and the sheets were allowed

to stand at 20°C for 7 days, to thereby obtain test sheets. The test sheets were tested for 200 hours with a salt spray testing machine described in JIS K 5600-7-1.

After that, X-shaped cuts were made using a cutter knife so that the cutter knife passed through the coating film on each of the test specimens and reached each of the steel sheets, and a pressure-sensitive adhesive cellophane tape was attached thereto and peeled off. The adhesive property of each of the steel sheets and the coating film was evaluated based on the same evaluation criteria as those for the low-temperature curability.

(Corrosion resistance evaluation B)

The adhesive property of each of the steel sheets and the coating film was evaluated in the same manner as in the corrosion resistance evaluation A except that the test sheets were immersed in water at 40°C for 336 hours instead of the 200-hr test using the salt spray testing machine described in JIS K 5600-7-1.

(Top coating property evaluation)

The aqueous coating compositions obtained in the foregoing were each spray-applied onto a shot blasted steel sheet with a size of 7 cm×15 cm so that a dried film thickness of 95 to 105 μm was achieved, and the sheet was allowed to stand at 20°C for 7 days and then exposed to an outdoor environment for 7 days.

Five steel sheets each thus having formed thereon a coating film were prepared. An oil-based coating material (manufactured by NIPPON PAINT MARINE COATINGS Co., Ltd., trade name "CR Marine Finish"), a solvent-type urethane-based coating material (manufactured by NIPPON PAINT MARINE COATINGS Co., Ltd., trade name "Polyuremytilac M"), a solvent-type epoxy-based coating material (manufactured by NIPPON PAINT MARINE COATINGS Co., Ltd., trade name "Epoxy Finish M"), an aqueous epoxy-based coating material (manufactured by NIPPON PAINT MARINE COATINGS Co., Ltd., trade name "ODEMARINE PF"), or an aqueous urethane-based coating material (manufactured by NIPPON PAINT Co., Ltd., trade name "ODE URE TOP") was spray-applied onto each of the prepared steel sheets so that a dried film thickness of 35 to 45 μm was achieved, and the sheets were allowed to stand at 20°C for 7 days, to thereby obtain test sheets.

The adhesive property of each of the steel sheets and the coating film formed using the aqueous coating composition obtained above was evaluated in the same manner as in the corrosion resistance evaluation A except that the test sheets were obtained as described above.

[0091] As clear from the results of Examples 1 to 22, the aqueous coating composition of the present invention exhibits excellent

low-temperature curability by containing the aqueous epoxy-based polyamine resin (A) and the compound (B). Meanwhile, as clear from a comparison between Examples 1 to 21 and Comparative Example 1, the aqueous coating composition of the present invention can form a coating film excellent in corrosion resistance by containing the alkoxysilane compound (C).

[0092] In addition, as clear from a comparison between Examples 1 to 22 and Comparative Example 3, when the content ratio of the alkoxysilane compound (C) is in a specific range, excellent low-temperature curability and corrosion resistance can be achieved. Further, as clear from a comparison between Examples 1 to 21 and Comparative Example 2, when the equivalent ratio of the aqueous epoxy-based polyamine resin (A) and the compound (B) is in a specific range, excellent low-temperature curability and corrosion resistance can be achieved.

[0093] Further, as clear from the results of Examples 12 to 16 and 20 to 22, the aqueous coating composition including the aqueous epoxy-based polyamine resin (A) obtained using the epoxy resin (a1) having an epoxy equivalent of 2,000 to 3,200 can form a coating film significantly excellent in initial rain resistance.

Industrial Applicability

[0094] The aqueous coating composition of the present invention

can be suitably used as an anticorrosive coating material in an inner or outer plate part of a ship and a submerged structure in seawater or freshwater. Specifically, the composition can be suitably used in: an inner or outer plate part of a ship such as deck, hatch coaming, upper structure part, hull part, engine room, living quarter, or car hold; a submerged structure in seawater or freshwater, such as a piping material; and the like.

Claims

[Claim 1] An aqueous coating composition, comprising:

(A) an aqueous epoxy-based polyamine resin having one or more primary amino groups and/or secondary amino groups in a molecule;

(B) a compound having one or more (meth)acryloyl groups in a molecule; and

(C) an alkoxysilane compound;

wherein an equivalent ratio of an amino group of the aqueous epoxy-based polyamine resin (A) and a (meth)acryloyl group of the compound (B) ((meth)acryloyl group/amino group) is 0.7 to 2.5; and a content of the alkoxysilane compound (C) in a solid content of the aqueous coating composition is 0.2 mass% to 5 mass%;

wherein the aqueous coating composition is a two-component aqueous coating composition comprising a base resin liquid for a coating material and a curing agent,

the base resin liquid for a coating material comprising the aqueous epoxy-based polyamine resin (A) and

the curing agent comprising the compound (B) and the alkoxysilane compound (C);

wherein the aqueous epoxy-based polyamine resin (A) has an amino group equivalent of 100 to 3,000; and

wherein the aqueous epoxy-based polyamine resin (A) is obtained by amine-modification of an epoxy resin, and the epoxy resin has an epoxy equivalent of 180 to 3,800.

[Claim 2] An aqueous coating composition according to claim 1, wherein the aqueous epoxy-based polyamine resin (A) is water-dispersible.

[Claim 3] An aqueous coating composition according to any one of claims 1 to 2, wherein the aqueous epoxy-based polyamine resin (A) comprises:

an aqueous epoxy-based polyamine resin (A1) obtained by amine-modification of an epoxy resin (a1) having an epoxy equivalent of 400 to 1,500; and

an aqueous epoxy-based polyamine resin (A2) obtained by amine-modification of an epoxy resin (a2) having an epoxy equivalent of 2,000 to 3,200.

[Claim 4] An aqueous coating composition according to claim 3, wherein a mass ratio of the epoxy resin (a1) and the epoxy resin (a2) ($a1/a2$) is 8/2 to 2/8.

[Claim 5] An aqueous coating composition according to any one of claims 1 to 4, wherein the aqueous epoxy-based polyamine resin (A) is obtained by neutralization of an amino group of an epoxy-based polyamine resin with an acid, and a neutralization ratio in the neutralization is 10% to 70%.

[Claim 6] An aqueous coating composition according to any one of claims 1 to 7, wherein the compound (B) has a viscosity at 25°C of 3,000 mPa·s or less.

[Claim 7] An aqueous coating composition according to any one of claims 1 to 6, further comprising a pigment, wherein the pigment has a pigment volume concentration of 20% to 50%.

[Claim 8] A method of forming a coating film, comprising applying the aqueous coating composition according to any one of claims 1 to 7 onto a substrate surface to form a coating film.

[Claim 9] A method of forming a coating film according to claim 8, further comprising applying a top coating material on the coating film to form a top coating layer.