

DESCRIPTION

TITLE OF THE INVENTION: AQUEOUS COATING MATERIAL, METHOD
FOR FORMING COATING FILM, AND TOP COATING SET

TECHNICAL FIELD

[0001]

The present invention relates to a novel aqueous coating material, a method for forming a film, and a top coating set.

BACKGROUND ART

[0002]

Conventionally, the surface of a building, a civil engineering structure, or the like is finished with a coating material. Such a coating material is required to exhibit excellent performance in weather resistance because it imparts aesthetics due to various colors, textures, and the like and also plays a role of protecting a substrate from wind and rain, direct sunlight, and the like. In recent years, aqueous coating materials using a resin emulsion as a binder have been increasingly used in consideration of pollution-free properties and safety.

[0003]

As one means for enhancing the weather resistance in the aqueous coating material, it is known to employ an

acrylic silicon resin emulsion as a binder. For example, Patent Document 1 describes an aqueous coating material containing a resin emulsion having a specific silicon content, acid value, and hydroxyl value, a cross-linking agent thereof, a pigment, and the like.

[0004]

By the way, the aqueous coating material to be applied to the building, the civil engineering structure, or the like is required to have performance (room-temperature curability) of film formation and curing in a temperature range of about 5 to 40°C because coating work is performed outdoors. However, in the above Patent Document, the consideration of such room-temperature curability is not sufficient, and when coating is performed at room temperature, there is a possibility that cracking or the like occurs in a coating film (film) or weather resistance or the like of the coating film becomes insufficient.

[0005]

In particular, among the substrates constituting the framework of the building, the civil engineering structure, or the like, for example, a cementitious substrate such as concrete or mortar may crack over time due to the influence of the shrinkage of the substrate itself, a load on the substrate, and the like. In building materials such as a

lightweight concrete plate, an aerated concrete plate, and a siding board plate, a joint portion between the building materials has a property of being easily displaced due to changes in temperature, humidity, and the like. Aqueous top coatings applied to the building, the civil engineering structure, or the like are also required to have cracking resistance to such a surface to be coated.

PRIOR ART DOCUMENT

PATENT DOCUMENT

[0006]

Patent Document 1: JP-A-08-12930

SUMMARY OF THE INVENTION

PROBLEMS TO BE SOLVED BY THE INVENTION

[0007]

The present invention has been made in view of the above-described problems, and an object of the present invention is to provide an aqueous coating material that is excellent in room-temperature curability and can exhibit excellent performance in cracking resistance, weather resistance, and the like.

[0008]

The present invention has been made in view of the above-described problems, and an object of the present

invention is to provide a method for forming a film that can exhibit excellent performance in cracking resistance, weather resistance, and the like.

MEANS FOR SOLVING THE PROBLEMS

[0009]

As a result of intensive studies to achieve the above object, the present inventors have conceived an acrylic silicon resin emulsion having a specific silica remaining amount ratio and a specific resin configuration, and an aqueous coating material containing a pigment, and have completed the present invention.

[0010]

As a result of intensive studies to achieve the above object, the present inventors have conceived a method for forming a film including applying a specific first top coating, and then applying an acrylic silicon resin emulsion having a specific resin configuration and a specific second top coating containing a pigment, and have completed the present invention.

[0011]

That is, the present invention has the following features.

1. An aqueous coating material having room-temperature curability, and containing an acrylic silicon

resin emulsion (A) and a pigment (B),

wherein a silica remaining amount ratio in a resin solid content of the acrylic silicon resin emulsion (A) is 1 to 40% by mass,

the acrylic silicon resin emulsion (A) has a glass transition temperature of 30°C or lower,

two or more kinds of (meth)acrylic acid alkyl esters (s) having an alkyl group having 4 or more carbon atoms are contained as monomers constituting the acrylic silicon resin emulsion (A), and

a homopolymer of the (meth)acrylic acid alkyl ester (s) having an alkyl group having 4 or more carbon atoms has a glass transition temperature of 0°C or lower.

In the present invention, "room temperature" refers to a temperature of 5 to 40°C.

2. The aqueous coating material according to claim 1, wherein the (meth)acrylic acid alkyl ester (s) having an alkyl group having 4 or more carbon atoms contains a (meth)acrylic acid alkyl ester (s1) having a branched alkyl group having 5 or more carbon atoms.

3. The aqueous coating material according to claim 2, wherein the branched alkyl group contains a methyl group.

4. The aqueous coating material according to claim 1, further comprising a cross-linking agent (C),

wherein the acrylic silicon resin emulsion (A) has a reactive functional group, and

the cross-linking agent (C) has a functional group capable of reacting with the reactive functional group.

5. A method for forming a film for forming a top coating film by sequentially applying a first top coating and a second top coating to a surface to be coated,

wherein the first top coating forms a film having an elongation percentage at -10°C of 20% or more,

the second top coating is the aqueous coating material according to any one of claims 1 to 4, and

the second top coating forms a film having an elongation percentage at -10°C less than that of the first top coating.

6. The method according to claim 5,

wherein the first top coating contains a resin emulsion and a pigment, and

two or more kinds of (meth)acrylic acid alkyl esters (s) having an alkyl group having 4 or more carbon atoms are contained as monomers constituting the resin emulsion, and a homopolymer of the (meth)acrylic acid alkyl ester (s) having an alkyl group having 4 or more carbon atoms has a glass transition temperature of 0°C or lower.

7. The method according to claim 6, wherein the (meth)acrylic acid alkyl ester (s) having an alkyl group

having 4 or more carbon atoms contains a (meth)acrylic acid alkyl ester (s1) having a branched alkyl group having 5 or more carbon atoms.

8. The method according to claim 7, wherein the branched alkyl group contains a methyl group.

9. A top coating set comprising the first top coating and the second top coating used in the method according to claim 5.

EFFECT OF THE INVENTION

[0012]

The aqueous coating material of the present invention is excellent in room-temperature curability, and can exhibit excellent performance in cracking resistance, weather resistance, and the like.

[0013]

According to the method for forming a film of the present invention, it is possible to form a film that exhibits excellent performance in cracking resistance, weather resistance, and the like.

MODE FOR CARRYING OUT THE INVENTION

[0014]

Hereinafter, a mode for carrying out the present invention will be described.

[0015]

[Aqueous coating material]

An aqueous coating material of the present invention contains a specific acrylic silicon resin emulsion (A) and a pigment (B). Such an aqueous coating material can form a colored coating film by curing at room temperature. Specifically, the acrylic silicon resin emulsion (A) has a silica remaining amount ratio in a resin solid content of 1 to 40% by mass, and a glass transition temperature (hereinafter also referred to as "Tg") of 30°C or lower, and contains two or more kinds of (meth)acrylic acid alkyl esters (s) having an alkyl group having 4 or more carbon atoms as monomers constituting the acrylic silicon resin emulsion (A), and the homopolymer of the (meth)acrylic acid alkyl ester (s) having an alkyl group having 4 or more carbon atoms has a glass transition temperature of 0°C or lower.

In the present invention, the monomer is a general term for compounds having a polymerizable unsaturated double bond (excluding compounds having a silicon atom).

[0016]

In general, a resin emulsion is formed by emulsifying and dispersing a resin in an aqueous medium (medium containing water).

In addition, the glass transition temperature of the

resin is a value determined by the Fox calculation formula based on the intrinsic Tg of each monomer constituting the resin (homopolymer Tg of each monomer) and the constituent ratio.

In the present invention, the acrylic silicon resin emulsion (A) is used as the resin emulsion. The acrylic silicon resin emulsion (A) is formed by emulsifying and dispersing an acrylic silicon resin in an aqueous medium.

The glass transition temperature of the acrylic silicon resin emulsion (A) is a value determined by the Fox calculation formula based on the intrinsic Tg of each monomer constituting the acrylic silicon resin emulsion (A) and the constituent ratio. However, in the present invention, an alkoxysilane compound is excluded in calculating the Tg of the acrylic silicon resin emulsion (A).

[0017]

<Component (A)>

In general, the resin emulsion can be cured at room temperature by setting the glass transition temperature to room temperature (5 to 40°C) or lower. The acrylic silicon resin emulsion can also be cured at room temperature by setting the glass transition temperature to room temperature or lower.

[0018]

However, in an aqueous coating material containing an acrylic silicon resin emulsion containing a large amount of a silicon component as a binder and further containing a pigment, defects such as cracking of a coating film or insufficient weather resistance of the coating film are apt to occur even when the glass transition temperature of the acrylic silicon resin emulsion is set low.

[0019]

In the present invention, in such an aqueous coating material, the acrylic silicon resin emulsion satisfying the above-described conditions is an essential component. The aqueous coating material of the present invention having such a specific configuration can exhibit excellent performance in cracking resistance, weather resistance, and the like.

Since the silica remaining amount ratio in the resin solid content of the acrylic silicon resin emulsion (A) is 1 to 40% by mass, the aqueous coating material of the present invention can exhibit stable performance even when a binder containing a silicon component at a high ratio is used, and therefore petroleum-derived organic components can be relatively reduced, which can also contribute to decarbonization. Furthermore, the aqueous coating material of the present invention can prolong the life of an object to be coated due to its excellent weather resistance, can

reduce the number of maintenances as a whole, and can contribute to decarbonization and the like from such a viewpoint.

[0020]

In the aqueous coating material of the present invention, the acrylic silicon resin emulsion (A) having a silica remaining amount ratio in the resin solid content of 1 to 40% by mass and a glass transition temperature of 30°C or lower (hereinafter referred to as "component (A)") is used as the binder.

[0021]

In the component (A), as a component (resin component) constituting the acrylic silicon resin, a component containing a (meth)acrylic acid alkyl ester monomer containing a (meth)acrylic acid alkyl ester (s) having an alkyl group having 4 or more carbon atoms and an alkoxy silane compound can be used. In the present invention, an acrylic acid alkyl ester and a methacrylic acid alkyl ester are collectively referred to as the (meth)acrylic acid alkyl ester. In the present invention, " α to β " is synonymous with " α or more and β or less".

[0022]

Examples of the (meth)acrylic acid alkyl ester include: (meth)acrylic acid alkyl esters having a homopolymer Tg of 15°C or higher such as methyl

methacrylate (Tg: 105°C), ethyl methacrylate (Tg: 65°C), n-propyl methacrylate (Tg: 35°C), isopropyl methacrylate (Tg: 81°C), n-butyl methacrylate (Tg: 20°C), tert-butyl acrylate (Tg: 43°C), tert-butyl methacrylate (Tg: 107°C), isobutyl methacrylate (Tg: 53°C), n-pentyl acrylate (Tg: 22°C), cyclohexyl acrylate (Tg: 15°C), cyclohexyl methacrylate (Tg: 83°C), stearyl acrylate (Tg: 35°C), hexadecyl acrylate (Tg: 35°C), hexadecyl methacrylate (Tg: 15°C), tetradecyl acrylate (Tg: 24°C), isobornyl acrylate (Tg: 94°C), isobornyl methacrylate (Tg: 155°C), dicyclopentanyl acrylate (Tg: 120°C), dicyclopentanyl methacrylate (Tg: 175°C), and dicyclopentenyl acrylate (Tg: 120°C); (meth)acrylic acid alkyl esters having a homopolymer Tg of higher than 0°C and lower than 15°C such as methyl acrylate (Tg: 8°C), n-propyl acrylate (Tg: 3°C), and n-lauryl acrylate (Tg: 10°C); and (meth)acrylic acid alkyl esters having a homopolymer Tg of 0°C or lower such as ethyl acrylate (Tg: -20°C), isopropyl acrylate (Tg: -3°C), n-butyl acrylate (Tg: -54°C), isobutyl acrylate (Tg: -26°C), n-pentyl methacrylate (Tg: -5°C), isoamyl acrylate (Tg: -45°C), n-hexyl acrylate (Tg: -57°C), n-hexyl methacrylate (Tg: -5°C), 2-ethylhexyl acrylate (Tg: -70°C), 2-ethylhexyl methacrylate (Tg: -10°C), n-octyl acrylate (Tg: -65°C), 2-octyl acrylate (Tg: -44°C), isooctyl methacrylate (Tg: -45°C), isooctyl acrylate (Tg: -70°C), isononyl acrylate

(Tg: -58°C), isodecyl acrylate (Tg: -60°C), isodecyl methacrylate (Tg: -41°C), tridecyl acrylate (Tg: -55°C), tridecyl methacrylate (Tg: -40°C), n-lauryl methacrylate (Tg: -65°C), and tetradecyl methacrylate (Tg: -72°C). These can be used singly or in combination of two or more kinds, and two or more kinds of the (meth)acrylic acid alkyl esters having a homopolymer Tg of 0°C or lower are contained.

[0023]

Examples of the alkoxysilane compound include: silane coupling agents (i) such as polymerizable unsaturated double bond-containing silane coupling agents (such as γ -methacryloxypropyltrimethoxysilane, γ -methacryloxypropylmethyldimethoxysilane, γ -methacryloxypropyltriethoxysilane, γ -methacryloxypropylmethyldiethoxysilane, vinyltrimethoxysilane, vinyltriethoxysilane, and vinyltriisopropoxysilane); epoxy group-containing silane coupling agents (such as γ -glycidoxypropyltrimethoxysilane, γ -glycidoxypropylmethyldimethoxysilane, γ -glycidoxypropyltriethoxysilane, γ -glycidoxypropylmethyldiethoxysilane, and 2-(3,4-epoxycyclohexyl)ethyltrimethoxysilane); amino group-containing silane coupling agents (such as N-2(aminoethyl)3-aminopropyltrimethoxysilane, N-

2 (aminoethyl) 3-aminopropylmethyldimethoxysilane, N-
2 (aminoethyl) 3-aminopropyltriethoxysilane, N-
2 (aminoethyl) 3-aminopropylmethyldiethoxysilane, 3-
aminopropyltrimethoxysilane, 3-aminopropyltriethoxysilane,
and N-phenyl-3-aminopropyltrimethoxysilane); mercapto
group-containing silane coupling agents (such as γ -
mercaptopropyltrimethoxysilane); ureide group-containing
silane coupling agents (such as 3-
ureidopropyltriethoxysilane); chloroalkyl group-containing
silane coupling agents (such as 3-
chloropropyltrimethoxysilane); sulfide group-containing
silane coupling agents (such as
bis(triethoxysilylpropyl)tetrasulfide); isocyanate group-
containing silane coupling agents (such as 3-
isocyanatopropyltriethoxysilane),

[0024]

alkoxysilanes (ii) such as tetrafunctional
alkoxysilanes (such as tetramethoxysilane,
tetraethoxysilane, tetra-n-propoxysilane, tetra-i-
propoxysilane, tetra-n-butoxysilane, tetra-i-butoxysilane,
tetra-t-butoxysilane, and tetraacetoxysilane); alkyl
alkoxysilanes (such as methyltrimethoxysilane,
methyltriethoxysilane, methyltripropoxysilane,
methyltributoxysilane, ethyltrimethoxysilane,
ethyltriethoxysilane, ethyltripropoxysilane,

ethyltributoxysilane, propyltrimethoxysilane,
propyltriethoxysilane, propyltripropoxysilane,
propyltributoxysilane, butyltrimethoxysilane,
butyltriethoxysilane, butyltripropoxysilane,
butyltributoxysilane, phenyltrimethoxysilane,
phenyltriethoxysilane, phenyltributoxysilane,
methyltriacetoxysilane, phenyltriacetoxysilane,
dimethyldimethoxysilane, dimethyldiethoxysilane,
dimethyldipropoxysilane, dimethyldibutoxysilane,
diethyldimethoxysilane, diethyldiethoxysilane,
diethyldipropoxysilane, diethyldibutoxysilane,
dipropyldimethoxysilane, dipropyldiethoxysilane,
dibutyldimethoxysilane, dibutyldiethoxysilane,
diphenyldimethoxysilane, diphenyldiethoxysilane,
diphenyldibutoxysilane, dimethoxymethylphenylsilane,
methylphenyldiethoxysilane,
cyclohexylmethyldimethoxysilane, dimethyldiacetoxysilane,
and diphenyldiacetoxysilane); or alkoxysilane-modified
products obtained by modifying at least a part of alkoxyl
groups of these tetrafunctional alkoxysilanes or alkyl
alkoxysilanes with a polyoxyalkylene group-containing
compound, a fluorine-containing compound, or the like, and
[0025]

cyclic siloxanes (iii) such as
hexamethylcyclotrisiloxane, octamethylcyclotetrasiloxane,

and decamethylcyclopentasiloxane. These can be used singly or in combination of two or more kinds thereof.

[0026]

The ratio of the alkoxysilane compound is preferably 2 to 100 parts by mass, more preferably 10 to 90 parts by mass, and still more preferably 20 to 85 parts by mass, with respect to 100 parts by mass of the (meth)acrylic acid alkyl ester. Such a ratio of the alkoxysilane compound is suitable from the viewpoint of cracking resistance, weather resistance, polymerization stability, and the like.

[0027]

The component (A) may contain monomers (other monomers) other than the above as the resin component. Examples of such other monomers include: carboxyl group-containing monomers such as acrylic acid (Tg: 106°C), methacrylic acid (Tg: 185°C), itaconic acid (Tg: 100°C), and maleic acid (Tg: 130°C); aromatic monomers such as styrene (Tg: 100°C) and α -methylstyrene (Tg: 168°C); carbonyl group-containing monomers such as acrolein (Tg: 60°C) and diacetone acrylamide (Tg: 65°C); hydroxyl group-containing monomers such as 2-hydroxyethyl acrylate (Tg: -15°C), 2-hydroxyethyl methacrylate (Tg: 55°C), 2-hydroxybutyl acrylate (Tg: -7°C), 2-hydroxybutyl methacrylate (Tg: 26°C), and 4-hydroxybutyl acrylate (Tg: -80°C); amino group-containing monomers such as N,N-

dimethylaminoethyl acrylate (Tg: 18°C), N,N-dimethylaminoethyl methacrylate (Tg: 18°C), and N,N-diethylaminoethyl methacrylate (Tg: 20°C); amide group-containing monomers such as acrylamide (Tg: 179°C) and N,N-dimethylaminopropylacrylamide (Tg: 134°C); nitrile group-containing monomers such as acrylonitrile (Tg: 125°C); epoxy group-containing monomers such as glycidyl methacrylate (Tg: 46°C); oxazoline group-containing monomers of 2-isopropenyl-2-oxazoline (Tg: 100°C); ethylenically unsaturated double bond-containing ultraviolet absorbers such as 2-[2'-hydroxy-5'-methacryloyloxyethylphenyl]-2H-benzotriazole (Tg: 100°C); ethylenically unsaturated double bond-containing light stabilizers such as 4-methacryloyloxy-1,2,2,6,6-pentamethylpiperidine (Tg: 130°C); and sulfonic acid-containing vinyl monomers, acid anhydrides, chlorine-containing monomers, fluorine-containing monomers, alkylene glycol monoallyl ethers, vinyl acetates, vinyl propionates, vinyl ethers, ethylenes, propylenes, and isobutylenes. These can be used singly or in combination of two or more kinds thereof.

[0028]

The ratio of the other monomers is preferably 0.1 to 20 parts by mass, more preferably 0.2 to 15 parts by mass, and still more preferably 0.3 to 10 parts by mass, with

respect to 100 parts by mass of the (meth)acrylic acid alkyl ester. By using the other monomers within such a range, various functions (for example, crosslinkability, stability, dispersibility, and the like) can be imparted.

[0029]

In the present invention, as the monomer constituting the component (A), a monomer obtained from a biologically derived resource, that is, a biomass-based monomer can be used. By introducing such a biomass-based monomer, the biomass degree of the component (A) and, by extension, the aqueous coating material can be increased, and the amount of a petroleum-derived compound used can be reduced. The use of such a material can also contribute to decarbonization. As the biomass-based monomer, for example, a monomer produced using a biologically derived alcohol, an organic acid, a hydrocarbon, or the like can be used. As the biomass-based monomer, many (meth)acrylic acid alkyl esters having an alkyl group having 4 or more carbon atoms have been put into practical use, and thus in the present invention, an aqueous coating material having a high biomass degree can be effectively obtained.

[0030]

The component (A) can be produced by polymerizing the above-described resin components. As the polymerization method, a known method may be employed, and in addition to

normal emulsion polymerization, soap-free emulsion polymerization, feed emulsion polymerization, seed emulsion polymerization, multi-stage emulsion polymerization, and the like can also be employed. The multi-stage emulsion polymerization can be performed by a two-stage or three-stage or more emulsion polymerization method or the like.

In the polymerization of the component (A), for example, an emulsifier, an initiator, a dispersant, a polymerization inhibitor, a polymerization suppressing agent, a buffer, a chain transfer agent, a pH adjuster, or the like can be used.

[0031]

Among them, as the emulsifier, various surfactants that can be used for emulsion polymerization can be used, and these may be of a reactive type (reactive surfactant) having a polymerizable unsaturated double bond.

As the emulsifier, for example, an anionic surfactant, a nonionic surfactant, a cationic surfactant, an amphoteric surfactant, and the like can be used. A polymer emulsifier such as a polyurethane resin, a polyacrylic acid-based resin, polyvinyl alcohol, or polyvinyl pyrrolidone can also be used. Such emulsifiers can also be used alone, or various emulsifiers can also be used in combination.

[0032]

The ratio of the emulsifier is preferably 0.3 to 10% by mass, and more preferably 0.5 to 5% by mass, with respect to the total amount of the resin components.

[0033]

The component (A) in the present invention contains, as the monomers constituting the acrylic silicon resin, two or more kinds of (meth)acrylic acid alkyl esters (s) having a homopolymer Tg of 0°C or lower (preferably -15°C or lower, more preferably -30°C or lower) and having an alkyl group having 4 or more carbon atoms (hereinafter, also referred to as "component (s)").

[0034]

Examples of the component (s) include n-butyl acrylate (Tg: -54°C), isobutyl acrylate (Tg: -26°C), n-pentyl methacrylate (Tg: -5°C), isoamyl acrylate (Tg: -45°C), n-hexyl acrylate (Tg: -57°C), n-hexyl methacrylate (Tg: -5°C), 2-ethylhexyl acrylate (Tg: -70°C), 2-ethylhexyl methacrylate (Tg: -10°C), n-octyl acrylate (Tg: -65°C), 2-octyl acrylate (Tg: -44°C), isooctyl methacrylate (Tg: -45°C), isooctyl acrylate (Tg: -70°C), isononyl acrylate (Tg: -58°C), isodecyl acrylate (Tg: -60°C), isodecyl methacrylate (Tg: -41°C), tridecyl acrylate (Tg: -55°C), tridecyl methacrylate (Tg: -40°C), n-lauryl methacrylate (Tg: -65°C), and tetradecyl methacrylate (Tg: -72°C).

These can be used in two or more kinds (preferably two to

five kinds, more preferably two to four kinds, and still more preferably two to three kinds). Among them, for example, isoamyl acrylate, n-hexyl acrylate, n-octyl acrylate, 2-octyl acrylate, n-lauryl methacrylate, and the like are also suitable in that they can be used as the biomass-based monomer.

[0035]

In the present invention, the component (A) has such a specific configuration, and thus excellent performance can be exhibited in cracking resistance, weather resistance, and the like. The reason why such performance is exhibited is not limited to the following, but it is considered that, for example, the coexistence of two or more kinds of alkyl groups having different chemical structures as described above as the component (s) provides an increase in film formability based on the action of these alkyl groups and imparts strength to the film after film formation, which contribute to the performance.

[0036]

The number of carbon atoms of the alkyl group in the component (s) is 4 or more, preferably 4 to 12, more preferably 4 to 10, and still more preferably 5 to 8. In the present invention, by using two or more kinds of components (s) having such a number of carbon atoms, excellent performance can be exhibited in cracking

resistance, weather resistance, and the like.

[0037]

The ratio of the component (s) can be preferably 20 to 80% by mass, and more preferably 30 to 70% by mass, in the total amount of the (meth)acrylic acid alkyl ester. The ratio of the component (s) having the highest ratio among the two or more kinds of the components (s) can be set to preferably 20 to 95% by mass, more preferably 25 to 85% by mass, and still more preferably 30 to 70% by mass, in the total amount of the component (s). The component (s) having such an aspect is suitable from the viewpoint of room-temperature curability, cracking resistance, weather resistance, and the like.

[0038]

In the component (A) in the present invention, at least one kind of the components (s) is desirably a (meth)acrylic acid alkyl ester (s1) having a branched alkyl group having 5 or more carbon atoms (hereinafter, also referred to as "component (s1)"). The number of carbon atoms of the alkyl group in the component (s1) is preferably 5 or more, more preferably 5 to 12, still more preferably 5 to 10, and particularly preferably 5 to 8. In the present application, the "branched alkyl group having 5 or more carbon atoms" means an alkyl group having a main chain and a side chain, in which the total number of carbon

atoms of the main chain and the side chain is 5 or more.

Examples of the component (s1) include isoamyl acrylate, 2-ethylhexyl acrylate, 2-ethylhexyl methacrylate, 2-octyl acrylate, isooctyl methacrylate, isooctyl acrylate, isononyl acrylate, isodecyl acrylate, and isodecyl methacrylate. The component (A) desirably contains at least one kind of the components (s1) as the monomer constituting the acrylic silicon resin, and more desirably contains two or more kinds thereof. The component (A) contains such a component (s1), and thus still more excellent performance can be exhibited in cracking resistance, blister resistance, weather resistance, and the like. The reason why such performance is exhibited is not limited to the following, but it is considered that, for example, the imparting of strength to the film after film formation based on the action of the branched alkyl group contributes to the performance.

[0039]

The ratio of the component (s1) can be preferably 20% by mass or more, more preferably 25% by mass or more, and still more preferably 30 to 100% by mass, in the total amount of the component (s). The component (s1) having such an aspect is suitable from the viewpoint of improving physical properties such as cracking resistance, blister resistance, and weather resistance.

[0040]

In the component (A) in the present invention, at least one kind of the components (s) is desirably a (meth)acrylic acid alkyl ester (s11) which has a branched alkyl group having 5 or more carbon atoms, the branched alkyl group having a methyl group (hereinafter, also referred to as "component (s11)"). The number of carbon atoms of the alkyl group in the component (s11) is preferably 5 or more, more preferably 5 to 12, still more preferably 5 to 10, and particularly preferably 5 to 8.

Examples of the component (s11) include isoamyl acrylate, 2-octyl acrylate, isooctyl methacrylate, isooctyl acrylate, isononyl acrylate, isodecyl acrylate, and isodecyl methacrylate. The component (A) desirably contains at least one kind of the components (s11) as the monomer constituting the acrylic silicon resin, and more desirably contains two or more kinds thereof. The component (A) contains such a component (s11), and thus still more excellent performance can be exhibited in cracking resistance, blister resistance, weather resistance, and the like. In particular, the component (s11) greatly contributes to water resistance, blister resistance, and the like at the initial stage of film formation. The reason why such performance is exhibited is not limited to the following, but it is considered that,

for example, the early imparting of strength to the film after film formation based on the action of the branched alkyl group having a methyl group contributes to the performance.

[0041]

The ratio of the component (s11) can be preferably 20% by mass or more, more preferably 25% by mass or more, and still more preferably 30 to 100% by mass, in the total amount of the component (s). The component (s11) having such an aspect is suitable from the viewpoint of improving physical properties such as cracking resistance, blister resistance, and weather resistance.

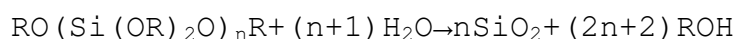
[0042]

In the component (A) in the present invention, the silica remaining amount ratio in the resin solid content is 1 to 40% by mass, preferably 5 to 35% by mass, and more preferably 10 to 30% by mass. The silica remaining amount ratio of the component (A) is within the above range, and thus a large amount of a silicon component is contained, and excellent weather resistance can be exhibited while physical properties such as cracking resistance are secured. When the silica remaining amount ratio is less than the above lower limit value, it is difficult to obtain sufficient physical properties in weather resistance and the like, and when the silica remaining amount ratio is

more than the above upper limit value, cracking resistance and the like become insufficient, and the case apt to be disadvantageous also in weather resistance.

[0043]

The silica remaining amount ratio is a ratio of a mass remaining as silica (SiO_2) when a component having a Si-O bond is fired at 900°C . In general, alkoxy silane reacts with water to cause a hydrolysis reaction, thereby forming silanol, and further has a property of causing a condensation reaction between silanols or between silanol and alkoxy. This reaction is ultimately carried out to give silica (SiO_2). These reactions are represented by the following general formula (reaction formula).



The silica remaining amount ratio is obtained by converting the amount of a silica component remaining based on this reaction formula.

[0044]

In the component (A), the type and ratio of the alkoxy silane compound in the resin component can be set so as to satisfy the silica remaining amount ratio. As shown in the above general formula, n moles of Si produces n moles of SiO_2 . Based on this, the silica remaining amount ratio of the component (A) can be set by a silicon atom ratio in one molecule of the alkoxy silane compound to be

used and the blending ratio thereof.

Examples of the alkoxysilane compound in the component (A) include (1) an aspect containing a silane coupling agent (i), (2) an aspect containing alkoxysilanes (ii) and/or cyclic siloxanes (iii), and (3) an aspect containing a silane coupling agent (i) and alkoxysilanes (ii) and/or cyclic siloxanes (iii). Among them, the aspect (2) or (3) (in particular, the aspect (3)) is suitable from the viewpoint of increasing the ratio of the silicon component and the like.

In the aspect (3), the ratio of the silane coupling agent (i) to the total amount of the silane coupling agent (i), the alkoxysilanes (ii), and the cyclic siloxanes (iii) is desirably 1 to 30% by mass, and more desirably 2 to 25% by mass.

[0045]

The glass transition temperature (T_g) of the component (A) is 30°C or lower, preferably -50°C to 25°C, more preferably -40°C to 20°C, and still more preferably -30°C to 15°C. When the T_g of the component (A) is within the above range, the case is suitable from the viewpoint of room-temperature curability, cracking resistance, weather resistance, contamination resistance, and the like. When the T_g is more than the above upper limit value, it is difficult to obtain sufficient physical properties in room-

temperature curability, cracking resistance, and the like. In the component (A), the type, ratio, and the like of the monomer to be used as the resin component can be set so as to satisfy the above glass transition temperature.

[0046]

The average particle size of the component (A) is preferably 300 nm or less, more preferably 20 to 250 nm, and still more preferably 50 to 200 nm. Here, the average particle size is a value measured by a dynamic light scattering method.

[0047]

The component (A) in the present invention can have an aspect in which a plurality of resin phases are mixed as long as the Tg is 30°C or lower. As the component (A), for example, a component can be used which contains a hard resin phase having a Tg of 15°C or higher and a soft resin phase having a Tg of 0°C or lower and in which the Tg of the entire resin constituting the component (A) is 30°C or lower.

Among them, the hard resin phase can be obtained by polymerization using one kind or two or more kinds (preferably two or more kinds) of the above-described monomers so that the Tg is 15°C or higher (more preferably 30°C or higher, still more preferably 50°C or higher).

The hard resin phase desirably contains, as a resin

component, a (meth)acrylic acid alkyl ester having a homopolymer Tg of 15°C or higher (more preferably 30°C or higher, still more preferably 50°C or higher).

[0048]

The soft resin phase can be obtained by polymerization using two or more kinds of the above-described monomers so that the Tg is 0°C or lower (more preferably -15°C or lower, still more preferably -30°C or lower).

The soft resin phase desirably contains, as a resin component, a (meth)acrylic acid alkyl ester having a homopolymer Tg of 0°C or lower (more preferably -15°C or lower, still more preferably -30°C or lower).

[0049]

The ratio between the hard resin phase and the soft resin phase in the component (A) may be set within a range in which the Tg of the entire resin is 30°C or lower. The ratio of the hard resin phase is preferably 10 to 90% by mass, more preferably 20 to 80% by mass, and still more preferably 30 to 70% by mass, in the resin solid content of the component (A). The ratio of the soft resin phase is preferably 10 to 90% by mass, more preferably 20 to 80% by mass, and still more preferably 30 to 70% by mass, in the resin solid content of the component (A). With such a mass ratio, the above-described effect of the present invention

can be easily obtained more stably. The component (A) may have, for example, an aspect containing two or more kinds of hard resin phases having different Tgs, an aspect containing two or more kinds of soft resin phases having different Tgs, or the like. The component (A) may have an aspect containing a resin phase (for example, a resin phase having an intermediate Tg (Tg is higher than 0°C and lower than 15°C) between the hard resin phase and the soft resin phase, and the like) different from the hard resin phase and the soft resin phase described above.

[0050]

When the component (A) contains the hard resin phase and the soft resin phase, the hard resin phase and the soft resin phase may coexist in the same emulsion particle or may exist in separate emulsion particles as long as the above-described conditions are satisfied. Specifically, for example, an aspect of (I) a multilayer structure type acrylic silicon resin emulsion containing a hard resin phase and a soft resin phase in the same emulsion particle, (II) a mixture of an acrylic silicon resin emulsion containing a hard resin phase and an acrylic silicon resin emulsion containing a soft resin phase, or the like can be adopted.

[0051]

<Component (B)>

The pigment (B) (hereinafter, also referred to as "component (B)") is a component that contributes to at least one of color developability, concealability, glossiness, aesthetics, strength, and the like. As the component (B), for example, a coloring pigment (B1) (hereinafter, also referred to as "component (B1)"), an extender pigment (B2) (hereinafter, also referred to as "component (B2)"), and the like can be used.

[0052]

The content of the component (B) is preferably 5 to 650 parts by mass, more preferably 10 to 500 parts by mass, still more preferably 15 to 300 parts by mass, and particularly preferably 20 to 200 parts by mass, with respect to 100 parts by mass of the solid content of the component (A).

[0053]

Examples of the coloring pigment (B1) include titanium oxide, zinc oxide, carbon black, graphite, black iron oxide, iron-manganese composite oxide, iron-copper-manganese composite oxide, iron-chromium composite oxide, iron-chromium-cobalt composite oxide, copper-chromium composite oxide, copper-manganese-chromium composite oxide, copper-magnesium composite oxide, bismuth-manganese composite oxide, red iron oxide, molybdate orange, permanent red, permanent carmine, anthraquinone red,

perylene red, quinacridone red, yellow iron oxide, titanium yellow, fast yellow, benzimidazolone yellow, chromium green, cobalt green, phthalocyanine green, ultramarine blue, Prussian blue, cobalt blue, phthalocyanine blue, quinacridone violet, dioxazine violet, an aluminum pigment, and a pearl pigment. These can be used singly or in combination of two or more kinds thereof.

[0054]

The average particle size of the component (B1) is preferably 2 μm or less, and more preferably 0.01 to 1 μm . The average particle size of the pigment (B) is a value measured by a laser diffraction particle size distribution measuring apparatus.

[0055]

The content of the component (B1) is preferably 250 parts by mass or less, more preferably 5 to 200 parts by mass, and still more preferably 10 to 150 parts by mass, with respect to 100 parts by mass of the solid content of the component (A). The content of the component (B1) within such a range is suitable from the viewpoint of color developability, concealability, aesthetics, and the like of the coating film, and is also advantageous from the viewpoint of the expression of the effect of the present invention.

[0056]

Examples of the extender pigment (B2) include heavy calcium carbonate, slight calcium carbonate, kaolin, clay, aluminum silicate, calcined clay, calcined kaolin, porcelain clay, china clay, diatomaceous earth, hydrous fine silicic acid, silica gel, zeolite, sodium sulfate, allophane, talc, mica, barite powder, barium sulfate, precipitated barium sulfate, barium carbonate, magnesium carbonate, silica powder, resin beads, aluminum hydroxide, porous calcium carbonate, siliceous shale, vermiculite, pearlite, Oya stone powder, activated clay, activated carbon, and shirasu balloon. These can be used singly or in combination of two or more kinds thereof.

[0057]

The average particle size of the extender pigment is preferably 0.1 to 100 μm , and more preferably 0.3 to 50 μm .

[0058]

The content of the component (B2) is preferably 400 parts by mass or less, more preferably 10 to 350 parts by mass, still more preferably 15 to 300 parts by mass, and particularly preferably 20 to 200 parts by mass, with respect to 100 parts by mass of the solid content of the component (A). The content of the component (B2) within such a range is suitable from the viewpoint of strength, aesthetics, and the like of the coating film, and is also advantageous from the viewpoint of the expression of the

effect of the present invention. The glossiness of the film can also be set to low gloss (for example, semi-gloss, 30% gloss, matte, and the like).

[0059]

<Component (C)>

In the aqueous coating material of the present invention, a cross-linking agent (C) (hereinafter also referred to as "component (C)") can be mixed together with the component (A). In this case, an acrylic silicon resin emulsion having a reactive functional group can be used as the component (A), and a cross-linking agent having a functional group capable of reacting with the reactive functional group can be used as the component (C). In the case of having such a component, it is considered that strength is imparted to the film during or after film formation by a cross-linking reaction between the component (A) and the cross-linking agent in addition to the action of the above-described component (s), and physical properties such as cracking resistance, blister resistance, and weather resistance can be enhanced.

[0060]

As the component (C), for example, a water-soluble cross-linking agent, a water-dispersible type cross-linking agent, a self-emulsifying type cross-linking agent, and the like are suitable.

[0061]

In the component (A) and the component (C), examples of the reactive functional group that can be used in such a cross-linking reaction include one or more kinds selected from a carboxyl group, a carbodiimide group, an epoxy group, an aziridine group, an oxazoline group, a hydroxyl group, an isocyanate group, a carbonyl group, a hydrazide group, an epoxy group, an amino group, an alkoxysilyl group, and the like.

In the component (A) and the component (C), such reactive functional groups may be used in combination. Examples of the combination of the reactive functional groups include combinations of a carboxyl group and a carbodiimide group, a carboxyl group and an epoxy group, a carboxyl group and an oxazoline group, a carboxyl group and an aziridine group, a hydroxyl group and an isocyanate group, a carbonyl group and a hydrazide group, an epoxy group and an amino group, and alkoxysilyl groups, and one kind or two or more kinds thereof can be used.

Suitable examples of the reactive functional group in the component (A) include a carboxyl group, a carbonyl group, an alkoxysilyl group, and the like.

[0062]

Specifically, when the component (A) has a carboxyl group, as the component (C), for example, a compound having

one or more reactive functional groups selected from a carbodiimide group, an epoxy group, an oxazoline group, and the like can be used. Among them, examples of the cross-linking agent having a carbodiimide group include those described in JP-A-10-60272, JP-A-10-316930, JP-A-11-60667, JP-A-2000-7642, JP-A-2000-119539, JP-A-2000-319351, JP-A-2013-112755, JP-A-2016-196612, JP-A-2016-196613, WO2017/6950, and the like. Examples of the cross-linking agent having an epoxy group include ethylene glycol diglycidyl ether, polyethylene glycol diglycidyl ether, propylene glycol diglycidyl ether, polypropylene glycol diglycidyl ether, glycerol polyglycidyl ether, diglycerol polyglycidyl ether, polyglycerol polyglycidyl ether, diglycerol polyglycidyl ether, polyhydroxyalkane polyglycidyl ether, and sorbitol polyglycidyl ether. Examples of the cross-linking agent having an oxazoline group include a resin obtained by copolymerizing a polymerizable oxazoline compound such as 2-vinyl-2-oxazoline, 2-vinyl-4-methyl-2-oxazoline, 2-vinyl-5-methyl-2-oxazoline, or 2-isopropenyl-2-oxazoline with a monomer copolymerizable with the compound. These can be used singly or in combination of two or more kinds thereof.

[0063]

The component (A) having a carboxyl group can be obtained by using, for example, a carboxyl group-containing

monomer such as acrylic acid, methacrylic acid, itaconic acid, or maleic acid as a resin component.

[0064]

When the component (A) has a carbonyl group, for example, a compound having a hydrazide group can be used as the component (C). Examples of the cross-linking agent having a hydrazide group include malonic acid dihydrazide, succinic acid dihydrazide, glutaric acid dihydrazide, adipic acid dihydrazide, sebacic acid dihydrazide, and maleic acid dihydrazide. These can be used singly or in combination of two or more kinds thereof.

[0065]

The component (A) having a carbonyl group can be obtained by using, for example, a carbonyl group-containing monomer such as acrolein or diacetone acrylamide as a resin component.

[0066]

When the component (A) has an alkoxysilyl group, for example, a compound having an alkoxysilyl group can be used as the component (C). Examples of the cross-linking agent having an alkoxysilyl group include the silane coupling agent described in the above-described component (A) and the alkoxysilane compounds such as alkoxysilanes. These can be used singly or in combination of two or more kinds thereof.

[0067]

The ratio of the component (C) is preferably 0.05 to 50 parts by mass, and more preferably 0.1 to 20 parts by mass, in terms of solid content, with respect to 100 parts by mass of the resin solid content of the component (A). With such a ratio, cracking resistance, blister resistance, weather resistance, and the like can be sufficiently enhanced.

[0068]

In the aqueous coating material of the present invention, various additives and the like can also be mixed in addition to the above-described components. Examples of such additives include a pigment dispersant, a viscosity modifier, a leveling agent, a coupling agent, a wetting agent, a film formation aid, a plasticizer, an anti-freezing agent, a pH adjuster, an antiseptic, an antifungal agent, an anti-algal agent, an antibacterial agent, an antifoaming agent, an adsorbent, a deodorant, an ultraviolet absorber, a light stabilizer, a hydrophilizing agent, an antioxidant, a catalyst, a solvent, and water. These can be used singly or in combination of two or more kinds thereof as necessary.

[0069]

Among them, the pigment dispersant is a component that contributes to the dispersion stabilization of the

component (B), the performance expression of the component (B), and the like.

[0070]

As the pigment dispersant, one kind or two or more kinds of commercially available or known products can be used, and for example, those having a styrene-maleic acid copolymer resin, a polyurethane resin, a polyester resin, an acrylic resin, or the like as a resin skeleton can be used.

[0071]

As the pigment dispersant in the aqueous coating material of the present invention, a pigment dispersant having an acid group and/or a basic group is suitable. Such a pigment dispersant can enhance the dispersion stability and the like of the component (B).

In general, in an aqueous coating material containing an acrylic silicon resin emulsion containing a large amount of a silicon component as a binder, a pigment dispersant excessively promotes the reaction of the silicon component, and the like, so that defects such as cracking or the like in a film and insufficient weather resistance or the like of the film tend to occur. However, in the present invention, even when such a pigment dispersant is used, excellent performance can be exhibited in cracking resistance, weather resistance or the like by employing the

component (A) having the above-described specific resin configuration, or the like.

[0072]

Examples of the acid group include a carboxy group, a sulfonic acid group, and a phosphoric acid group. Examples of the basic group include a primary amino group, a secondary amino group, a tertiary amino group, and a quaternary ammonium base. The component (C) may have one kind or two or more kinds of these acid groups and basic groups. Suitable examples of the component (C) include polycarboxylic acid type dispersants such as polyacrylic acid, polymethacrylic acid, and a styrene-maleic acid copolymer resin; sulfonic acid type dispersants such as lignin sulfonic acid and naphthalene sulfonic acid; phosphoric acid type dispersants such as a phosphoric acid ester compound; and polymer dispersants having an acid value and/or an amine value.

[0073]

The content of the component (C) is preferably 0.01 to 20 parts by mass, and more preferably 0.1 to 10 parts by mass, in terms of solid content, with respect to 100 parts by mass of the solid content of the component (A).

[0074]

<Component (D)>

The aqueous coating material of the present invention

can be used by being mixed with an ether or ester solvent (D) (hereinafter also referred to as "component (D)") in addition to the above components. Among the components (D), the ether solvent is a solvent having an ether bond in the molecule, and the ester solvent is a solvent having an ester bond in the molecule.

In the present invention, an ether or ester solvent (D1) having a solubility in water of 0.5 to 50 g/100 gH₂O (hereinafter also referred to as "component (D1)") can be contained as the component (D), and an ether solvent having a solubility in water of 0.5 to 50 g/100 gH₂O and/or an ester solvent having a solubility in water of 0.5 to 50 g/100 gH₂O can be used. By containing such a component (D1), the aqueous coating material of the present invention can exhibit more excellent performance in cracking resistance, weather resistance, and the like. When the aqueous coating material is a glossy type, glossiness and the like can also be enhanced.

The solubility in water in the present invention is a maximum mass (g) that can be dissolved in 100 g of water. The measurement temperature is 20°C.

[0075]

As the component (D1), an ether solvent or an ester solvent having a solubility in water within the above range can be used, and examples of a specific compound include:

ethylene glycol monohexyl ether (solubility in water: 0.99 g/100 gH₂O, boiling point: 208°C), propylene glycol phenyl ether (solubility in water: 1 g/100 gH₂O, boiling point: 243°C), ethylene glycol monobutyl ether acetate (solubility in water: 1.1 g/100 gH₂O, boiling point: 188°C), diethylene glycol monohexyl ether (solubility in water: 1.7 g/100 gH₂O, boiling point: 258°C), ethylene glycol monophenyl ether (solubility in water: 2.6 g/100 gH₂O, boiling point: 245°C), tripropylene glycol monobutyl ether (solubility in water: 3 g/100 gH₂O, boiling point: 274°C), diethylene glycol monophenyl ether (solubility in water: 3.4 g/100 gH₂O, boiling point: 283°C), dipropylene glycol monobutyl ether (solubility in water: 5 g/100 gH₂O, boiling point: 229°C), propylene glycol monobutyl ether (solubility in water: 6 g/100 gH₂O, boiling point: 170°C), diethylene glycol monobutyl ether acetate (solubility in water: 6.5 g/100 gH₂O, boiling point: 247°C), propylene glycol diacetate (solubility in water: 8 g/100 gH₂O, boiling point: 161°C), propylene glycol monomethyl ether acetate (solubility in water: 16 g/100 gH₂O, boiling point: 146°C), dipropylene glycol monopropyl ether (solubility in water: 19 g/100 gH₂O, boiling point: 212°C), dipropylene glycol monomethyl ether acetate (solubility in water: 19 g/100 gH₂O, boiling point: 209°C), ethylene glycol diethyl ether (solubility in water: 20 g/100 gH₂O, boiling point: 121°C),

and ethylene glycol monoethyl ether acetate (solubility in water: 23 g/100 gH₂O, boiling point: 156°C). These can be used singly or in combination of two or more kinds thereof.

[0076]

The solubility of the component (D1) in water is 0.5 to 50 g/100 gH₂O, preferably 0.8 to 25 g/100 gH₂O, and more preferably 1 to 10 g/100 gH₂O. The boiling point of the component (D1) is preferably 150°C or higher, more preferably 200°C or higher, and still more preferably 220°C or higher. The component (D1) satisfying such physical property values is suitable from the viewpoint of the expression of the effect of the present invention.

The reason why the effect of the present invention is exerted by the component (D1) is not limited to the following, but it is presumed that, for example, the component (D1) having intermediate properties of both hydrophobicity and hydrophilicity, and the increase of the affinity with the acrylic component and the silicon component by these properties contribute to the effect.

As the component (D1), a component having a hydrophobic group having 4 or more carbon atoms is preferable, a component having a hydrophobic group having 6 or more carbon atoms is more preferable, and a component having a phenyl group is particularly suitable.

[0077]

The content of the component (D1) is preferably 1 to 40 parts by mass, more preferably 2 to 30 parts by mass, still more preferably 3 to 25 parts by mass, and particularly preferably 4 to 20 parts by mass, with respect to 100 parts by mass of the solid content of the component (A). When the content of the component (D1) is within such a range, still more excellent performance can be exhibited in room-temperature curability, cracking resistance, weather resistance, and the like.

[0078]

In the present invention, two or more kinds of the components (D1) can be contained as the component (D). For example, an aspect containing two kinds of the components (D1) in which the difference in solubility in water is preferably 0.5 to 15 g/100 gH₂O (more preferably 0.8 to 10 g/100 gH₂O, still more preferably 1 to 5 g/100 gH₂O) can be adopted. Such an aspect is suitable from the viewpoint of improving the glossiness effect of the present invention.

[0079]

In the present invention, as the component (D), in addition to the above-described component (D1), an ether or ester solvent (D2) having a solubility in water of more than 50 g/100 gH₂O (hereinafter, also referred to as "component (D2)") can be contained.

As the component (D2), an ether solvent having a

solubility in water of more than 50 g/100 gH₂O and/or an ester solvent having a solubility in water of more than 50 g/100 gH₂O can be used, and examples of a specific compound include: ethylene glycol monomethyl ether (solubility in water: ∞, boiling point: 125°C), ethylene glycol monoethyl ether (solubility in water: ∞, boiling point: 135°C), ethylene glycol monopropyl ether (solubility in water: ∞, boiling point: 150°C), ethylene glycol monoisopropyl ether (solubility in water: ∞, boiling point: 143°C), ethylene glycol monobutyl ether (solubility in water: ∞, boiling point: 171°C), ethylene glycol monoisobutyl ether (solubility in water: ∞, boiling point: 161°C), ethylene glycol monotertiary-butyl ether (solubility in water: ∞, boiling point: 153°C), ethylene glycol monomethyl ether acetate (solubility in water: ∞, boiling point: 145°C), ethylene glycol monoethyl ether acetate (solubility in water: ∞, boiling point: 156°C), ethylene glycol dimethyl ether (solubility in water: ∞, boiling point: 85°C), diethylene glycol monomethyl ether (solubility in water: ∞, boiling point: 194°C), diethylene glycol monoethyl ether (solubility in water: ∞, boiling point: 202°C), diethylene glycol monobutyl ether (solubility in water: ∞, boiling point: 230°C), diethylene glycol monoisobutyl ether (solubility in water: ∞, boiling point: 220°C), diethylene glycol monoethyl ether acetate (solubility in water: ∞,

boiling point: 217°C), diethylene glycol dimethyl ether (solubility in water: ∞ , boiling point: 162°C), diethylene glycol diethyl ether (solubility in water: ∞ , boiling point: 189°C), triethylene glycol monomethyl ether (solubility in water: ∞ , boiling point: 249°C), triethylene glycol monobutyl ether (solubility in water: ∞ , boiling point: 271°C), triethylene glycol monoethyl ether (solubility in water: ∞ , boiling point: 255°C), propylene glycol monomethyl ether (solubility in water: ∞ , boiling point: 120°C), propylene glycol monoethyl ether (solubility in water: ∞ , boiling point: 133°C), propylene glycol monopropyl ether (solubility in water: ∞ , boiling point: 150°C), dipropylene glycol monomethyl ether (solubility in water: ∞ , boiling point: 190°C), dipropylene glycol dimethyl ether (solubility in water: 53 g/100 gH₂O, boiling point: 175°C), tripropylene glycol monomethyl ether (solubility in water: ∞ , boiling point: 242°C), and butylene glycol monomethyl ether (solubility in water: ∞ , boiling point: 161°C). These can be used singly or in combination of two or more kinds thereof.

[0080]

The solubility of the component (D2) in water is more than 50 g/100 gH₂O, and preferably ∞ . The boiling point of the component (D2) is preferably 150°C or higher. The component (D2) satisfying such physical property values is

suitable from the viewpoint of improving the effect of the present invention.

[0081]

In the present invention, as the component (D), in addition to the above-described component (D1), an ether or ester solvent (D3) having a solubility in water of less than 0.5 g/100 gH₂O (hereinafter, also referred to as "component (D3)") can be contained.

As the component (D3), an ether solvent having a solubility in water of less than 0.5 g/100 gH₂O and/or an ester solvent having a solubility in water of less than 0.5 g/100 gH₂O can be used, and examples of a specific compound include: diethylene glycol dibutyl ether (solubility in water: 0.3 g/100 gH₂O, boiling point: 255°C), diethylene glycol mono-2-ethylhexyl ether (solubility in water: 0.3 g/100 gH₂O, boiling point: 272°C), ethylene glycol mono-2-ethylhexyl ether (solubility in water: 0.2 g/100 gH₂O, boiling point: 229°C), ethylene glycol dibutyl ether (solubility in water: 0.2 g/100 gH₂O, boiling point: 203°C), 2,2,4-trimethyl-1,3-pentanediol monoisobutyrate (solubility in water: 0.09 g/100 gH₂O, boiling point: 255°C), and 2,2,4-trimethyl-1,3-pentanediol diisobutyrate (solubility in water: 0.04 g/100 gH₂O, boiling point: 282°C). These can be used singly or in combination of two or more kinds thereof.

[0082]

The solubility of the component (D3) in water is less than 0.5 g/100 gH₂O, preferably 0.4 g/100 gH₂O or less, and more preferably 0.01 to 0.4 g/100 gH₂O. The boiling point of the component (D3) is preferably 200°C or higher, and more preferably 220°C or higher. The component (D3) satisfying such physical property values is suitable from the viewpoint of improving the effect of the present invention.

[0083]

In the present invention, as the component (D), an aspect containing the component (D1), an aspect containing the component (D1) and the component (D2), an aspect containing the component (D1) and the component (D3), an aspect containing the component (D1), the component (D2), and the component (D3), and the like can be adopted. In each of such aspects, two or more kinds of the components (D1) can also be included.

[0084]

When the component (D2) is contained as the component (D), the content of the component (D2) is preferably 0.5 to 30 parts by mass, and more preferably 1 to 20 parts by mass, with respect to 100 parts by mass of the solid content of the component (A). In this case, the mass ratio of the component (D1) to the component (D2) ((D1) : (D2))

is preferably 95 : 5 to 10 : 90, more preferably 90 : 10 to 10 : 90, and still more preferably 80 : 20 to 20 : 80.

When the component (D3) is contained as the component (D), the content of the component (D3) is preferably 1 to 30 parts by mass, and more preferably 2 to 30 parts by mass, with respect to 100 parts by mass of the solid content of the component (A). In this case, the mass ratio of the component (D1) to the component (D3) ((D1) : (D3)) is preferably 95 : 5 to 5 : 95, more preferably 90 : 10 to 10 : 90, and still more preferably 80 : 20 to 20 : 80. Such an aspect is suitable from the viewpoint of improving the effect of the present invention.

[0085]

In the aqueous coating material of the present invention, in addition to the above-described components, a resin emulsion other than the component (A), a water-soluble resin, and the like can also be mixed.

Examples of the resin emulsion other than the component (A) include an acrylic resin emulsion, a urethane resin emulsion, a fluororesin emulsion, and an epoxy resin emulsion. An acrylic silicon resin emulsion other than the component (A) can also be used.

Examples of the water-soluble resin include a polyurethane resin, a polyacrylic acid-based resin, polyvinyl alcohol, and polyvinyl pyrrolidone. These can be

used singly or in combination of two or more kinds thereof as necessary. Among them, resin emulsions such as a urethane resin emulsion and a fluororesin emulsion are suitable from the viewpoint of improving weather resistance and the like.

[0086]

The aqueous coating material of the present invention can be produced by uniformly mixing the above-described component (A), component (B), and if necessary, the component (C), various additives, and the like by a conventional method.

[0087]

[Method for forming film]

The aqueous coating material of the present invention can be preferably applied to, for example, surface finishing for the surface to be coated of a building, a civil engineering construction, or the like. Examples of the surface to be coated as a coating target in the present invention include the exterior surfaces (for example, outer wall, roof, and the like) of the building and the civil engineering structure and the like.

[0088]

Examples of the substrate constituting the surface to be coated include a concrete, a mortar, a porcelain tile, a fiber-blended cement board, a cement calcium silicate

board, a slag cement perlite board, a cement board, an ALC board, a siding board, a plasterboard, a plywood, an extruded board, a steel plate, and a plastic plate. When the surface to be coated is formed of a plurality of plate-shaped substrates, a seam between the plate-shaped substrates may be filled with a sealing material, a joint sealing material such as a dry joint sealing material, or the like.

The surfaces of these substrates may be subjected to some surface treatments (for example, a treatment with a putty, a sealer, a surfacer, or a filler) or the like. Those on which a coating film is already formed (for example, those having an existing coating film) may be used.

[0089]

The surface to be coated may include an existing coating film. Such an existing coating film is formed by, for example, one kind or two or more kinds of coating agents.

[0090]

As the coating agent, various coating agents such as colored or uncolored, or opaque or transparent coating agents can be used, and examples thereof include those containing one or more resins selected from a vinyl acetate resin, an alkyd resin, an epoxy resin, an acrylic resin, a

urethane resin, an acrylic silicon resin, a silicon resin, a fluororesin, and the like. The existing coating film includes one or two or more films, and may be, for example, any of an elastic type, a hard type, and the like.

[0091]

The aqueous coating material of the present invention can also be coated directly to such a surface to be coated, or can be coated after the surface to be coated is treated by coating an undercoating, a base adjustment coating, or the like (for example, a sealer, a primer, a surfacer, a filler, a putty, and the like) on the surface to be coated.

[0092]

The aqueous coating material of the present invention can also be coated after forming an elastic film by coating an elastic coating material on a surface to be coated.

[0093]

Examples of the elastic coating material include, among coating materials for textured finishes of buildings specified in JIS A6909:2021, those exhibiting flexibility or waterproofness, and liquid-applied compounds for waterproofing membrane coating of buildings specified in JIS A6021:2022. Specifically, examples of the elastic coating material include a flexible type exterior silicate-based thin finishing coating (flexible type exterior thin coating Si), a flexible type exterior synthetic resin

emulsion-based thin finishing coating (flexible type exterior thin coating E), a waterproof type exterior synthetic resin emulsion-based thin finishing coating (waterproof type exterior thin coating E), a flexible type polymer cement-based multilayer finishing coating (flexible type multilayer coating CE), a waterproof type polymer cement-based multilayer finishing coating (waterproof type multilayer coating CE), a waterproof type synthetic resin emulsion-based multilayer finishing coating (waterproof type multilayer coating E), a waterproof type reaction curable type synthetic resin emulsion-based multilayer finishing coating (waterproof type multilayer coating RE), a waterproof type synthetic resin solution-based multilayer finishing coating (waterproof type multilayer coating RS), a flexible type synthetic resin emulsion-based finishing coating for modification (flexible type modification coating E), a flexible type reaction curable type synthetic resin emulsion-based finishing coating for modification (flexible type modification coating RE), a flexible type polymer cement-based finishing coating for modification (flexible type modification coating CE), an acrylic rubber-based coating film waterproof material for roof, a urethane rubber-based coating film waterproof material for roof, an acrylic rubber-based coating film waterproof material for outer wall, and a urethane rubber-based coating film

prevention material for outer wall.

[0094]

The coating method of the elastic coating material is not particularly limited, and a coating method corresponding to each material can be adopted. As the coating tool, for example, a spray, a roller, a trowel, a brush, or the like can be used.

[0095]

The application amount of the elastic coating material is preferably 0.2 to 5 kg/m², and more preferably 0.3 to 4 kg/m². At the time of coating, the elastic coating material can also be appropriately diluted as necessary.

[0096]

Drying after the coating of the elastic coating material may be performed at room temperature (5 to 40°C), and heating can also be performed as necessary.

[0097]

The elastic coating material can also be coated directly to the surface to be coated, or can also be coated after the surface to be coated is treated by coating an undercoating, a base adjustment coating, or the like (for example, a sealer, a primer, a surfacer, a filler, a putty, and the like) to the surface to be coated.

[0098]

The elastic film (film of elastic coating material) is desirably one in which the single film forms a film having an elongation percentage at -10°C of 20% or more. Such an elastic film can exhibit advantageous effects, for example, from the viewpoint of followability to the displacement of the surface to be coated, the prevention of ingress of water, carbon dioxide, and the like into the inside surface to be coated, and the like.

In the present invention, the elongation percentage at -10°C is a value measured according to a method defined in "Elongation Test" in JIS A6909:2021. The single film of the elastic film having a dry film thickness of 1 mm is subjected to the elongation test.

[0099]

When the aqueous coating material of the present invention is coated, for example, various coating tools such as a spray, a roller, and a brush can be used. Among these, as the roller, for example, a short-, medium-, or long-fiber roller (wool roller or the like) can be used.

[0100]

During coating, it is also possible to dilute the aqueous coating material with water. The mixing amount of water may be appropriately set in consideration of the type of the coating tool, the state of the surface to be coated, the temperature at the time of coating, and the like, and

is preferably 0 to 20% by mass with respect to the entire aqueous coating material.

[0101]

The application amount of the aqueous coating material of the present invention is preferably 0.05 to 1 kg/m², more preferably 0.1 to 0.8 kg/m², and still more preferably 0.15 to 0.6 kg/m². By coating the aqueous coating material with such an application amount, a coating film sufficiently excellent in aesthetics, weather resistance, and the like can be formed.

[0102]

The aqueous coating material of the present invention can be used as a room-temperature curable type aqueous coating material. Therefore, the aqueous coating material of the present invention can be coated and dried after being coated under an environment of room temperature (5 to 40°C). However, heating can also be performed as necessary.

The drying time is preferably about 0.5 to 4 hours at room temperature.

The number of times of application can be 1 or 2 or more (preferably 1 to 2). When the number of times of application is 2 or more, the total application amount is desirably within the above range.

[0103]

The aqueous coating material of the present invention can be preferably used as a top coating.

[0104]

The present invention is a method for forming a film in which a top coating film is formed by sequentially applying (coating) two specific top coatings (a first top coating and a second top coating) to a surface to be coated.

[0105]

<Top coating>

In the present invention, a film is formed by sequentially applying a first top coating and a second top coating to a surface to be coated. Before the coating of the first top coating, one or more kinds selected from an undercoating, a base adjustment coating, an elastic coating material, and the like can also be coated as described above.

[0106]

In the present invention, as the first top coating, one that forms a film having an elongation percentage at -10°C of 20% or more can be used, and as the second top coating, the above-described aqueous coating material of the present invention can be used. In the present invention, by sequentially applying such a first top coating and a second top coating to form a film, excellent

performance in cracking resistance, weather resistance, and the like can be exhibited.

[0107]

In the present invention, as the second top coating, in addition to the above-described conditions, one that forms a film in which the elongation percentage at -10°C is smaller than the elongation percentage at -10°C of the first top coating is used.

[0108]

The elongation percentage at -10°C of the top second coating is preferably 30% or less, more preferably 1 to 30%, still more preferably 5 to 28%, and particularly preferably 10 to 26%. In the present invention, by using such a second top coating, a film exhibiting excellent performance in blister resistance, contamination resistance, and the like can be formed.

The elongation percentage at -10°C of the second top coating is a value measured according to a method defined in "Elongation Test" in JIS A6909:2021. A test body to be subjected to Elongation Test is obtained by applying and laminating a second top coating film having a dry film thickness of 80 μm on the surface of a waterproof type multilayer coating E main material (the single film satisfies the elongation percentage definition at -10°C defined in JIS A6909:2021) having a dry film thickness of 1

mm.

[0109]

The elongation percentage at -10°C of the second top coating can be adjusted by the T_g of the component (A), the content of the component (B), and the like in the second top coating.

The T_g of the component (A) is 30°C or lower, preferably -50°C to 25°C , more preferably -40°C to 20°C , and still more preferably -30°C to 15°C .

The content of the component (B) is preferably 5 to 500 parts by mass, more preferably 10 to 300 parts by mass, and still more preferably 10 to 200 parts by mass, with respect to 100 parts by mass of the solid content of the component (A).

[0110]

<First top coating>

In the present invention, as the first top coating, one that forms a film having an elongation percentage at -10°C of 20% or more (preferably 20 to 50%, more preferably 22 to 40%) is used. The elongation percentage at -10°C of the first top coating is larger than the elongation percentage at -10°C of the second top coating. This makes it possible to form a film exhibiting excellent performance in cracking resistance, weather resistance, and the like.

The elongation percentage at -10°C of the first top

coating is a value measured according to a method defined in "Elongation Test" in JIS A6909:2021. A test body to be subjected to Elongation Test is obtained by applying and laminating a first top coating film having a dry film thickness of 80 μm on the surface of a waterproof type multilayer coating E main material (the single film satisfies the elongation percentage definition at -10°C defined in JIS A6909:2021) having a dry film thickness of 1 mm.

[0111]

As the first top coating, a material containing a resin emulsion and a pigment can be used. Such a first top coating can form a colored film by curing at room temperature.

Among these, examples of the resin emulsion include a vinyl acetate resin emulsion, a vinyl chloride resin emulsion, an epoxy resin emulsion, an alkyd resin emulsion, a urethane resin emulsion, an acrylic resin emulsion, an acrylic silicon resin emulsion, a fluororesin emulsion, or a composite thereof. These can be used singly or in combination of two or more kinds thereof.

[0112]

As the resin emulsion in the first top coating, an aspect containing one or more kinds selected from an acrylic resin emulsion and an acrylic silicon resin

emulsion is suitable.

As the acrylic resin emulsion, one containing a (meth)acrylic acid alkyl ester as a resin component can be used.

As the acrylic silicon resin emulsion, one containing a (meth)acrylic acid alkyl ester and an alkoxy silane compound as a resin component can be used. As the (meth)acrylic acid alkyl ester and the alkoxy silane compound, the same compounds as those for the second top coating (the above-described aqueous coating material of the present invention) can be used.

[0113]

The resin emulsion in the first top coating may contain, as monomers constituting the resin, two or more kinds of (meth)acrylic acid alkyl esters (s) having a homopolymer T_g of 0°C or lower (preferably -15°C or lower, more preferably -30°C or lower) and having an alkyl group having 4 or more carbon atoms. In the present invention, the resin emulsion in the first top coating has such a specific configuration, and thus it is possible to exhibit still more excellent performance in cracking resistance, blister resistance, weather resistance, and the like. The reason why such performance is exhibited is not limited to the following, but it is considered that, for example, the coexistence of two or more kinds of alkyl groups having

different chemical structures provides an increase in film formability based on the action of these alkyl groups, and imparts strength to the film after film formation, and the presence of the alkyl group similar to that of the second top coating provides an increase in adhesion, which contribute to the performance.

As the component (s), the same components as those described in detail in the second top coating can be used.
[0114]

The resin emulsion in the first top coating can also have an aspect containing, as a monomer constituting the resin, a (meth)acrylic acid alkyl ester (s1) having a homopolymer Tg of 0°C or lower (preferably -15°C or lower, more preferably -30°C or lower) and having a branched alkyl group having 5 or more carbon atoms.

Also as the component (s1), the same components as those described in detail in the second top coating can be used.

The resin emulsion in the first top coating desirably contains, as a monomer constituting the resin, at least one kind of the components (s1), and more desirably contains two or more kinds of the components (s1). As a result, it is possible to exhibit still more excellent performance in cracking resistance, blister resistance, weather resistance, and the like. The reason why such performance

is exhibited is not limited to the following, but it is considered that, for example, the imparting of strength to the film after film formation based on the action of the branched alkyl group, and the enhancement of the adhesion due to the presence of the alkyl group similar to that of the second top coating contribute to the performance.

[0115]

In the resin emulsion in the first top coating, the branched alkyl group of the component (s1) desirably contains a methyl group. Examples of the component (s1) in which the branched alkyl group contains the methyl group (hereinafter, also referred to as "component (s11)") include isoamyl acrylate, 2-octyl acrylate, isooctyl methacrylate, isooctyl acrylate, isononyl acrylate, isodecyl acrylate, and isodecyl methacrylate. The resin emulsion in the first top coating desirably contains at least one kind of the components (s11) as the monomer constituting the resin, and more desirably contains two or more kinds thereof. The resin emulsion in the first top coating contains such a component (s11), and thus still more excellent performance can be exhibited in cracking resistance, blister resistance, weather resistance, and the like. The reason why such performance is exhibited is not limited to the following, but it is considered that, for example, the early imparting of strength to the film after

film formation based on the action of the branched alkyl group having a methyl group contributes to the performance.

[0116]

In the resin emulsion in the first top coating, the silica remaining amount ratio in the resin solid content is preferably 0.5 to 40% by mass, more preferably 2 to 30% by mass, and still more preferably 4 to 25% by mass. This is more suitable from the viewpoint of cracking resistance, weather resistance, and the like.

[0117]

The resin emulsion in the first top coating has a glass transition temperature (T_g) of preferably 30°C or lower, more preferably -50°C to 30°C, and still more preferably -40°C to 25°C, which is more suitable from the viewpoint of room-temperature curability, cracking resistance, and the like.

Specifically, the T_g of the acrylic resin emulsion is preferably -40°C to 30°C, more preferably -30°C to 25°C, and still more preferably -20°C to 20°C.

The T_g of the acrylic silicon resin emulsion is preferably -50 to 20 °C, more preferably -40°C to 10°C, and still more preferably -30°C to 5°C.

In the resin emulsion in the first top coating, the type, ratio, and the like of the monomer to be used as the resin component can be set so as to satisfy the glass

transition temperature.

[0118]

The average particle size of the resin emulsion in the first top coating is preferably 300 nm or less, more preferably 20 to 250 nm, and still more preferably 50 to 200 nm. Here, the average particle size is a value measured by a dynamic light scattering method.

[0119]

The first top coating can contain, in addition to the resin emulsion, a pigment (B) which is an essential raw material of the above-described aqueous coating material of the present invention.

The pigment (B) is a component that contributes to at least one of color developability, concealability, strength, and the like, and as with the second top coating, for example, the coloring pigment (B1), the extender pigment (B2), and the like can be used.

[0120]

The content of the component (B) is preferably 5 to 300 parts by mass, more preferably 10 to 200 parts by mass, and still more preferably 20 to 100 parts by mass, with respect to 100 parts by mass of the solid content of the resin emulsion. By mixing the component (B), the color tone of the first top coating can also be set to the approximate color of the second top coating. As the

coloring pigment (B1) and the extender pigment (B2),

the same coloring pigment and extender pigment as those of the second top coating (the above-described aqueous coating material of the present invention) can be used.

[0121]

The average particle size of the component (B1) is preferably 2 μm or less, and more preferably 0.01 to 1 μm . The content of the component (B1) is preferably 250 parts by mass or less, more preferably 5 to 200 parts by mass, and still more preferably 10 to 100 parts by mass, with respect to 100 parts by mass of the solid content of the resin emulsion. The content of the component (B1) within such a range is more suitable from the viewpoint of the color developability, concealability, and the like of the film.

[0122]

The average particle size of the component (B2) is preferably 0.1 to 100 μm , and more preferably 0.3 to 50 μm . The content of the component (B2) is preferably 200 parts by mass or less, more preferably 100 parts by mass or less, and still more preferably 50 parts by mass or less, with respect to 100 parts by mass of the solid content of the resin emulsion. An aspect not containing the component (B2) is also suitable.

[0123]

In the first top coating, the cross-linking agent (C) can be mixed together with the resin emulsion. In this case, a resin emulsion having a reactive functional group can be used as the resin emulsion, and a cross-linking agent capable of reacting with the reactive functional group can be used as the component (C). In the case of having such a component, strength is imparted to the film during or after film formation by a cross-linking reaction between the resin emulsion and the cross-linking agent, and physical properties such as cracking resistance, blister resistance, and weather resistance can be further enhanced.

[0124]

As the component (C), the same component as that of the second top coating (the above-described aqueous coating material of the present invention) can be used.

[0125]

The ratio of the component (C) is preferably 0.05 to 50 parts by mass, and more preferably 0.1 to 20 parts by mass, in terms of solid content, with respect to 100 parts by mass of the resin solid content of the resin emulsion. With such a ratio, cracking resistance, blister resistance, weather resistance, and the like can be sufficiently enhanced.

[0126]

In the first top coating, various additives and the like can also be mixed in addition to the above-described components. Examples of such additives include a pigment dispersant, a viscosity modifier, a leveling agent, a coupling agent, a wetting agent, a film formation aid, a plasticizer, an anti-freezing agent, a pH adjuster, an antiseptic, an antifungal agent, an anti-algal agent, an antibacterial agent, an antifoaming agent, an adsorbent, a deodorant, an ultraviolet absorber, a light stabilizer, a hydrophilizing agent, an antioxidant, a catalyst, a solvent, and water. These can be used singly or in combination of two or more kinds thereof as necessary. Among them, as the pigment dispersant, the same pigment dispersant as that of the second top coating (the above-described aqueous coating material of the present invention) can be used, and the content thereof is preferably 0.01 to 20 parts by mass, and more preferably 0.1 to 10 parts by mass, in terms of solid content, with respect to 100 parts by mass of the solid content of the resin emulsion. In the same manner as the second top coating, an ether or ester solvent (D) (one or more kinds selected from the component (D1), the component (D2), the component (D3), and the like) can also be mixed with the first top coating.

[0127]

In the first top coating, a water-soluble resin or the like can also be mixed in addition to the above-described components. Examples of the water-soluble resin include a polyurethane resin, a polyacrylic acid-based resin, polyvinyl alcohol, and polyvinyl pyrrolidone. These can be used singly or in combination of two or more kinds thereof as necessary.

[0128]

The first top coating can be produced by uniformly mixing the above-described components and, if necessary, various additives and the like by a conventional method.

[0129]

The elongation percentage at -10°C of the first top coating can be adjusted by the T_g of the resin emulsion, the content of the component (B), and the like in the first top coating.

The T_g of the resin emulsion in the first top coating is preferably 30°C or lower, more preferably -50°C to 30°C , and still more preferably -40°C to 25°C .

The content of the component (B) is preferably 5 to 300 parts by mass, more preferably 10 to 200 parts by mass, and still more preferably 20 to 100 parts by mass, with respect to 100 parts by mass of the solid content of the resin emulsion.

[0130]

<Method for forming film >

In the present invention, a top coating film is formed by applying (coating) a top coating (a first top coating and a second top coating) to a surface to be coated. That is, the first top coating and the second top coating are sequentially applied to the surface to be coated to form a top coating film. Before the coating of the first top coating, one or more kinds selected from an undercoating, a base adjustment coating, an elastic coating material, and the like can also be coated as described above.

[0131]

In the present invention, it is desirable to apply the first top coating, dry the film, and then apply the second top coating. As the first top coating and the second top coating, those described above can be used. In the present invention, by forming a laminated film using such two specific kinds of top coatings, excellent performance in cracking resistance, weather resistance, and the like can be exhibited.

[0132]

In the application of each top coating, a known coating tool can be used. As the coating tool, for example, a spray, a roller, a brush, or the like can be used. At the time of coating, each top coating can also be

appropriately diluted as necessary.

[0133]

The mixing amount of water may be appropriately set in consideration of the type of the coating tool, the state of the surface to be coated, the temperature at the time of coating, and the like, and is preferably 0 to 20% by mass.

[0134]

Both the first top coating and the second top coating can be used as a room-temperature curable type aqueous top coating. Therefore, each top coating can be coated or dried after being coated under an environment of room temperature (5 to 40°C). However, heating can also be performed as necessary. The drying time is preferably about 0.5 to 4 hours at room temperature.

[0135]

The application amount of each of the first top coating and the second top coating is preferably 0.05 to 0.4 kg/m², and more preferably 0.08 to 0.3 kg/m².

[0136]

The dry film thickness of each of the first top coating and the second top coating is preferably 20 to 300 μm, and more preferably 30 to 200 μm. This makes it possible to form a film exhibiting excellent performance in weather resistance, cracking resistance, and the like while making use of the texture and the like of the base before

the coating of the top coating.

[0137]

The film thickness ratio {(dry film thickness of first top coating film) : (dry film thickness of second top coating film)} between the first top coating film and the second top coating film is preferably 80 : 20 to 20 : 80, more preferably 70 : 30 to 30 : 70, and still more preferably 65 : 35 to 35 : 65. Such an aspect makes it possible to stably obtain more excellent performance in weather resistance, cracking resistance, and the like.

[0138]

In the method for forming a film of the present invention, for example, after one or more kinds selected from an undercoating, a base adjustment coating, an elastic coating material, and the like are coated to a surface to be coated as necessary, the first top coating and the second top coating can be applied in order. The second top coating is desirably applied after the film of the first top coating is dried (after drying for preferably 1 hour or more, more preferably 2 hours or more).

[0139]

[Top coating set]

In the present invention, the first top coating and the second top coating described above can be used as a top coating set including a set of these two kinds. That is,

as a top coating set for forming a top coating film on a surface to be coated, one made of the first top coating and the second top coating described above can be used.

EXAMPLES

[0140]

Hereinafter, Examples are shown to make the features of the present invention clearer, but the present invention is not limited to these Examples.

[0141]

(Production of aqueous coating material)

In the production of an aqueous coating material in Examples, the following raw materials were used.

[0142]

- Resin 1: Acrylic silicon resin emulsion (emulsion polymer containing cyclohexyl methacrylate-2-ethylhexyl acrylate-n-octyl acrylate-methacrylic acid-silane coupling agent-alkoxysilanes (mass ratio 38 : 14 : 12.5 : 1.5 : 1.5 : 32.5) as main components, glass transition temperature: 3°C, silica remaining amount ratio in resin solid content: 15% by mass, solid content: 40% by mass)

- Resin 2: Acrylic silicon resin emulsion (emulsion polymer containing cyclohexyl methacrylate-2-octyl acrylate-n-octyl acrylate-methacrylic acid-silane coupling agent-alkoxysilanes (mass ratio 33 : 18.5 : 13 : 1.5 :

1.5 : 32.5) as main components, glass transition temperature: 3°C, silica remaining amount ratio in resin solid content: 15% by mass, solid content: 40% by mass)

- Resin 3: Acrylic silicon resin emulsion (emulsion polymer containing methyl methacrylate-cyclohexyl methacrylate-2-ethylhexyl acrylate-isoamyl acrylate-methacrylic acid-silane coupling agent-alkoxysilanes (mass ratio 8 : 27 : 17 : 12.5 : 1.5 : 1.5 : 32.5) as main components, glass transition temperature: 3°C, silica remaining amount ratio in resin solid content: 15% by mass, solid content: 40% by mass)

[0143]

- Resin 4: Acrylic silicon resin emulsion (emulsion polymer containing methyl methacrylate-cyclohexyl methacrylate-2-ethylhexyl acrylate-isoamyl acrylate-diacetone acrylamide-methacrylic acid-silane coupling agent-alkoxysilanes (mass ratio 8 : 25 : 16 : 14 : 1.5 : 1.5 : 32.5) as main components, glass transition temperature: 3°C, silica remaining amount ratio in resin solid content: 15% by mass, solid content: 40% by mass)

- Resin 5: Acrylic silicon resin emulsion (emulsion polymer containing methyl methacrylate-cyclohexyl methacrylate-2-ethylhexyl acrylate-isoamyl acrylate-diacetone acrylamide-methacrylic acid-silane coupling agent-alkoxysilanes (mass ratio 8 : 28 : 13 : 14 : 1.5 :

1.5 : 1.5 : 32.5) as main components, glass transition temperature: 10°C, silica remaining amount ratio in resin solid content: 15% by mass, solid content: 40% by mass)

• Resin 6: Acrylic silicon resin emulsion (emulsion polymer containing methyl methacrylate-cyclohexyl methacrylate-2-ethylhexyl acrylate-isoamyl acrylate-diacetone acrylamide-methacrylic acid-silane coupling agent-alkoxysilanes (mass ratio 8 : 15.5 : 13 : 15.5 : 1.5 : 1.5 : 1.5 : 43.5) as main components, glass transition temperature: -4°C, silica remaining amount ratio in resin solid content: 20% by mass, solid content: 40% by mass)

[0144]

• Resin 7: Acrylic silicon resin emulsion (emulsion polymer containing cyclohexyl methacrylate-2-ethylhexyl acrylate-2-octyl acrylate-diacetone acrylamide-methacrylic acid-silane coupling agent-alkoxysilanes (mass ratio 32.5 : 12 : 18.5 : 1.5 : 1.5 : 1.5 : 32.5) as main components, glass transition temperature: 3°C, silica remaining amount ratio in resin solid content: 15% by mass, solid content: 40% by mass)

• Resin 8: Acrylic silicon resin emulsion (emulsion polymer containing methyl methacrylate-cyclohexyl methacrylate-isoamyl acrylate-2-octyl acrylate-diacetone acrylamide-methacrylic acid-silane coupling agent-

alkoxysilanes (mass ratio 5 : 22.5 : 17 : 18.5 : 1.5 : 1.5 : 1.5 : 32.5) as main components, glass transition temperature: 3°C, silica remaining amount ratio in resin solid content: 15% by mass, solid content: 40% by mass)

• Resin 9: Acrylic silicon resin emulsion (emulsion polymer containing cyclohexyl methacrylate-isobornyl acrylate-isoamyl acrylate-2-octyl acrylate-diacetone acrylamide-methacrylic acid-silane coupling agent-alkoxysilanes (mass ratio 23 : 5 : 18 : 17 : 1.5 : 1.5 : 1.5 : 32.5) as main components, glass transition temperature: 3°C, silica remaining amount ratio in resin solid content: 15% by mass, solid content: 40% by mass)
[0145]

• Resin 10: Acrylic silicon resin emulsion (emulsion polymer containing cyclohexyl methacrylate-2-ethylhexyl acrylate-n-octyl acrylate-diacetone acrylamide-methacrylic acid-silane coupling agent-alkoxysilanes (mass ratio 36.5 : 13 : 13.5 : 1.5 : 1.5 : 1.5 : 32.5) as main components, glass transition temperature: 3°C, silica remaining amount ratio in resin solid content: 15% by mass, solid content: 40% by mass)

• Resin 11: Acrylic silicon resin emulsion (emulsion polymer containing cyclohexyl methacrylate-2-octyl acrylate-n-octyl acrylate-diacetone acrylamide-methacrylic acid-silane coupling agent-alkoxysilanes (mass ratio 32 :

16 : 15 : 1.5 : 1.5 : 1.5 : 32.5) as main components, glass transition temperature: 3°C, silica remaining amount ratio in resin solid content: 15% by mass, solid content: 40% by mass)

[0146]

• Resin 12: Acrylic silicon resin emulsion (emulsion polymer containing cyclohexyl methacrylate-2-ethylhexyl acrylate-2-octyl acrylate-diacetone acrylamide-methacrylic acid-silane coupling agent-alkoxysilanes (mass ratio 39.5 : 16.5 : 18 : 1.5 : 1.5 : 1.5 : 21.5) as main components, glass transition temperature: 3°C, silica remaining amount ratio in resin solid content: 10% by mass, solid content: 40% by mass)

In the resins 1 to 12, γ -methacryloxypropyltrimethoxysilane was used as the silane coupling agent, and methyltrimethoxysilane was used as one of the alkoxysilanes.

[0147]

• Resin 13: Acrylic silicon resin emulsion (emulsion polymer containing cyclohexyl methacrylate-n-hexyl acrylate-2-octyl acrylate-diacetone acrylamide-methacrylic acid-silane coupling agent-alkoxysilanes (mass ratio 36.5 : 19 : 18.5 : 1.5 : 1.5 : 1.5 : 21.5) as main components, glass transition temperature: 3°C, silica remaining amount ratio in resin solid content: 10% by mass, solid content:

40% by mass)

In the resin 13, γ -methacryloxypropyltrimethoxysilane was used as the silane coupling agent, and methyltrimethoxysilane and phenyltrimethoxysilane (mass ratio: 19.5 : 2) were used as the alkoxysilanes.

• Resin 14: Acrylic silicon resin emulsion (emulsion polymer containing cyclohexyl methacrylate-n-butyl acrylate-2-octyl acrylate-diacetone acrylamide-methacrylic acid-silane coupling agent-alkoxysilanes-cyclic siloxanes (mass ratio 36 : 17 : 22 : 1.5 : 1.5 : 1.5 : 17.5 : 3) as main components, glass transition temperature: 3°C, silica remaining amount ratio in resin solid content: 10% by mass, solid content: 40% by mass)

In the resin 14, γ -methacryloxypropyltrimethoxysilane was used as the silane coupling agent, and methyltrimethoxysilane and phenyltrimethoxysilane (mass ratio: 14.5 : 3) were used as the alkoxysilanes.

[0148]

• Resin 15: Acrylic silicon resin emulsion (emulsion polymer containing methyl methacrylate-cyclohexyl methacrylate-isoamyl acrylate-2-octyl acrylate-diacetone acrylamide-methacrylic acid-silane coupling agent-alkoxysilanes (mass ratio 5 : 24 : 29 : 21 : 1.5 : 1.5 : 1.5 : 16.5) as main components, glass transition temperature: -6°C, silica remaining amount ratio in resin

solid content: 8% by mass, solid content: 40% by mass)

• Resin 16: Acrylic resin emulsion (emulsion polymer containing methyl methacrylate-cyclohexyl methacrylate-2-ethylhexyl acrylate-n-butyl acrylate-diacetone acrylamide-methacrylic acid (mass ratio 15 : 41.5 : 20 : 20.5 : 1.5 : 1.5) as main components, glass transition temperature: 8°C, solid content: 40% by mass)

[0149]

• Resin 17: Acrylic silicon resin emulsion (emulsion polymer containing cyclohexyl methacrylate-n-octyl acrylate-methacrylic acid-silane coupling agent-alkoxysilanes (mass ratio 37 : 27.5 : 1.5 : 1.5 : 32.5) as main components, glass transition temperature: 3°C, silica remaining amount ratio in resin solid content: 15% by mass, solid content: 40% by mass)

• Resin 18: Acrylic silicon resin emulsion (emulsion polymer containing cyclohexyl methacrylate-n-octyl acrylate-diacetone acrylamide-methacrylic acid-silane coupling agent-alkoxysilanes (mass ratio 35.8 : 27.2 : 1.5 : 1.5 : 1.5 : 32.5) as main components, glass transition temperature: 3°C, silica remaining amount ratio in resin solid content: 15% by mass, solid content: 40% by mass)

In the resin 15, the resin 17, and the resin 18, γ -methacryloxypropyltrimethoxysilane was used as the silane

coupling agent, and methyltrimethoxysilane was used as one of the alkoxysilanes.

[0150]

- Resin 19: Urethane resin emulsion (aqueous dispersion liquid of polycarbonate-based polyurethane resin, solid content: 30% by mass)

[0151]

- Coloring pigment 1: Titanium oxide (average particle size: 0.3 μm)

- Pigment dispersant 1: Polycarboxylic acid type dispersant (aqueous solution of ammonium polycarboxylate, solid content: 30% by mass)

- Coloring liquid 1: Aqueous dispersion liquid of yellow iron oxide (average particle size: 0.5 μm) [coloring pigment ratio: 50% by mass, solid content ratio of pigment dispersant {polycarboxylic acid type dispersant (styrene-maleic acid-based copolymer resin)}: 2% by mass]

- Coloring liquid 2: Aqueous dispersion liquid of carbon black (average particle size: 0.1 μm) [coloring pigment ratio: 20% by mass, solid content ratio of pigment dispersant {polymer dispersant having acid value and amine value, and phosphoric acid type dispersant (phosphoric acid ester compound)}: 2% by mass]

- Solvent 1: Ether solvent (tripropylene glycol monobutyl ether, solubility in water: 3 g/100 gH₂O, boiling

point: 274°C)

- Solvent 2: Ether solvent (dipropylene glycol monobutyl ether, solubility in water: 5 g/100 gH₂O, boiling point: 229°C)

- Solvent 3: Ether solvent (ethylene glycol monophenyl ether, solubility in water: 2.6 g/100 gH₂O, boiling point: 245°C)

- Solvent 4: Ether solvent (ethylene glycol monotertiary-butyl ether, solubility in water: ∞, boiling point: 153°C)

- Solvent 5: Ether solvent (diethylene glycol monobutyl ether, solubility in water: ∞, boiling point: 230°C)

- Solvent 6: Ether solvent (diethylene glycol dibutyl ether, solubility in water: 0.3 g/100 gH₂O, boiling point: 255°C)

- Solvent 7: Ether solvent (ethylene glycol mono2-ethylhexyl ether, solubility in water: 0.2 g/100 gH₂O, boiling point: 229°C)

- Solvent 8: Ether solvent (diethylene glycol monophenyl ether, solubility in water: 3.4 g/100 gH₂O, boiling point: 283°C),

- Solvent 9: Ester solvent (2,2,4-trimethyl-1,3-pentanediol monoisobutyrate, solubility in water: 0.09 g/100 gH₂O, boiling point: 255°C)

- Thickener 1: Cellulosic thickener
- Thickener 2: Polyurethane-based associative thickener
- Antifoaming agent 1: Mineral oil-based antifoaming agent
- Antifoaming agent 2: Silicone-based antifoaming agent
- Cross-linking agent 1: Adipic acid dihydrazide
- Cross-linking agent 2: Carbodiimide resin aqueous dispersion (solid content: 40% by mass)
- Cross-linking agent 3: γ -Glycidoxypropyltrimethoxysilane

[0152]

The formal names of abbreviations in Tables are shown below.

2EHA: 2-Ethylhexyl acrylate

nOA: n-Octyl acrylate

2OA: 2-Octyl acrylate

IAA: Isoamyl acrylate

nHA: n-Hexyl acrylate

nBA: n-Butyl acrylate

[0153]

<Aqueous coating material 1>

0.4 parts by mass of a thickener 1, 0.1 parts by mass of an antifoaming agent 1, 2.5 parts by mass of a pigment

dispersant 1, and 70 parts by mass of a coloring pigment 1 were mixed and stirred with 27 parts by mass of water to produce a coloring pigment dispersion liquid.

Subsequently, 250 parts by mass of a resin 1 (100 parts by mass in terms of solid content), 18 parts by mass of a solvent 1, 2 parts by mass of a thickener 2, and 0.2 parts by mass of an antifoaming agent 2 were mixed and stirred with 100 parts by mass of the coloring pigment dispersion liquid to produce an aqueous coating material 1.

[0154]

<Aqueous coating material 2>

250 parts by mass of a resin 2 (100 parts by mass in terms of solid content), 18 parts by mass of a solvent 1, 2 parts by mass of a thickener 2, and 0.2 parts by mass of an antifoaming agent 2 were mixed and stirred with 100 parts by mass of a coloring pigment dispersion liquid similar to that in Example 1 to produce an aqueous coating material 2.

[0155]

<Aqueous coating material 3>

250 parts by mass of a resin 3 (100 parts by mass in terms of solid content), 18 parts by mass of a solvent 1, 2 parts by mass of a thickener 2, and 0.2 parts by mass of an antifoaming agent 2 were mixed and stirred with 100 parts by mass of a coloring pigment dispersion liquid similar to that in Example 1 to produce an aqueous coating material 3.

[0156]

<Aqueous coating material 4>

250 parts by mass of a resin 4 (100 parts by mass in terms of solid content), 18 parts by mass of a solvent 1, 2 parts by mass of a thickener 2, 0.2 parts by mass of an antifoaming agent 2, and 1 part by mass of a cross-linking agent 1 were mixed and stirred with 100 parts by mass of a coloring pigment dispersion liquid similar to that in Example 1 to produce an aqueous coating material 4.

[0157]

<Aqueous coating material 5>

250 parts by mass of a resin 5 (100 parts by mass in terms of solid content), 18 parts by mass of a solvent 1, 2 parts by mass of a thickener 2, 0.2 parts by mass of an antifoaming agent 2, and 1 part by mass of a cross-linking agent 1 were mixed and stirred with 100 parts by mass of a coloring pigment dispersion liquid similar to that in Example 1 to produce an aqueous coating material 5.

[0158]

<Aqueous coating material 6>

250 parts by mass of a resin 6 (100 parts by mass in terms of solid content), 18 parts by mass of a solvent 1, 2 parts by mass of a thickener 2, 0.2 parts by mass of an antifoaming agent 2 , and 1 part by mass of a cross-linking agent 1 were mixed and stirred with 100 parts by mass of a

coloring pigment dispersion liquid similar to that in Example 1 to produce an aqueous coating material 6.

[0159]

<Aqueous coating material 7>

250 parts by mass of a resin 7 (100 parts by mass in terms of solid content), 18 parts by mass of a solvent 1, 2 parts by mass of a thickener 2, 0.2 parts by mass of an antifoaming agent 2 , and 1 part by mass of a cross-linking agent 1 were mixed and stirred with 100 parts by mass of a coloring pigment dispersion liquid similar to that in Example 1 to produce an aqueous coating material 7.

[0160]

<Aqueous coating material 8>

250 parts by mass of a resin 8 (100 parts by mass in terms of solid content), 18 parts by mass of a solvent 1, 2 parts by mass of a thickener 2, 0.2 parts by mass of an antifoaming agent 2 , and 1 part by mass of a cross-linking agent 1 were mixed and stirred with 100 parts by mass of a coloring pigment dispersion liquid similar to that in Example 1 to produce an aqueous coating material 8.

[0161]

<Aqueous coating material 9>

250 parts by mass of a resin 9 (100 parts by mass in terms of solid content), 18 parts by mass of a solvent 1, 2 parts by mass of a thickener 2, 0.2 parts by mass of an

antifoaming agent 2 , and 1 part by mass of a cross-linking agent 1 were mixed and stirred with 100 parts by mass of a coloring pigment dispersion liquid similar to that in Example 1 to produce an aqueous coating material 9.

[0162]

<Aqueous coating material 10>

250 parts by mass of a resin 8 (100 parts by mass in terms of solid content), 18 parts by mass of a solvent 2, 2 parts by mass of a thickener 2, 0.2 parts by mass of an antifoaming agent 2 , and 1 part by mass of a cross-linking agent 1 were mixed and stirred with 100 parts by mass of a coloring pigment dispersion liquid similar to that in Example 1 to produce an aqueous coating material 10.

[0163]

<Aqueous coating material 11>

250 parts by mass of a resin 8 (100 parts by mass in terms of solid content), 12 parts by mass of a solvent 2, 6 parts by mass of a solvent 3, 2 parts by mass of a thickener 2, 0.2 parts by mass of an antifoaming agent 2, and 1 part by mass of a cross-linking agent 1 were mixed and stirred with 100 parts by mass of a coloring pigment dispersion liquid similar to that in Example 1 to produce an aqueous coating material 11.

[0163]

<Aqueous coating material 12>

250 parts by mass of a resin 8 (100 parts by mass in terms of solid content), 12 parts by mass of a solvent 2, 6 parts by mass of a solvent 4, 2 parts by mass of a thickener 2, 0.2 parts by mass of an antifoaming agent 2, and 1 part by mass of a cross-linking agent 1 were mixed and stirred with 100 parts by mass of a coloring pigment dispersion liquid similar to that in Example 1 to produce an aqueous coating material 12.

[0165]

<Aqueous coating material 13>

250 parts by mass of a resin 8 (100 parts by mass in terms of solid content), 12 parts by mass of a solvent 2, 6 parts by mass of a solvent 5, 2 parts by mass of a thickener 2, 0.2 parts by mass of an antifoaming agent 2, and 1 part by mass of a cross-linking agent 1 were mixed and stirred with 100 parts by mass of a coloring pigment dispersion liquid similar to that in Example 1 to produce an aqueous coating material 13.

[0166]

<Aqueous coating material 14>

250 parts by mass of a resin 8 (100 parts by mass in terms of solid content), 12 parts by mass of a solvent 2, 6 parts by mass of a solvent 6, 2 parts by mass of a thickener 2, 0.2 parts by mass of an antifoaming agent 2, and 1 part by mass of a cross-linking agent 1 were mixed

and stirred with 100 parts by mass of a coloring pigment dispersion liquid similar to that in Example 1 to produce an aqueous coating material 14.

[0167]

<Aqueous coating material 15>

250 parts by mass of a resin 8 (100 parts by mass in terms of solid content), 12 parts by mass of a solvent 2, 6 parts by mass of a solvent 7, 2 parts by mass of a thickener 2, 0.2 parts by mass of an antifoaming agent 2, and 1 part by mass of a cross-linking agent 1 were mixed and stirred with 100 parts by mass of a coloring pigment dispersion liquid similar to that in Example 1 to produce an aqueous coating material 15.

[0168]

<Aqueous coating material 16>

250 parts by mass of a resin 9 (100 parts by mass in terms of solid content), 12 parts by mass of a solvent 2, 6 parts by mass of a solvent 3, 2 parts by mass of a thickener 2, 0.2 parts by mass of an antifoaming agent 2, and 1 part by mass of a cross-linking agent 1 were mixed and stirred with 100 parts by mass of a coloring pigment dispersion liquid similar to that in Example 1 to produce an aqueous coating material 16.

[0169]

<Aqueous coating material 17>

250 parts by mass of a resin 10 (100 parts by mass in terms of solid content), 18 parts by mass of a solvent 1, 2 parts by mass of a thickener 2, 0.2 parts by mass of an antifoaming agent 2, and 1 part by mass of a cross-linking agent 1 were mixed and stirred with 100 parts by mass of a coloring pigment dispersion liquid similar to that in Example 1 to produce an aqueous coating material 17.

[0170]

<Aqueous coating material 18>

250 parts by mass of a resin 11 (100 parts by mass in terms of solid content), 18 parts by mass of a solvent 1, 2 parts by mass of a thickener 2, 0.2 parts by mass of an antifoaming agent 2, and 1 part by mass of a cross-linking agent 1 were mixed and stirred with 100 parts by mass of a coloring pigment dispersion liquid similar to that in Example 1 to produce an aqueous coating material 18.

[0171]

<Aqueous coating material 19>

250 parts by mass of a resin 3 (100 parts by mass in terms of solid content), 18 parts by mass of a solvent 1, 2 parts by mass of a thickener 2, 0.2 parts by mass of an antifoaming agent 2, and 3 part by mass of a cross-linking agent 2 were mixed and stirred with 100 parts by mass of a coloring pigment dispersion liquid similar to that in Example 1 to produce an aqueous coating material 19.

[0172]

<Aqueous coating material 20>

250 parts by mass of a resin 12 (100 parts by mass in terms of solid content), 18 parts by mass of a solvent 1, 2 parts by mass of a thickener 2, 0.2 parts by mass of an antifoaming agent 2, and 1 part by mass of a cross-linking agent 1 were mixed and stirred with 100 parts by mass of a coloring pigment dispersion liquid similar to that in Example 1 to produce an aqueous coating material 20.

[0173]

<Aqueous coating material 21>

250 parts by mass of a resin 13 (100 parts by mass in terms of solid content), 18 parts by mass of a solvent 1, 2 parts by mass of a thickener 2, 0.2 parts by mass of an antifoaming agent 2, and 1 part by mass of a cross-linking agent 1 were mixed and stirred with 100 parts by mass of a coloring pigment dispersion liquid similar to that in Example 1 to produce an aqueous coating material 21.

[0174]

<Aqueous coating material 22>

250 parts by mass of a resin 14 (100 parts by mass in terms of solid content), 18 parts by mass of a solvent 1, 2 parts by mass of a thickener 2, 0.2 parts by mass of an antifoaming agent 2, and 1 part by mass of a cross-linking agent 1 were mixed and stirred with 100 parts by mass of a

coloring pigment dispersion liquid similar to that in Example 1 to produce an aqueous coating material 22.

[0175]

<Aqueous coating material 23>

250 parts by mass of a resin 9 (100 parts by mass in terms of solid content), 2 parts by mass of a solvent 2, 2 parts by mass of a solvent 8, 11 parts by mass of a solvent 9, 2 parts by mass of a thickener 2, 0.2 parts by mass of an antifoaming agent 2, and 1 part by mass of a cross-linking agent 1 were mixed and stirred with 100 parts by mass of a coloring pigment dispersion liquid similar to that in Example 1 to produce an aqueous coating material 23.

[0176]

<Aqueous coating material 24>

250 parts by mass of a resin 9 (100 parts by mass in terms of solid content), 2 parts by mass of a solvent 2, 2 parts by mass of a solvent 8, 11 parts by mass of a solvent 9, 2 parts by mass of a thickener 2, 0.2 parts by mass of an antifoaming agent 2, 1 part by mass of a cross-linking agent 1, and 10 parts by mass of a coloring liquid 1 were mixed and stirred with 100 parts by mass of a coloring pigment dispersion liquid similar to that in Example 1 to produce an aqueous coating material 24.

[0177]

<Aqueous coating material 25>

250 parts by mass of a resin 9 (100 parts by mass in terms of solid content), 2 parts by mass of a solvent 2, 2 parts by mass of a solvent 8, 11 parts by mass of a solvent 9, 2 parts by mass of a thickener 2, 0.2 parts by mass of an antifoaming agent 2, 1 part by mass of a cross-linking agent 1, and 10 parts by mass of a coloring liquid 2 were mixed and stirred with 100 parts by mass of a coloring pigment dispersion liquid similar to that in Example 1 to produce an aqueous coating material 25.

[0178]

<Aqueous coating material 26>

250 parts by mass of a resin 9 (100 parts by mass in terms of solid content), 2 parts by mass of a solvent 2, 2 parts by mass of a solvent 8, 11 parts by mass of a solvent 9, 2 parts by mass of a thickener 2, 0.2 parts by mass of an antifoaming agent 2, and 1 part by mass of a cross-linking agent 3 were mixed and stirred with 100 parts by mass of a coloring pigment dispersion liquid similar to that in Example 1 to produce an aqueous coating material 26.

[0179]

<Aqueous coating material 27>

220 parts by mass of a resin 10 (88 parts by mass in terms of solid content), 18 parts by mass of a solvent 1, 2

parts by mass of a thickener 2, 0.2 parts by mass of an antifoaming agent 2, 1 part by mass of a cross-linking agent 1, and 40 parts by mass of a resin 19 (12 parts by mass in terms of solid content) were mixed and stirred with 100 parts by mass of a coloring pigment dispersion liquid similar to that in Example 1 to produce an aqueous coating material 27.

[0180]

<Aqueous coating material 28>

220 parts by mass of a resin 9 (88 parts by mass in terms of solid content), 2 parts by mass of a solvent 2, 2 parts by mass of a solvent 8, 11 parts by mass of a solvent 9, 2 parts by mass of a thickener 2, 0.2 parts by mass of an antifoaming agent 2, 1 part by mass of a cross-linking agent 1, and 40 parts by mass of a resin 19 (12 parts by mass in terms of solid content) were mixed and stirred with 100 parts by mass of a coloring pigment dispersion liquid similar to that in Example 1 to produce an aqueous coating material 28.

[0181]

<Aqueous coating material 29>

250 parts by mass of a resin 17 (100 parts by mass in terms of solid content), 18 parts by mass of a solvent 1, 2 parts by mass of a thickener 2, and 0.2 parts by mass of an antifoaming agent 2 were mixed and stirred with 100 parts

by mass of a coloring pigment dispersion liquid similar to that in Example 1 to produce an aqueous coating material 29.

[0182]

<Aqueous coating material 30>

250 parts by mass of a resin 17 (100 parts by mass in terms of solid content), 2 parts by mass of a thickener 2, and 0.2 parts by mass of an antifoaming agent 2 were mixed and stirred with 100 parts by mass of a coloring pigment dispersion liquid similar to that in Example 1 to produce an aqueous coating material 30.

[0183]

<Aqueous coating material 31>

250 parts by mass of a resin 18 (100 parts by mass in terms of solid content), 18 parts by mass of a solvent 1, 2 parts by mass of a thickener 2, 0.2 parts by mass of an antifoaming agent 2, and 1 part by mass of a cross-linking agent 1 were mixed and stirred with 100 parts by mass of a coloring pigment dispersion liquid similar to that in Example 1 to produce an aqueous coating material 31.

[0184]

<Aqueous coating material 32>

250 parts by mass of a resin 17 (100 parts by mass in terms of solid content), 18 parts by mass of a solvent 1, 2 parts by mass of a thickener 2, and 0.2 parts by mass of an

antifoaming agent 2 were mixed and stirred to produce an aqueous coating material 32.

[0185]

(Test method)

Each aqueous coating material was tested by the following methods.

[0186]

[Test 1]

As a test substrate, a slate plate having a convex-concave pattern (height difference: about 1.5 mm) formed by a synthetic resin emulsion-based thick finishing coating was prepared. When each aqueous coating material was spray-coated on the test substrate at an application amount of 0.3 kg/m², and dried for 168 hours in a state where the coating surface was horizontally placed in a thermostat at a temperature of 5°C, the appearance of the coating film was observed. As the evaluation criteria, those in which no cracks were recognized were evaluated as "A", those in which cracks were slightly recognized were evaluated as "B", and those in which cracks were obviously recognized were evaluated as "C". A practically problematic level is "C".

[0187]

[Test 2]

When each aqueous coating material was applied to one

surface of a glass plate using a film applicator having a gap of 150 μm , and dried in a standard state (temperature: 23°C, relative humidity: 50%) for 48 hours in a state where the coating surface was horizontally placed, a 20-degree mirror surface glossiness (measurement angle: 20 degrees) was measured. As the evaluation criteria, those having a 20-degree mirror surface glossiness of 46 or more were evaluated as "AA", those having a 20-degree mirror surface glossiness of 43 or more and less than 46 were evaluated as "A", those having a 20-degree mirror surface glossiness of 40 or more and less than 43 were evaluated as "B", and those having a 20-degree mirror surface glossiness of less than 40 were evaluated as "C". A practically problematic level is "C".

[0188]

[Test 3]

The test plate subjected to the Test 1 was dried in a standard state (temperature: 23°C, relative humidity: 50%) for 14 days, and then exposed for 1000 hours with an accelerated weather resistance tester (xenon weather meter). Then, the appearance of the coating film was observed. As the evaluation criteria, those in which no cracks were recognized were evaluated as "A", those in which cracks were slightly recognized were evaluated as "B", and those in which cracks were obviously recognized

were evaluated as "C". A practically problematic level is "C".

[0189]

[Test 4]

As a test substrate, a slate plate having a coating film (coating film thickness: 0.5 mm) formed by a flexible type synthetic resin emulsion-based finishing coating for modification was prepared. Each aqueous coating material was spray-coated on the test substrate at an application amount of 0.3 kg/m², and dried for 24 hours in a state where the coating surface was horizontally placed in a thermostat at a temperature of 5°C to prepare a test body. When this test body was immersed in water at 23°C for 24 hours, the appearance of the coating film was observed. As the evaluation criteria, those in which no blistering was observed were evaluated as "AA", those in which blistering was very slightly observed were evaluated as "A", those in which blistering was slightly observed were evaluated as "B", and those in which blistering was obviously observed were evaluated as "C". A practically problematic level is "C".

[0190]

(Test results)

The test results are shown in Table 1. In Test 1, good results were obtained in Examples 1 to 28 (in

particular, Examples 3 to 28), and excellent cracking resistance was obtained. In Test 2, good results were obtained in Examples 1 to 28 (in particular Examples 11 to 16, 23 to 26 and 28), and excellent glossiness was obtained. Also in Test 3, good results were obtained in Examples 3 to 28 (in particular, Examples 4 to 16 and 18 to 28), and excellent cracking resistance and weather resistance were obtained. In Test 4, good results were obtained in Examples 1 to 28 (in particular, Examples 2 to 16 and 18 to 28), the strength of the coating film was early expressed, and excellent blister resistance was obtained.

Because of insufficient results in Test 1 in Comparative Examples 1 to 3, Test 3 in Comparative Examples 1 to 3 was not performed. Since Comparative Example 4 does not contain a pigment or the like and is outside the scope of the present invention, Tests 2 and 3 are not performed.

[0191]

[Table 1]

Composition and evaluation			Examples											
			1	2	3	4	5	6	7	8	9	10	11	12
Aqueous coating material	Type		1	2	3	4	5	6	7	8	9	10	11	12
	Parts by mass		100	100	100	100	100	100	100	100	100	100	100	100
Resin component	Type	Resin	1	2	3	4	5	6	7	8	9	8	8	8
	Parts by mass		250	250	250	250	250	250	250	250	250	250	250	250

	Component (s)	Type	2EHA nOA	2OA nOA	2EHA IAA	2EHA IAA	2EHA IAA	2EHA IAA	2EHA 2OA	IAA 2OA	IAA 2OA	IAA 2OA	IAA 2OA	IAA 2OA
	Glass transition temperature	°C	3	3	3	3	10	-4	3	3	3	3	3	3
	Silica remaining amount ratio	% By mass	15	15	15	15	15	20	15	15	15	15	15	15
Component (D) solvent			Type	1	1	1	1	1	1	1	1	2	2	2
			Parts by mass	18	18	18	18	18	18	18	18	18	12	12
			Type	-	-	-	-	-	-	-	-	-	3	4
			Parts by mass	-	-	-	-	-	-	-	-	-	6	6
			Type	-	-	-	-	-	-	-	-	-	-	-
			Parts by mass	-	-	-	-	-	-	-	-	-	-	-
Thickener 2			Parts by mass	2	2	2	2	2	2	2	2	2	2	2
Antifoaming agent 2			Parts by mass	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Component (C) cross-linking agent			Type	-	-	-	1	1	1	1	1	1	1	1
			Parts by mass	-	-	-	1	1	1	1	1	1	1	1
Others			Type	-	-	-	-	-	-	-	-	-	-	-
			Parts by mass	-	-	-	-	-	-	-	-	-	-	-
Evaluation	Test 1		B	B	A	A	A	A	A	A	A	A	A	A
	Test 2		B	B	B	B	B	B	B	B	B	B	AA	A
	Test 3		-	-	B	A	A	A	A	A	A	A	A	A
	Test 4		B	A	A	A	A	A	A	AA	AA	AA	AA	AA

[0192]

[Table 2]

Composition and evaluation			Examples											
			13	14	15	16	17	18	19	20	21	22		
Aqueous coating material		Type	13	14	15	16	17	18	19	20	21	22		

Component (B) - containing coloring pigment dispersion liquid		Parts by mass	100	100	100	100	100	100	100	100	100	100
Resin component	Resin	Type	8	8	8	9	10	11	3	12	13	14
		Parts by mass	250	250	250	250	250	250	250	250	250	250
	Component (s)	Type	IAA	IAA	IAA	IAA	2EHA	2OA	2EHA	2EHA	nHA	nBA
			2OA	2OA	2OA	2OA	nOA	nOA	IAA	2OA	2OA	2OA
	Glass transition temperature	°C	3	3	3	3	3	3	3	3	3	3
	Silica remaining amount ratio	% By mass	15	15	15	15	15	15	15	10	10	10
Component (D) solvent		Type	2	2	2	2	1	1	1	1	1	1
		Parts by mass	12	12	12	12	18	18	18	18	18	18
		Type	5	6	7	3	-	-	-	-	-	-
		Parts by mass	6	6	6	6	-	-	-	-	-	-
		Type	-	-	-	-	-	-	-	-	-	-
		Parts by mass	-	-	-	-	-	-	-	-	-	-
Thickener 2		Parts by mass	2	2	2	2	2	2	2	2	2	2
Antifoaming agent 2		Parts by mass	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Component (C) cross- linking agent		Type	1	1	1	1	1	1	2	1	1	1
		Parts by mass	1	1	1	1	1	1	3	1	1	1
Others		Type	-	-	-	-	-	-	-	-	-	-
		Parts by mass	-	-	-	-	-	-	-	-	-	-
Evaluation	Test 1		A	A	A	A	A	A	A	A	A	A
	Test 2		A	A	A	AA	B	B	B	B	B	B
	Test 3		A	A	A	A	B	A	A	A	A	A
	test 4		AA	AA	AA	AA	B	A	A	A	A	A

[0193]

[Table 3]

Composition and evaluation			Examples						Comparative Examples			
			23	24	25	26	27	28	1	2	3	4
Aqueous coating material	Type		23	24	25	26	27	28	29	30	31	32
Component (B)- containing coloring pigment dispersion liquid	Parts by mass		100	100	100	100	100	100	100	100	100	-
Resin component	Resin	Type	9	9	9	9	10	9	17	17	18	17
		Parts by mass	250	250	250	250	220	220	250	250	250	250
	Component (s)	Type	IAA	IAA	IAA	IAA	2EHA	IAA	nOA	nOA	nOA	nOA
			20A	20A	20A	20A	nOA	20A	-	-	-	-
	Glass transition temperature	°C	3	3	3	3	3	3	3	3	3	3
	Silica remaining amount ratio	% By mass	15	15	15	15	15	15	15	15	15	15
Component (D) solvent		Type	2	2	2	2	1	2	1	-	1	1
		Parts by mass	2	2	2	2	18	2	18	-	18	18
		Type	8	8	8	8	-	8	-	-	-	-
		Parts by mass	2	2	2	2	-	2	-	-	-	-
		Type	9	9	9	9	-	9	-	-	-	-
		Parts by mass	11	11	11	11	-	11	-	-	-	-
Thickener 2	Parts by mass		2	2	2	2	2	2	2	2	2	2
Antifoaming agent 2	Parts by mass		0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Component (C) cross- linking agent	Type		1	1	1	3	1	1	-	-	1	-
	Parts by mass		1	1	1	1	1	1	-	-	1	-
Others	Type		-	Coloring liquid 1	Coloring liquid 2	-	Resin 19	Resin 19	-	-	-	-

		Parts by mass	-	10	10	-	40	40	-	-	-	-
Evaluation	Test 1		A	A	A	A	A	A	C	C	C	B
	Test 2		AA	AA	AA	AA	B	AA	B	C	B	-
	Test 3		A	A	A	A	A	A	-	-	-	-
	Test 4		AA	AA	AA	AA	A	AA	C	C	C	C

[0194]

<Top coating 1>

0.4 parts by mass of a thickener 1, 0.1 parts by mass of an antifoaming agent 1, 2.5 parts by mass of a pigment dispersant 1, and 70 parts by mass of a coloring pigment 1 were mixed and stirred with 27 parts by mass of water to produce a coloring pigment dispersion liquid.

Subsequently, 250 parts by mass of a resin 1 (100 parts by mass in terms of solid content), 6 parts by mass of a solvent 8, 12 parts by mass of a solvent 9, 2 parts by mass of a thickener 2, and 0.2 parts by mass of an antifoaming agent 2 were mixed and stirred with 100 parts by mass of the coloring pigment dispersion liquid to produce a top coating 1.

The elongation percentage at -10°C of the top coating 1 was 17%.

[0195]

<Top coating 2>

250 parts by mass of a resin 2 (100 parts by mass in terms of solid content), 6 parts by mass of a solvent 8, 12 parts by mass of a solvent 9, 2 parts by mass of a

thickener 2, and 0.2 parts by mass of an antifoaming agent 2 were mixed and stirred with 100 parts by mass of a coloring pigment dispersion liquid similar to that of the top coating 1 to produce a top coating 2.

The elongation percentage at -10°C of the top coating 2 was 18%.

[0196]

<Top coating 3>

250 parts by mass of a resin 3 (100 parts by mass in terms of solid content), 6 parts by mass of a solvent 8, 12 parts by mass of a solvent 9, 2 parts by mass of a thickener 2, and 0.2 parts by mass of an antifoaming agent 2 were mixed and stirred with 100 parts by mass of a coloring pigment dispersion liquid similar to that of the top coating 1 to produce a top coating 3.

The elongation percentage at -10°C of the top coating 3 was 18%.

[0197]

<Top coating 4>

250 parts by mass of a resin 10 (100 parts by mass in terms of solid content), 6 parts by mass of a solvent 8, 12 parts by mass of a solvent 9, 2 parts by mass of a thickener 2, and 0.2 parts by mass of an antifoaming agent 2, and 1 parts by mass of a cross-linking agent 1 were mixed and stirred with 100 parts by mass of a coloring

pigment dispersion liquid similar to that of the top coating 1 to produce a top coating 4.

The elongation percentage at -10°C of the top coating 4 was 18%.

[0198]

<Top coating 5>

250 parts by mass of a resin 11 (100 parts by mass in terms of solid content), 6 parts by mass of a solvent 8, 12 parts by mass of a solvent 9, 2 parts by mass of a thickener 2, and 0.2 parts by mass of an antifoaming agent 2, and 1 parts by mass of a cross-linking agent 1 were mixed and stirred with 100 parts by mass of a coloring pigment dispersion liquid similar to that of the top coating 1 to produce a top coating 5.

The elongation percentage at -10°C of the top coating 5 was 18%.

[0199]

<Top coating 6>

250 parts by mass of a resin 3 (100 parts by mass in terms of solid content), 6 parts by mass of a solvent 8, 12 parts by mass of a solvent 9, 2 parts by mass of a thickener 2, 0.2 parts by mass of an antifoaming agent 2, and 3 parts by mass of a cross-linking agent 2 were mixed and stirred with 100 parts by mass of a coloring pigment dispersion liquid similar to that of the top coating 1 to

produce a top coating 6.

The elongation percentage at -10°C of the top coating 6 was 20%.

[0200]

<Top coating 7>

250 parts by mass of a resin 4 (100 parts by mass in terms of solid content), 6 parts by mass of a solvent 8, 12 parts by mass of a solvent 9, 2 parts by mass of a thickener 2, and 0.2 parts by mass of an antifoaming agent 2, and 1 parts by mass of a cross-linking agent 1 were mixed and stirred with 100 parts by mass of a coloring pigment dispersion liquid similar to that of the top coating 1 to produce a top coating 7.

The elongation percentage at -10°C of the top coating 7 was 20%.

[0201]

<Top coating 8>

250 parts by mass of a resin 5 (100 parts by mass in terms of solid content), 6 parts by mass of a solvent 8, 12 parts by mass of a solvent 9, 2 parts by mass of a thickener 2, and 0.2 parts by mass of an antifoaming agent 2, and 1 parts by mass of a cross-linking agent 1 were mixed and stirred with 100 parts by mass of a coloring pigment dispersion liquid similar to that of the top coating 1 to produce a top coating 8.

The elongation percentage at -10°C of the top coating 8 was 14%.

[0202]

<Top coating 9>

250 parts by mass of a resin 6 (100 parts by mass in terms of solid content), 6 parts by mass of a solvent 8, 12 parts by mass of a solvent 9, 2 parts by mass of a thickener 2, and 0.2 parts by mass of an antifoaming agent 2, and 1 parts by mass of a cross-linking agent 1 were mixed and stirred with 100 parts by mass of a coloring pigment dispersion liquid similar to that of the top coating 1 to produce a top coating 9.

The elongation percentage at -10°C of the top coating 9 was 26%.

[0203]

<Top coating 10>

250 parts by mass of a resin 12 (100 parts by mass in terms of solid content), 6 parts by mass of a solvent 8, 12 parts by mass of a solvent 9, 2 parts by mass of a thickener 2, 0.2 parts by mass of an antifoaming agent 2, and 1 part by mass of a cross-linking agent 1 were mixed and stirred with 100 parts by mass of a coloring pigment dispersion liquid similar to that of the top coating 1 to produce a top coating 10.

The elongation percentage at -10°C of the top coating

10 was 23%.

[0204]

<Top coating 11>

250 parts by mass of a resin 8 (100 parts by mass in terms of solid content), 6 parts by mass of a solvent 8, 12 parts by mass of a solvent 9, 2 parts by mass of a thickener 2, 0.2 parts by mass of an antifoaming agent 2, and 1 part by mass of a cross-linking agent 1 were mixed and stirred with 100 parts by mass of a coloring pigment dispersion liquid similar to that of the top coating 1 to produce a top coating 11.

The elongation percentage at -10°C of the top coating 11 was 20%.

[0205]

<Top coating 12>

250 parts by mass of a resin 9 (100 parts by mass in terms of solid content), 6 parts by mass of a solvent 8, 12 parts by mass of a solvent 9, 2 parts by mass of a thickener 2, 0.2 parts by mass of an antifoaming agent 2, and 1 part by mass of a cross-linking agent 1 were mixed and stirred with 100 parts by mass of a coloring pigment dispersion liquid similar to that of the top coating 1 to produce a top coating 12.

The elongation percentage at -10°C of the top coating 12 was 18%.

[0206]

<Top coating 13>

250 parts by mass of a resin 8 (100 parts by mass in terms of solid content), 6 parts by mass of a solvent 2, 6 parts by mass of a solvent 8, 6 parts by mass of a solvent 9, 2 parts by mass of a thickener 2, 0.2 parts by mass of an antifoaming agent 2, and 1 part by mass of a cross-linking agent 1 were mixed and stirred with 100 parts by mass of a coloring pigment dispersion liquid similar to that of the top coating 1 to produce a top coating 13.

The elongation percentage at -10°C of the top coating 13 was 21%.

[0207]

<Top coating 14>

250 parts by mass of a resin 8 (100 parts by mass in terms of solid content), 12 parts by mass of a solvent 2, 6 parts by mass of a solvent 8, 2 parts by mass of a thickener 2, 0.2 parts by mass of an antifoaming agent 2, and 1 part by mass of a cross-linking agent 1 were mixed and stirred with 100 parts by mass of a coloring pigment dispersion liquid similar to that of the top coating 1 to produce a top coating 14.

The elongation percentage at -10°C of the top coating 14 was 20%.

[0208]

<Top coating 15>

250 parts by mass of a resin 13 (100 parts by mass in terms of solid content), 6 parts by mass of a solvent 8, 12 parts by mass of a solvent 9, 2 parts by mass of a thickener 2, 0.2 parts by mass of an antifoaming agent 2, and 1 part by mass of a cross-linking agent 1 were mixed and stirred with 100 parts by mass of a coloring pigment dispersion liquid similar to that of the top coating 1 to produce a top coating 15.

The elongation percentage at -10°C of the top coating 15 was 18%.

[0209]

<Top coating 16>

250 parts by mass of a resin 14 (100 parts by mass in terms of solid content), 6 parts by mass of a solvent 8, 12 parts by mass of a solvent 9, 2 parts by mass of a thickener 2, 0.2 parts by mass of an antifoaming agent 2, and 1 part by mass of a cross-linking agent 1 were mixed and stirred with 100 parts by mass of a coloring pigment dispersion liquid similar to that of the top coating 1 to produce a top coating 16.

The elongation percentage at -10°C of the top coating 16 was 19%.

[0210]

<Top coating 17>

250 parts by mass of a resin 17 (100 parts by mass in terms of solid content), 6 parts by mass of a solvent 8, 12 parts by mass of a solvent 9, 2 parts by mass of a thickener 2, and 0.2 parts by mass of an antifoaming agent 2 were mixed and stirred with 100 parts by mass of a coloring pigment dispersion liquid similar to that of the top coating 1 to produce a top coating 17.

The elongation percentage at -10°C of the top coating 17 was 18%.

[0211]

<Top coating 18>

250 parts by mass of a resin 18 (100 parts by mass in terms of solid content), 6 parts by mass of a solvent 8, 12 parts by mass of a solvent 9, 2 parts by mass of a thickener 2, 0.2 parts by mass of an antifoaming agent 2, and 1 part by mass of a cross-linking agent 1 were mixed and stirred with 100 parts by mass of a coloring pigment dispersion liquid similar to that of the top coating 1 to produce a top coating 18.

The elongation percentage at -10°C of the top coating 18 was 18%.

[0212]

<Top coating 19>

250 parts by mass of a resin 15 (100 parts by mass in terms of solid content), 6 parts by mass of a solvent 8, 12

parts by mass of a solvent 9, 2 parts by mass of a thickener 2, 0.2 parts by mass of an antifoaming agent 2, and 1 part by mass of a cross-linking agent 1 were mixed and stirred with 100 parts by mass of a coloring pigment dispersion liquid similar to that of the top coating 1 to produce a top coating 19.

The elongation percentage at -10°C of the top coating 19 was 32%.

[0213]

<Top coating 20>

125 parts by mass of a resin 8 (50 parts by mass in terms of solid content), 125 parts by mass of a resin 16 (50 parts by mass in terms of solid content), 6 parts by mass of a solvent 8, 12 parts by mass of a solvent 9, 2 parts by mass of a thickener 2, 0.2 parts by mass of an antifoaming agent 2, and 1 part by mass of a cross-linking agent 1 were mixed and stirred with 100 parts by mass of a coloring pigment dispersion liquid similar to that of the top coating 1 to produce a top coating 20.

The elongation percentage at -10°C of the top coating 20 was 30%.

[0214]

<Top coating 21>

250 parts by mass of a resin 16 (100 parts by mass in terms of solid content), 6 parts by mass of a solvent 8, 12

parts by mass of a solvent 9, 2 parts by mass of a thickener 2, 0.2 parts by mass of an antifoaming agent 2, and 1 part by mass of a cross-linking agent 1 were mixed and stirred with 100 parts by mass of a coloring pigment dispersion liquid similar to that of the top coating 1 to produce a top coating 21.

The elongation percentage at -10°C of the top coating 21 was 38%.

[0215]

The elongation percentage at -10°C of each top coating is a value measured according to a method defined in "Elongation Test" in JIS A6909:2021. Test body subjected to Elongation Test is obtained by applying and laminating a top coating film having a dry film thickness of 80 μm on the surface of a film having a dry film thickness of 1 mm and containing a waterproof type multilayer coating E main material which corresponds to JIS A6909:2021 {a mixture of acrylic resin emulsion (Tg-28°C), titanium oxide (average particle size: 0.3 μm), heavy calcium carbonate (average particle size: 12 μm), etc., elongation percentage at -10°C of 38% of a single film}.

[0216]

(Test method)

Each top coating was tested by the following method.

[0217]

[Test 5]

As a test substrate, there was prepared a slate plate having a convex-concave pattern (height difference: about 1.5 mm) formed by a waterproof type multilayer coating E main material which corresponds to JIS A6909:2021 {a mixture of acrylic resin emulsion (Tg: -28°C), titanium oxide (average particle size: 0.3 μm), heavy calcium carbonate (average particle size: 12 μm), etc., elongation percentage at -10°C of 38% of a single film}. A first top coating was spray-coated on the test substrate at an application amount of 0.15 kg/m², and dried for 2 hours. Then, a second top coating was spray-coated at an application amount of 0.15 kg/m², dried, and cured for 168 hours to prepare a test body. Coating, drying, and curing were all performed in a standard state (temperature: 23°C, relative humidity: 50%).

[0218]

The test body obtained by the above method was subjected to a total of 10 cycles of a repeated warm and cold test as one cycle of immersion in water for 18 hours, leaving to stand at -20°C for 3 hours, and leaving to stand at 50°C for 3 hours. Then, the appearance of the film was confirmed, and the state of occurrence of defects (blistering, peeling, cracking, etc.) was evaluated. The evaluation was performed in four stages (excellent:

A>B>C>D: poor), in which one in which the occurrence of defects was not recognized was evaluated as "A", and one in which the occurrence of defects was clearly recognized was evaluated as "D". Practically problematic levels are "C" and "D".

[0219]

[Test 6]

A test body obtained in the same manner as in Test 5 was exposed for 1000 hours with an accelerated weather resistance tester (xenon weather meter), and then the appearance of the film was observed. The evaluation was performed in four stages (excellent: A>B>C>D: poor), in which one in which the occurrence of defects was not recognized was evaluated as "A", and one in which the occurrence of defects was clearly recognized was evaluated as "D". Practically problematic levels are "C" and "D".

[0220]

(Test results)

The test results are shown in Table 6. In Examples 29 to 47, good results were obtained in Test 5 and Test 6, and excellent cracking resistance, weather resistance, and the like were obtained.

[0221]

[Table 4]

	Top coating
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			1	2	3	4	5	6	7	8	9	10		
Component (B)- containing coloring pigment dispersion liquid		Parts by mass	100	100	100	100	100	100	100	100	100	100		
Resin component	Resin	Type	1	2	3	10	11	3	4	5	6	12		
		Parts by mass	250	250	250	250	250	250	250	250	250	250	250	
	Component (s)	Type	2EHA nOA	2OA nOA	2EHA IAA	2EHA nOA	2OA nOA	2EHA IAA	2EHA IAA	2EHA IAA	2EHA IAA	2EHA IAA	2EHA 2OA	
		Glass transition temperature	°C	3	3	3	3	3	3	3	10	-4	3	
	Silica remaining amount ratio	% By mass	15	15	15	15	15	15	15	15	15	20	10	
	Component (D) solvent		Type	8	8	8	8	8	8	8	8	8	8	8
Parts by mass			6	6	6	6	6	6	6	6	6	6	6	6
Type			9	9	9	9	9	9	9	9	9	9	9	9
Parts by mass			12	12	12	12	12	12	12	12	12	12	12	12
Type			-	-	-	-	-	-	-	-	-	-	-	-
Parts by mass			-	-	-	-	-	-	-	-	-	-	-	-
Thickener 2		Parts by mass	2	2	2	2	2	2	2	2	2	2	2	
Antifoaming agent 2		Parts by mass	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	
Component (C) cross- linking agent		Type	-	-	-	1	1	2	1	1	1	1	1	
		Parts by mass	-	-	-	1	1	3	1	1	1	1	1	1
Elongation percentage at -10°C		%	17	18	18	18	18	20	20	14	26	23		

[0222]

[Table 5]

			Top coating										
			11	12	13	14	15	16	17	18	19	20	21
Component (B) - containing coloring pigment dispersion liquid		Parts by mass	100	100	100	100	100	100	100	100	100	100	100
Resin component	Resin	Type	8	9	8	8	13	14	17	18	15	8	16
		Parts by mass	250	250	250	250	250	250	250	250	250	125	250
		Type	-	-	-	-	-	-	-	-	-	16	-
		Parts by mass	-	-	-	-	-	-	-	-	-	125	-
	Component (s)	Type	IAA	IAA	IAA	IAA	nHA	nBA	nOA	nOA	IAA	IAA	2EHA
			2OA	2OA	2OA	2OA	2OA	2OA	-	-	2OA	2OA	nBA
			-	-	-	-	-	-	-	-	-	2EHA	-
			-	-	-	-	-	-	-	-	-	nBA	-
	Glass transition temperature	°C	3	3	3	3	3	3	3	3	-6	6	8
	Silica remaining amount ratio	% By mass	15	15	15	15	10	10	15	15	8	8	0
Component (D) solvent		Type	8	8	2	2	8	8	8	8	8	8	8
		Parts by mass	6	6	6	12	6	6	6	6	6	6	6
		Type	9	9	8	8	9	9	9	9	9	9	9
		Parts by mass	12	12	6	6	12	12	12	12	12	12	12
		Type	-	-	9	-	-	-	-	-	-	-	-
		Parts by mass	-	-	6	-	-	-	-	-	-	-	-
Thickener 2		Parts by mass	2	2	2	2	2	2	2	2	2	2	2
Antifoaming agent 2		Parts by mass	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Component (C) cross-linking agent		Type	1	1	1	1	1	1	-	1	1	1	1
		Parts by mass	1	1	1	1	1	1	-	1	1	1	1

Elongation percentage at -10°C	%	20	18	21	20	18	19	18	18	32	30	38
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Note) Except for "Resin 16" included in "Resin component" in Table 5 above, an acrylic silicon resin is contained, and the "Resin 16" does not contain a silicon component.

[0223]

[Table 6]

Composition and evaluation		First top coating		Second top coating		Evaluation	
		Type of top coating	Elongation percentage at -10°C (%)	Type of top coating	Elongation percentage at -10°C (%)	Test 5	Test 6
Examples	29	19	32	1	17	B	B
	30	19	32	2	18	B	B
	31	19	32	3	18	A	B
	32	19	32	4	18	A	B
	33	19	32	5	18	A	A
	34	19	32	6	20	A	A
	35	19	32	7	20	A	A
	36	19	32	8	14	A	A
	37	19	32	9	26	A	A
	38	19	32	10	23	A	A
	39	19	32	11	20	A	A
	40	19	32	12	18	A	A
	41	19	32	13	21	A	A
	42	19	32	14	20	A	A
	43	20	30	13	21	A	A
	44	21	38	13	21	A	B
	45	10	23	8	14	A	A
	46	19	32	15	18	A	A
	47	19	32	16	19	A	A
Comparative Examples	5	19	32	17	18	C	D
	6	19	32	18	18	C	D
Reference Example	1	1	17	1	17	C	C

CLAIMS

[Claim 1] An aqueous coating material having room-temperature curability, and containing an acrylic silicon resin emulsion (A) and a pigment (B),

wherein a silica remaining amount ratio in a resin solid content of the acrylic silicon resin emulsion (A) is 1 to 40% by mass,

the acrylic silicon resin emulsion (A) has a glass transition temperature of 30°C or lower,

two or more kinds of (meth)acrylic acid alkyl esters (s) having an alkyl group having 4 or more carbon atoms are contained as monomers constituting the acrylic silicon resin emulsion (A), and

a homopolymer of the (meth)acrylic acid alkyl ester (s) having an alkyl group having 4 or more carbon atoms has a glass transition temperature of 0°C or lower.

[Claim 2] The aqueous coating material according to claim 1, wherein the (meth)acrylic acid alkyl ester (s) having an alkyl group having 4 or more carbon atoms contains a (meth)acrylic acid alkyl ester (s1) having a branched alkyl group having 5 or more carbon atoms.

[Claim 3] The aqueous coating material according to claim

2, wherein the branched alkyl group contains a methyl group.

[Claim 4] The aqueous coating material according to claim 1, further comprising a cross-linking agent (C),

wherein the acrylic silicon resin emulsion (A) has a reactive functional group, and

the cross-linking agent (C) has a functional group capable of reacting with the reactive functional group.

[Claim 5] A method for forming a film for forming a top coating film by sequentially applying a first top coating and a second top coating to a surface to be coated,

wherein the first top coating forms a film having an elongation percentage at -10°C of 20% or more,

the second top coating is the aqueous coating material according to any one of claims 1 to 4, and

the second top coating forms a film having an elongation percentage at -10°C less than that of the first top coating.

[Claim 6] The method according to claim 5,

wherein the first top coating contains a resin emulsion and a pigment, and

two or more kinds of (meth)acrylic acid alkyl esters

(s) having an alkyl group having 4 or more carbon atoms are contained as monomers constituting the resin emulsion, and a homopolymer of the (meth)acrylic acid alkyl ester (s) having an alkyl group having 4 or more carbon atoms has a glass transition temperature of 0°C or lower.

[Claim 7] The method according to claim 6, wherein the (meth)acrylic acid alkyl ester (s) having an alkyl group having 4 or more carbon atoms contains a (meth)acrylic acid alkyl ester (s1) having a branched alkyl group having 5 or more carbon atoms.

[Claim 8] The method according to claim 7, wherein the branched alkyl group contains a methyl group.

[Claim 9] A top coating set comprising the first top coating and the second top coating used in the method according to claim 5.