

AQUEOUS COATING COMPOSITION

Technical Field

[0001] The present invention relates to an aqueous coating composition.

Background Art

[0002] In recent years, from an environmental standpoint, conversion of a solvent-based coating material into an aqueous coating material has been socially required. Example of the aqueous coating material includes a two-component aqueous coating composition containing an epoxy resin and a polyamine compound (Patent Document 1). The aqueous coating composition may exhibit sufficient curability at a temperature equal to or more than a room temperature, and may form a normal coating film. However, the composition is inferior in curability at a low temperature (for example, about 5°C). Therefore, in the case where the composition is used at a low-temperature place (for example, outdoor in winter season), the composition involves such a problem that it is difficult to exert inherent sufficient coating film properties.

Prior Art Documents

Patent Document

[0003] [Patent Document 1] JP 11-166153 A

Summary

Problem to be solved by the Invention

[0004] The present invention has been made to solve the above-mentioned conventional problem, and an object of the present invention is to provide an aqueous coating composition having excellent low-temperature curability.

Means for solving the Problems

[0005] An aqueous coating composition of the present invention includes: (A) a water-soluble or water-dispersible polyamine resin having one or more primary amine groups and/or secondary amine groups in a molecule; and (B) a compound having one or more (meth)acryloyl groups in a molecule; in which: the polyamine resin (A) has an amine equivalent of 100 to 3,000, and the compound (B) has a viscosity at 25°C of 3,000 mPa·s or less.

[0005a] In a first aspect, there is provided an aqueous coating composition, comprising: (A) a water-dispersible polyamine resin having one or more primary amine groups and/or secondary amine groups in a molecule; and (B) a compound having one or more (meth) acryloyl groups in a molecule; wherein: the aqueous coating composition is a two-component aqueous coating composition that a base coating solution comprises the polyamine resin (A) and a curing agent comprises the compound (B), the polyamine resin (A) has an amine equivalent of 100 to 3, 000, the polyamine resin (A) has a neutralization ratio of 10 to 70%, and the compound (B) has a viscosity at 25°C of 3,000 mPa s or less.

[0006] In a preferred example, the aqueous coating composition is a two-component aqueous coating composition; a base coating solution comprises the polyamine resin (A); and a curing agent comprises the compound (B).

[0007] In a preferred embodiment, the polyamine resin (A) is an acrylic polyamine resin or an epoxy-based polyamine resin.

[0008] In a preferred embodiment, the compound (B) has a

molecular weight of 150 or more and 2,000 or less.

[0009] In a preferred embodiment, the compound (B) is a water-soluble compound, and the polyamine resin (A) is a water-dispersible resin.

[0010] In a preferred embodiment, the compound (B) is a self-emulsifying compound.

[0011] In a preferred embodiment, the compound (B) is emulsified or dispersed by the polyamine resin (A).

[0012] In a preferred embodiment, the compound (B) is a mixture of a water-soluble compound and a non-water-soluble compound.

[0013] In a preferred embodiment, the compound (B) is an emulsified compound.

[0014] In a preferred embodiment, the curing agent further comprises an emulsifier.

Effects of the Invention

[0015] The aqueous coating composition of the present invention exhibits excellent low-temperature curability by containing: (A) a water-soluble or water-dispersible polyamine resin having one

or more primary amine groups and/or secondary amine groups in a molecule; and (B) a compound having one or more (meth)acryloyl groups in a molecule. That is, when the polyamine resin (A) and the compound (B) are used, the resin and compound becomes highly reactive with each other to promote a reaction even at a low temperature. Therefore, an aqueous coating composition having excellent low-temperature curability can be obtained. Further, a product obtained by the reaction of the polyamine resin (A) and the compound (B) may have a structure formed by crosslinking of the polyamine resin (A) by the compound (B), and hence an aqueous coating composition having excellent coating film properties can be obtained.

Description of Embodiments

[0016] A. Summary of aqueous coating composition

The aqueous coating composition of the present invention contains: (A) a water-soluble or water-dispersible polyamine resin having one or more primary amine groups and/or secondary amine groups in a molecule; and (B) a compound having one or more (meth)acryloyl groups in a molecule, and the composition cures by the reaction of the polyamine resin (A) and the compound (B), to thereby obtain a coating film.

[0017] The aqueous coating composition of the present invention is preferably a two-component aqueous coating composition including a base coating solution and a curing agent, in which the base coating

solution contains the polyamine resin (A), and the curing agent contains the compound (B). When the polyamine resin (A) and the compound (B) are used as the two-component aqueous coating composition, a combination of the polyamine resin (A) and the compound (B) in which the resin and compound are highly reactive with each other can be selected, to thereby obtain an aqueous coating composition having excellent low-temperature curability.

[0018] The content of the polyamine resin in terms of a solid content is preferably 5 to 95 wt%, more preferably 10 to 90 wt% with respect to the total solid content of the aqueous coating composition.

[0019] The content of the compound (B) is preferably 2 to 40 wt%, more preferably 5 to 30 wt% with respect to the total solid content of the aqueous coating composition.

[0020] The ratio of the number of the amine groups in the polyamine resin (A) to the number of the (meth)acryloyl groups in the compound (B) (amine group:acryloyl group) is preferably 1:0.5 to 1:1.5, more preferably 1:0.75 to 1:1.25, particularly preferably 1:0.9 to 1:1.1. It should be noted that, the phrase "number of amine groups" as used herein refers to the number of the primary amine groups (that is, the number of the secondary amine groups is excluded) in the case where the polyamine resin (A) has the primary amine

groups in a molecule (including the case where the polyamine resin (A) has the primary amine groups and the secondary amine groups), or refers to the number of the secondary amine groups in the case where the polyamine resin (A) has only the secondary amine groups in a molecule.

[0021] A pigment, a solvent, an additive, or the like may be blended, as required, into the aqueous coating composition of the present invention. Examples of the pigment include: coloring pigments such as titanium oxide, yellow iron oxide, red iron oxide, carbon black, phthalocyanine blue, phthalocyanine green, azo red, quinacridone red, and benzimidazolone yellow; and extender pigments such as calcium carbonate, barium sulfate, kaolin, clay, and talc. 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 (CS-12), 2,2,4-trimethyl-1,3-pentanediol diisobutyrate (CS-16), diethyl adipate, and diisobutyl adipate. Examples of the additive include a dispersant, a viscosity adjuster, a curing catalyst, a surface modifier, an antifoaming agent, a

plasticizer, a film-forming aid, a UV absorbing agent, and an antioxidant.

[0022] B. Polyamine resin (A)

The polyamine resin (A) to be used in the aqueous coating composition of the present invention may be any appropriate resin as long as the resin has one or more primary amine groups and/or secondary amine groups, and is a water-soluble or water-dispersible resin. Examples of the resin include an aliphatic polyamine resin, an aromatic polyamine resin, and an alicyclic polyamine resin.

[0023] The amount of the amine groups in the polyamine resin (A) is, as an amine equivalent, 100 to 3,000, more preferably 500 to 2,000, particularly preferably 800 to 1,500. If the amine equivalent of the polyamine resin (A) is in such range, the polyamine resin (A) is water-soluble or water-dispersible, and a coating film having excellent low-temperature curability can be obtained. The amine equivalent is represented by the molecular weight of a resin solid content per primary amine group in the case where the polyamine resin (A) has the primary amine groups, or is represented by the molecular weight of a resin solid content per secondary amine group in the case where the polyamine resin (A) has no primary amine group. The amine equivalent of the polyamine resin (A) can be determined from the blending amounts of raw materials.

[0024] The molecular weight (number average) of the polyamine resin (A) may be any appropriate molecular weight depending on desired coating film properties. The molecular weight is preferably 500 to 20,000, more preferably 1,000 to 3,000 in terms of standard polystyrene measured by gel permeation chromatography (GPC). If the molecular weight of the polyamine resin (A) is in such range, the polyamine resin (A) can react efficiently with the compound (B) because the resin can be easily mixed with the compound. Meanwhile, if the molecular weight of the polyamine resin (A) is in such range, a coating film having excellent anticorrosion property, water resistance, and adhesive property can be obtained.

[0025] The glass-transition temperature of the polyamine resin (A) may be any appropriate glass-transition temperature depending on desired coating film properties. The glass-transition temperature is preferably -50 to 100°C, more preferably 0 to 50°C.

[0026] The polyamine resin (A) may be converted into an aqueous resin by neutralization of the amine groups with an acid before use. The type of the acid and a neutralization ratio (neutralization ratio with respect to the amine groups in the polyamine resin before conversion into an aqueous resin) may be any appropriate type and neutralization ratio depending on desired state of the polyamine resin (A) (water-soluble to water-dispersible form). Examples of the acid include an acetic acid, a formic acid, a lactic acid, and

a phosphoric acid. The neutralization ratio (neutralization ratio with respect to the amine groups in the polyamine resin before conversion into an aqueous resin) is preferably 10 to 70%, more preferably 15 to 50%.

[0027] The polyamine resin (A) is preferably an epoxy-based polyamine resin obtained by amine-denaturation of an epoxy resin or an acrylic polyamine resin obtained by amine-denaturation of an acrylic resin. Of those, the epoxy-based polyamine resin is particularly preferred. This is because, if the resin is the epoxy-based polyamine resin, it is possible to obtain an aqueous coating composition which is more excellent in anticorrosion property. That is, when the epoxy-based polyamine resin serving as the polyamine resin (A) and the compound (B) are used, it is possible to obtain an aqueous coating composition which can form a coating film that exerts excellent anticorrosion property comparable to or superior to that of a conventional epoxy resin coating composition including an epoxy resin and a polyamine compound even at a low temperature.

[0028] The epoxy-based polyamine resin and acrylic polyamine resin can be obtained by any appropriate denaturation method. Examples of the denaturation method include: a method of adding a primary amine group-containing polyamine to an epoxy resin or an acrylic resin; and a method of adding a ketiminated amine

group-containing compound to an epoxy resin or an acrylic resin. The polyamine resin (A) obtained as described above has one or more primary amine groups and/or secondary amine groups, and secondary hydroxyl groups in a molecule. The polyamine resin may be a resin obtained by a reaction of part of the primary amine groups, secondary amine groups, and/or hydroxyl groups in the polyamine resin (A) with a compound having a functional group such as an epoxy group, an acid anhydride group, an acid halogen group, or an isocyanate group. If a polyamine resin obtained by a reaction of such functional group is included as part of the polyamine resin to be used, physical properties of a resultant coating film can be adjusted.

[0029] The method of adding the primary amine group-containing polyamine to the epoxy resin or acrylic resin is a method involving reacting a primary amine group in the primary amine group-containing polyamine with a reactive group in the epoxy resin or acrylic resin (such as an epoxy group) to form a secondary amine group, resulting in producing the epoxy-based polyamine resin or acrylic polyamine resin having the secondary amine group.

[0030] The method of adding the ketiminated amine group-containing compound to the epoxy resin or acrylic resin is a method involving reacting the ketiminated amine group-containing compound with the epoxy resin or acrylic resin and then hydrolyzing the ketimine group to form a primary amine group, resulting in

producing the epoxy-based polyamine resin or acrylic polyamine resin having the primary amine group. It should be noted that the reaction of the ketiminated amine group-containing compound with the epoxy resin or acrylic resin may be carried out in the presence of a secondary amine such as diethanolamine, methylethanolamine, or diethylamine.

[0031] As the epoxy resin, any appropriate epoxy resin may be used. The resin is preferably a bisphenol A-type epoxy resin or a bisphenol F-type epoxy resin, and is particularly preferably a bisphenol A-type epoxy resin.

[0032] The epoxy equivalent of the epoxy resin may be determined depending on desired coating film properties. The epoxy equivalent is preferably 180 to 2,000, more preferably 400 to 1,500. If the epoxy equivalent of the epoxy resin is in such range, a coating film having excellent water resistance, anticorrosion property, and adhesive property can be obtained.

[0033] Chain elongation of the epoxy resin may be carried out by 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 denature the resin. Examples of the active hydrogen-containing compound include a bifunctional compound such as a dimer acid, diamine, or polyether polyol.

[0034] Depending on applications, before amine denaturation, the number of epoxy groups in the epoxy resin may be decreased by adding a fatty acid to reduce sites to be amine-denatured and lower the reactivity before use.

[0035] Any appropriate acrylic resin may be used as the acrylic resin. An acrylic resin obtained by copolymerizing a monomer composition containing a radical polymerizable monomer having an epoxy group and/or a glycidyl group is preferred. Examples of the radical polymerizable monomer having an epoxy group and/or a glycidyl group include glycidyl acrylate, glycidyl methacrylate, methyl glycidyl acrylate, methyl glycidyl methacrylate, 3,4-epoxycyclohexylmethyl acrylate, and 3,4-epoxycyclohexylmethyl methacrylate.

[0036] Examples of the primary amine group-containing polyamine include diethylenetriamine, dipropylenetriamine, dibutylenetriamine, and triethylenetetramine. They may be used alone or in combination.

[0037] The ketiminated amine group-containing compound can be obtained by reacting a primary amine group-containing compound with ketone. Examples of the primary amine group-containing compound include: primary amine 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.

[0038] C. Compound (B)

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

[0039] 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. If the molecular weight of the compound (B) is in such range, the polyamine resin (A) and the compound (B) can be easily mixed without using a special mixing device, to thereby obtain a coating composition having excellent dispersibility. As a result, the polyamine resin (A) and the compound (B) can react with each other efficiently, to thereby obtain an aqueous coating composition having excellent curability. It should be noted that the molecular weight of the compound (B) can be calculated from the chemical formula.

[0040] The number of the (meth)acryloyl group in the compound (B) is 1 or more, preferably 2 to 4. The number of the (meth)acryloyl group in the compound (B) may be determined depending on desired

coating film properties.

[0041] The viscosity of the compound (B) at 25°C is 3,000 mPa·s or less, preferably 50 mPa·s or more and 3,000 mPa·s or less, more preferably 50 mPa·s or more and 2,200 mPa·s or less, particularly preferably 50 mPa·s or more and 1,100 mPa·s or less. If the viscosity of the compound (B) is in such range, the polyamine resin (A) and the compound (B) can be easily mixed without using a special mixing device, to thereby obtain a coating composition having excellent dispersibility. As a result, the polyamine resin (A) and the compound (B) can react with each other efficiently, to thereby obtain an aqueous coating composition having excellent curability.

[0042] 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 monomer and
 carboxyl group-containing, ethylenically unsaturated monomer (such
 as a reaction product between glycidyl acrylate or glycidyl
 methacrylate and an acrylic acid, a methacrylic acid, a crotonic
 acid, or a maleic acid), and polymerizable unsaturated
 monocarboxylic acid amide compounds of polyamines (such as
 ethylenediamine diacrylate). They may be used alone or in
 combination.

[0043] As described above, the compound (B) is required to be
 capable of being easily mixed with (capable of reacting with) the
 polyamine resin (A). Preferably, the polyamine resin (A) and the
 compound (B) are used in an inhomogeneous state in such a range
 that the resin and compound can be easily mixed (can react with
 each other). More preferably, the compound (B) and the polyamine
 resin (A) are used in different phase states. In such states, an

acute reaction progress of the polyamine resin (A) and the compound (B) can be inhibited to appropriately adjust the reactivity. Therefore, for example, in the case of using the aqueous coating composition of the present invention is used as a two-component coating material, an aqueous coating composition having excellent handling property can be obtained. Preferred examples of the states include: a case where the compound (B) is a water-soluble compound, and the polyamine resin (A) is a water-dispersible resin; a case where the compound (B) is self-emulsifying; and a case where the compound (B) is emulsified or dispersed by the polyamine resin (A). It should be noted that a determination of whether the compound (B) is "non-water-soluble", "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 the state visually. After allowing the mixture to stand still, if the mixture contains precipitate, the compound is judged to be "non-water-soluble", 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".

[0044] In the case where the compound (B) has been denatured by, for example, polyethylene oxide, the compound may be converted into a water-soluble or self-emulsifying compound by increasing

the ethylene oxide addition mole number to enhance its hydrophilicity.

[0045] Examples of the water-soluble compound (B) 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 the molecule.

[0046] Examples of the self-emulsifying compound (B) 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.

[0047] Examples of the compound (B) that may be emulsified or dispersed by the polyamine resin (A) include polyethylene glycol #200 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.

[0048] The compound (B) may be preferably used as a mixture of a water-soluble compound and a non-water-soluble compound. If such mixture of the water-soluble compound and the non-water-soluble compound is used, the non-water-soluble compound can be easily introduced into a reaction system by the water-soluble compound. Further, the resultant coating material is excellent in low-temperature curability. Examples of the water-soluble compound having one or more (meth)acryloyl groups in a molecule include the above-mentioned water-soluble compound (B). Examples of the non-water-soluble compound having one or more (meth)acryloyl groups in a molecule include a compound which is not completely soluble in water, such as propoxylated bisphenol A diacrylate (PO 4 mol). The mixing ratio of the water-soluble compound (B) and the non-water-soluble compound (B) (water-soluble/non-water-soluble) is preferably 1/9 to 9/1, more preferably 2/8 to 8/2.

[0049] In one embodiment, before mixing of the polyamine resin (A) and the compound (B), the compound (B) may be diluted with an organic solvent. Examples of the organic solvent include ethylene

glycol monobutyl ether (BC) and diethylene glycol monobutyl ether (BDG). When the compound (B) is diluted in advance with an organic solvent as described above, the polyamine resin (A) and the compound (B) can be easily mixed without using a special mixing device, to thereby obtain a coating composition having excellent dispersibility. As a result, the polyamine resin (A) and the compound (B) can react with each other efficiently.

[0050] In another embodiment, the compound (B) is an emulsion. That is, before mixing of the polyamine resin (A) and the compound (B), an emulsifier may be mixed with the compound (B), or the compound (B) may be emulsified or dispersed by a dispersant, an emulsifier, or an aqueous resin. Moreover, in the case where the aqueous coating composition of the present invention is a two-component aqueous coating composition, an emulsifier may further be added to the above-mentioned curing agent. If such treatment is carried out, the polyamine resin (A) and the compound (B) can be mixed without using a special mixing device, to thereby obtain a coating composition having excellent dispersibility. As a result, the polyamine resin (A) and the compound (B) can react with each other efficiently. Further, if such treatment is carried out, the compound (B) can be treated as a nonhazardous material. A nonionic emulsifier, an anionic emulsifier, or the like may be used as the emulsifier. Examples of the nonionic emulsifier include a polyoxyethylene alkylphenol ether, a 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 sulfosuccinic 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 sodium polyacrylate and an ammonium salt of a half ester of a styrene-maleic acid copolymer. Examples of the aqueous resin include a sodium salt of a polyacrylic acid ester.

[0051] In still another embodiment, before mixing of the polyamine resin (A) and the compound (B), the compound (B) may be dispersed in a dispersing element of a resin different from the polyamine resin (A). Examples of the dispersing element of the resin include an emulsion and dispersion of an acrylic resin and an emulsion and dispersion of a urethane resin. When the compound (B) is dispersed in the dispersing element of the resin in advance as described above, the polyamine resin (A) and the compound (B) can be mixed without using a special mixing device, to thereby obtain a coating composition having excellent dispersibility. As a result, the polyamine resin (A) and the compound (B) can react with each other efficiently.

[0052] D. Coating method

The aqueous coating composition of the present invention may be applied to any appropriate matter to be coated. A typical matter to be coated is a surface of iron.

[0053] Examples of a method of applying the aqueous coating composition of the present invention include brush coating, air spray, airless spray, and roller application.

[0054] The application amount of the aqueous coating composition of the present invention may be set to any appropriate application amount depending on applications. In general, the amount is preferably 10 to 300 g/m².

[0055] A method of drying the aqueous coating composition of the present invention may be any appropriate drying method. The method is preferably natural drying or heat drying. That is, the aqueous coating composition of the present invention may be used as a coating composition capable of curing at ordinary temperature, or may be used as a coating composition capable of curing by heating. In the case of natural drying, the drying time is preferably 24 hours or more, more preferably 1 week or more.

Examples

[0056] 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 by weight. Further, evaluation items in the examples are as follows.

[0057] (Coating film condition)

Coating materials obtained in Examples and Comparative Examples were each applied onto a glass plate and dried (for 24 hours) at 25°C, and the coated glass plate was visually observed to evaluate the coating film for its burnish, transparency, and coating film defects such as blisters and cissings.

Burnish o: Highly burnished

 Δ: Moderately burnished

 x: Not burnished

Transparency o: No or little turbidity

 Δ: Moderate turbidity

 x: Severe turbidity

Coating film defects o: No or few blisters and cissings

 Δ: A few blisters and cissings

 x: blisters and cissings across the
surface

(Curability)

The coating materials obtained in Examples and Comparative Examples were each applied onto glass plates and dried (for 24 hours) at 25°C and 5°C to obtain coating films. The coating films were

each rubbed with gauze impregnated with methyl ethyl ketone (MEK) at the same temperature as that in its application and drying, and the number of times of reciprocation until a glass base material was exposed was measured. It should be noted that the notation ">200" in the tables means that the glass base material was not exposed even when the number reached 200. Further, if the number of times of reciprocation until exposure is 100 or more, the coating film is evaluated to be acceptable.

(Anticorrosion property)

The coating films obtained in Examples were each applied onto a sandblast plate using a brush at 200 g/m² and dried at 20°C for seven days, to thereby obtain a test specimen. A cycle corrosion test, specified in JIS K 5600 7-7, was carried out for the test specimen. After 120 cycles, the coating film condition was confirmed based on the following criteria.

The ratio of a corrosion area in a coating film with respect to the surface of the test specimen.

◎: less than 0.05%

○: 0.05% or more and less than 0.1%

△: 0.1% or more and less than 0.3%

×: 0.3% or more

[0058] [Production Example 1] Preparation of polyamine resin (epoxy-based polyamine resin)

702 parts of an epoxy resin having an epoxy equivalent of 188,

which was synthesized from bisphenol A and epichlorohydrin, 269 parts of bisphenol A, 108 parts of 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 in the presence of 1 part of benzyldimethylamine at 117°C until the epoxy equivalent reached 1,270. After that, 255 parts of a ketimine compound of aminoethylethanolamine (73 wt% MIBK solution) were added thereto, and the mixture was allowed to react at 117°C for one 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 a number average molecular weight of 2,400 and an amine equivalent of 1,184.

[0059] [Production Example 2] Emulsification of epoxy-based polyamine resin

Acetic acid was added to the epoxy-based polyamine resin obtained in Production Example 1 so that a neutralization ratio (neutralization ratio of the resin based on amine 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 wt% was achieved, to thereby prepare Emulsion I.

[0060] [Production Example 3] Preparation of polyamine resin

(acrylic polyamine resin)

670 parts of MIBK were fed to a reactor equipped with a stirrer, a cooler, a nitrogen injection tube, a thermometer, and a dropping funnel, and the mixture was heated to 110°C. A solution containing 540 parts of styrene, 400 parts of n-butyl acrylate, 140 parts of glycidyl methacrylate, 100 parts of MIBK, and 20 parts of t-butyl peroctoate was added dropwise over three hours to the reactor using the dropping funnel. After completion of the dropwise addition, the mixture was maintained at 110°C for 30 minutes, and then a solution containing 2 parts of t-butyl peroctoate and 50 parts of MIBK was added dropwise over 30 minutes. After completion of the dropwise addition, the reaction was further continued at 110°C for one hour, to thereby obtain an acrylic resin varnish having a nonvolatile content (including epoxy groups) of 60%. To 1,920 parts of the resultant varnish were added 255 parts of a ketimine compound of aminoethylethanolamine (73 wt% MIBK solution), and the mixture was allowed to react at 117°C for one hour, to thereby obtain an acrylic polyamine resin having a number average molecular weight of 10,000 and an amine equivalent of 1,184.

[0061] [Production Example 4] Emulsification of acrylic polyamine resin

Acetic acid was added to the acrylic polyamine resin obtained in Production Example 3 so that a neutralization ratio (neutralization ratio of the resin based on amine 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 wt% was achieved, to thereby prepare Emulsion II.

[0062] [Production Example 5] Preparation of polyamine resin (epoxy-based polyamine resin)

742 parts of an epoxy resin having an epoxy equivalent of 188, 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 in the presence of 1 part of benzyldimethylamine at 117°C until an epoxy equivalent of 1,270 was achieved. After that, 350 parts of a ketimine compound of diethylenetriamine (73 wt% 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 (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 a number average molecular weight of 2,600 and an amine equivalent of 947.

[0063] [Production Example 6] Emulsification of epoxy-based polyamine resin

Acetic acid was added to the epoxy-based polyamine resin obtained in Production Example 5 so that a neutralization ratio (neutralization ratio of the resin based on cationic 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 wt% was achieved, to thereby prepare Emulsion III.

[0064] [Example 1]

To 2,960 parts of Emulsion I obtained in Production Example 2 as a polyamine resin (A) were added 118 parts of dipropylene glycol n-butyl ether (DPnB) while stirring with a disper, and then 392 parts of ethoxylated trimethylolpropane triacrylate (EO 20 mol) (manufactured by Shin-Nakamura Chemical Co., Ltd., product name "AT-20E") were further added thereto as a compound (B) while stirring with a disper, followed by stirring for 10 minutes, to thereby obtain a clear coating material. The resultant coating material was applied onto glass plates using a 6-mil applicator under environments of 25°C and 5°C, and the material was dried for 24 hours under the same environments as in its application, to thereby obtain coating films. After that, the coating film condition and curability of each of the resultant coating films were evaluated. Table 2 shows the results.

[0065] [Examples 2 to 10]

Coating films were attained in the same manner as in Example 1 except that the compound (B) was replaced by 392 parts of ethoxylated trimethylolpropane triacrylate (EO 20 mol), and the compounds (B) shown in Table 1 were used at the contents shown in Table 2. After that, the coating film condition and curability of each of the resultant coating films were evaluated. Table 2 shows the results.

[0066] [Example 11]

Coating films were obtained in the same manner as in Example 10 except that the polyamine resin (A) was replaced by Emulsion I, and Emulsion II obtained in Production Example 4 was used. After that, the coating film condition and curability of each of the resultant coating films were evaluated. Table 2 shows the results.

[0067] [Example 12]

159 parts of ion-exchange water and 16 parts of Newcol 740 (manufactured by Nippon Nyukazai Co., Ltd., nonionic emulsifier) were dissolved homogeneously by stirring with a disper, to thereby prepare an aqueous emulsifier solution. After that, 143 parts of a compound (B), i.e., ethoxylated trimethylolpropane triacrylate (EO 3 mol) were added thereto, and the mixture was stirred with a disper for 10 minutes to roughly disperse the compound. The compound was further dispersed using an ultrasonic homogenizer until an average particle size of 350 nm was achieved, to thereby obtain an emulsion of the compound (B).

To 2,367 parts of Emulsion III obtained in Production Example 6 as a polyamine resin (A) were added 118 parts of dipropylene glycol n-butyl ether (DPnB) while stirring with a disper, and then 318 parts of the emulsion of the compound (B) obtained in the foregoing (content of the compound (B): 143 parts) were further added thereto while stirring with a disper, followed by stirring for 10 minutes, to thereby obtain a clear coating material. The resultant coating material was subjected to the same procedure as in Example 1, to thereby obtain coating films. After that, the coating film condition and curability of each of the resultant coating films were evaluated. Table 2 shows the results.

[0068] [Table 1]

Compound (B) No.	Compound (B)	Molecular weight	Viscosity (mPa·s)	Number of functional groups	Acryloyl group equivalent	Property*
1	Ethoxylated trimethylolpropane triacrylate (EO 20 mol)	1,176	350	3	392	Water-soluble
2	Ethoxylated triacrylate (EO 20 mol) glycerin	1,130	190	3	377	Water-soluble
3	Polyethylene glycol #400 diacrylate (EO 9 mol)	508	58	2	254	Self-emulsifying
4	Ethoxylated bisphenol A diacrylate (EO 10 mol)	776	620	2	388	Self-emulsifying
5	Ethoxylated bisphenol A diacrylate (EO 20 mol)	1,200	700	2	600	Self-emulsifying
6	Ethoxylated triacrylate (EO 9 mol) glycerin	650	95	3	217	Self-emulsifying
7	Ethoxylated bisphenol A diacrylate (EO 4 mol)	512	1,100	2	256	Capable of being emulsified/dispersed by the polyamine resin (A)
8	Trimethylolpropane triacrylate	296	95	3	99	Capable of being emulsified/dispersed by the polyamine resin (A)
9	Pentaerythritol triacrylate	298	700	3	99	Capable of being emulsified/dispersed by the polyamine resin (A)
10	Propoxylated bisphenol A diacrylate (PO 4 mol)	568	2,200	2	284	Non-water-soluble
11	Ethoxylated trimethylolpropane acrylate (EO 3 mol)	428	60	3	143	Non-water-soluble

* 5 g of the compound (B) were added to 100 g of water, and the mixture was stirred and allowed to stand still, followed by visual observation. If the mixture contained precipitates, the compound was evaluated to be "non-water-soluble", if the mixture contained no precipitates and was clear, the compound was evaluated to be "water-soluble", and if the mixture contained no precipitates and was turbid, the compound was evaluated to be "self-emulsifying".

[0069] [Table 2]

Compound (B) No.		Example 1	Example 2	Example 3	Example 4	Example 5	Example 6
Composition of coating material	Polyamine resin (A) (parts)	1 2,960	2 2,960	3 2,960	4 2,960	5 2,960	6 2,960
	Emulsion I	-	-	-	-	-	-
	Emulsion II	-	-	-	-	-	-
	DPnB (parts)	118	118	118	118	118	118
	Compound (B) (parts)	392	377	254	388	600	217
	Burnish	o	o	o	o	o	o
Coating film condition	Transparency	o	o	o	o	o	o
	blisters/cissings	o	o	o	o	o	o
	25°C	>200	>200	120	150	150	>200
Curability	5°C	150	150	100	100	100	200

Compound (B) No.		Example 7	Example 8	Example 9	Example 10	Example 11	Example 12
Composition of coating material	Polyamine resin (A) (parts)	7 2,960	8 2,960	9 2,960	2 2,960	10 2,960	11 2,960
	Emulsion I	-	-	-	-	-	-
	Emulsion II	-	-	-	-	-	-
	Emulsion III	-	-	-	-	-	-
	DPnB (parts)	118	118	118	118	118	118
	Compound (B) (parts)	256	99	99	189	133	189
Coating film condition	Burnish	o	o	o	o	o	o
	Transparency	o	o	Δ	o	o	o
	blisters/cissings	o	o	o	o	o	o
Curability	25°C	150	150	>200	>200	>200	>200
	5°C	130	110	130	>200	>200	>200

* The number in the parentheses represents an amount in terms of an emulsion.

[0070] [Example 13]

A pigment-dispersed composition containing 100 parts of tap water, 34 parts of DISPERBYK-190 (manufactured by BYK, pigment dispersant), 2 parts of BYK-019 (manufactured by BYK, antifoaming agent), 170 parts of calcium carbonate, 185 parts of titanium oxide, and 2 parts of a calcium-based anticorrosion pigment was dispersed with a disper for 30 minutes. Subsequently, 450 parts of Emulsion I obtained in Production Example 2 as a polyamine resin (A), 18 parts of DPnB, and 10 parts of Adecanol UH-420 (manufactured by ADECA CORPORATION, associated thickener) were added and mixed, to thereby prepare a base coating solution. Further, a solution obtained by dissolving 41 parts of a compound (B), i.e., propoxylated bisphenol A diacrylate (PO 4 mol) in 41 parts of DPnB was added while stirring with a disper, and the mixture was stirred for 10 minutes, to thereby obtain an enamel coating material. The resultant coating material was applied onto glass plates using a 6-mil applicator under environments of 25°C and 5°C, and the material was dried for 24 hours under the same environments as in its application, to thereby obtain coating films. After that, the coating film condition, curability, and anticorrosion property of each of the resultant coating films were evaluated. Table 3 shows the results.

[0071] [Example 14]

Coating films were obtained in the same manner as in Example 13 except that 33 parts of ethoxylated glycerin triacrylate (EO

9 mol) (manufactured by Shin-Nakamura Chemical Co., Ltd., product name "A-GLY-9E", Compound(B) No.6) were used instead of 41 parts of propoxylated bisphenol A diacrylate (PO 4 mol). After that, the coating film condition, curability, and anticorrosion property of each of the resultant coating films were evaluated. Table 3 shows the results.

[0072] [Example 15]

Coating films were obtained in the same manner as in Example 13 except that 450 parts of Emulsion II obtained in Production Example 4 were used as a polyamine resin (A) instead of 450 parts of Emulsion I obtained in Production Example 2. The coating film condition, curability, and anticorrosion property of each of the resultant coating films were evaluated. Table 3 shows the results.

[0073] Coating films were obtained in the same manner as in Example 13 except that 450 parts of Emulsion III obtained in Production Example 6 were used as a polyamine resin (A) instead of 450 parts of Emulsion I obtained in Production Example 2, and 61 parts of the emulsion of ethoxylated trimethylolpropane triacrylate (EO 3 mol) produced in Example 12 were used as a compound (B) instead of the solution obtained by dissolving 41 parts of propoxylated bisphenol A diacrylate (PO 4 mol) in 41 parts of DPnB. The coating film condition, curability, and anticorrosion property of each of the resultant coating films were evaluated. Table 3 shows the

results.

[0074] [Table 3]

		Example 13	Example 14	Example 15	Example 16
Compound (B) No.		10	6	10	11
Composition of coating material	Base coating solution (parts)	971	971	971	971
	Emulsion contained in base coating solution	Emulsion I	Emulsion I	Emulsion II	Emulsion III
	Compound (B) (parts)	41(82)*	33	41(82)*	27(61)*
Curability	25°C	>200	>200	>200	>200
	5°C	120	150	120	150
Anticorrosion property		◎	○	Δ	◎

* The numbers in the parentheses each represent an amount in terms of a solution or an emulsion.

[0075] [Comparative Example 1]

Coating films were obtained in the same manner as in Example 1 except that the compound (B) was not used. After that, the coating film condition and curability of each of the resultant coating films were evaluated. Table 4 shows the results.

[0076] [Comparative Example 2]

Coating films were obtained in the same manner as in Example 1 except that 2,100 parts of urethane acrylate having a molecular weight of 4,200, a viscosity of 30,000 mPa·s, and 2 functional groups (UA-W2, manufactured by Shin-Nakamura Chemical Co., Ltd.) were used instead of the compound (B). After that, the coating film condition

and curability of each of the resultant coating films were evaluated. Table 4 shows the results.

[0077] [Comparative Example 3]

Coating films were obtained in the same manner as in Example 1 except that 94 parts of dipentaerythritol hexaacrylate having a molecular weight of 562, a viscosity of 6,600 mPa·s, and 6 functional groups were used instead of the compound (B). After that, the coating film condition and curability of each of the resultant coating films were evaluated. Table 4 shows the results.

[0078] [Comparative Example 4]

Coating films were obtained in the same manner as in Example 1 except that 255 parts of a bisphenol type epoxy resin having a molecular weight of 510, a viscosity of 100,000 mPa·s, and 2 acryloyl groups (Ripoxy VR-77, manufactured by SHOWA HIGHPOLYMER CO., LTD.) were used instead of the compound (B). After that, the coating film condition and curability of each of the resultant coating films were evaluated. Table 4 shows the results.

[0079] [Table 4]

		Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4
Coating film condition	Burnish	o	o	x	x
	Transparency	o	o	Δ	x
	blisters /cissings	o	o	x	x
Curability	25°C	20	30	50	50
	5°C	20	20	30	30

[0080] [Comparative Example 5]

1,000 parts of Adeka Resin EM-101-50 (aqueous epoxy resin emulsion manufactured by ADEKA CORPORATION; epoxy equivalent 1000, solid content 50%) and 50 parts of DPnB were mixed to prepare a base coating solution.

Subsequently, 200 parts of SUNMIDE WH-900 (manufactured by Air Products and Chemicals, Inc., denatured aliphatic polyamine, nonvolatile content 60%, amine number 220) were added as a curing agent to the base coating solution, and mixing was carried out by stirring with a disper. The resultant coating material was applied onto glass plates using a 6-mil applicator under environments of 25°C and 5°C, and the material was dried for 24 hours under the same environments as in its application, to thereby obtain coating films. The curability of each of the resultant coating films was evaluated. As a result, the curability at 25°C was good (MEK resistance >200 times), and the material did not cure at all at 5°C (the material was easily dissolved in MEK).

[0081] As is clear from Tables 2 and 3, the aqueous coating

composition of the present invention can achieve sufficient low-temperature curability, which cannot be achieved in the case of the conventional aqueous coating material (Comparative Example 5).

[0082] Further, as is clear from the results of Examples 13, 14, and 16 (Table 3), when each of the epoxy-based polyamine resins is used as a polyamine resin, it is possible to obtain an aqueous coating composition which can produce a coating film having excellent anticorrosion property in addition to the low-temperature curability.

Industrial Applicability

[0083] The aqueous coating composition of the present invention can be suitably used as a construction coating material or a heavy-duty coating material in an anticorrosive, a sealer, a primer, or the like for a bridge, a building exterior, a floor, a building product, or the like.

Claims

[Claim 1] An aqueous coating composition, comprising:

(A) a water-dispersible polyamine resin having one or more primary amine groups and/or secondary amine groups in a molecule; and

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

wherein:

the aqueous coating composition is a two-component aqueous coating composition that a base coating solution comprises the polyamine resin (A) and a curing agent comprises the compound (B),

the polyamine resin (A) has an amine equivalent of 100 to 3,000,

the polyamine resin (A) has a neutralization ratio of 10 to 70%, and

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

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

[Claim 3] An aqueous coating composition according to claims 1 and 2, wherein the compound (B) has a molecular weight of 150 or more and 2,000 or less.

[Claim 4] An aqueous coating composition according to any one of claims 1 to 3, wherein the compound (B) is a water-soluble compound, and the polyamine resin (A) is a water-dispersible resin.

[Claim 5] An aqueous coating composition according to any one of claims 1 to 3, wherein the compound (B) is a self-emulsifying compound.

[Claim 6] An aqueous coating composition according to any one of claims 1 to 3, wherein the compound (B) is emulsified or dispersed by the polyamine resin (A).

[Claim 7] An aqueous coating composition according to any one of claims 1 to 3, wherein the compound (B) is a mixture of a water-soluble compound and a non-water-soluble compound.

[Claim 8] An aqueous coating composition according to any one of claims 1 to 3, wherein the compound (B) is an emulsified compound.

[Claim 9] An aqueous coating composition according to any one of claims 1 to 3, wherein the curing agent further comprises an emulsifier.