

Description

Title of Invention: METHOD FOR FORMING COATING FILM

Technical Field

[0001] The present invention relates to 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 of Invention

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 a method for forming a coating film which is excellent in low-temperature curability.

Means for solving the Problems

[0006] A method of forming a coating film according to an embodiment of the present invention includes coating a substrate with an aqueous coating composition to form a coating film, wherein the aqueous coating composition includes: an aqueous epoxy-based polyamine resin (A) having one or more primary amino groups and/or secondary amino groups in a molecule; and a compound (B) having one or more (meth)acryloyl groups in a molecule.

In a preferred embodiment of the invention, the aqueous coating composition is a two-component aqueous coating composition including 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).

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) in the aqueous coating composition 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 compound (B) has a molecular weight of 150 or more and 2,000 or less.

In a preferred embodiment of the invention, the method of forming a coating film further includes forming a top coating layer on the coating film after the forming of the coating film with the aqueous coating composition.

In a preferred embodiment of the invention, the method of forming a coating film further includes forming an intermediate coating layer after the forming of the coating film with the aqueous coating composition and before the forming of the top coating layer.

In a preferred embodiment of the invention, the method of forming a coating film further includes forming a undercoating layer

on substrate before the forming of the coating film with the aqueous coating composition.

Effects of the Invention

[0007] According to the method of forming a coating film according to the present invention, it is possible to obtain a coating film which exerts practical performance even at low temperature (for example, 5°C or less) by using an aqueous coating composition including an aqueous epoxy-based polyamine resin (A) having one or more primary amino groups and/or secondary amino groups in a molecule and a compound (B) having one or more (meth)acryloyl groups in a molecule. More specifically, the aqueous coating composition utilizes, for a curing reaction, a Michael addition reaction at a high reactivity, and hence a cured coating film can be obtained even at low temperature (for example, 5°C or less). Further, in the case where the aqueous epoxy-based polyamine resin (A) is water-dispersible, the aqueous coating composition has good stability at ordinary temperature in spite of very high reactivity of the Michael addition reaction itself and is excellent in workability compared with a solvent-based coating composition. In addition, the epoxy resin is used as a binder, and hence a coating film excellent in corrosion resistance can be obtained.

Description of Embodiments

[0008] A. Method of forming coating film

A method of forming a coating film according to the present invention includes coating a substrate with an aqueous coating composition to form a coating film.

[0009] A-1. Outline of aqueous coating composition

The aqueous coating composition includes: an aqueous epoxy-based polyamine resin (A) having one or more primary amino groups and/or secondary amino groups in a molecule; and a compound (B) having one or more (meth)acryloyl groups in a molecule. In the aqueous coating composition, a curing reaction (Michael addition 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 curing reaction of the aqueous epoxy-based polyamine resin (A) and the compound (B) can be performed even at low temperature (for example, 5°C), and hence the aqueous coating composition is excellent in low-temperature curability.

[0010] The aqueous coating composition 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). When the aqueous coating composition 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.

[0011] Before mixing of the aqueous epoxy-based polyamine resin (A) and the compound (B), the aqueous coating composition 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 and capable of allowing the aqueous epoxy-based polyamine resin (A) and the compound (B) to react with each other efficiently.

[0012] 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.

[0013] 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 in water with the dispersant, the emulsifier, or the 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, an ammonium salt of a half ester of a styrene-maleic acid copolymer, and a polyethylene oxide adduct of a half ester of a styrene-maleic acid copolymer. Examples of the aqueous resin include a sodium salt of polyacrylic acid ester. It should be noted that, in the case where the aqueous coating composition is a two-component composition, the dispersant, the emulsifier, or the aqueous resin may be incorporated into the curing agent.

[0014] Examples of the dispersing element to be used when the compound (B) is dispersed in the dispersing element of a resin different from the aqueous epoxy-based polyamine resin (A) include an emulsion and dispersion of an acrylic resin, an emulsion and dispersion of a urethane resin, and an aqueous epoxy-based polyamine

resin having no primary amino group and no secondary amino group.

[0015] The content of the aqueous epoxy-based polyamine resin (A) in terms of a solid content is preferably 5 to 95 mass%, more preferably 10 to 90 mass% with respect to the total solid content of the aqueous coating composition.

[0016] The content of the compound (B) is preferably 2 to 30 mass%, more preferably 5 to 25 mass% with respect to the total solid content of the aqueous coating composition.

[0017] An equivalent ratio of the (meth)acryloyl group of the compound (B) and the amino group of the aqueous epoxy-based polyamine resin (A) ((meth)acryloyl group/amino group) is preferably 0.7 to 2.5, more 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.

[0018] The aqueous coating composition 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: color pigments such as titanium oxide, yellow iron oxide, red iron oxide, carbon black, phthalocyanine blue, phthalocyanine green, azo red, quinacridone red, and benzimidazolone yellow; extender pigments such as calcium carbonate, barium sulfate, kaolin, clay, talc, and mica; and anti-rust pigments such as zinc phosphate and calcium 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. It should be noted that 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] The aqueous coating composition may include water, a solvent, or an additive. 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 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] The aqueous coating composition may include an alkoxysilane compound as an additive. The aqueous coating

composition including the alkoxysilane compound can form a coating film excellent in adhesive property to the substrate.

[0023] Specific examples of the alkoxysilane compound 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. They may be used alone or
in combination. They may be partially subjected to hydrolysis and/or
hydrolysis dehydration condensation.

[0024] When the alkoxysilane compound is incorporated, its content is preferably 0.3 to 3 mass%, more preferably 0.5 to 2 mass% with respect to the total solid content of the aqueous coating composition.

[0025] A-2. Aqueous epoxy-based polyamine resin (A)

The aqueous coating composition includes the aqueous epoxy-based polyamine resin (A) having one or more primary amino

groups and/or secondary amino groups in a molecule. The aqueous coating composition including such resin as a binder can form a coating film excellent in corrosion resistance. It should be noted that the concept of "aqueous" as used herein comprehends "water-soluble" and "water-dispersible."

[0026] The aqueous epoxy-based polyamine resin (A) is preferably water-dispersible. When a water-dispersible aqueous epoxy-based polyamine resin (A) is used, a coating film excellent in water resistance can be formed. 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 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.

[0027] 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, for example, neutralization of an amino group with an acid, to thereby obtain the aqueous epoxy-based polyamine resin (A).

[0028] The epoxy resin is preferably a bisphenol A-type epoxy resin or a bisphenol F-type epoxy resin, particularly preferably a bisphenol A-type epoxy resin.

[0029] 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.

[0030] 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.

[0031] 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.

[0032] As the epoxy resin, two or more kinds of epoxy resins may be used in combination.

[0033] 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.

[0034] 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.

[0035] 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.

[0036] 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.

[0037] Examples of the primary amino group-containing polyamine include diethylenetriamine, dipropylenetriamine, dibutylenetriamine, and triethylenetetramine. They may be used alone or in combination.

[0038] 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.

[0039] 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.

[0040] 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.

[0041] 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.

[0042] 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.

[0043] 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.

[0044] The aqueous coating composition may include two or more kinds of the aqueous epoxy-based polyamine resins (A).

[0045] The aqueous coating composition 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.

[0046] 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.

[0047] A-3. Compound (B)

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

[0048] 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.

[0049] 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.

[0050] The viscosity of the compound (B) at 25°C is preferably 3,000 mPa·s or less, more preferably 50 to 3,000 mPa·s, particularly preferably 50 to 2,200 mPa·s, most preferably 50 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.

[0051] 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.

[0052] 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 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; and a case where the compound (B) is self-emulsifying or is water-insoluble.

[0053] As a method of providing the inhomogeneous state, any appropriate method may be employed depending on the dissolution property of the compound (B) in water. For example, in the case where the compound (B) is water-soluble, the compound (B) may be used without any modification. In this case, the aqueous epoxy-based polyamine resin (A) is preferably a water-dispersible resin. On the other hand, in the case where the compound (B) is self-emulsifying, the compound (B) may be used without any modification or may be emulsified or dispersed in water with an emulsifier, a dispersant, or an aqueous resin before use. In the case where the compound (B) is water-insoluble, the compound (B) may be emulsified or dispersed in water with an emulsifier, a dispersant, or an aqueous resin before use. In such cases, the form of the aqueous epoxy-based polyamine resin (A) may be water-soluble or water-dispersible, and is preferably water-dispersible. 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."

[0054] The compound (B) may be converted into a water-soluble or self-emulsifying compound, for example, by modifying the compound with polyethylene oxide and increasing the ethylene oxide addition mole number to enhance its hydrophilicity.

[0055] 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.

[0056] Examples of the compound (B) that is self-emulsifying

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.

[0057] Examples of the compound (B) that is water-insoluble 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.

[0058] 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), and hence a coating film excellent in low-temperature curability can be obtained. 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.

[0059] A-4. Method for coating with aqueous coating composition

Any appropriate substrate may be coated with the aqueous coating composition. Examples of the substrate include metal, wood, plastics, rubber, stone, slate, concrete, mortar, fiber, paper, glass, ceramics, porcelain, a film, and complexes thereof. Further, for example, when the substrate is an inorganic substrate such as slate or concrete, a sealer may be applied onto a surface of the substrate in advance. The aqueous coating composition is preferably applied to metal in consideration of its characteristics. Examples of the metal include iron, copper, tin, zinc, aluminum, and stainless steel.

[0060] Examples of an object to be coated having metal on its surfaces (outer and inner surfaces) include architectural structures, ships, vehicles (e.g., railway vehicles, large vehicles), aircraft,

bridges, marine structures, plants, tanks (e.g., petroleum tanks), pipes, steel tubes, and cast iron tubes. The method of forming a coating film according to the present invention is applicable to architectural structures and civil engineering structures as well as the foregoing.

[0061] As the coating method, there is typically given a method involving applying the aqueous coating composition onto an object to be coated, followed by drying. As an application method, any appropriate method may be adopted depending on the kind of the object to be coated (substrate) and the like. Examples thereof include application by means of a brush, a roller, an air spray, an airless spray, a trowel, or the like, and immersion.

[0062] The application amount of the aqueous coating composition may be set to any appropriate application amount depending on intended use. The application amount is preferably 10 to 350 g/m².

[0063] As the drying method, any appropriate method may be adopted. Air drying or heat drying is preferred. In the case of the air drying, a drying time is preferably 2 hours or more, more preferably 24 hours or more, particularly preferably 1 week or more. According to the method of forming a coating film according to the present invention, it is possible to form a coating film excellent

in corrosion resistance even when the drying is performed at low temperature (for example, 5°C or less).

[0064] The coating film to be formed through coating with the aqueous coating composition has a thickness of preferably 20 to 150 μm , more preferably 30 to 120 μm in terms of thickness of a dried coating film. When the thickness of the dried coating film is more than 150 μm , a problem such as the occurrence of dripping may occur at the time of the formation of the coating film.

[0065] The coating film to be obtained by using the aqueous coating composition has excellent corrosion resistance, and the use of only the coating film is sufficient for a part not requiring weatherability, such as an inner surface of a bridge girder.

[0066] B. Method of forming multilayer coating film

An additional coating film may be formed before and/or after the formation of a coating film through coating with the aqueous coating composition. In an embodiment, after coating with the aqueous coating composition has been performed to form a coating film, the coating film is coated with a top coating material to form a top coating layer. The formation of the top coating layer additionally improves outer appearance, corrosion resistance, and water-resistant adhesive property.

[0067] Any appropriate coating material may be adopted as the top coating material. Examples thereof include an epoxy/amine-based coating material, a two-component urethane curing type coating material, a one-component urethane curing type coating material, a carbodiimide curing type coating material, an acrylic resin-based coating material, an alkyd resin-based coating material, and a silicon resin-based coating material. The top coating material may be a solvent type or an aqueous one, and is preferably an aqueous one because an environmental load may be reduced. The top coating material is more preferably an aqueous two-component urethane curing type coating material, an aqueous one-component urethane curing type coating material, an aqueous silicon resin-based coating material, or an aqueous carbodiimide curing type coating material. When the top coating material is any of such aqueous coating materials, the resultant coating film has excellent weatherability and can achieve protection of good appearance for a long period of time.

[0068] The top coating layer is typically formed by applying the top coating material and drying (thermally treating) the material. As an application method, any appropriate method may be adopted depending on the kind of the top coating material and the like. Examples thereof include application by means of a brush, a roller, an air spray, an airless spray, a trowel, or the like, and immersion.

[0069] The application amount of the top coating material may

be set to any appropriate application amount depending on the kind of the coating material, purposes of coating, and the like. The application amount is preferably 30 to 400 g/m².

[0070] A method of drying (heating) the top coating material may be any appropriate drying (heating) method depending on the kind of the top coating material and the like. Examples thereof include air drying, forced drying, and baking.

[0071] The thickness of the top coating layer may be set to any appropriate thickness depending on the kind of the coating material and purposes of coating. The thickness is preferably 10 to 150 μm .

[0072] Before the formation of a coating film with the aqueous coating composition, the surface of the substrate may be coated with an undercoating material to form an undercoating layer. The formation of the undercoating layer provides additionally excellent corrosion resistance and water-resistant adhesive property, which are well applicable to a case requiring high corrosion resistance, such as a bridge, a plant, or a tank.

[0073] Any appropriate coating material may be adopted as the undercoating material. Examples thereof include an organic or inorganic zinc-rich coating material. When such coating material

containing zinc powder is used, an undercoating layer which has extremely high corrosion resistance can be formed. In addition, the coating material has good workability and can form a uniform undercoating layer. The undercoating material may be a solvent type or an aqueous one, and is preferably an aqueous one because an environmental load may be reduced.

[0074] As a method of forming the undercoating layer, the same method as in the case of the upper coating layer may be adopted. The application amount of the undercoating material may be set to any appropriate application amount depending on the kind of the coating material, purposes of coating, and the like. The application amount is preferably 80 to 1,200 g/m². The thickness of the undercoating layer may be set to any appropriate thickness depending on the kind of the coating material, purposes of coating, and the like. The thickness is preferably 20 to 200 μm.

[0075] After the formation of a coating film through coating with the aqueous coating composition, the coating film may be coated with an intermediate coating material to form an intermediate coating layer. The formation of the intermediate coating layer may provide a coating film additionally excellent in corrosion resistance and water-resistant adhesive property. The top coating layer is preferably formed on the intermediate coating layer.

[0076] Any appropriate coating material may be adopted as the intermediate coating material. Examples thereof include an epoxy/amine-based coating material, a two-component urethane curing type coating material, and a one-component urethane curing type coating material. The intermediate coating material may be a solvent type or an aqueous one, and is preferably an aqueous one because an environmental load may be reduced. The intermediate coating material is more preferably an aqueous epoxy/amine-based coating material or an aqueous two-component urethane curing type coating material. Such aqueous coating material can form a multilayer coating film which has good adhesiveness to the top coating layer and is strong.

[0077] As a method of forming the intermediate coating layer, the same method as in the case of the upper coating layer may be adopted. The application amount of the intermediate coating material may be set to any appropriate application amount depending on the kind of the coating material, purposes of coating, and the like. The application amount is preferably 20 to 400 g/m². The thickness of the intermediate coating layer may be set to any appropriate thickness depending on the kind of the coating material, purposes of coating, and the like. The thickness is preferably 10 to 100 μm .

[0078] 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-1. The number, kinds, and amounts of pigments and additives to be added may be selected as appropriate depending on purposes.

Examples

[0079] 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. Further, evaluations in the examples were carried out for the following items.

[0080] (Corrosion resistance)

The resultant coating film was subjected to a cyclic corrosion test defined in JIS K 5600 7-7, and the state of the coating film after 120 cycles was evaluated based on the following criteria.

Ratio of area of rust generated on the coating film to the area of the resultant coating film

A: Less than 0.05%

B: 0.05% or more and less than 0.1%

(Initial rain resistance)

A coating film was immersed together with a substrate in water

at 5°C, lifted up after a lapse of 24 hours, and allowed to stand still at 5°C for 24 hours, and the outer appearance of the coating film was then visually observed and evaluated based on the following criteria.

AA: No abnormality in outer appearance observed

A: Slight changes in burnish and color observed but no mark of crack or swelling observed

C: Mark of crack or swelling observed

(Water-resistant adhesive property)

A coating film was immersed together with an object coated therewith in water at 20°C and lifted up after a lapse of 7 days, and then in accordance with a cross-cut method of JIS K 5600-5.6 (2006), 5×5 squares each measuring 3 mm×3 mm were formed on the coating film. A pressure-sensitive adhesive tape was attached to a surface thereof and then rapidly peeled off, and evaluation was performed based on the following criteria.

10 points: No peeled square and no peeling along the cut part observed (peeling area: 0%)

8 points: No peeling of the squares but slight peeling along the cut part observed (peeling area: more than 0% and less than 5%)

6 points or less: Some peeled squares or significant peeling along the cut part observed (peeling area: 5% or more)

[0081] (Production of aqueous coating composition)

(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.

[0082] (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.

[0083] (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.

[0084] (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.

[0085] (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.

[0086] (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.

[0087] [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))								
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
Epoxy-based polyamine resin								
	255	-	-	-	-	-	-	-
	-	350	350	350	350	350	350	350
	-	27	27	-	27	27	27	-
	-	188	188	-	188	188	188	-
	-	-	-	1,060	-	-	-	-
	35	35	20	40	100	65	20	40
	40	40	40	40	40	40	40	40
	1,079	1,079	730	3,000	1,079	1,079	1,079	2,200
Epoxy equivalent of epoxy resin	1,184	1,093	810	1,550	1,093	1,093	1,093	1,150
Amino group equivalent of aqueous epoxy-based polyamine resin	Water-dispersible	Water-dispersible	Water-dispersible	Water-dispersible	Water-soluble	Water-dispersible	Water-dispersible	Water-dispersible
State	Milky white	Milky white	Milky white	Milky white	Clear	Milky white	Milky white	Milky white
Outer appearance								

[0088] (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.

[0089] (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.

[0090] (Production Example 11) Production of base resin liquid for coating material I

110 parts of water, 32 parts of a pigment dispersant (manufactured by BYK-Chemie, trade name "Disperbyk-190"), 4 parts of a defoamer (manufactured by BYK-Chemie, trade name "BYK-019"), 179 parts of calcium carbonate (manufactured by MARUO CALCIUM CO., LTD, trade name "N Ground Calcium Carbonate"), 172 parts of titanium oxide (manufactured by Du Pont, trade name "TI-PUR R706"), and 25 parts of a calcium-based anti-rust pigment (manufactured by Toho Ganryo Kogyo Co., Ltd., trade name "EXPERT NP1007") were mixed, 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 ADEKA 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.

[0091] (Production Examples 12 to 18) Production of base resin liquids for coating material II to VIII

Base resin liquids for a coating material II to VII were obtained in the same manner as in Production Example 11 except that aqueous epoxy-based polyamine resins (A) shown in Table 2 were used instead of the aqueous epoxy-based polyamine resin (A) I.

[0092] [Table 2]

	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 resin
Production Example 11	I	I (Production Example 1)	1,079	1,184
Production Example 12	II	II (Production Example 2)	1,079	1,093
Production Example 13	III	III (Production Example 3)	730	810
Production Example 14	IV	IV (Production Example 4)	3,000	1,550
Production Example 15	V	V (Production Example 5)	1,079	1,093
Production Example 16	VI	VI (Production Example 6)	1,079	1,093
Production Example 17	VII	VII (Production Example 7)	1,079	1,093
Production Example 18	VIII	VIII (Production Example 8)	2,200	1,150

[0093] (Production Example 19) Production of curing agent I
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) as the compound (B) were mixed, and the mixture was stirred using a homogenizer for 10 minutes to give a curing agent I.

[0094] (Production Examples 20 to 28) Production of curing agents II to X

Curing agents II to X containing compounds (B) were prepared according to the method of Production Example 19 using the compounds (B) shown in Table 3 at blending ratios shown in Table 3 by mixing methods shown in Table 3. 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, V, VIII, and IX. Table 3 shows the viscosity at 25°C, molecular weight, number of functional groups, acryloyl group equivalent, and property (self-emulsifying, water-insoluble, or water-soluble) of the compound (B) used in each of Production 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 for 3 minutes 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."

[0095] [Table 3]

Curing agent No. Kind	Production Example 19	Production Example 20	Production Example 21	Production Example 22	Production Example 23
	I	II	III	IV	V
Compound B	Polyethylene glycol #400 dimethacrylate (EO 9 mol)	Pentaerythritol acrylate	Trimethylolpropane acrylate	Propoxylated bisphenol A diacrylate (EO 04 mol)	Ethoxylated bisphenol A diacrylate (EO 04 mol)
	58	700	95	2,200	1,100
	Viscosity (mPa·s)			568	85
	Molecular weight	298	296	512	470
	Number of functional groups	3	3	2	3
	Acryloyl group equivalent	2	99	284	256
	Property				
	Self-emulsifying	Water-insoluble	Water-insoluble	Water-insoluble	Water-insoluble
	Blending amount (parts)	50	50	50	25
	DPnB (parts)	10	10	10	10
Compound B	Water (parts)	35	-	35	35
	Emulsifier (parts)	40	-	-	5
	Mixing method				
	Homogenizer	Homogenizer	Disper	Homogenizer	Homogenizer
Curing agent No. Kind	Production Example 24	Production Example 25	Production Example 26	Production Example 27	Production Example 28
Compound B	VI	VII	VIII	IX	X
	Ethoxylated bisphenol A diacrylate (EO 10 mol)	Ethoxylated glycerin triacrylate (EO 09 mol)	Ethoxylated bisphenol A diacrylate (EO 04 mol)	Propoxylated trimethylolpropane acrylate (EO 03 mol)	Ethoxylated bisphenol A diacrylate (EO 30 mol)
	620	95	1,100	85	800
	Viscosity (mPa·s)			470	1,656
	Molecular weight	776	512	2	2
	Number of functional groups	2	3	3	2
	Acryloyl group equivalent	388	217	256	828
	Property				
	Self-emulsifying	Water-insoluble	Water-insoluble	Water-insoluble	Water-soluble
	Blending amount (parts)	50	50	50	50
Compound B	DPnB (parts)	10	50	10	-
	Water (parts)	40	-	35	50
	Emulsifier (parts)	-	-	5	-
	Mixing method				
	Homogenizer	Disper	Homogenizer	Homogenizer	Disper

[0096] (Production Examples 29 to 47) Production of aqueous coating compositions 1 to 19

The base resin liquid for a coating material obtained in Production Examples 11 to 18 and the curing agents obtained in Production Examples 19 to 27 were mixed in blending amounts shown in Table 4, and the mixtures were stirred for 10 minutes with a disper to give aqueous coating compositions 1 to 19.

[0097] (Production of top coating material and intermediate coating material)

(Production Example 48) Production of aqueous epoxy/amine-based coating material A

34.5 parts of ion-exchange water and 0.3 part of a sodium alkyl diphenyl ether disulfonate (manufactured by Kao Corporation, trade name "PELEX SS-H") were loaded and heated in a nitrogen atmosphere to 80°C. Next, a monomer mixed solution including, as monomers, 14 parts of styrene, 58 parts of 2-ethylhexyl acrylate, 22 parts of methyl methacrylate, 4 parts of ethylene glycol dimethacrylate, and 2 parts of methacrylic acid, and as a chain transfer agent, 0.5 part of lauryl mercaptan was prepared. The resultant monomer mixed solution had an acid value of 13 mgKOH/g. The monomer mixed solution was added to an emulsifier aqueous solution of 1.2 parts of a sodium alkyl diphenyl ether disulfonate (manufactured by Kao Corporation, trade name "PELEX SS-H") in 50 parts of ion-exchange water, and the mixture was emulsified with a mixer to prepare a

pre-emulsion.

The thus-obtained pre-emulsion and an initiator aqueous solution of 0.3 part of ammonium persulfate in 13 parts of ion-exchange water were added dropwise into the separable flask from different dropping funnels simultaneously. Dropwise addition at constant rates over 120 minutes for the former and over 150 minutes for the latter was started. After the completion of the dropwise addition, a reaction was continued at the same temperature as above for an additional 120 minutes. The resultant was cooled and then neutralized with aqueous ammonia corresponding to 10 mol% of the methacrylic acid used. The neutralization product was filtered with a 200-mesh metal screen to give an acrylic emulsion resin.

Subsequently, 1.9 parts of a pigment dispersant (manufactured by BYK-Chemie, trade name "Disperbyk-190"), 0.3 part of a defoamer (manufactured by BYK-Chemie, trade name "BYK-019"), 18.6 parts of titanium oxide, 10.9 parts of calcium carbonate, 8.5 parts of talc, 2.9 parts of an anti-rust agent (manufactured by KIKUCHI COLOR & CHEMICALS CORPORATION, trade name "LF BOUSEI PM-303W"), and 12.1 parts of water were mixed with each other and dispersed with a disper.

To the dispersion were added 41 parts of an emulsified epoxy resin (manufactured by ADEKA CORPORATION, trade name "ADEKA RESIN EM-101-50," epoxy equivalent: 500 g/equivalent, solid content: 47%),

1.7 parts of a film forming aid (manufactured by CHISSO CORPORATION, "CS-12"), 0.4 part of an anti-rust agent, 0.2 part of a defoamer, and 17 parts of the acrylic emulsion resin produced in the foregoing to give a base resin liquid for a coating material.

Further, 8.9 parts of a water-soluble polyamine resin Sunmide (manufactured by Air Products and Chemicals, Inc., trade name "WH-910," active hydrogen equivalent: 135 g/equivalent (in terms of solid content), solid content: 60%) and 11.2 parts of water were mixed with each other to give a curing agent.

The base resin liquid for a coating material and the curing agent were mixed with each other and stirred with a disper to give an aqueous epoxy/amine-based coating material A.

[0098] (Production Example 49) Production of aqueous epoxy/amine-based coating material B

An aqueous epoxy/amine-based coating material B was obtained in the same manner as in Production Example 48 except that the blend of the base resin liquid for a coating material was changed by using 4 parts of the acrylic emulsion resin instead of 17 parts of the acrylic emulsion resin.

[0099] (Production Example 50) Production of aqueous two-component urethane-based coating material A

22 parts of water, 6 parts of a pigment dispersant (manufactured by BYK-Chemie, trade name "Disperbyk-190"), 70 parts of titanium oxide, 1 part of a defoamer (manufactured by BYK-Chemie, trade name "BYK-011," diluted to 10% before use), and 0.4 part of a dimethylethanolamine aqueous solution (25 mass%) were mixed with each other and stirred with a disper to give a pigment paste.

39 parts of the resultant pigment paste, 58 parts of an aqueous acrylic polyol (manufactured by DIC Corporation, trade name "BURNOCK WE-306"), 0.4 part of a surface conditioner (manufactured by BYK-Chemie, trade name "BYK-346"), 0.05 part of a leveling agent (manufactured by BYK-Chemie, trade name "BYK-333"), 0.4 part of a surfactant (manufactured by Air Products and Chemicals, Inc., trade name "DYNOL 604"), 0.5 part of a viscosity adjuster (manufactured by Rohm and Haas Company, trade name "Primal RM-8W"), 0.1 part of a dimethylethanolamine aqueous solution (25 mass%), and 2 parts of a defoamer (manufactured by SAN NOPCO LIMITED, trade name "SN-Defoamer 373") were mixed with each other and stirred with a disper to give a base resin liquid for a coating material.

100 parts of the base resin liquid for a coating material were mixed with 17 parts of a water dispersible polyisocyanate (manufactured by DIC Corporation, trade name "BURNOCK DNW-5000"), and the mixture was stirred with a disper to give an aqueous two-component urethane-based coating material A.

[0100] (Production Example 51) Production of aqueous carbodiimide-based coating material

100 parts of 4,4-dicyclohexylmethane diisocyanate were subjected to a reaction in the presence of 1 part of 3-methyl-1-phenyl-2-phospholene-1-oxide as a carbodiimidation catalyst at 170°C for 8 hours to give a carbodiimide compound having about 3 carbodiimide groups per molecule and having isocyanate groups at both terminals (isocyanate equivalent: 450 g/equivalent).

To 360 parts of a solution obtained by diluting the carbodiimide compound with methyl isobutyl ketone to 50 mass% were added 0.02 part of dibutyltin laurate and 165 parts of polypropylene glycol having a molecular weight of 2,000, and the mixture was subjected to a reaction at 85°C for 1 hour. Subsequently, 125 parts of polyethylene glycol monomethyl ether having 15 repeat units were added thereto, and the resultant mixture was subjected to a reaction at 85°C for 1.5 hours.

After the confirmation of disappearance of the isocyanate groups with an infrared spectrophotometer, 920 parts of deionized water were added, and the mixture was stirred to homogeneity. Methyl isobutyl ketone and water were distilled off at 40°C under reduced pressure so that an effective component was adjusted to 40 mass% to give an aqueous carbodiimide curing agent having a carbodiimide

equivalent of 825 g/equivalent.

Next, to 35 parts of a pigment paste obtained by mixing and dispersing, with a disper, 6.8 parts of water, 1 part of a pigment dispersant (manufactured by BYK-Chemie, trade name "Disperbyk-190"), 1 part of ethylene glycol, 0.2 part of a defoamer, 2 parts of barium sulfate, and 24 parts of titanium oxide were added 35 parts of an acrylic emulsion (acid value: 30 mgKOH/g, solid content: 55 mass%), 8 parts of a water-soluble acrylic resin (acid value: 55 mgKOH/g, hydroxyl value: 70 mgKOH/g, mass average molecular weight: 9,000, solid content: 30 mass%), 3 parts of a film forming aid (manufactured by CHISSO CORPORATION, trade name "CS-12"), 1 part of a viscosity agent, and 1 part of a defoamer to give a base resin liquid for a coating material.

To the resultant base resin liquid for a coating material were added 35 parts of the aqueous carbodiimide curing agent produced previously, and the mixture was stirred with a disper to give an aqueous carbodiimide-based coating material.

[0101] (Production of undercoating material)

(Production Example 52) Production of aqueous organic zinc-rich coating material

8.8 parts of a water-soluble polyamine resin (manufactured by Air Products and Chemicals, Inc., trade name "Sunmide WH-910,"

active hydrogen equivalent: 135 g/equivalent (in terms of solid content), solid content: 60%), 1.2 parts of a viscosity agent, and 6 parts of water were mixed with each other to give a curing agent.

The curing agent, 16 parts of an emulsified epoxy resin (manufactured by ADEKA CORPORATION, trade name "ADEKA RESIN EM-101-50," epoxy equivalent: 500 g/equivalent, solid content: 47%), and 68 parts of zinc powder were mixed, and the mixture was stirred with a disper to give an aqueous organic zinc-rich coating material.

[0102] (Example 1) Formation of single-layer coating film

An aqueous coating composition 1 was prepared under an environment of 30°C by the method of Production Example 29, and 24 hours after the preparation, the aqueous coating composition 1 was applied onto a sandblasted steel sheet with a brush in an application amount of 200 g/m² and dried under an environment of 20°C for 7 days to form a single-layer coating film (thickness after drying: 60 μm) formed with the aqueous coating composition 1. At that time, the aqueous coating composition 1 did not gelate and was able to be applied with good workability. The resultant single-layer coating film subjected to the evaluation for "corrosion resistance." Table 4 shows the evaluation results.

[0103] (Examples 2 to 19) Formation of single-layer coating film

Single-layer coating films were obtained in the same manner as in Example 1 except that the aqueous coating compositions shown in Table 4 were used instead of the aqueous coating composition 1. It should be noted that, although the aqueous coating compositions were used 24 hours after the preparation in all Examples, none of the aqueous coating compositions gelled. The resultant single-layer coating films were subjected to the same evaluation as in Example 1. Table 4 shows the evaluation results.

[0104] (Example 20) Formation of single-layer coating film

The aqueous coating composition 1 was prepared under an environment of 5°C by the method of Production Example 29, and 1 hour after the preparation, the aqueous coating composition 1 was applied onto a polished steel sheet with a brush in an application amount of 200 g/m² and dried under an environment of 5°C for 24 hours to form a single-layer coating film (thickness after drying: 60 μm) formed with the aqueous coating composition 1. At that time, the aqueous coating composition 1 did not gelate and was able to be applied with good workability. The resultant coating film was subjected to the evaluation for "initial rain resistance." Table 4 shows the evaluation results.

[0105] (Examples 21 to 38) Formation of single-layer coating film

Single-layer coating films were obtained in the same manner

as in Example 20 except that the aqueous coating compositions shown in Table 4 were used instead of the aqueous coating composition 1. It should be noted that, although the aqueous coating compositions were used 1 hour after the preparation in all Examples, none of the aqueous coating compositions gelled. The resultant single-layer coating films were subjected to the same evaluation as in Example 20. Table 4 shows the evaluation results.

[0106] (Example 39) Formation of single-layer coating film

The aqueous coating composition 1 was prepared under an environment of 23°C by the method of Production Example 29, and 24 hours after the preparation, the aqueous coating composition 1 was applied onto a polished steel sheet degreased with xylene with a brush in an application amount of 200 g/m² and dried under an environment of 23°C for 7 days to form a single-layer coating film (thickness after drying: 60 μm) formed with the aqueous coating composition 1. At that time, the aqueous coating composition 1 did not gelate and was able to be applied with good workability. The resultant coating film was subjected to the evaluation for "water-resistant adhesive property." Table 4 shows the evaluation results.

[0107] (Examples 40 to 57) Formation of single-layer coating film

Single-layer coating films were obtained in the same manner

as in Example 39 except that the aqueous coating compositions shown in Table 4 were used instead of the aqueous coating composition 1. It should be noted that, although the aqueous coating compositions were used 24 hours after the preparation in all Examples, none of the aqueous coating compositions gelled. The resultant single-layer coating films were subjected to the same evaluation as in Example 39. Table 4 shows the evaluation results.

[0108] [Table 4]

No.	State	Epoxy group equivalent	Amino group equivalent	Blending amount (parts)									
				Example 1 20 39	Example 2 21 40	Example 3 22 41	Example 4 23 42	Example 5 24 43	Example 6 25 44	Example 7 26 45	Example 8 27 46	Example 9 28 47	Example 10 29 48
				Aqueous coating composition 1 (Production Example 29)	Aqueous coating composition 2 (Production Example 30)	Aqueous coating composition 3 (Production Example 31)	Aqueous coating composition 4 (Production Example 32)	Aqueous coating composition 5 (Production Example 33)	Aqueous coating composition 6 (Production Example 34)	Aqueous coating composition 7 (Production Example 35)	Aqueous coating composition 8 (Production Example 36)	Aqueous coating composition 9 (Production Example 37)	Aqueous coating composition 10 (Production Example 38)
I	Water-dispersible	1,079	1,184	500		500		500		500		500	
II	Water-dispersible	1,079	1,093		500		500		500		500		500
III	Water-dispersible	730	810										
IV	Water-dispersible	3,000	1,550										
V	Water-soluble	1,079	1,093										
VI	Water-dispersible	1,079	1,093										
VII	Water-dispersible	1,079	1,093										
VIII	Water-dispersible	2,200	1,150										
Base resin liquid for coating material				Blending amount (parts)									
No.	Property	Acryloyl group equivalent											
I	Self-emulsifying	254		40									
II	Water-insoluble	99			20								
III	Water-insoluble	99				10							
IV	Water-insoluble	284					85						
V	Water-insoluble	207						45					60
VI	Self-emulsifying	388							65				

NPP11067PCT

	VII	Water-insoluble	217													
	VIII	Water-insoluble	256										60			
	IX	Water-insoluble	157											20		
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 3,200: a1/a2																
Acryloyl group equivalent/amino group equivalent			10/0	10/0	10/0	10/0	10/0	10/0	10/0	10/0	10/0	10/0	10/0	10/0	10/0	10/0
Corrosion resistance (Examples 1 to 19) Initial rain resistance (Examples 20 to 38) Water-resistant adhesive property (Examples 39 to 57)			1.1	1.3	0.7	1.9	1.5	1.1	1.3	1.5	0.9	1.8				
			A	A	A	A	A	A	A	A	A	A	A	A	A	A
			A	A	A	A	A	A	A	A	A	A	A	A	A	A
			10 points	10 points	10 points	10 points	10 points	10 points	10 points	10 points	10 points	10 points	10 points	10 points	10 points	10 points

Curing agent	VIII	Water-dispersible	2,200	1,150															
	No.	Property	Acryloyl group equivalent		Blending amount (parts)														
	I	Self-emulsifying	254																
	II	Water-insoluble	99																
	III	Water-insoluble	99																
	IV	Water-insoluble	284	75															
	V	Water-insoluble	207																
	VI	Self-emulsifying	388																
	VII	Water-insoluble	217																
	VIII	Water-insoluble	256																
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 3,200: a1/a2	IX	Water-insoluble	157		25	30	30	30	1.7	1.0	1.9	2.0	2.0	35	35	35		10/0	10/0
	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 3,200: a1/a2			10/0	7/3	3/7	3/7	0/10	5/5	4/6	10/0	10/0	10/0	10/0	10/0	10/0	10/0	10/0	10/0
	Acryloyl group equivalent/amino group equivalent			1.2	1.1	1.5	1.5	1.7	1.0	1.9	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
	Corrosion resistance (Examples 1 to 19)			A	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A
Water-resistant adhesive property (Examples 39 to 57)	Initial rain resistance (Examples 20 to 38)			A	AA	AA	AA	AA	AA	AA	AA	AA	AA	AA	AA	AA	AA	AA	AA
	Water-resistant adhesive property (Examples 39 to 57)			10 points	10 points	10 points	10 points	8 points	10 points	10 points	10 points	10 points	10 points	10 points	10 points	10 points	10 points	10 points	10 points

[0109] (Example 58) Formation of multilayer coating film (two layers)

As a substrate, a polished steel sheet degreased with xylene was used. The aqueous coating composition 12 obtained in Production Example 40 was applied under an environment of 5°C onto the substrate with a brush in an application amount of 200 g/m² and then dried for 24 hours at the same environment as in application to give a coating film (thickness after drying: 60 μm) formed with the aqueous coating composition I. The resultant coating film had no finger feeling (specifically, no sticky feeling) and a top coating material was able to be applied thereonto.

A solvent type epoxy/amine-based coating material A (manufactured by NIPPON PAINT Co., Ltd., trade name "Epotal NB-20") was applied as the top coating material onto the resultant coating film under an environment of 5°C with a brush in an application amount of 200 g/m² and then dried at 25°C for 24 hours to form a topcoatinglayer (thicknessafterdrying: 60 μm). Thus, a multilayer coating film (two layers) was obtained.

The resultant multilayer coating film (two layers) was subjected to the evaluation for "water-resistant adhesive property." Table 5 shows the evaluation results.

[0110] (Examples 59 to 68) Formation of multilayer coating film

(two layers)

Multilayer coating films (two layers) were obtained using the substrates, aqueous coating compositions, and top coating materials shown in Table 5 under the conditions shown in Table 5 in accordance with the method described in Example 58. The top coating materials used in Examples 59 to 68 and shown in Table 5 are as follows. It should be noted that the polished steel sheet used in Example 59 had been degreased with xylene in advance, and the slate sheet used in Example 65 had had an aqueous sealer for an inorganic material (manufactured by NIPPON PAINT CO., LTD., trade name "Ultra Sealer III") applied onto its surface in advance.

Any of the coating films formed with the aqueous coating compositions had no finger feeling (specifically, no sticky feeling) and the top coating materials were able to be applied thereonto.

In addition, the resultant multilayer coating films (two layers) were subjected to the same evaluation as in Example 58. Table 5 shows the evaluation results.

(Top coating material)

1. Solvent type epoxy/amine-based coating material A

As the solvent type epoxy/amine-based coating material A, "Epotal NB-20" (trade name) manufactured by NIPPON PAINT Co., Ltd. was used.

2. Solvent two-component urethane-based coating material A

As the solvent two-component urethane-based coating material A, "HI-PON 50 FINE" (trade name) manufactured by NIPPON PAINT Co., Ltd. was used.

3. Solvent two-component urethane-based coating material B

As the solvent two-component urethane-based coating material B, "NIPPE URETOP ECO" (trade name) manufactured by NIPPON PAINT Co., Ltd. was used.

4. Aqueous epoxy/amine-based coating material A

As the aqueous epoxy/amine-based coating material A, the aqueous epoxy/amine-based coating material A produced in Production Example 48 was used.

5. Aqueous two-component urethane-based coating material A

As the aqueous two-component urethane-based coating material A, the aqueous two-component urethane-based coating material A produced in Production Example 50 was used.

6. Aqueous emulsion-based coating material

As the aqueous emulsion-based coating material, "ODE COAT G" (trade name) manufactured by NIPPON PAINT Co., Ltd. was used.

7. Aqueous carbodiimide-based coating material

As the aqueous carbodiimide-based coating material, the aqueous carbodiimide-based coating material produced in Production Example 51 was used.

[0111] [Table 5]

Substrate	Example 58		Example 59		Example 60		Example 61		Example 62		Example 63	
	Kind of coating material	Polished steel sheet	Aqueous coating composition 12	Polished steel sheet	Aqueous coating composition 2	Zinc-plated steel sheet	Aqueous coating composition 2	Zinc-plated steel sheet	Aqueous coating composition 13	Galvalume steel sheet	Aqueous coating composition 13	Galvalume steel sheet
Aqueous coating composition	Application environment	5°C	Brush	25°C	Brush	5°C	Brush	25°C	Brush	5°C	Brush	25°C
	Application method											
	Application amount	200 g/m ²	Brush	200 g/m ²	Brush	200 g/m ²	Brush	200 g/m ²	Brush	180 g/m ²	Brush	210 g/m ²
	Drying environment	5°C×1 day		25°C×1 day		5°C×1 day		25°C×1 day		5°C×1 day		25°C×1 day
	Thickness	60 μm		60 μm		60 μm		60 μm		60 μm		60 μm
100 Coating material	Kind of coating material	Solvent type epoxy/amine-based coating material A	Solvent type epoxy/amine-based coating material A	Solvent type epoxy/amine-based coating material A	Solvent type epoxy/amine-based coating material A	Solvent type epoxy/amine-based coating material A	Solvent type epoxy/amine-based coating material A	Solvent type epoxy/amine-based coating material A	Aqueous epoxy/amine-based coating material A	Aqueous epoxy/amine-based coating material A	Aqueous epoxy/amine-based coating material A	Aqueous epoxy/amine-based coating material A
	Application environment	5°C		25°C		5°C		25°C		5°C		25°C
	Application method	Brush	Brush	Brush	Brush	Brush	Brush	Brush	Brush	Brush	Brush	Brush
	Application amount	200 g/m ²		200 g/m ²		100 g/m ²		100 g/m ²		130 g/m ²		130 g/m ²
	Drying environment	25°C×1 day		25°C×1 day		25°C×1 day		25°C×1 day		25°C×1 day		25°C×1 day
Water-resistant adhesive property	Thickness	60 μm		60 μm		60 μm		60 μm		60 μm		60 μm
	Water-resistant adhesive property	10 points		10 points		10 points		10 points		10 points		10 points

Substrate	Example 64	Example 65	Example 66	Example 67	Example 68
	Glass sheet	slate sheet	Stainless steel sheet	Dull steel sheet	Zinc phosphate-treated steel sheet

Aqueous coating composition	Kind of coating material	Aqueous coating composition 5	Aqueous coating composition 10	Aqueous coating composition 17	Aqueous coating composition 7	Aqueous coating composition 8
	Application environment	25°C	25°C	25°C	25°C	25°C
	Application method	Spray	Roller	Roller	Airless spray	Airless spray
	Application amount	140 g/m ²	240 g/m ²	100 g/m ²	200 g/m ²	200 g/m ²
	Drying environment	25°C×1 day	25°C×1 day	25°C×1 day	80°C×20 min	80°C×20 min
Top coating material	Thickness	60 μm	60 μm	60 μm	60 μm	60 μm
	Kind of coating material	Aqueous two-component urethane-based coating material A	Aqueous emulsion-based coating material	Aqueous carbodiimide-based coating material	Solvent two-component urethane-based coating material B	Solvent two-component urethane-based coating material B
	Application environment	25°C	25°C	25°C	25°C	25°C
	Application method	Spray	Roller	Roller	Airless spray	Airless spray
	Application amount	100 g/m ²	120 g/m ²	100 g/m ²	80 g/m ²	80 g/m ²
Water-resistant adhesive property	Drying environment	25°C×1 day	25°C×1 day	25°C×1 day	80°C×20 min	80°C×20 min
	Thickness	60 μm	60 μm	60 μm	60 μm	60 μm
	Water-resistant adhesive property	10 points	10 points	10 points	10 points	10 points

[0112] (Example 69) Formation of multilayer coating film (four layers)

A sandblasted steel sheet was coated with a solvent type organic zinc-rich coating material (manufactured by NIPPON PAINT Co., Ltd., trade name "N Zinky 8000 NB") as an undercoating material so that a thickness after drying of 70 μm was achieved to form an undercoating layer.

After that, the aqueous coating composition 13 obtained in Production Example 41 was applied under an environment of 5°C with a brush onto the undercoating layer so that a thickness after drying of 60 μm was achieved, and then dried under the same environment as in its application for 1 day to give a coating film formed with the aqueous coating composition 13.

A solvent type epoxy/amine-based coating material B (manufactured by NIPPON PAINT Co., Ltd., trade name "HI-PON 30 FINE Intermediate coating") was applied as an intermediate coating material under an environment of 25°C with a brush onto the resultant coating film so that a thickness after drying of 30 μm was achieved, and then dried under the same environment as in its application for 1 day to give an intermediate coating layer.

A solvent two-component urethane-based coating material A (manufactured by NIPPON PAINT Co., Ltd., trade name "HI-PON 50 FINE")

was applied as a top coating material under an environment of 25°C with an air spray onto the intermediate coating layer so that a thickness after drying of 30 μm was achieved, and then dried under the same environment as in its application for 7 days to form a top coating layer. Thus, a multilayer coating film (four layers).

The resultant multilayer coating film (four layers) was subjected to the evaluations for "water-resistant adhesive property" and "corrosion resistance." Table 6 shows the evaluation results.

[0113] (Example 70) Formation of multilayer coating film (four layers)

A multilayer coating film (four layers) was obtained in the same manner as in Example 69 except that the undercoating material, aqueous coating composition, intermediate coating material, and top coating material shown in Table 6 were used. It should be noted that the undercoating material, intermediate coating material, and top coating material shown in Table 6 and used in Example 70 are as follows.

The resultant multilayer coating film (four layers) was subjected to the same evaluations as in Example 69. Table 6 shows the evaluation results.

(Undercoating material)

The aqueous organic zinc-rich coating material obtained in Production Example 52 was used.

(Intermediate coating material)

As the aqueous epoxy/amine-based coating material B, the aqueous epoxy/amine-based coating material B obtained in Production Example 49 was used.

(Top coating material)

As an aqueous carbodiimide-based coating material, the aqueous carbodiimide-based coating material produced in Production Example 51 was used.

[0114] [Table 6]

	Example 69	Example 70
Undercoating material	Solvent type organic zinc-rich coating material	Aqueous organic zinc-rich coating material
Aqueous coating composition	Aqueous coating composition 13	Aqueous coating composition 13
Intermediate coating material	Solvent type epoxy/amine-based coating material B	Aqueous epoxy/amine-based coating material B
Top coating material	Solvent two-component urethane-based coating material A	Aqueous carbodiimide-based coating material
Water-resistant adhesive property	10 points	10 points
Corrosion resistance	A	A

[0115] (Comparative Example 1)

A coating film formed with the solvent type epoxy/amine-based coating material A on a substrate was obtained in the same manner as in Example 58 except that the solvent type epoxy/amine-based coating material A (manufactured by NIPPON PAINT Co., Ltd., trade name "Epotal NB-20") was used instead of the aqueous coating composition 12 obtained in Production Example 40. The resultant coating film was sticky, and hence it was impossible to apply a top coating material.

[0116] As shown in each of Examples 1 to 19, according to the method of forming a coating film according to the present invention, it was possible to give a coating film excellent in corrosion resistance.

[0117] As shown in each of Examples 1 to 19 and 39 to 57, in the case of using the water-dispersible aqueous epoxy-based polyamine resin (A), the aqueous coating composition which had been stored for a long period of time did not gelate, was excellent in workability, and allowed a coating film excellent in corrosion resistance to be formed.

[0118] As shown in each of Examples 20 to 38, 58, 60, and 62, the coating film formed by the method of forming a coating film according to the present invention exhibited sufficient curability even at low temperature. On the other hand, as shown in Comparative

Example 1, the coating film formed with the conventional epoxy/amine-based coating material had insufficient curability at low temperature.

[0119] As shown in each of Examples 31 to 35, when 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 is used, a coating film excellent in initial rain resistance can be formed. Meanwhile, as shown in each of Examples 31, 32, 34, 35, 50, 51, 53, and 54, when the aqueous coating composition including the aqueous epoxy-based polyamine resin (A1) obtained using an epoxy resin (a1) having an epoxy equivalent of 400 to 1,500 and an aqueous epoxy-based polyamine resin (A2) obtained using an epoxy resin (a2) having an epoxy equivalent of 2,000 to 3,200 at a specific mass ratio (a1/a2) is used, a coating film excellent in initial rain resistance and water-resistant adhesive property can be formed.

[0120] As shown in each of Examples 58 to 68, a coating film excellent in water-resistant adhesive property was able to be obtained according to the method of forming a coating film according to the present invention by forming the top coating layer.

[0121] As shown in each of Examples 69 and 70, a coating film excellent in water-resistant adhesive property and corrosion

resistance was able to be obtained according to the method of forming a coating film according to the present invention by forming the undercoating layer, the intermediate coating layer, and the top coating layer.

Industrial Applicability

[0122] The method of forming a coating film according to the present invention can be suitably used in, for example, an anticorrosive application. Specifically, the method can be suitably applied to, for example, ships, vehicles (e.g., railway vehicles, large vehicles), aircraft, bridges, marine structures, plants, tanks (e.g., petroleum tanks), pipes, steel tubes, and cast iron tubes as well as metal parts included in architectural structures, such as doors and window frames.

Claims

[Claim 1] A method of forming a coating film, comprising coating a substrate with an aqueous coating composition to form a coating film, wherein the aqueous coating composition comprises: an aqueous epoxy-based polyamine resin (A) having one or more primary amino groups and/or secondary amino groups in a molecule; and a compound (B) having one or more (meth)acryloyl groups in a molecule.

[Claim 2] A method of forming a coating film according to claim 1, 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).

[Claim 3] A method of forming a coating film according to claim 1 or 2, wherein the aqueous epoxy-based polyamine resin (A) is water-dispersible.

[Claim 4] A method of forming a coating film according to any one of claims 1 to 3, wherein the aqueous epoxy-based polyamine resin (A) has an amino group equivalent of 100 to 3,000.

[Claim 5] A method of forming a coating film according to any one

of claims 1 to 4, 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 6] A method of forming a coating film according to any one of claims 1 to 4, wherein the aqueous epoxy-based polyamine resin (A) in the aqueous coating composition 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 7] A method of forming a coating film according to claim 6, wherein a mass ratio of the epoxy resin (a1) and the epoxy resin (a2) ($a1/a2$) is 8/2 to 2/8.

[Claim 8] A method of forming a coating film according to any one of claims 1 to 7, 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 9] A method of forming a coating film according to any one

of claims 1 to 8, wherein the compound (B) has a viscosity at 25°C of 3,000 mPa·s or less.

[Claim 10] A method of forming a coating film according to any one of claims 1 to 9, wherein the compound (B) has a molecular weight of 150 or more and 2,000 or less.

[Claim 11] A method of forming a coating film according to any one of claims 1 to 10, further comprising forming a top coating layer on the coating film after the forming of the coating film with the aqueous coating composition.

[Claim 12] A method of forming a coating film according to claim 11, further comprising forming an intermediate coating layer after the forming of the coating film with the aqueous coating composition and before the forming of the top coating layer.

[Claim 13] A method of forming a coating film according to any one of claims 1 to 12, further comprising forming a undercoating layer on substrate before the forming of the coating film with the aqueous coating composition.