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(54) Title: AQUEOUS RESIN COMPOSITION, AQUEOUS COATING MATERIAL AND ARTICLE HAVING CURED COATING FILM OF THE AQUEOUS COATING MATERIAL

(57) Abstract: Provided is an aqueous resin composition containing, as dispersed in an aqueous medium, a self-emulsifying aqueous resin (E) that includes a modified epoxy resin (D) in an acrylic resin (C) which is a carboxyl group-having polymer (A) neutralized with a basic compound (B), wherein the acid value of the polymer (A) is within the range of 40 to 90 mg KOH/g, the basic compound (B) contains an alkylamine (b1) in an amount of 55 mol% or more, and the modified epoxy resin (D) is a reaction product of an epoxy resin (d1), a monocarboxylic acid (d2) and a compound (d3) having a hydroxyl group bonding to a phosphorus atom. The cured coating film obtained from the aqueous resin composition has a high hardness and is excellent in adhesion to a substrate, acid resistance and corrosion resistance.

DESCRIPTION

Title of the Invention:

AQUEOUS RESIN COMPOSITION, AQUEOUS COATING MATERIAL AND ARTICLE HAVING CURED COATING FILM OF THE AQUEOUS COATING MATERIAL

Technical Field

[0001]

The present invention relates to an aqueous resin composition, an aqueous coating material and an article having a cured coating film of the aqueous coating material.

Background Art

[0002]

Heretofore, as a coating material for metal articles such as construction materials, steel furniture, fancy accessories and others, a baking coating material that uses a solvent-based acrylic resin coating material or a solvent-based alkyd resin coating material as the main ingredient and uses an amino resin as the curing agent is employed. Recently, however, in an overall field of coating materials, from the viewpoint of environmental protection by reducing volatile substances such as an organic solvent which is released from coating materials and the tendency toward non-hazardous coating materials,

solvent-based coating materials are being replaced with aqueous coating materials, and also for baking coating materials, replacement toward aqueous coating materials is strongly demanded.

[0003]

In general, baking coating materials are cured at high temperatures of 120°C or higher, but recently, from the viewpoint of energy cost reduction and application to substrates such as plastics and the like that could hardly undergo high-temperature baking treatment, it is desired to lower the baking temperature.

[0004]

As resins for such aqueous baking coating materials, for example, an aqueous resin composition including a modified epoxy resin has been proposed (for example, see PTL 1). However, the aqueous resin composition contains an emulsifier, and therefore, for example, in a salt water spray test with a steel plate having cross-cuts which are formed on the surface thereto and reach the base substrate, there occurs a problem that the plate would rust or blister.

[0005]

An aqueous resin composition where a self-emulsifying acrylic resin including a modified epoxy resin therein is dispersed has been proposed (for example, see PTL 2). However, the aqueous resin composition is problematic in that, when

cured at lower than 120°C, the hardness of the coating film is low and the acid resistance thereof is poor.

[0006]

Given the situation, a coating composition is desired that can form a cured coating film having a high coating film hardness and excellent in coating film properties such as acid resistance and others, even under a low-temperature curing condition.

Citation List

Patent Literature

[0007]

PTL 1: JP-A 2003-2950

PTL 2: JP-A 2012-92198

Summary of Invention

Technical Problem

[0008]

A problem that the invention is to solve is to provide an aqueous resin composition and an aqueous coating material that can form a cured coating film having a high cured coating film hardness and excellent in substrate adhesion, acid resistance and corrosion resistance, even under a low-temperature curing condition, and to provide an article having a cured coating film of the aqueous coating material.

Solution to Problem

[0009]

The present inventors have assiduously studied for the purpose of solving the above-mentioned problem and, as a result, have found that an aqueous resin composition containing, as dispersed in an aqueous medium, a self-emulsifying aqueous resin in which a specific modified epoxy resin is included in a carboxyl group-having acrylic resin neutralized with a specific base compound can be used as an aqueous coating material, and that an aqueous coating material containing the aqueous resin composition and a curing agent can form a cured coating film having a high coating film hardness and excellent in substrate adhesion, acid resistance and corrosion resistance, thereby completing the present invention.

[0010]

Specifically, the present invention relates to an aqueous resin composition containing, as dispersed in an aqueous medium, a self-emulsifying aqueous resin (E) in which a modified epoxy resin (D) is included in an acrylic resin (C) which is a carboxyl group-having polymer (A) neutralized with a basic compound (B), wherein the acid value of the polymer (A) is within a range of 40 to 90 mg KOH/g, the basic compound (B) contains an alkylamine (b1) in an amount of 55 mol% or more, and the modified epoxy resin (D) is a reaction product of an epoxy resin (d1), a monocarboxylic acid (d2) and a compound (d3) having a hydroxyl group bonding to a phosphorus atom, to

an aqueous coating material containing the composition and a curing agent (F), and further to an article having a cured coating film of the aqueous coating material.

Advantageous Effects of Invention

[0011]

The aqueous resin composition of the present invention can be used as an aqueous coating composition. In addition, the aqueous coating material containing the aqueous resin composition and a curing agent can form a cured coating film having a high coating film hardness and excellent in substrate adhesion, acid resistance and corrosion resistance, and therefore can be favorably used for metal members such as belts, fasteners, bags, key holders, accessories, etc.; construction members such as steel furniture, external walls, roofs, etc.; civil engineering members such as guard rails, sound barriers, drainage ports, etc.; various types of metal substrates of household electric appliances, industrial machines, automobiles, etc.

Description of Embodiments

[0012]

The aqueous resin composition of the present invention is an aqueous resin composition where a self-emulsifying aqueous resin (E) in which a modified epoxy resin (D) is included in an acrylic resin (C) which is a carboxyl group-having polymer (A) neutralized with a basic compound (B),

is dispersed in an aqueous medium, wherein the acid value of the polymer (A) is within a range of 40 to 90 mg KOH/g, the basic compound (B) contains an alkylamine (b1) in an amount of 55 mol% or more, and the modified epoxy resin (D) is a reaction product of an epoxy resin (d1), a monocarboxylic acid (d2) and a compound (d3) having a hydroxyl group bonding to a phosphorus atom.

[0013]

First, the carboxyl group-having polymer (A) is described. The polymer (A) is obtained, for example, by copolymerizing a carboxyl group-having unsaturated monomer (a1) and an unsaturated monomer (a2) except the carboxyl group-having unsaturated monomer (a1).

[0014]

The unsaturated monomer (a1) includes, for example, (meth)acrylic acid, crotonic acid, isocrotonic acid, 2-(meth)acryloyloxyehtylsuccinic acid, 2-(meth)acryloyloxyhexahydrophthalic acid, 2-(meth)acryloyloxyethyl glutarate; a dicarboxylic acid such as maleic acid, fumaric acid, itaconic acid, etc., and an anhydride thereof; a monoalkyl ester of a dicarboxylic acid such as monomethyl maleate, monoethyl maleate, monobutyl maleate, monooctyl maleate, monomethyl fumarate, monoethyl fumarate, monobutyl fumarate, monooctyl fumarate, monomethyl itaconate, monoethyl itaconate, monobutyl itaconate,

monooctyl itaconate, etc. Among the unsaturated monomers (a1), (meth)acrylic acid is preferred as a resin having a low viscosity and excellent in dispersibility can be obtained. One alone or two or more of these unsaturated monomers (a1) can be used either singly or as combined.

[0015]

In the present invention, "(meth)acrylic acid" means one or both of methacrylic acid and acrylic acid; "(meth)acryloyl" means one or both of methacryloyl and acryloyl; and "(meth)acrylate" means one or both of methacrylate and acrylate.

[0016]

The other unsaturated monomer (a2) than the unsaturated monomer (a1) includes, for example, alkyl (meth)acrylates such as methyl (meth)acrylate, ethyl (meth)acrylate, n-propyl (meth)acrylate, iso-propyl (meth)acrylate, n-butyl (meth)acrylate, iso-butyl (meth)acrylate, tert-butyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, lauryl (meth)acrylate, octadecyl (meth)acrylate, docosanyl (meth)acrylate, cyclopentyl (meth)acrylate, cyclohexyl (meth)acrylate, bornyl (meth)acrylate, isobornyl (meth)acrylate, dicyclopentanyl (meth)acrylate, cycloalkyl (meth)acrylate, etc.; hydroxyl group-having unsaturated monomers such as hydroxyalkyl (meth)acrylates such as hydroxyethyl (meth)acrylate, hydroxypropyl (meth)acrylate,

hydroxybutyl (meth)acrylate, etc., and adducts of lactone compounds such as ε-caprolactone, γ-valerolactone or the like to the hydroxyalkyl (meth)acrylates; aromatic vinyl compounds such as styrene, p-tert-butylstyrene, α-methylstyrene, vinyltoluene, etc.; ω-alkoxyalkyl (meth)acrylates such as 2-methoxyethyl (meth)acrylate, 4-methoxybutyl (meth)acrylate, etc.; tertiary amide group-having unsaturated monomers such as N,N-dimethyl(meth)acrylamide, etc.; polyalkylene oxide structure-having unsaturated monomers such as methoxypolyethylene glycol (meth)acrylate, polyethylene glycol (meth)acrylate, methoxypolypropylene glycol (meth)acrylate, polypropylene glycol (meth)acrylate, etc.; N-alkoxymethyl(meth)acrylamides such as
N-methylol(meth)acrylamide,
N-methoxymethyl(meth)acrylamide,
N-ethoxymethyl(meth)acrylamide,
N-n-butoxymethyl(meth)acrylamide,
N-iso-butoxymethyl(meth)acrylamide, etc.; secondary amino group-having unsaturated monomers such as methylaminoethyl (meth)acrylate, etc.; active methylene group-having unsaturated monomers such as vinyl acetoacetate, 2-acetoacetoxyethyl (meth)acrylate, etc.; hydrolysable silyl group-having unsaturated monomers such as vinyltrimethoxysilane,
3-(meth)acryloyloxypropyltrimethoxysilane, etc.; silyl ester

group-having unsaturated monomers such as trimethylsilyl (meth)acrylate, etc.; epoxy group-having unsaturated monomers such as glycidyl (meth)acrylate, methylglycidyl (meth)acrylate, 3,4-epoxycyclohexyl (meth)acrylate, glycidyl vinyl ether, allyl glycidyl ether, etc.; isocyanate group-having unsaturated monomers such as 2-isocyanatopropene, 2-isocyanatoethyl vinyl ether, 2-isocyanatoethyl methacrylate, m-isopropenyl-α,α-dimethylbenzyl isocyanate, etc. One alone or two or more of these unsaturated monomers (a2) may be used either singly or as combined.

[0017]

The production method for the polymer (A) includes, for example, the following two solution polymerization methods.

[0018]

A method 1 is a method of dropwise adding the unsaturated monomer (a1) and the unsaturated monomer (a2) to an organic solvent along with a polymerization initiator, and polymerizing them with stirring under heat.

[0019]

Another method 2 is a method of dropwise adding a monomer mixture (I) of the unsaturated monomer (a1) and/or the unsaturated monomer (a2) to an organic solvent along with a polymerization initiator, polymerizing them with stirring under heat, and further adding a monomer mixture (II) containing the unsaturated monomer (a1) as the main ingredient,

and polymerizing them with stirring under heat. From the viewpoint that the storage stability of the aqueous resin composition to be obtained betters more, preferably, the ratio of the molar ratio (x) of the unsaturated monomer (a1) in the unsaturated monomer mixture (I) to the molar ratio (y) of the unsaturated monomer (a1) in the unsaturated monomer mixture (II) [(x)/(y)] falls within a range of less than 1, more preferably within a range of less than 0.5.

[0020]

The ratio by mass of the unsaturated monomer mixture (I) to the unsaturated monomer mixture (II) [(I)/(II)] is preferably within a range of 20/80 to 85/15, more preferably 30/70 to 75/25.

[0021]

As in the above-mentioned method 2, by copolymerizing two types of mixtures differing in point of the composition of the unsaturated monomers to form the polymer (A) in two stages, the carboxyl group can be eccentrically located in the polymer (A), and the polymer includes the modified epoxy resin (C) and at the same time when the polymer is dispersed in the aqueous medium, the carboxyl group that the polymer (A) to be the shell part of the self-emulsifying aqueous resin (E) has is positioned on the aqueous phase side, and in addition, the hydrophobic part of the acrylic resin polymer (A) is positioned on the core side of the self-emulsifying aqueous resin (E),

and accordingly, the stability of the resin in an aqueous medium is further more improved.

[0022]

The organic solvent to be used in producing the polymer (A) is preferably a water-miscible organic solvent that is miscible with water with no separation, and above all, an organic solvent having a solubility in water (gram of organic solvent dissolving in 100 g of water) at 25°C of 3 g or more is preferred. The water-miscible organic solvent of the type includes, for example, alcohol solvents such as methanol, ethanol, propanol, butanol, etc.; ketone solvents such as acetone, methyl ethyl ketone, etc.; glycol ether solvents such as ethylene glycol monomethyl ether, ethylene glycol dimethyl ether, ethylene glycol monoethyl ether, ethylene glycol diethyl ether, ethylene glycol monopropyl ether, ethylene glycol monoisopropyl ether, ethylene glycol monobutyl ether, diethylene glycol monomethyl ether, diethylene glycol dimethyl ether, diethylene glycol monoethyl ether, diethylene glycol diethyl ether, diethylene glycol monoisopropyl ether, diethylene glycol monobutyl ether, triethylene glycol monomethyl ether, triethylene glycol dimethyl ether, propylene glycol monomethyl ether, propylene glycol dimethyl ether, propylene glycol monopropyl ether, propylene glycol monobutyl ether, dipropylene glycol monomethyl ether, dipropylene glycol dimethyl ether, etc. One alone or two or

more of these water-miscible organic solvents may be used either singly or as combined.

[0023]

The polymerization initiator for use in producing the polymer (A) includes, for example, azo compounds such as 2,2'-azobis(isobutyronitrile), 2,2'-azobis(2-methylbutyronitrile), azobiscyanovaleric acid, etc.; organic peroxides such as tert-butylperoxy pivalate, tert-butylperoxy benzoate, tert-butylperoxy 2-ethylhexanoate, di-tert-butyl peroxide, cumene hydroperoxide, benzoyl peroxide, t-butyl hydroperoxide, etc.; inorganic peroxides such as hydrogen peroxide, ammonium persulfate, potassium persulfate, sodium persulfate, etc. One alone or two or more of these polymerization initiators may be used either singly or as combined. Preferably, the polymerization initiator is used in an amount falling within a range of 0.1 to 10% by mass relative to the total of the unsaturated monomers to form the polymer (A).

[0024]

The nonvolatile content in the reactor in producing the polymer (A) is preferably within a range of 30 to 90% by mass, more preferably within a range of 50 to 85% by mass.

[0025]

It is important that the acid value of the polymer (A) is within a range of 40 to 90 mg KOH/g, for imparting excellent

low-temperature curability to the composition.

[0026]

The hydroxy value of the polymer (A) is preferably within a range of 5 to 100 mg KOH/g for further bettering the low-temperature curability.

[0027]

The weight-average molecular weight of the polymer (A) is, as being able to provide an aqueous resin composition and a coating material excellent in storage stability with no viscosity increase, preferably within a range of 5,000 to 100,000, more preferably within a range of 10,000 to 50,000.

[0028]

In the present invention, the acid value and the hydroxyl value are those determined through calculation from the starting material, unsaturated monomer composition. The weight-average molecular weight is one determined through gel permeation chromatography (hereinafter abbreviated as "GPC").

[0029]

It is important that, from the viewpoint of the coating film hardness, the glass transition temperature of the polymer (A) falls within a range of 50 to 100°C.

[0030]

In the present invention, the glass transition temperature is one determined through calculation according to the following FOX equation.

FOX Equation: 1/Tg = W1/Tg1+W2/Tg2+...

(Tg: glass transition temperature to be determined, W1: weight fraction of component 1, Tg1: glass transition temperature of homopolymer of component 1)

As the value of the glass transition temperature of the homopolymer of each component, one described in "Adhesion Technology Handbook" by Nikkan Kogyo Shimbun, Ltd., or "Polymer Handbook" by Wiley-Interscience Publication is exemplified. Hereinafter, the glass transition temperature is referred to as "Tg".

[0031]

The acrylic resin (C) is one prepared by neutralizing the polymer (A) with the basic compound (B), and from the viewpoint of acid resistance, it is important that the basic compound (B) contains an alkylamine (b1) in an amount of 55 mol% or more, preferably 70 mol% or more.

[0032]

The alkylamine (b1) includes, for example, monomethylamine, dimethylamine, trimethylamine, monoethylamine, diethylamine, triethylamine, monopropylamine, dipropylamine, tripropylamine, etc. From the viewpoint of easiness in controlling temperature in the neutralization step, triethylamine is preferred. One alone or two or more of these alkylamines (b1) may be used either singly or as combined.

[0033]

The other basic compound (b2) than the alkylamine (b1) usable as the basic compound (B) includes organic amines such as alkanolamines such as monoethanolamine, diethanolamine, monoiropropanolamine, diisopropanolamine, N-methylethanolamine, N,N-dimethylethanolamine, N,N-diethylethanolamine, 2-amino-2-methylpropanol, 2-(dimethylamino)-2-methylpropanol, N-methyldiethanolamine, etc.; polyamines such as ethylenediamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine, etc.; and ammonia (aqueous), etc. One alone or two or more of these basic compounds (b2) can be used either singly or as combined.

[0034]

The degree of neutralization of the carboxyl group that the acrylic resin (C) has is, from the viewpoint of more bettering the dispersion stability, preferably within a range of 50 to 100%.

[0035]

The modified epoxy resin (D) is a reaction product of an epoxy resin (d1), a monocarboxylic acid (d2) and a compound (d3) having a hydroxyl group bonding to a phosphorus atom.

[0036]

The epoxy resin (d1) includes, for example, aliphatic polyol diglycidyl ether-type epoxy resins with ethylene glycol, propylene glycol, hexanediol, neopentyl glycol, trimethylolethane, trimethylolpropane, pentaerythritol,

glycerin, diglycerin, sorbitol, spiroglycol, hydrogenated bisphenol A or the like;

[0037]

Aromatic epoxy resins such as diglycidyl ether-type epoxy resins with bisphenol A, bisphenol F, bisphenol S, bisphenol AD or the like; novolak-type epoxy resins that are glycidyl ethers of phenol-novolak resins, cresol-novolak resins or the like; diglycidyl ether-type epoxy resins with polyols such as ethylene oxide or propylene oxide adducts of aromatic polyhydroxy compounds;

[0038]

Polyglycidyl ether-type epoxy resins with polyether polyol such as polyethylene glycol, polypropylene glycol, polytetramethylene glycol, etc.; cyclic aliphatic polyepoxy resins such as bis(3,4-epoxycyclohexylmethyl) adipate,3,4-epoxycyclohexylmehtyl-3',4'-epoxycyclohexyl carboxylate, etc.;

[0039]

Polyglycidyl ester-type epoxy resins with a polycarboxylic acid such as propanetricarboxylic acid, butanetetracarboxylic acid, adipic acid, phthalic acid, terephthalic acid, trimellitic acid, etc.; bisepoxy resins with hydrocarbon dienes such as butadiene, hexadiene, octadiene, dodecadiene, cyclooctadiene, α-pinene, vinylchyclohexene, etc.;

[0040]

Epoxy resins with diene polymers such as polybutadiene, polyisoprene, etc.; glycidylamine-type epoxy resins with tetraglycidyldiaminodiphenylmethane, tetraglycidylbisaminomethylcyclohexane, diglycidyl aniline, tetraglycidylmetaxylylenediamine, etc.; epoxy resins having various hetero rings such as triazine, hydantoin, etc. One alone or two or more of these epoxy resins (c1) can be used either singly or as combined.

[0041]

Among these epoxy resins, aromatic epoxy resins capable of more improving corrosion resistance are preferred, and bisphenol A-type epoxy resins are more preferred.

[0042]

The monocarboxylic acid (d2) includes, for example, saturated carboxylic acids such as propionic acid, lactic acid, butyric acid, valeric acid, etc.; ethylenic unsaturated monocarboxylic acids such as (meth)acrylic acid, vinylacetic acid, crotonic acid, tiglic acid, 3,3-dimethylacrylic acid, pentenoic acid, etc. Among these, ethylenic unsaturated monocarboxylic acids capable of more improving adhesion to substrates are preferred, ethylenic unsaturated monocarboxylic acids having 3 to 5 carbon atoms are more preferred, and (meth)acrylic acid is even more preferred. One alone or two or more of these monocarboxylic acids (d2) can

be used either singly or as combined.

[0043]

The compound (d3) having a hydroxyl group bonding to the phosphorus atom includes, for example, phosphoric acid, phosphorous acid, hypophosphorous acid; phosphoric monoesters such as monomethyl phosphate, monoethyl phosphate, monopropyl phosphate, monobutyl phosphate, etc. Compounds having 2 or more hydroxyl groups bonding to a phosphorus atom are preferred as being able to further improve corrosion resistance; and phosphoric acid is more preferred.

[0044]

The reaction of the epoxy resin (d1), the monocarboxylic acid (d2) and the compound (d3) having a hydroxyl group bonding to a phosphorus atom in producing the modified epoxy resin (D) is preferably such that the total molar number of the molar number of the carboxyl group in the monocarboxylic acid (d2) and the molar number of the hydroxyl group bonding to a phosphorus atom in the compound (d3), relative to one mol of the epoxy group in the epoxy resin (d1), is 0.9 to 1 mol.

[0045]

The production method for the modified epoxy resin (D) includes, for example, the following methods (1) to (3).

[0046]

Method (1): The epoxy resin (d1), the monocarboxylic acid (d2) and the compound (d3) are reacted all at a time.

[0047]

Method (2): The epoxy resin (d1) is reacted with the monocarboxylic acid (d2) and then with the compound (d3).

[0048]

Method (3): The epoxy resin (d1) is reacted with the compound (d3) and then with the monocarboxylic acid (d2).

[0049]

Among these methods, the method (2) is preferred as excellent in reaction efficiency.

[0050]

In these methods, if desired, an organic solvent, a catalyst or the like may be used, and as the catalyst, use of a triphenyl phosphine, an amine compound or the like is preferred.

[0051]

The self-emulsifying aqueous resin (E) includes the modified epoxy resin (D) in the acrylic resin (C), and is obtained, for example, through phase inversion emulsification with water of a solution prepared by mixing the polymer (A), the modified resin (D) and the basic compound (B).

[0052]

The ratio by mass of the polymer (A) and the modified epoxy resin (D) [(A)/(D)] in the self-emulsifying aqueous resin (E) is, from the viewpoint of bettering storage stability and corrosion resistance of the coating film to be formed,

preferably within a range of 70/30 to 97/3.

[0053]

The aqueous resin composition of the present invention contains the self-emulsifying aqueous resin (E) dispersed in an aqueous medium. As the aqueous medium, water as well as a water-miscible organic solvent that has been listed hereinabove as the organic solvent usable in producing the polymer (A) can be used. One alone or two or more of these aqueous media can be used either singly or as combined.

[0054]

The aqueous resin composition of the present invention is one prepared by dispersing the self-emulsifying aqueous resin (E) in an aqueous medium, and by further incorporating a curing agent (F) thereinto, the composition can be the aqueous coating material of the present invention. The curing agent (F) includes, for example, an amino resin, a blocked isocyanate resin, etc.

[0055]

The amino resin includes, for example, alkylol group-having amino resins to be obtained by reacting an amino group-having compound such as melamine, benzoguanamine, acetoguanamide, urea or the like with an aldehyde compound such as formaldehyde, acetaldehyde or the like; alkoxyalkyl group-having amino resins to be obtained by reacting the alkylol group-having amino resin and a lower alcohol such as

methanol, ethanol, n-butanol, iso-butanol or the like, etc.

[0056]

The blocked isocyanate resin includes, for example, blocked isocyanates to be obtained by blocking an adduct of an organic diisocyanate compound and a polyalcohol, a low-molecular-weight hydroxyl group-containing polyester resin, a low-molecular-weight hydroxyl group-containing alkyd resin, water or the like, or a polymer produced through polymerization of the organic diisocyanate compound (including an isocyanurate-type polyisocyanate compound, an uretdione compound), with various types of blocking agents including an oxime compound, a phenol compound, an alcohol compound, a diketone compound or the like.

[0057]

The organic diisocyanate compound includes, for example, alicyclic diisocyanates such as isophorone diisocyanate, etc.; aromatic diisocyanates such as xylylene diisocyanate, tolylene diisocyanate, 4,4-diphenylmethane diisocyanate, etc.; aliphatic diisocyanates such as hexamethylene diisocyanate, trimethylhexamethylene diisocyanate, etc.

[0058]

The blending amount of the curing agent (F) is, from the viewpoint of further improving the curability of the aqueous coating material of the present invention and improving the coating film appearance and the durability of the cured coating

film, preferably such that the ratio by mass of [self-emulsifying aqueous resin (E)/curing agent (F)] is within a range of 50/50 to 95/5, more preferably within a range of 70/30 to 90/10.

[0059]

Further, if desired, the aqueous coating material of the present invention may contain, as other blending components, various additives such as an inorganic pigment, an organic pigment, an extender pigment, a wax, a surfactant, a stabilizer, a flowability regulator, a dye, a leveling agent, a rheology controlling agent, a UV absorbent, an antioxidant, a plasticizer, an antistatic agent, a defoaming agent, a viscosity improver, a lightproof stabilizer, a weatherproof stabilizer, a heat-resistant stabilizer, a pigment dispersant, etc.

[0060]

The coating method with the coating composition of the present invention varies, depending on the articles to be coated, and includes, for example, methods with a gravure coater, a roll coater, a comma coater, a knife coater, an air knife coater, a curtain coater, a kiss coater, a shower coater, a wheeler coater, a spin coater, dipping, screen printing, a spray, an applicator, a bar coater, etc.

[0061]

The aqueous coating material of the present invention

can form a cured coating film excellent in acid resistance, on the surfaces of various articles.

[0062]

The coating composition of the present invention can be directly applied to articles that are to be objects to be coated, or after the objects to be coated are first coated with a primer coating material suitable to the objects, and then coated with the coating composition of the present invention.

[0063]

The material of the articles that are to be objects to be coated includes various metals such as iron, copper, zinc, aluminum, magnesium or the like and alloys thereof; various resins such as polycarbonate (PC), acrylonitrile-butadiene-styrene copolymer (ABS), PC-ABS polymer alloy, polymethyl methacrylate (PMMA), polyethylene terephthalate (PET), polyamide (PA), polypropylene (PP), etc.; fiber-reinforced plastics (FRP) prepared by incorporating a filler such as glass fibers or the like into these resins; etc.

[0064]

Articles that can be coated with the aqueous coating material of the present invention include metal parts of belts, bags, accessories, etc.; construction members of steel furniture, external walls, roofs, etc.; civil engineering members such as guard rails, sound barriers, drainage ports,

etc.; various types of metal substrates of household electric appliances, industrial machines, automobiles, etc.

Examples

[0065]

The present invention is described in more detail with reference to specific examples to be given hereunder. The viscosity of the water-based resin composition is a value measured with a BM viscometer manufactured by Toki Sangyo Co., Ltd., "TVB10 Model Viscometer"; the mean particle size of the resin particles in the water-based resin composition is a value measured with "Nanotrac UPA-150" manufactured by Nikkiso Co., Ltd. The weight-average molecular weight (Mw) was measured under the measurement condition mentioned below.

[0066]

[Weight-Average Molecular Weight Measurement Condition]

Measurement apparatus: High-speed GPC apparatus ("HLC-8220GPC" manufactured by Tosoh Corporation)

Columns: The following columns manufactured by Tosoh Corporation were connected in series and used.

"TSKgel G5000" (7.8 mm I.D. × 30 cm) × one

"TSKgel G4000" (7.8 mm I.D. × 30 cm) × one

"TSKgel G3000" (7.8 mm I.D. × 30 cm) × one

"TSKgel G2000" (7.8 mm I.D. × 30 cm) × one

Detector: RI (differential refractometer)

Column temperature: 40°C

Eluent: tetrahydrofuran (THF)

Flow rate: 1.0 mL/min

Injection amount: 100 μL (tetrahydrofuran solution having a sample concentration of 0.4% by mass)

Standard samples: Using the following standard polystyrenes, a calibration curve was formed.

[0067]

(Standard Polystyrenes)

"TSKgel Standard Polystyrene A-500" manufactured by Tosoh Corporation

"TSKgel Standard Polystyrene A-1000" manufactured by Tosoh Corporation

"TSKgel Standard Polystyrene A-2500" manufactured by Tosoh Corporation

"TSKgel Standard Polystyrene A-5000" manufactured by Tosoh Corporation

"TSKgel Standard Polystyrene F-1" manufactured by Tosoh Corporation

"TSKgel Standard Polystyrene F-2" manufactured by Tosoh Corporation

"TSKgel Standard Polystyrene F-4" manufactured by Tosoh Corporation

"TSKgel Standard Polystyrene F-10" manufactured by Tosoh Corporation

"TSKgel Standard Polystyrene F-20" manufactured by Tosoh Corporation

"TSKgel Standard Polystyrene F-40" manufactured by Tosoh Corporation

"TSKgel Standard Polystyrene F-80" manufactured by Tosoh Corporation

"TSKgel Standard Polystyrene F-128" manufactured by Tosoh Corporation

"TSKgel Standard Polystyrene F-288" manufactured by Tosoh Corporation

"TSKgel Standard Polystyrene F-550" manufactured by Tosoh Corporation

[0068]

(Synthesis Example 1: Synthesis of modified epoxy resin (D-1))

545.5 parts by mass of a bisphenol A-type epoxy resin ("Epikote 1001" manufactured by Mitsubishi Chemical Corporation) and 259.0 parts by mass of diethylene glycol dimethyl ether were put in a reactor equipped with a stirrer, a thermometer, a reflux condenser and a nitrogen gas introducing duct, and heated up to 80°C while dissolved. After the dissolution, 59.7 parts by mass of acrylic acid was added thereto at 80°C, and heated up to 110°C with stirring, taking 1 hour. The reaction was continued at 110°C for 3 hours, and when the acid value of reaction product reached 1.0 mg KOH/g or less, the system was cooled down to 80°C. A mixture of 12.1

parts by mass of 85% by mass phosphoric acid and 70.2 parts by mass of diethylene glycol dimethyl ether was continuously dropwise added thereto, taking 1 hour. After the dropwise addition, the system was still kept reacted at 80°C for 4 hours, and then 50.5 parts by mass of diethylene glycol dimethyl ether was added thereto to give a modified epoxy resin (D-1) having a nonvolatile content of 64.0% by mass and an acid value of 9.0 mg KOH/g.

[0069]

(Example 1: Synthesis of aqueous resin composition (1))

766.8 parts by mass of diethylene glycol dimethyl ether and 27.0 parts by mass of fumaric acid were put into a reactor equipped with a reflux condenser, a stirrer and a nitrogen gas introducing duct, and stirred with heating up to 135°C. In a nitrogen stream atmosphere, a monomer mixture of 637.2 parts by mass of styrene, 145.8 parts by mass of methyl methacrylate, 62.6 parts by mass of n-butyl acrylate, 108.0 parts by mass of 2-hydoxyethyl methacrylate and 16.2 parts by mass of acrylic acid, and 39.6 parts by mass of t-butylperoxy-2-ethylhexanoate were continuously dropwise added thereto, taking 3 hours. Subsequently, a monomer mixture of 424.8 parts by mass of styrene, 97.2 parts by mass of methyl methacrylate, 41.8 parts by mass of n-butyl acrylate, 72.0 parts by mass of 2-hydroxyethyl methacrylate and 145.8 parts by mass of acrylic acid, and 30.6 parts by mass of t-butylperoxy-2-ethylhexanoate

were continuously dropwise added thereto, taking 2 hours. At the same temperature, this was stirred for 2 hours and the reaction was finished to give a solution of a polymer (A-1) having Tg of 80°C, an acid value of 85 mg KOH/g and a hydroxyl value of 43 mg KOH/g. 149.4 parts by mass of a modified epoxy resin (D-1) was mixed in the solution, then neutralized with 117.0 parts by mass of triethylamine, and processed for phase inversion emulsification using 2105.0 parts by mass of ion-exchanged water to give an aqueous resin composition (1) with a self-emulsifying aqueous resin dispersed in an aqueous medium. The aqueous resin composition (1) had a nonvolatile content of 44.0% by mass and a pH of 7.5.

[0070]

(Example 2: Synthesis of aqueous resin composition (2))

234.4 parts by mass of diethylene glycol dimethyl ether was put into a reactor equipped with a reflux condenser, a stirrer and a nitrogen gas introducing duct, and stirred with heating up to 135°C. In a nitrogen stream atmosphere, a monomer mixture of 227.2 parts by mass of styrene, 58.8 parts by mass of methyl methacrylate, 21.6 parts by mass of n-butyl acrylate, 38.5 parts by mass of 2-hydoxyethyl methacrylate and 5.0 parts by mass of acrylic acid, and 14.1 parts by mass of t-butylperoxy-2-ethylhexanoate were continuously dropwise added thereto, taking 3.5 hours. Subsequently, a monomer mixture of 97.4 parts by mass of styrene, 25.1 parts by mass

of methyl methacrylate, 9.2 parts by mass of n-butyl acrylate, 16.5 parts by mass of 2-hydroxyethyl methacrylate and 44.5 parts by mass of acrylic acid, and 7.7 parts by mass of t-butylperoxy-2-ethylhexanoate were continuously dropwise added thereto, taking 1.5 hours. At the same temperature, this was stirred for 2 hours and the reaction was finished to give a solution of a polymer (A-2) having Tg of 80°C, an acid value of 70 mg KOH/g and a hydroxyl value of 43 mg KOH/g. 45.8 parts by mass of a modified epoxy resin (D-1) was mixed in the solution, then neutralized with 34.7 parts by mass of triethylamine, and processed for phase inversion emulsification using 485.7 parts by mass of ion-exchanged water to give an aqueous resin composition (2) with a self-emulsifying aqueous resin dispersed in an aqueous medium. The aqueous resin composition (2) had a nonvolatile content of 47.0% by mass and a pH of 7.5.

[0071]

(Example 3: Synthesis of aqueous resin composition (3))

255.8 parts by mass of diethylene glycol dimethyl ether and 9.0 parts by mass of fumaric acid were put into a reactor equipped with a reflux condenser, a stirrer and a nitrogen gas introducing duct, and stirred with heating up to 135°C. In a nitrogen stream atmosphere, a monomer mixture of 212.4 parts by mass of styrene, 64.9 parts by mass of methyl methacrylate, 23.4 parts by mass of n-butyl acrylate, 36.0 parts by mass of 2-hydoxyethyl methacrylate, 1.5 parts by mass of acrylic acid

and 0.7 parts by mass of methacrylic acid, and 13.6 parts by mass of t-butylperoxy-2-ethylhexanoate were continuously dropwise added thereto, taking 3 hours. Subsequently, a monomer mixture of 141.6 parts by mass of styrene, 43.3 parts by mass of methyl methacrylate, 15.6 parts by mass of n-butyl acrylate, 24.0 parts by mass of 2-hydroxyethyl methacrylate, 13.9 parts by mass of acrylic acid and 6.5 parts by mass of methacrylic acid, and 9.8 parts by mass of t-butylperoxy-2-ethylhexanoate were continuously dropwise added thereto, taking 2 hours. At the same temperature, this was stirred for 2 hours and the reaction was finished to give a solution of a polymer (A-3) having Tg of 80°C, an acid value of 42 mg KOH/g and a hydroxyl value of 43 mg KOH/g. 50.0 parts by mass of a modified epoxy resin (D-1) was mixed in the solution, then neutralized with 30.1 parts by mass of triethylamine, and processed for phase inversion emulsification using 725.0 parts by mass of ion-exchanged water to give an aqueous resin composition (3) with a self-emulsifying aqueous resin dispersed in an aqueous medium. The aqueous resin composition (3) had a nonvolatile content of 36.5% by mass and a pH of 7.4.

[0072]

(Example 4: Synthesis of aqueous resin composition (4))

255.0 parts by mass of diethylene glycol dimethyl ether and 9.0 parts by mass of fumaric acid were put into a reactor equipped with a reflux condenser, a stirrer and a nitrogen gas

introducing duct, and stirred with heating up to 135°C. In a nitrogen stream atmosphere, a monomer mixture of 212.4 parts by mass of styrene, 60.8 parts by mass of methyl methacrylate, 21.6 parts by mass of n-butyl acrylate, 36.0 parts by mass of 2-hydoxyethyl methacrylate and 3.3 parts by mass of acrylic acid, and 13.3 parts by mass of t-butylperoxy-2-ethylhexanoate were continuously dropwise added thereto, taking 3 hours. Subsequently, a monomer mixture of 141.6 parts by mass of styrene, 40.2 parts by mass of methyl methacrylate, 14.4 parts by mass of n-butyl acrylate, 24.0 parts by mass of 2-hydroxyethyl methacrylate and 29.7 parts by mass of acrylic acid, and 10.0 parts by mass of t-butylperoxy-2-ethylhexanoate were continuously dropwise added thereto, taking 2 hours. At the same temperature, this was stirred for 2 hours and the reaction was finished to give a solution of a polymer (A-4) having Tg of 80°C, an acid value of 57 mg KOH/g and a hydroxyl value of 43 mg KOH/g. 50.0 parts by mass of a modified epoxy resin (D-1) was mixed in the solution, then neutralized with 39.0 parts by mass of triethylamine, and processed for phase inversion emulsification using 735.0 parts by mass of ion-exchanged water to give an aqueous resin composition (4) with a self-emulsifying aqueous resin dispersed in an aqueous medium. The aqueous resin composition (4) had a nonvolatile content of 40.5% by mass and a pH of 7.5.

[0073]

(Example 5: Synthesis of aqueous resin composition (5))

256.5 parts by mass of diethylene glycol dimethyl ether and 9.0 parts by mass of fumaric acid were put into a reactor equipped with a reflux condenser, a stirrer and a nitrogen gas introducing duct, and stirred with heating up to 135°C. In a nitrogen stream atmosphere, a monomer mixture of 212.4 parts by mass of styrene, 67.0 parts by mass of methyl methacrylate, 22.0 parts by mass of n-butyl acrylate, 36.0 parts by mass of 2-hydoxyethyl methacrylate and 2.1 parts by mass of acrylic acid, and 13.6 parts by mass of t-butylperoxy-2-ethylhexanoate were continuously dropwise added thereto, taking 3 hours. Subsequently, a monomer mixture of 141.6 parts by mass of styrene, 44.6 parts by mass of methyl methacrylate, 14.8 parts by mass of n-butyl acrylate, 24.0 parts by mass of 2-hydroxyethyl methacrylate and 19.1 parts by mass of acrylic acid, and 10.0 parts by mass of t-butylperoxy-2-ethylhexanoate were continuously dropwise added thereto, taking 2 hours. At the same temperature, this was stirred for 2 hours and the reaction was finished to give a solution of a polymer (A-5) having Tg of 80°C, an acid value of 42 mg KOH/g and a hydroxyl value of 43 mg KOH/g. 50.0 parts by mass of a modified epoxy resin (D-1) was mixed in the solution, then neutralized with 29.8 parts by mass of triethylamine, and processed for phase inversion emulsification using 725.0 parts by mass of ion-exchanged water to give an aqueous resin composition (5)

with a self-emulsifying aqueous resin dispersed in an aqueous medium. The aqueous resin composition (5) had a nonvolatile content of 32.0% by mass and a pH of 7.6.

[0074]

(Example 6: Synthesis of aqueous resin composition (6))

256.4 parts by mass of diethylene glycol dimethyl ether and 9.0 parts by mass of fumaric acid were put into a reactor equipped with a reflux condenser, a stirrer and a nitrogen gas introducing duct, and stirred with heating up to 135°C. In a nitrogen stream atmosphere, a monomer mixture of 212.4 parts by mass of styrene, 67.0 parts by mass of methyl methacrylate, 22.0 parts by mass of n-butyl acrylate, 36.0 parts by mass of 2-hydoxyethyl methacrylate and 2.1 parts by mass of acrylic acid, and 13.6 parts by mass of t-butylperoxy-2-ethylhexanoate were continuously dropwise added thereto, taking 3 hours. Subsequently, a monomer mixture of 141.6 parts by mass of styrene, 44.6 parts by mass of methyl methacrylate, 14.8 parts by mass of n-butyl acrylate, 24.0 parts by mass of 2-hydroxyethyl methacrylate and 19.1 parts by mass of acrylic acid, and 10.0 parts by mass of t-butylperoxy-2-ethylhexanoate were continuously dropwise added thereto, taking 2 hours. At the same temperature, this was stirred for 2 hours and the reaction was finished to give a solution of a polymer (A-6) having Tg of 80°C, an acid value of 43 mg KOH/g and a hydroxyl value of 43 mg KOH/g. 50.0 parts by mass of a modified epoxy

resin (D-1) was mixed in the solution, then neutralized with 22.3 parts by mass of triethylamine and 7.2 parts by mass of 25 mass% aqueous ammonia, and processed for phase inversion emulsification using 835.0 parts by mass of ion-exchanged water to give an aqueous resin composition (6) with a self-emulsifying aqueous resin dispersed in an aqueous medium. The aqueous resin composition (6) had a nonvolatile content of 32.0% by mass and a pH of 7.6.

[0075]

(Comparative Example 1: Preparation of aqueous resin composition (R1))

255.6 parts by mass of diethylene glycol dimethyl ether and 9.0 parts by mass of fumaric acid were put into a reactor equipped with a reflux condenser, a stirrer and a nitrogen gas introducing duct, and stirred with heating up to 135°C. In a nitrogen stream atmosphere, a monomer mixture of 212.4 parts by mass of styrene, 48.6 parts by mass of methyl methacrylate, 20.9 parts by mass of n-butyl acrylate, 36.0 parts by mass of 2-hydoxyethyl methacrylate and 5.4 parts by mass of acrylic acid, and 13.0 parts by mass of t-butylperoxy-2-ethylhexanoate were continuously dropwise added thereto, taking 3 hours. Subsequently, a monomer mixture of 141.6 parts by mass of styrene, 32.4 parts by mass of methyl methacrylate, 13.9 parts by mass of n-butyl acrylate, 24.0 parts by mass of 2-hydroxyethyl methacrylate and 48.6 parts by mass of acrylic

acid, and 10.4 parts by mass of t-butylperoxy-2-ethylhexanoate were continuously dropwise added thereto, taking 2 hours. At the same temperature, this was stirred for 2 hours and the reaction was finished to give a solution of a polymer (RA-1) having Tg of 80°C, an acid value of 85 mg KOH/g and a hydroxyl value of 43 mg KOH/g. The solution was neutralized with 38.8 parts by mass of triethylamine added thereto, and processed for phase inversion emulsification using 870.0 parts by mass of ion-exchanged water to give an aqueous resin composition (R1) with a self-emulsifying aqueous resin dispersed in an aqueous medium. The aqueous resin composition (R1) had a nonvolatile content of 36.5% by mass and a pH of 7.5.

[0076]

(Comparative Example 2: Preparation of aqueous resin composition (R2))

766.8 parts by mass of diethylene glycol dimethyl ether and 27.0 parts by mass of fumaric acid were put into a reactor equipped with a reflux condenser, a stirrer and a nitrogen gas introducing duct, and stirred with heating up to 135°C. In a nitrogen stream atmosphere, a monomer mixture of 637.2 parts by mass of styrene, 145.8 parts by mass of methyl methacrylate,62.6 parts by mass of n-butyl acrylate, 108.0 parts by mass of 2-hydoxyethyl methacrylate and 16.2 parts by mass of acrylic acid, and 39.6 parts by mass of t-butylperoxy-2-ethylhexanoate were continuously dropwise

added thereto, taking 3 hours. Subsequently, a monomer mixture of 424.8 parts by mass of styrene, 97.2 parts by mass of methyl methacrylate, 41.8 parts by mass of n-butyl acrylate, 72.0 parts by mass of 2-hydroxyethyl methacrylate and 145.8 parts by mass of acrylic acid, and 30.6 parts by mass of t-butylperoxy-2-ethylhexanoate were continuously dropwise added thereto, taking 2 hours. At the same temperature, this was stirred for 2 hours and the reaction was finished to give a solution of a polymer (RA-2) having Tg of 80°C, an acid value of 85 mg KOH/g and a hydroxyl value of 43 mg KOH/g. 149.4 parts by mass of a modified epoxy resin (D-1) was mixed in the solution, and then the solution was neutralized with 103.0 parts by mass of dimethylethanolamine, and processed for phase inversion emulsification using 2105.0 parts by mass of ion-exchanged water to give an aqueous resin composition (R2) with a self-emulsifying aqueous resin dispersed in an aqueous medium. The aqueous resin composition (R2) had a nonvolatile content of 44.0% by mass and a pH of 7.5.

[0077]

(Comparative Example 3: Preparation of aqueous resin composition (R3))

327.7 parts by mass of diethylene glycol dimethyl ether was put into a reactor equipped with a reflux condenser, a stirrer and a nitrogen gas introducing duct, and stirred with heating up to 135°C. In a nitrogen stream atmosphere, a monomer

mixture of 212.8 parts by mass of styrene, 83.7 parts by mass of methyl methacrylate, 390.9 parts by mass of n-butyl acrylate, 129.8 parts by mass of 2-hydoxyethyl methacrylate and 243.0 parts by mass of an unsaturated fatty acid hydroxyalkyl ester-modified epsilon-caprolactone ("Placcel FM1" manufactured by Daicel Corporation), and 33.6 parts by mass of t-butylperoxy-2-ethylhexanoate were continuously dropwise added thereto, taking 3.5 hours. Subsequently, a monomer mixture of 91.2 parts by mass of styrene, 35.8 parts by mass of methyl methacrylate, 167.5 parts by mass of n-butyl acrylate, 55.6 parts by mass of 2-hydroxyethyl methacrylate, 104.2 parts by mass of the unsaturated fatty acid hydroxyalkyl ester-modified epsilon-caprolactone ("Placcel FM1" manufactured by Daicel Corporation), 39.0 parts by mass of acrylic acid and 16.0 parts by mass of methoxypolyethylene glycol methacrylate ("NK Ester M-230G" manufactured by Shin-Nakamura Chemical Co., Ltd.), and 14.4 parts by mass of t-butylperoxy-2-ethylhexanoate were continuously dropwise added thereto, taking 1.5 hours. At the same temperature, this was stirred for 1 hour, then the temperature is reduced to 120°C, and 16.0 parts by mass of styrene and 5.9 parts by mass of t-butyl peroxybenzoate were added thereto, and further stirred for 2 hours to finish the reaction, thereby giving a solution of a polymer (RA-3) having Tg of 0°C, an acid value of 20 mg KOH/g and a hydroxyl value of 100 mg KOH/g. 302.4 parts by

mass of a modified epoxy resin (D-1) was mixed in the solution, and then this was neutralized with 44.6 parts by mass of dimethylethanolamine, and processed for phase inversion emulsification using 1856.3 parts by mass of ion-exchanged water to give an aqueous resin composition (R3) with a self-emulsifying aqueous resin dispersed in an aqueous medium. The aqueous resin composition (R3) had a nonvolatile content of 44.0% by mass and a pH of 8.3.

[0078]

(Comparative Example 4: Preparation of aqueous resin composition (R4))

329. parts by mass of diethylene glycol dimethyl ether was put into a reactor equipped with a reflux condenser, a stirrer and a nitrogen gas introducing duct, and stirred with heating up to 135°C. In a nitrogen stream atmosphere, a monomer mixture of 214.1 parts by mass of styrene, 240.8 parts by mass of methyl methacrylate, 396.3 parts by mass of n-butyl acrylate, 78.3 parts by mass of 2-hydoxyethyl methacrylate and 47.0 parts by mass of an unsaturated fatty acid hydroxyalkyl ester-modified epsilon-caprolactone ("Placcel FM1" manufactured by Daicel Corporation), and 39.4 parts by mass of t-butylperoxy-2-ethylhexanoate were continuously dropwise added thereto, taking 3.5 hours. Subsequently, a monomer mixture of 91.7 parts by mass of styrene, 103.2 parts by mass of methyl methacrylate, 169.8 parts by mass of n-butyl acrylate,

33.6 parts by mass of 2-hydroxyethyl methacrylate, 63.0 parts by mass of the unsaturated fatty acid hydroxyalkyl ester-modified epsilon-caprolactone ("Placcel FM1" manufactured by Daicel Corporation), 39.3 parts by mass of acrylic acid and 16.0 parts by mass of "NK Ester M-230G", and 16.9 parts by mass of t-butylperoxy-2-ethylhexanoate were continuously dropwise added thereto, taking 1.5 hours. At the same temperature, this was stirred for 1 hour, then the temperature is reduced to 120°C, and 16.1 parts by mass of styrene and 4.8 parts by mass of t-butyl peroxybenzoate were added thereto, and further stirred for 2 hours to finish the reaction, thereby giving a solution of a polymer (RA-4) having Tg of 10°C, an acid value of 20 mg KOH/g and a hydroxyl value of 49 mg KOH/g. 307.2 parts by mass of a modified epoxy resin (D-1) was mixed in the solution, and then this was neutralized with 41.4 parts by mass of dimethylethanolamine, and processed for phase inversion emulsification using 1891.2 parts by mass of ion-exchanged water to give an aqueous resin composition (R4) with a self-emulsifying aqueous resin dispersed in an aqueous medium. The aqueous resin composition (R4) had a nonvolatile content of 44.0% by mass and a pH of 7.8.

[0079]

(Comparative Example 5: Preparation of aqueous resin composition (R5))

255.6 parts by mass of diethylene glycol dimethyl ether

and 9.0 parts by mass of fumaric acid were put into a reactor equipped with a reflux condenser, a stirrer and a nitrogen gas introducing duct, and stirred with heating up to 135°C. In a nitrogen stream atmosphere, a monomer mixture of 212.4 parts by mass of styrene, 38.9 parts by mass of methyl methacrylate, 20.1 parts by mass of n-butyl acrylate, 36.0 parts by mass of 2-hydoxyethyl methacrylate and 5.4 parts by mass of acrylic acid, and 12.6 parts by mass of t-butylperoxy-2-ethylhexanoate were continuously dropwise added thereto, taking 3 hours. Subsequently, a monomer mixture of 141.6 parts by mass of styrene, 25.9 parts by mass of methyl methacrylate, 13.4 parts by mass of n-butyl acrylate, 24.0 parts by mass of 2-hydroxyethyl methacrylate and 66.0 parts by mass of acrylic acid, and 10.8 parts by mass of t-butylperoxy-2-ethylhexanoate were continuously dropwise added thereto, taking 2 hours. At the same temperature, this was stirred for 2 hours to finish the reaction, thereby giving a solution of a polymer (RA-5) having Tg of 80°C, an acid value of 107 mg KOH/g and a hydroxyl value of 43 mg KOH/g. 50.0 parts by mass of a modified epoxy resin (D-1) was mixed in the solution, and then this was neutralized with 37.8 parts by mass of triethylamine, and processed for phase inversion emulsification using 835.0 parts by mass of ion-exchanged water to give an aqueous resin composition (R5) with a self-emulsifying aqueous resin dispersed in an aqueous medium. The aqueous resin composition

(R5) had a nonvolatile content of 40.0% by mass and a pH of 7.4.

[0080]

(Comparative Example 6: Preparation of aqueous resin composition (R6))

255.4 parts by mass of diethylene glycol dimethyl ether and 9.0 parts by mass of fumaric acid were put into a reactor equipped with a reflux condenser, a stirrer and a nitrogen gas introducing duct, and stirred with heating up to 135°C. In a nitrogen stream atmosphere, a monomer mixture of 212.4 parts by mass of styrene, 70.2 parts by mass of methyl methacrylate, 22.4 parts by mass of n-butyl acrylate, 36.0 parts by mass of 2-hydoxyethyl methacrylate and 1.6 parts by mass of acrylic acid, and 13.7 parts by mass of t-butylperoxy-2-ethylhexanoate were continuously dropwise added thereto, taking 3 hours. Subsequently, a monomer mixture of 141.6 parts by mass of styrene, 46.8 parts by mass of methyl methacrylate, 14.9 parts by mass of n-butyl acrylate, 24.0 parts by mass of 2-hydroxyethyl methacrylate and 13.8 parts by mass of acrylic acid, and 9.4 parts by mass of t-butylperoxy-2-ethylhexanoate were continuously dropwise added thereto, taking 2 hours. At the same temperature, this was stirred for 2 hours to finish the reaction, thereby giving a solution of a polymer (RA-6) having Tg of 80°C, an acid value of 43 mg KOH/g and a hydroxyl value of 43 mg KOH/g. 50.0 parts by mass of a modified epoxy

resin (D-1) was mixed in the solution, and then this was neutralized with 21.5 parts by mass of triethylamine, and processed for phase inversion emulsification using 500.0 parts by mass of ion-exchanged water. However, an aqueous resin composition with a self-emulsifying aqueous resin dispersed in an aqueous medium could not be obtained.

[0081]

(Comparative Example 7: Preparation of aqueous resin composition (R7))

255.0 parts by mass of diethylene glycol dimethyl ether and 9.0 parts by mass of fumaric acid were put into a reactor equipped with a reflux condenser, a stirrer and a nitrogen gas introducing duct, and stirred with heating up to 135°C. In a nitrogen stream atmosphere, a monomer mixture of 212.4 parts by mass of styrene, 60.8 parts by mass of methyl methacrylate, 21.6 parts by mass of n-butyl acrylate, 36.0 parts by mass of 2-hydoxyethyl methacrylate and 3.3 parts by mass of acrylic acid, and 13.3 parts by mass of t-butylperoxy-2-ethylhexanoate were continuously dropwise added thereto, taking 3 hours. Subsequently, a monomer mixture of 141.6 parts by mass of styrene, 40.2 parts by mass of methyl methacrylate, 14.4 parts by mass of n-butyl acrylate, 24.0 parts by mass of 2-hydroxyethyl methacrylate and 29.7 parts by mass of acrylic acid, and 10.0 parts by mass of t-butylperoxy-2-ethylhexanoate were continuously dropwise added thereto, taking 2 hours. At

the same temperature, this was stirred for 2 hours to finish the reaction, thereby giving a solution of a polymer (RA-7) having Tg of 80°C, an acid value of 57 mg KOH/g and a hydroxyl value of 43 mg KOH/g. 50.0 parts by mass of a modified epoxy resin (D-1) was mixed in the solution, and then this was neutralized with 19.5 parts by mass of triethylamine, and processed for phase inversion emulsification using 500.0 parts by mass of ion-exchanged water. However, an aqueous resin composition with a self-emulsifying aqueous resin dispersed in an aqueous medium could not be obtained.

[0082]

The physical data of the aqueous resin compositions (1) to (6) and (R1) to (R5) obtained in the above are shown in Tables 1 and 2. In the Tables, "TEA" represents triethylamine, and "DMEA" represents dimethylethanolamine. In Comparative Examples 6 and 7, an aqueous resin composition with a self-emulsifying aqueous resin dispersed in an aqueous medium could not be obtained, and therefore physical data were not measured.

[0083]
Table 1

		Example 1	Example 2	Example 3	Example 4	Example 5	Example 6
Aqueous Resin Composition		(1)	(2)	(3)	(4)	(5)	(6)
Acid Value of Polymer (A) (mg KOH/g)		85	70	42	57	42	43
Basic Compound (B)		TEA	TEA	TEA	TEA	TEA	TEA 25 mass% aqueous ammonia
Content of Alkylamine (b1) in Basic Compound (B) (mol%)		100	100	100	100	100	75
Ratio by Mass of Polymer (A) to Modified Epoxy Resin (D([(A)/(D)]		100/5	100/5	100/5	100/5	100/5	100/5
Physical Data	Nonvolatile Content (mass%)	44.0	47.0	36.5	40.5	32.0	32.0
	pH	7.5	7.5	7.4	7.5	7.6	7.6
	Viscosity (mPa·s)	390	1,150	7,400	310	450	700
	Mean Particle Size (nm)	120	190	200	90	160	140

[0084]
Table 2

		Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4	Comparative Example 5	Comparative Example 6	Comparative Example 7
Aqueous Resin Composition		(R1)	(R2)	(R3)	(R4)	(R5)	(R6)	(R7)
Acid Value of Polymer (A) (mg KOH/g)		85	85	20	20	107	35	57
Basic Compound (B)		TEA	DMEA	DMEA	DMEA	TEA	TEA	TEA 25 mass% aqueous ammonia
Content of Alkylamine (b1) in Basic Compound (B) (mol%)		100	0	0	0	100	100	50
Ratio by Mass of Polymer (A) to Modified Epoxy Resin (D([(A)/(D)]		100/0	100/5	100/12	100/13	100/5	100/5	100/5
Physical Data	Nonvolatile Content (mass%)	36.5	44.0	44.0	44.0	40.0	Not Measured	Not Measured
	pH	7.5	7.5	8.3	7.8	7.4		
	Viscosity (mPa·s)	50	200	500	450	100		
	Mean Particle Size (nm)	105	105	120	140	210		

[0085]

(Examples 7 to 12: Preparation and Evaluation of Aqueous Coating Materials (1) to (6))

[Preparation of Aqueous Coating Materials]

Each aqueous resin composition (1) to (6) obtained in Examples 1 to 6 and a curing agent (melamine resin) were blended as in Table 3 below, stirred and mixed to give aqueous coating materials (1) to (6). Next, the resultant aqueous coating materials were formed into coating films and evaluated as mentioned below.

[0086]

[Formation of Coating Film for Evaluation]

Each aqueous coating material (1) to (6) obtained in the above was applied to a tin plate so that the dry thickness of the coating film could be 30 μm, using a bar coater. After coated, the tin plate was cured at 25°C for 20 minutes and then dried at 110°C for 25 minutes to form thereon a coating film for evaluation (1) to (6).

[0087]

[Evaluation of Coating Film Hardness (pencil hardness)]

The surface of the cured coating film form evaluation, as obtained in the above, was tested according to a scratch test (pencil method) of JIS K 5600-5-4:1999. The hardness of the hardest pencil not leaving a scar on the surface was referred to as the pencil hardness of the coating film, and

the coating film hardness was evaluated according to the following criteria.

A: 2H or more

B: H

C: F or less

[0088]

[Evaluation of Adhesion to Substrate]

The coating film for evaluation obtained in the above was checked for adhesion according to JIS K 5600-5-6:1999 (cross-cut method). Using a cutter, 100 cross-cuts of 1 mm each were formed in the surface of the cured coating film, and an adhesive tape (manufactured by Nichiban Co., Ltd.) was stuck thereto to coat all the cross-cuts, and then immediately peeled. From the ratio of the cross-cuts having remained on the surface, the adhesion to substrate was evaluated according to the following criteria.

A: Less than 5% of the cross-cuts peeled.

B: 5% or more and less than 15% of the cross-cuts peeled.

C: 15% or more of the cross-cuts peeled.

[0089]

[Evaluation of Acid Resistance]

2 ml of 50 mass% nitric acid was dropped onto the coating film for evaluation obtained in the above, and after 90 seconds, the nitric acid was wiped off, and thereafter the surface of the coating film was observed, and the acid resistance thereof

was evaluated according to the following criteria.

A: No change before and after the test.

B: Some slight scarring, lifting and yellowing were seen.

C: Significant scarring, lifting and yellowing were seen.

[0090]

[Evaluation of Corrosion Resistance]

The coating film for evaluation obtained in the above was tested according to a saline water spray test of JIS K 5600-7-:2006. Using a cutter knife, scratches (cross-cuts) to reach the substrate were formed in the cured coating film, and using a saline water spray tester manufactured by Suga Test Instruments Co., Ltd., the coating film was tested. After 72 hours, the tested sample was visually checked for rusting and evaluated according to the following criteria.

A: Rusting was not seen or was seen slightly around the cross-cuts, and peeling of the coating film owing to the rusting was not seen.

B: Rusting was seen widely around the cross-cuts, and peeling or lifting of the coating film owing to the rusting was seen, but spreading of rust was not seen.

C: Rusting was seen widely around the cross-cuts, and peeling or lifting of the coating film owing to the rusting was seen, and further, rust spread to contaminate the coating film therearound.

[0091]

(Comparative Examples 8 to 12: Preparation and evaluation of aqueous coating materials (R1) to (R5))

In the same manner as in Examples 7 to 12 except that the blending formulations were changed as in Table 4 below, aqueous coating materials (R1) to (R5) were prepared and evaluated for the performance of the resultant coating films.

[0092]

The blending formulations and the evaluation results of the aqueous coating materials (1) to (6) obtained in the above are shown in Table 3.

[0093]
Table 3

			Example 7	Example 8	Example 9	Example 10	Example 11	Example 12
Aqueous Coating Material			(1)	(2)	(3)	(4)	(5)	(6)
Formulation (part by mass)	Main Ingredient	Aqueous Resin Composition (1)	30					
		Aqueous Resin Composition (2)		30				
		Aqueous Resin Composition (3)			30			
		Aqueous Resin Composition (4)				30		
		Aqueous Resin Composition (5)					30	
		Aqueous Resin Composition (6)						30
	Curing Agent	Melamine Resin (1)	3.7	3.9	3.0			
		Melamine Resin (2)				3.5	2.7	2.7
Coating Film Evaluation		Coating Film Hardness (pencil hardness)	A (3H)	A (3H)	A (2H)	A (2H)	A (2H)	A (2H)
		Adhesion to Substrate	A	A	A	A	A	A
		Acid Resistance	A	B	A	A	A	A
		Corrosion Resistance	A	B	B	B	A	A

[0094]

The blending formulations and the evaluation results of the aqueous coating materials (R1) to (R5) obtained in the above are shown in Table 4.

[0095]
Table 4

			Comparative Example 8	Comparative Example 9	Comparative Example 10	Comparative Example 11	Comparative Example 12
Aqueous Coating Material			(R1)	(R2)	(R3)	(R4)	(R5)
Formulation (part by mass)	Main Ingredient	Aqueous Resin Composition (R1)	30				
		Aqueous Resin Composition (R2)		30			
		Aqueous Resin Composition (R3)			30		
		Aqueous Resin Composition (R4)				30	
		Aqueous Resin Composition (R5)					30
	Curing Agent	Melamine Resin (1)	3.0	3.7	3.7	3.7	3.3
Coating Film Evaluation		Coating Film Hardness (pencil hardness)	A (3H)	A (3H)	B (H)	B (H)	A (2H)
		Adhesion to Substrate	C	A	A	A	C
		Acid Resistance	C	C	C	C	A
		Corrosion Resistance	C	C	B	B	C

[0096]

It is confirmed that the aqueous resin materials using the aqueous resin compositions of the present invention of Examples 1 to 6 are excellent in various coating film properties.

[0097]

On the other hand, Comparative Example 1 is an example not including a modified epoxy resin, and it is confirmed that this is poor in adhesion to substrate, acid resistance and corrosion resistance.

[0098]

Comparative Examples 2 to 4 are examples using dimethylethanolamine as a basic compound, and it is confirmed that these are poor in acid resistance.

[0099]

Comparative Example 5 is an example where the acid value of the polymer is 107 mg KOH/g that is larger than the upper limit, 90 mg KOH/g in the present invention, and it is confirmed that this is poor in adhesion to substrate and corrosion resistance.

[0100]

Comparative Example 6 is an example where the acid value of the polymer is 35 mg KOH/g that is smaller than the lower limit, 40 mg KOH/g in the present invention, and in this case, an aqueous dispersion could not be formed.

[0101]

Comparative Example 7 is an example where an alkylamine and aqueous ammonia are used together as a basic compound and the alkylamine is in an amount of 50 mol% that is smaller than the lower limit 55 mol% in the present invention, and in this case, an aqueous dispersion could not be formed.

CLAIMS

[Claim 1]

An aqueous resin composition comprising, as dispersed in an aqueous medium, a self-emulsifying aqueous resin (E) in which a modified epoxy resin (D) is included in an acrylic resin (C) which is a carboxyl group-having polymer (A) neutralized with a basic compound (B), wherein the acid value of the polymer (A) is within a range of 40 to 90 mg KOH/g, the basic compound (B) contains an alkylamine (b1) in an amount of 55 mol% or more, and the modified epoxy resin (D) is a reaction product of an epoxy resin (d1), a monocarboxylic acid (d2) and a compound (d3) having a hydroxyl group bonding to a phosphorus atom.

[Claim 2]

The aqueous resin composition according to claim 1, wherein the monocarboxylic acid (d2) is an ethylenic unsaturated carboxylic acid.

[Claim 3]

An aqueous coating material comprising the aqueous resin composition of claim 1 or 2, and a curing agent (F).

[Claim 4]

An article having a cured coating film of the aqueous coating material of claim 3.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CN2017/080741

A. CLASSIFICATION OF SUBJECT MATTER

C09D 5/02(2006.01)i; C09D 163/00(2006.01)i; C09D 163/10(2006.01)i; C09D 133/00(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

CNPAT,CNKI,DWPI:aqueous,self-emulsifying,epoxy,carboxyl,amine,phosphorus,acrylic,acrylate

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 2012092198 A (DAINIPPON INK & CHEMICALS) 17 May 2012 (2012-05-17) abstract, and description, paragraphs [0020], [0030], [0037], [0046], [0047], [0052] and [0059]	1-4
X	JP H09263625 A (DAINIPPON INK & CHEMICALS) 07 October 1997 (1997-10-07) description, paragraphs [0010]-[0131]	1-4
X	JP H08325509 A (DAINIPPON INK & CHEMICALS) 10 December 1996 (1996-12-10) description, paragraphs [0010]-[0139]	1-4
X	JP H07242854 A (DAINIPPON INK & CHEMICALS) 19 September 1995 (1995-09-19) description, paragraphs [0009]-[0100]	1-4
A	US 5087645 A (TOYO SEIKAN KAISHA LTD) 11 February 1992 (1992-02-11) the whole document	1-4

☐ Further documents are listed in the continuation of Box C. ☑ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

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"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
22 December 2017	**11 January 2018**

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/CN2017/080741

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				WO	8805455	A1	28 July 1988