

Description

Title of Invention: WATER-BASED COATING COMPOSITION, AND PROCESS FOR FORMATION OF COATING FILM AND PROCESS FOR FORMATION OF MULTILAYER COATING FILM, WHICH COMPRISE USING THE WATER-BASED COATING COMPOSITION

Technical Field

[0001] The present invention relates to an aqueous coating composition, and a method of forming a coating film and a method of forming a multilayer coating film each using the aqueous coating composition.

Background Art

[0002] As an anticorrosive coating material, a one-component solvent type coating material containing an alkyd resin as a main component is generally used. Meanwhile, there is a demand for an aqueous anticorrosive coating material as an environmentally friendly material. For example, an epoxy ester dispersion resin has been proposed as a main binder suitable for the aqueous anticorrosive coating material (see Non Patent Literature 1). The epoxy ester dispersion resin has been reported to be excellent in salt spray resistance, moisture resistance, water resistance, and the like as compared to a water-soluble alkyd resin and an acrylic emulsion resin.

[0003] However, the alkyd resin has a problem in that formaldehyde is generated when the resin is cured. Further, the epoxy ester dispersion resin has a problem in that its corrosion resistance is not sufficient. Accordingly, there is a demand for an anticorrosive coating material having additionally excellent performance.

[0004] Although a coating film formed with the anticorrosive coating material may, of course, be used by itself, an additional improvement in coating film performance may be attained when the coating film is processed into a multilayer through formation of another coating film (for example, on the coating film formed with the anticorrosive coating material). However, there is a problem in that, when adhesiveness between the coating films (interlayer adhesiveness) is low, sufficient performance may not be exerted.

Citation List

Non Patent Literature

[0005] [NPL 1] "Introduction to Environmentally Friendly Technologies, Environmentally Friendly Totally Water Based Anticorrosive Coating System," RUST PREVENTION & CONTROL JAPAN, 46, No. 1, 2002, p. 36-39

Summary

Technical Problem

[0006] The present disclosure has been made in order to solve the conventional problem, and a main object of the present disclosure is to provide an aqueous coating composition excellent in corrosion resistance. Another object of the present disclosure is to provide a method of forming a coating film having excellent corrosion resistance and being excellent in interlayer adhesiveness.

[0006a] In a first aspect of the present disclosure, there is provided a method of forming a coating film, comprising:

coating a substrate with an aqueous coating composition comprising:

an amine-modified epoxy resin (A) which is obtained by modifying an epoxy resin having a molecular weight of 2,000 or more, which is calculated with "epoxy equivalent x 2", and having a bisphenol skeleton with an amine compound; and

a plasticizer (C) which has a boiling point of 200°C or more and is water-insoluble; and
subjecting the aqueous coating composition to air drying.

[0006b] In a second aspect of the present disclosure, there is provided a method of forming a multilayer coating film, comprising:

coating a substrate with the aqueous coating composition as defined above to form a coating film; and

forming a top coating layer on the coating film.

Means for solving the Problems

[0007] According to one aspect of the present invention, an aqueous coating composition is provided. The aqueous coating composition includes an amine-modified epoxy resin (A) which is obtained by modifying an epoxy resin having a molecular weight of 2,000 or more and having a bisphenol skeleton with an amine compound and a plasticizer (C) which has a boiling point of 200°C or more and is water-insoluble.

In one embodiment of the invention, a content of the plasticizer (C) is 10 to 30 parts by mass with respect to 100 parts by mass in total of the amine-modified epoxy resin (A) and the plasticizer (C).

In another embodiment of the invention, the amine-modified epoxy resin (A) has an amino group neutralized with an acid compound (B).

In still another embodiment of the invention, the amine-modified epoxy resin (A) has a neutralization ratio of 10 to 80%.

In still another embodiment of the invention, the amine-modified epoxy resin (A) has a modification rate of 1 to 10 mass%.

In still another embodiment of the invention, the plasticizer (C) has a water solubility of 10 parts by mass or less in 100 parts by mass of water.

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

According to still another aspect of the invention, a method of forming a multilayer coating film is provided. The method of forming a multilayer coating film includes coating a substrate with the aqueous coating composition to form a coating film and forming a top coating layer on the coating film.

In one embodiment of the invention, the method of forming a multilayer 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 another embodiment of the invention, the method of forming a multilayer coating film further includes forming an undercoating layer on the substrate before the forming of the coating film with the aqueous coating composition.

Advantageous Effects of Invention

[0008] According to the aqueous coating composition of the present invention, a coating film to be obtained includes a rigid bisphenol skeleton in a large amount and is excellent in corrosion resistance. Basically, an epoxy resin formed of a bisphenol skeleton has high rigidity proportional to its molecular weight. As rigidity increases, corrosion resistance improves. However, a glass transition point also increases, which makes it difficult to form a coating film. According to the present invention, a hard component which, as it is, may not be formed into a coating film as described above and a plasticizer satisfying specific features are combined, and thus the aqueous coating composition that achieves excellent corrosion resistance can be obtained.

[0009] Specifically, a coating film formed with the aqueous coating composition of the present invention is estimated to have such a structure that an amine-modified epoxy resin including a

rigid bisphenol skeleton in a large amount includes the plasticizer to form a film. A part of the plasticizer included in the aqueous coating composition volatilizes at the time of film formation (coating) and at the time of drying, but a large part of the plasticizer is considered to form a coating film in a state of being included in the amine-modified epoxy resin. The plasticizer has a low water solubility and a high boiling point, and hence is suppressed from volatilizing out of the coating film as much as possible. This is considered to contribute to additionally excellent corrosion resistance. Further, the coating film formed with the aqueous coating composition of the present invention is excellent in adhesiveness for other layers. Accordingly, a multilayer coating film formed according to the the present invention can have not only additionally improved corrosion resistance due to being a multilayer but also a characteristic of having a function possessed by a top coating layer and corrosion resistance in combination.

[0010] The aqueous coating composition of the present invention, because of being aqueous, is excellent from an environmental perspective. Further, the aqueous coating composition does not utilize oxidative polymerization, and hence a problem such as the generation of formaldehyde does not occur. In addition, in the formation of a coating film, no curing agent needs to be used, and hence the aqueous coating composition can be used as a one-component type. Accordingly, a problem in storage stability or workability

based on a curing reactivity does not occur. As described above, through the use of the epoxy resin having a high molecular weight itself as a component for forming a coating film to make the most of the characteristic of the epoxy resin, an aqueous coating composition having sufficient performance as an anticorrosive coating material can be obtained. Further, through the use of such aqueous coating composition, a method of forming a coating film provided with excellent corrosion resistance and excellent from an environmental perspective as well can be obtained.

Description of Embodiments

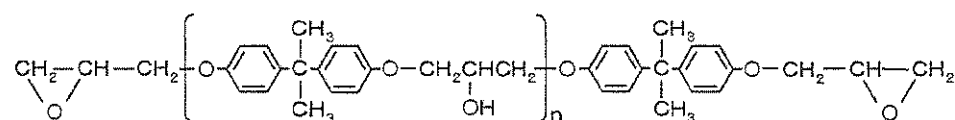
[0011] A. Aqueous coating composition

An aqueous coating composition of the present invention includes an amine-modified epoxy resin (A) and a plasticizer (C) which has a boiling point of 200°C or more and is water-insoluble. The plasticizer (C), when mixed with the amine-modified epoxy resin (A) at a mass ratio of 1:1, is capable of dissolving the amine-modified epoxy resin (A). The aqueous coating composition of the present invention is preferably a water dispersion or an aqueous solution of the amine-modified epoxy resin (A).

[0012] The amine-modified epoxy resin (A) is typically obtained by modifying an epoxy resin with an amine compound. The epoxy resin constituting the amine-modified epoxy resin (A) is an epoxy resin having a bisphenol skeleton. The epoxy resin having a bisphenol

skeleton has high rigidity and the resin itself has excellent corrosion resistance. The epoxy resin having a bisphenol skeleton typically has a structure in which bisphenol A and diglycidyl ether of bisphenol A are condensed with each other, and the structure is represented by the following general formula (n represents an integer).

[Chem. 1]



[0013] The bisphenol skeleton preferably accounts for 90 mass% or more of the epoxy resin. The use of the epoxy resin thus having high rigidity can provide excellent corrosion resistance.

[0014] The epoxy resin (before modification) has a molecular weight of 2,000 or more, more preferably 2,000 to 8,500, still more preferably 3,000 to 8,000. When the molecular weight is less than 2,000, corrosion resistance may reduce. When the molecular weight is more than 8,500, the amine-modified epoxy resin (A) to be obtained is difficult to disperse or dissolve in water, which may result in phase separation. Herein, the term "molecular weight" refers to a value calculated with "epoxy equivalent $\times$ 2" on the assumption of having the above-mentioned structural formula.

[0015] As the epoxy resin, a commercially available product may be used as it is, or one synthesized by condensing bisphenol A and diglycidyl ether of bisphenol A as described above may be used. As a method for the synthesis, any appropriate method may be adopted. As a specific example thereof, there is given a method for synthesis involving blending an excess amount of diglycidyl ether of bisphenol A in bisphenol A, and heating the resultant in an organic solvent such as methyl isobutyl ketone with an organic base such as dimethylbenzylamine as a catalyst. An epoxy equivalent is preferably measured to monitor the reaction so that the reaction may be terminated when the epoxy equivalent reaches a value of interest. The epoxy resin is preferably synthesized in consideration of, for example, the facts that the modification with an amine compound is performed in an organic solvent such as methyl isobutyl ketone and it takes effort to dissolve a solid epoxy resin in the organic solvent. It should be noted that the aqueous coating composition may include the organic solvent used in the synthesis of the amine-modified epoxy resin (A) but is preferably substantially free of the organic solvent.

[0016] The modification is typically performed by causing ring-opening addition of an amine compound having active hydrogen to epoxy groups of an epoxy resin which is to serve as a raw material. Substantially all the epoxy groups are preferably modified.

Specifically, the epoxy groups are modified at a ratio of preferably 90% or more.

[0017] The amine-modified epoxy resin (A) has a modification rate of preferably 1 to 10 mass%, more preferably 3 to 8 mass%. When the modification rate is less than 1 mass%, the amine-modified epoxy resin (A) is difficult to disperse or dissolve in water, which may result in phase separation. When the modification rate is more than 10 mass%, corrosion resistance or adhesiveness may reduce. Further, an excessively long drying time may be required to obtain a coating film. Herein, the "modification rate" is determined with "amount of amine compound/(amount of epoxy resin+amount of amine compound)." It should be noted that, when a diketiminated product to be described later is used as the amine compound, the "amount of amine compound" refers to the amount of an amine compound to be produced in the resin after hydrolysis.

[0018] Examples of the amine compound include a ketiminated product of butylamine, octylamine, diethylamine, dibutylamine, methylbutylamine, monoethanolamine, diethanolamine, N-methylethanolamine, or aminoethylethanolamine and a diketiminated product of diethylenetriamine. They may be used alone or in combination. Of those, a ketiminated product is preferred. The use of the ketiminated product allows a primary amino group to appear upon neutralization to be described later, which improves

coating film physical properties such as adhesiveness.

[0019] As a method for the modification with an amine compound (ring-opening addition), any appropriate method may be adopted. For example, there is given a method involving dissolving an epoxy resin which is to serve as a raw material in an organic solvent, adding an amine compound in a substantially equivalent amount to that of an epoxy group possessed by the epoxy resin, and then heating the mixture as required.

[0020] The amine-modified epoxy resin (A) preferably has an amino group neutralized with an acid compound (B). This is because the neutralization allows the amine-modified epoxy resin (A) to be satisfactorily dispersed or dissolved in water.

[0021] Examples of the acid compound (B) include: inorganic acids such as hydrochloric acid, nitric acid, and phosphoric acid; and organic acids such as carboxylic acid compounds including formic acid, acetic acid, propionic acid, and lactic acid, and sulfamic acid. They may be used alone or in combination. Of those, organic acids are preferred, and carboxylic acid compounds are particularly preferred. This is because an aqueous coating composition to be obtained may have additionally excellent corrosion resistance (particularly when drying is performed at ordinary temperature). Of the carboxylic acid compounds, acetic acid is preferred in

consideration of volatility.

[0022] A neutralization ratio (ratio of an acid equivalent to the equivalent of an amino group possessed by the amine-modified epoxy resin (A)) is preferably 10 to 80%, more preferably 15 to 80%. When the neutralization ratio is less than 10%, the amine-modified epoxy resin (A) is difficult to disperse or dissolve in water, which may result in phase separation. When the neutralization ratio is more than 80%, water resistance may reduce.

[0023] Whether the amine-modified epoxy resin (A) is dispersed in water or dissolved therein may be determined through adjustments of, for example, the molecular weight and amount of amino groups of the amine-modified epoxy resin (A), the kind of amine compound to be used in the modification, the kind of acid compound (B) to be used, and the blending amount of the acid compound (B) (neutralization ratio). The amine-modified epoxy resin (A) is preferably formed into a water dispersion. When the amine-modified epoxy resin (A) is a water dispersion, additionally excellent corrosion resistance may be provided.

[0024] As described above, the aqueous coating composition of the present invention includes the plasticizer (C). The use of the plasticizer (C) allows the provision of an aqueous coating composition having sufficient performance as an anticorrosive

coating material without sacrificing the rigidity (corrosion resistance) of the epoxy resin. The plasticizer (C), when mixed with the amine-modified epoxy resin (A) at a mass ratio of 1:1, is capable of dissolving the amine-modified epoxy resin (A). When the dissolution property of the plasticizer (C) is not sufficient, a problem such as phase separation may occur and an aqueous coating composition may not be obtained in a satisfactory manner.

[0025] The plasticizer (C) is water-insoluble. As the plasticizer (C) is water-insoluble, excellent corrosion resistance may be provided. Herein, the term "water-insoluble" refers to a state of being not freely miscible with water and refers to a state of being substantially insoluble in water. Specifically, the plasticizer (C) preferably has a water solubility of 10 parts by mass or less in 100 parts by mass of water. When the water solubility is more than 10 parts by mass in 100 parts by mass of water, corrosion resistance may reduce.

[0026] The plasticizer (C) is liquid at room temperature (25°C) and has a viscosity of preferably 1,000 mPa·s or less, more preferably 500 mPa·s or less.

[0027] The plasticizer (C) has a boiling point of preferably 200°C or more. When the boiling point of the plasticizer (C) is less than 200°C, corrosion resistance may reduce.

[0028] Specific examples of the plasticizer (C) include: glycol ether-based compounds such as diethylene glycol dibutyl ether (dibutyl diglycol, DBDG), ethylene glycol monophenyl ether (phenyl glycol, PhG), diethylene glycol monophenyl ether (phenyl diglycol, PhDG), ethylene glycol monobenzyl ether (benzyl glycol, BzG), propylene glycol monophenyl ether (phenyl propylene glycol PhFG), dipropylene glycol monopropyl ether (propyl propylene diglycol, PFDG), dipropylene glycol monobutyl ether (DPnB, butyl propylene diglycol, BFDG), tripropylene glycol monobutyl ether (TPnB), and polypropylene glycol #1000; and carboxylic acid ester-based compounds such as DBE (dibasic acid esters), dibutyl phthalate (DBP), di-2-ethylhexyl phthalate (DOP), diisononyl phthalate (DINP), diisodecyl phthalate (DIDP), diheptyl phthalate (DHP), di-n-octyl phthalate (N-DOP), butylbenzyl phthalate (BBP), ethylphthalylethyl glycolate, di-2-ethylhexyl adipate (DOA), and dibutyl diglycol adipate (BXA). Further, as a commercially available product, Solvesso 200 (manufactured by Exxon Chemical Company) may be used. They may be used alone or in combination. Of those, a compound having no ester bond in the molecule is preferably used in consideration of long-term stability. Further, a glycol ether-based compound is preferably used in consideration of odor.

[0029] The content of the plasticizer (C) is preferably 10 to 30 parts by mass, more preferably 15 to 30 parts by mass with respect

to 100 parts by mass in total of the amine-modified epoxy resin (A) and the plasticizer (C) ((A)+(C)). When the content is less than 10 parts by mass, a crack may occur in a coating film. When the content is more than 30 parts by mass, an excessively long drying time may be required to obtain a coating film. Further, the content of the plasticizer (C) in the aqueous coating composition is preferably 10 mass% or less from the viewpoint of using a volatile organic compound (VOC) in an amount as small as possible.

[0030] The aqueous coating composition of the present invention preferably includes an aqueous medium containing water as a main component. The aqueous medium may contain an organic solvent that is soluble in water. Specific examples of the organic solvent include ethylene glycol, propylene glycol, ethylene glycol monobutyl ether, propylene glycol monobutyl ether, diethylene glycol, dipropylene glycol, and diethylene glycol monobutyl ether. From the viewpoint of using the VOC in an amount as small as possible, the amount of the organic solvent is preferably as small as possible.

[0031] The total of the content of the amine-modified epoxy resin (A) and the content of the plasticizer (C) in the aqueous coating composition is preferably 15 to 40 mass%. When the total content is less than 15 mass%, an appropriate coating film may not be obtained. When the total content is more than 40 mass%, the stability of the coating material may reduce.

[0032] The aqueous coating composition of the present invention may include a pigment. 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, and talc; and anti-rust pigments. The concentration of the pigment in the aqueous coating composition is preferably 10 to 50 mass%.

[0033] The aqueous coating composition of the present invention may include an additive. 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, an ultraviolet absorbing agent, an antioxidant, and a curing agent. It should be noted that, although the aqueous coating composition of the present invention does not need a curing agent, the curing agent may be used as appropriate when, for example, a coating film is required to have a characteristic at an additionally high level. As the curing agent, there may be used, for example, an isocyanate compound and a melamine compound. Alternatively, when the amine-modified epoxy resin (A) has a primary or secondary amino group, a compound having a plurality of (math)acryloyl groups or a compound having a plurality of epoxy groups may be used.

[0034] The aqueous coating composition of the present invention is preferably obtained by mixing the amine-modified epoxy resin (A), the plasticizer (C), and the aqueous medium with each other. When the acid compound (B) is used, the acid compound (B) is added at any appropriate timing. The acid compound (B) is preferably added after the amine-modified epoxy resin (A) obtained by modifying an epoxy resin with an amine compound and the plasticizer (C) have been mixed with each other. In an embodiment, the plasticizer (C) is added to a solution of the amine-modified epoxy resin (A) in an organic solvent, and the acid compound (B) is further added thereto to prepare a mixture. After that, the resultant mixture is added dropwise to the aqueous medium, or the aqueous medium is added to the resultant mixture to disperse or dissolve the mixture, and the organic solvent is then distilled off. Thus, the aqueous coating composition is produced. The amine-modified epoxy resin (A) may be obtained as an organic solvent solution, and hence, as in this embodiment, the organic solvent is preferably eventually distilled off.

[0035] The plasticizer (C) may be used as an organic solvent in the production of the amine-modified epoxy resin (A) and thus be blended into the aqueous coating composition. The use of the plasticizer (C) as an organic solvent can suppress the total usage of organic solvents. In the production of the aqueous coating composition, the above-mentioned other components may each be added

at any appropriate timing.

[0036] B. Method of forming (multilayer) coating film

Any appropriate substrate may be coated with the aqueous coating composition of the present invention. 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.

[0037] Examples of an object to be coated having metal on its surfaces (outer and inner surfaces) include 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 aqueous coating composition is applicable to architectural structures and civil engineering structures as well as the foregoing.

[0038] As a typical coating method, there is given a method involving applying the aqueous coating composition onto an object to be coated (substrate), followed by drying. The aqueous coating

composition of the present invention allows coating to be performed in such a simple manner that, for example, a step such as electrodeposition is not necessary. 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.

[0039] The application amount the aqueous coating composition may be set to any appropriate application amount depending on intended use and the like. The application amount is preferably 10 to 400 g/m².

[0040] As a 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.

[0041] The coating film to be formed through coating with the aqueous coating composition has a thickness of preferably 10 to 100 μm , more preferably 20 to 100 μm . When the thickness is more than 100 μm , a problem such as the occurrence of dripping may occur at the time of coating.

[0042] An additional coating film (layer) 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 and corrosion resistance.

[0043] 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 alkyd resin-based coating material, an acrylic resin-based coating material, and an acrylic silicone 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.

[0044] 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. The thickness of the top 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 150 μm .

[0045] Before the formation of a coating film through coating with the aqueous coating composition, 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, which is well applicable to a case requiring high corrosion resistance, such as a bridge, a plant, or a tank.

[0046] Any appropriate coating material may be adopted as the undercoating material. Examples thereof include an organic or inorganic zinc-rich coating material. 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.

[0047] 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 μ m.

[0048] 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 additionally excellent corrosion resistance. The top coating layer is preferably formed after the formation of the intermediate coating layer.

[0049] 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.

[0050] 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 μ m.

[0051] The top coating material, the intermediate coating material, and the undercoating material may each contain a pigment, an additive, and the like. Examples of the pigment and the additive

include the pigments and additives described in the above-mentioned section A. The number, kinds, and amounts of pigments and additives to be added may be selected as appropriate depending on purposes.

[0052] As an application method and drying method for each of the top coating material, the intermediate coating material, and the undercoating material, any appropriate methods may be adopted depending on the kind of the coating material to be used. Examples of the application method and drying method for each of the top coating material, the intermediate coating material, and the undercoating material include the same methods described above for the application method and drying method for the aqueous coating composition.

Examples

[0053] 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.

[0054] (Production Example 1) Production of pigment paste
10 parts of water, 0.1 part of hydroxyethyl cellulose, 3 parts of a pigment dispersant (manufactured by BYK-Chemie, trade name "Disperbyk-190"), 10 parts of talc, 8 parts of calcium carbonate, 17 parts of titanium oxide, and 2 parts of a calcium-based anti-rust

pigment were mixed with each other and stirred for 30 minutes with a disper to produce a pigment-dispersed paste.

[0055] (Example 1)

1,005 parts of diglycidyl ether of bisphenol A and 495 parts of bisphenol A were dissolved in 500 parts of methyl isobutyl ketone (hereinafter, referred to as "MIBK"). To the solution were added 2 parts of dimethylbenzylamine, and the mixture was subjected to a reaction continuously until an epoxy equivalent reached 1,500 to give an epoxy resin having a bisphenol skeleton which was to serve as a raw material.

After the completion of the reaction, 123 parts of dibutylamine were added and the mixture was subjected to a reaction at 120°C for 1 hour to give the amine-modified epoxy resin (A) having a bisphenol skeleton.

286 parts of dipropylene glycol n-butyl ether as the plasticizer (C) (15 mass% with respect to the total amount of the amine-modified epoxy resin (A) and the plasticizer (C)) were added, and 3 parts of 90% acetic acid as the acid compound (B) were then added to perform neutralization (neutralization ratio: 20%). While the resultant was kept at 90°C with stirring, 2,600 parts of water were gradually added thereto to achieve homogeneity. In addition, under reduced pressure at 50°C, 1,000 parts of a mixture of MIBK

and water were distilled off to give a clear type aqueous coating composition (water dispersion).

50 parts of the clear type aqueous coating composition and 50 parts of the pigment paste obtained in the production example described above were mixed with each other and stirred with a disper for 10 minutes to give a white aqueous coating composition.

[0056] (Example 2)

1,939 parts of diglycidyl ether of bisphenol A and 1,061 parts of bisphenol A were dissolved in 1,000 parts of MIBK. To the solution were added 4 parts of dimethylbenzylamine, and the mixture was subjected to a reaction continuously until an epoxy equivalent reached 3,000 to give an epoxy resin having a bisphenol skeleton which was to serve as a raw material.

After the completion of the reaction, 249 parts of an MIBK diketiminated product of diethylenetriamine (hereinafter, referred to as DETA diketimine) were added and the mixture was subjected to a reaction at 120°C for 1 hour to give the amine-modified epoxy resin (A) having a bisphenol skeleton.

1,059 parts of dipropylene glycol n-butyl ether as the plasticizer (C) (25 mass% with respect to the total amount of the amine-modified epoxy resin (A) and the plasticizer (C)) were added,

and 48 parts of 90% acetic acid as the acid compound (B) were then added to perform neutralization (neutralization ratio: 38%). While the resultant was kept at 90°C with stirring, 4,631 parts of water were gradually added thereto to achieve homogeneity. In addition, under reduced pressure at 50°C, 2,324 parts of a mixture of MIBK and water were distilled off to give a clear type aqueous coating composition (water dispersion). Further, a white aqueous coating composition was obtained in the same manner as in Example 1.

[0057] (Example 3)

A clear type aqueous coating composition (water dispersion) was prepared in the same manner as in Example 2 except that an equal amount of DBE (dibasic acid ester) was used as the plasticizer (C) in place of dipropylene glycol n-butyl ether. Then, a white aqueous coating composition was obtained.

[0058] (Example 4)

4,000 parts of an epoxy resin having an epoxy equivalent of 4,000 (manufactured by Japan Epoxy Resins Co. Ltd., grade: 1010) as the epoxy resin having a bisphenol skeleton which was to serve as a raw material were added to 1,167 parts of MIBK under heating, 100 parts of diethanolamine were further added thereto, and the mixture was subjected to a reaction at 120°C for 1 hour to give the amine-modified epoxy resin (A) having a bisphenol skeleton.

1,543 parts of tripropylene glycol n-butyl ether as the plasticizer (C) (30 mass% with respect to the total amount of the amine-modified epoxy resin (A) and the plasticizer (C)) were added, and 38 parts of 90% acetic acid as the acid compound (B) were then added to perform neutralization (neutralization ratio: 60%). While the resultant was kept at 90°C with stirring, 5,773 parts of water were gradually added thereto to achieve homogeneity. In addition, under reduced pressure at 50°C, 2,333 parts of a mixture of MIBK and water were distilled off to give a clear type aqueous coating composition (water dispersion). Further, a white aqueous coating composition was obtained in the same manner as in Example 1.

[0059] (Comparative Example 1)

A white aqueous coating composition was obtained in the same manner as in Example 1 except that an equal amount of butyl diglycol was used as the plasticizer (C) in place of dipropylene glycol n-butyl ether.

[0060] (Comparative Example 2)

A white aqueous coating composition was obtained in the same manner as in Example 2 except that an equal amount of propylene glycol n-butyl ether was used as the plasticizer (C) in place of dipropylene glycol n-butyl ether.

[0061] (Comparative Example 3)

A white aqueous coating composition was obtained in the same manner as in Example 1 except that the epoxy resin having a bisphenol skeleton which was to serve as a raw material was changed to 925 parts of an epoxy resin having an epoxy equivalent of 925 (manufactured by Japan Epoxy Resins Co. Ltd., grade: 1004).

[0062] (Comparative Example 4)

A white aqueous coating composition was obtained in the same manner as in Example 1 except that, in obtaining the epoxy resin having a bisphenol skeleton which was to serve as a raw material, the amounts of diglycidyl ether of bisphenol A and bisphenol A were changed to 528 parts and 410 parts, respectively, 563 parts of polypropylene glycol diglycidyl ether having a molecular weight of 630 were used, and the plasticizer (C) was not used.

[0063] The details of the plasticizer (C) used in each of the Examples and Comparative Examples are as follows.

Dipropylene glycol n-butyl ether (DPnB): viscosity: 5 mPa·s; boiling point: 229°C; water solubility: 6

DBE: viscosity: 6 mPa·s; boiling point: 200°C; water solubility: 5

Tripropylene glycol n-butyl ether (TPnB): viscosity: 10 mPa·s; boiling point: 274°C; water solubility: 3

Butyl diglycol (BDG): viscosity: 5 mPa·s; boiling point: 230°C; water solubility: ∞

Propylene glycol n-butyl ether (PnB): viscosity: 3 mPa·s; boiling point: 170°C; water solubility: 6

[0064] <Evaluations>

The aqueous coating compositions obtained in the foregoing were evaluated by the following methods. Table 1 shows the results.

(Outer appearance of coating film)

A polished steel sheet degreased with xylene was coated with each coating composition in an amount of 140 g/m² using a brush, and the resultant was dried at room temperature for 24 hours. The outer appearance of the thus-obtained coating film was visually observed and evaluated based on the following criteria.

○: No abnormality

×: Occurrence of a crack or peeling

(Drying time)

A polished steel sheet degreased with xylene was coated with each coating composition in an amount of 140 g/m² using a brush, and the resultant was dried at room temperature for 24 hours. A finger was pressed against the thus-obtained coating film, and a degree of dryness was evaluated based on the following criteria.

○: No sticky feeling at the finger tip, and no fingerprint left on the coating film upon release of the finger

×: Sticky feeling at the finger tip, or a fingerprint left

on the coating film upon release of the finger

(Water-resistant adhesiveness)

A polished steel sheet degreased with xylene was coated with each coating composition in an amount of 140 g/m² using a brush, and the resultant was dried at room temperature for 24 hours to give a test sheet.

The test sheet was immersed in water at 23°C for 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 thereon. 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 with the number of squares left on the surface.

- o: All squares left on the surface
- x: Some squares left on the surface
- xx: No square left on the surface

(Corrosion resistance)

The obtained coating composition was applied onto a sandblasted steel sheet at 140 g/m² with a brush and dried at 20°C for 7 days to give a test sheet.

The resultant test sheet 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 surface of test sheet

◎: 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

(Storage stability)

The obtained white aqueous coating composition was stored at room temperature, and a state change during the storage was visually observed.

◎: No change even after a lapse of 1 month

○: A slight precipitation observed after a lapse of 1 month

×: A precipitation observed after a lapse of 1 day

[0065] [Table 1]

		Example 1	Example 2	Example 3	Example 4
Amine-modified epoxy resin (A)	Molecular weight	3,000	6,000	6,000	8,000
	Amine compound	Dibutylamine	DETA diketimine	DETA diketimine	Diethanolamine
	Modification rate	8%	3%	3%	3%
Acid compound (B)	Kind	90% Acetic acid	—	—	—
	Neutralization ratio	20%	38%	38%	60%
Plasticizer (C)	Kind	DPnB Glycol ether	DPnB Glycol ether	DBE Dibasic acid ester	TPnB Glycol ether
	Boiling point	229	229	200	274
	Solubility	6	6	5	3
	Content	15%	25%	25%	30%
Evaluations	Outer appearance of coating film	○	○	○	○
	Drying time	○	○	○	○
	Water-resistant adhesiveness	○	◎	◎	○
	Corrosion resistance	◎	◎	◎	◎
	Storage stability	◎	◎	○	◎

		Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4
Amine-modified epoxy resin (A)	Molecular weight	3,000	6,000	1,850	3,000
	Amine compound	Dibutylamine	DETA diketimine	Dibutylamine	Dibutylamine
	Modification rate	8%	3%	8%	12%
Acid compound (B)	Kind	90% Acetic acid	—	—	—
	Neutralization ratio	20%	38%	20%	20%
Plasticizer (C)	Kind	BDG Glycol	PnB Glycol ether	DPnB Glycol ether	—
	Boiling point	230	170	229	—
	Solubility	∞	6	6	—
	Content	15%	25%	15%	—
Evaluations	Outer appearance of coating film	○	○	○	○
	Drying time	○	○	○	○
	Water-resistant adhesiveness	×	×	×	×
	Corrosion resistance	×	×	×	×
	Storage stability	◎	◎	◎	◎

[0066] From each of the aqueous coating compositions of Examples 1 to 4, a coating film having excellent corrosion resistance and water-resistant adhesiveness was obtained. On the other hand, sufficient corrosion resistance was not obtained with each of the aqueous coating compositions of Comparative Examples.

[0067] (Examples A to K) Formation of multilayer coating film

A substrate was coated with the aqueous coating composition of Example 1 or Example 2 above to form a coating film, and then coated with a top coating material to form a multilayer coating film.

[0068] The details of the top coating material used are as follows.

(Top coating material)

1. Solvent type epoxy/amine-based coating material

As the solvent type epoxy/amine-based coating material, "HI-PON 40 TOP COATING" (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

As the aqueous epoxy/amine-based coating material, an aqueous epoxy/amine-based coating material produced in Production Example 2 below was used.

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

As the aqueous two-component urethane-based coating material A, an aqueous two-component urethane-based coating material produced in Production Example 3 below was used.

6. Aqueous two-component urethane-based coating material B

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

7. Aqueous emulsion-based coating material

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

8. Aqueous carbodiimide-based coating material

As the carbodiimide-based coating material, a carbodiimide-based coating material produced in Production Example 4 below was used.

[0069] (Production Example 2) Production of aqueous epoxy/amine-based coating material

34.5 parts of ion-exchanged 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-exchanged 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-exchanged 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.

[0070] (Production Example 3) Production of aqueous two-component urethane-based coating material

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.

[0071] (Production Example 4) 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

ion-exchanged 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.

[0072] The resultant multilayer coating film was evaluated for

its water-resistant adhesiveness by the same method employed for the evaluation of the single-layer coating film in the foregoing.

[0073] Table 2 shows the evaluation results together with details of the substrates and coating conditions. It should be noted that the polished steel sheet used in each of Example A and Example B had been degreased with xylene in advance and the slate sheet used in Example H 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.

[0074] [Table 2]

Substrate		Example A	Example B	Example C	Example D	Example E	Example F
		Polished steel sheet	Polished steel sheet	Zinc-plated steel sheet	Zinc-plated steel sheet	Aluminum sheet	Aluminum sheet
Aqueous coating composition	Kind of coating material	Example 1	Example 1	Example 2	Example 2	Example 2	Example 2
	Application environment	5°C	25°C	5°C	25°C	5°C	25°C
	Application method	brush	brush	brush	brush	brush	brush
	Application amount	140 g/m ²	140 g/m ²	140 g/m ²	140 g/m ²	100 g/m ²	140 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
Top coating material	Kind of coating material	Solvent type epoxy/amine-based coating material	Solvent type epoxy/amine-based coating material	Solvent type 2K urethane coating material A	Solvent type 2K urethane coating material A	Aqueous epoxy/amine-based coating material	Aqueous epoxy/amine-based coating material
	Application environment	25°C	25°C	25°C	25°C	25°C	25°C
	Application method	brush	brush	brush	brush	brush	brush
	Application amount	200 g/m ²	200 g/m ²	100 g/m ²	100 g/m ²	140 g/m ²	140 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 adhesiveness		o	o	o	o	o	o

Substrate		Example G	Example H	Example I	Example J	Example K
		Glass sheet	Slate sheet	Plastic sheet	Dull steel sheet	Zinc phosphate-treated steel sheet
Aqueous coating composition	Kind of coating material	Example 1	Example 2	Example 2	Example 1	Example 2
	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	250 g/m ²	140 g/m ²	250 g/m ²	140 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	Kind of coating material	Aqueous 2K urethane-based coating material A	Aqueous emulsion-based coating material	Aqueous carbodiimide-based coating material	Solvent type 2K urethane coating material B	Aqueous 2K 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	120 g/m ²	120 g/m ²	120 g/m ²	120 g/m ²	120 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
Water-resistant adhesiveness		o	o	o	o	o

[0075] (Comparative Examples)

Multilayer coating films were each obtained in the same manner as in Example B except that any one of the aqueous coating compositions of Comparative Examples 1 to 4 was used in place of the aqueous coating composition of Example 1.

Each of the resultant multilayer coating films was evaluated for its water-resistant adhesiveness and marked with Symbol "x".

[0076] As shown in Table 2, in each of Examples, the multilayer coating film formed by the method of forming a multilayer coating film according to the present invention was excellent in water-resistant adhesiveness. The multilayer coating film formed by the method of forming a multilayer coating film according to the present invention was excellent in water-resistant adhesiveness and corrosion resistance, which suggested sufficient adhesiveness between the coating film formed with the aqueous coating composition used in the the present invention and a top coating layer in the multilayer coating film.

On the other hand, the multilayer coating film of each of Comparative Examples was poor in water-resistant adhesiveness. This is probably because the performance of the coating film formed with the aqueous coating composition of each of Comparative Examples is insufficient.

Industrial Applicability

[0077] The aqueous coating composition of the present invention can be suitably used as, for example, an anticorrosive coating material. Specifically, the aqueous coating composition of the present invention can be suitably applied to ships, vehicles (e.g., railway vehicles, large vehicles), aircraft, bridges, marine structures, plants, tanks (e.g., petroleum tanks), pipes, steel tubes, cast iron tubes, and the like 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 comprising:

5 an amine-modified epoxy resin (A) which is obtained by modifying an epoxy resin having a molecular weight of 2,000 or more, which is calculated with "epoxy equivalent x 2", and having a bisphenol skeleton with an amine compound; and

 a plasticizer (C) which has a boiling point of 200°C
10 or more and is water-insoluble; and

subjecting the aqueous coating composition to air drying.

[Claim 2] A method of forming a coating film according to claim 1, wherein a content of the plasticizer (C) is 10 to 30 parts by
15 mass with respect to 100 parts by mass in total of the amine-modified epoxy resin (A) and the plasticizer (C).

[Claim 3] A method of forming a coating film according to claim 1 or 2, wherein the amine-modified epoxy resin (A) has an amino
20 group neutralized with an acid compound (B).

[Claim 4] A method of forming a coating film according to claim 3, wherein the amine-modified epoxy resin (A) has a neutralization ratio of 10 to 80%.

- 5 [Claim 5] A method of forming a coating film according to any one of claims 1 to 4, wherein the amine-modified epoxy resin (A) has a modification rate of 1 to 10 mass%.

[Claim 6] A method of forming a coating film according to any one of claims 1 to 5, wherein the plasticizer (C) has a water solubility of 10 parts by mass or less in 100 parts by mass of water.

5

[Claim 7] A method of forming a multilayer coating film, comprising:
coating a substrate with the aqueous coating composition according to any one of claims 1 to 6 to form a coating film; and forming a top coating layer on the coating film.

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[Claim 8] A method of forming a multilayer coating film according to claim 7, 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.

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[Claim 9] A method of forming a multilayer coating film according to claim 7 or 8, further comprising forming an undercoating layer on the substrate before the forming of the coating film with the aqueous coating composition.

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