

TWO-PACKAGE AQUEOUS COATING COMPOSITION

BACKGROUND OF THE INVENTION

[0001] The present invention relates to a two-package aqueous coating
5 composition containing a carbodiimide curing agent.

[0002] In the field of a coating material, there have previously been many
solvent-based coating materials, but from the viewpoint of an environmental
problem, they have been replaced with an aqueous coating material having a
small content of an organic solvent in recent years. The aqueous coating
10 material contains a water-soluble or water-dispersible resin, and forms a coating
film by volatilization of a solvent component such as water, after coating.

[0003] However, a hydrophilic functional group such as a carboxyl group is
attached to a resin in an aqueous coating material in order to develop water
solubility or water dispersibility. For this reason, there is a problem that a large
15 amount of hydrophilic functional groups remain also in a formed coating film,
and as a result, a water resistance of the coating film is reduced.

[0004] Then, recently, trials have been attempted to improve performance such
as a water resistance of a coating film by containing a compound having a
carbodiimide group as a curing agent in an aqueous coating material, and
20 reacting the group with a carboxyl group of a resin to allow the carboxyl group
to be eliminated (Patent Documents 1 to 4).

[0005]

[Patent Document 1] JP-A No. 2000-007642

[Patent Document 2] JP-A No. 2011-132374

[Patent Document 3] JP-A No. 2000-313825

[Patent Document 4] JP-A No. 2010-260001

SUMMARY OF THE INVENTION

[0006] However, there has arisen new problems that, when the aqueous coating materials of the above-mentioned Patent Documents 1 to 4 are used outdoors in order to coat large structures such as an outer wall for a house, a bridge, an industrial machine and the like, water resistances at the initial stage after coating are not sufficiently obtained, and gloss is not sufficiently obtained.

Concerning the water resistances at the initial stage, more particularly, although the aqueous coating materials have been apparently dried at the initial stage after coating, a curing reaction has not sufficiently progressed yet, and the water resistances at the initial stage are not sufficient, and thus when exposed to rainfall soon after execution outdoors, a blister may be generated in a part of a coating film. Further, when temperature becomes lower, since an elongation ratio of a coating film is reduced, a cracking may be generated at a site where a blister is generated. It is difficult to use an aqueous coating material by which sufficient gloss is not obtained as a topcoat coating material. Further, in the field of a coating material, long term storage stabilities of a coating material are required, but there is also a problem that, when the aqueous coating material is used after long term preservation, sufficient performance of a coating film is not obtained.

[0007] Therefore, an object of the present invention is to provide an aqueous two-package coating composition which is excellent in long term storage stabilities, is also excellent in water resistances at the initial stage and gloss of a coating film, and is good for the environment.

[0008] In order to achieve the object, the present inventors have conducted intensive studies, and as a result, found out that the object is achieved by using, for a two-package aqueous coating composition, a carbodiimide compound including a residue of polyethylene glycol monoalkyl ether (PEG portion), a residue of polypropylene glycol monoalkyl ether (PPG portion) and a carbodiimide portion, wherein number average repetition numbers of ethylene glycol (EG) units in the PEG portion and propylene glycol (PG) units in the PPG portion are in the specific ranges, and further, a molar ratio of the PEG portion and the PPG portion is in the specific range, as a curing agent, resulting in completion of the present invention.

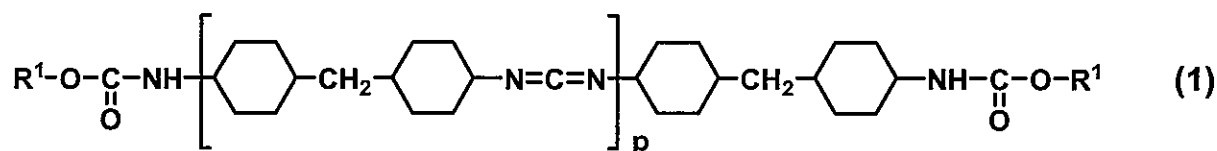
[0009] That is, the present invention provides a two-package aqueous coating composition containing:

(A) an aqueous acrylic resin having a carboxyl group, and

(B) a carbodiimide compound represented by the general formula (1):

[0010]

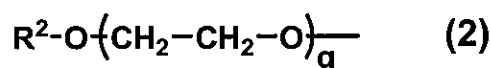
[Chemical formula 1]



wherein p represents an integer of 1 to 5, and two R¹s are independently a residue of polyethylene glycol monoalkyl ether represented by the general formula (2):

[0011]

[Chemical formula 2]

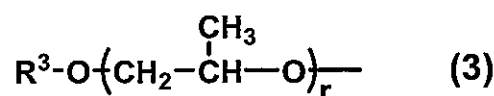


wherein a number average repetition number q is in the range of 6 to 40, and R^2 represents an alkyl group having 1 to 8 carbon atoms, or a phenyl group

and/or a residue of polypropylene glycol monoalkyl ether represented by the general formula (3):

[0012]

[Chemical formula 3]



wherein a number average repetition number r is in the range of 4 to 14, and R^3 represents an alkyl group having 1 to 8 carbon atoms, or a phenyl group,

wherein, in the R^1 's in the general formula (1), a molar ratio between the residue of polyethylene glycol monoalkyl ether represented by the general formula (2) and the residue of polypropylene glycol monoalkyl ether represented by the general formula (3) is 1:1 to 1:15.

[0013] The two-package aqueous coating composition of the present invention uses, as a curing agent, a carbodiimide compound including a PEG portion, a PPG portion and a carbodiimide portion, and in the structure thereof, the number average repetition number q of EG units in the PEG portion is in the range of 6 to 40, the number average repetition number r of PG units in the PPG portion is in the range of 4 to 14, and the molar ratio of the PEG portion and the PPG portion is in the specific range of 1:1 to 1:15, and thus it is

excellent in long term preserving properties, and is also excellent in water resistances at the initial stage and gloss of a coating film.

[0014] Since the two-package aqueous coating composition of the present invention is also excellent in a curing reactivity at low temperature, it can form a coating film excellent in water resistances at the initial stage in a relative short time, even when the curing temperature is relatively low. For example, in the aqueous coating composition of the present invention, only by being used and aged under the temperature environment having a curing temperature of -10 to 50°C, a curing reaction effectively progresses in a few hours, and a coating film excellent in water resistances at the initial stage and gloss can be formed.

Since the two-package aqueous coating composition of the present invention also relates to an aqueous coating material, it can effectively reduce the content of an organic solvent. For this reason, a discharge amount of a volatile organic compound and a discharge amount of an environmental pollutant based on the PRTR law (Law Concerning Reporting, etc. of Releases to the Environment of Specific Chemical Substances and Promoting Improvements in Their Management) can be considerably reduced as compared with a previous solvent-based coating material.

DETAILED DESCRIPTION OF THE INVENTION

[0015] Hereinafter, the present invention will be described in detail in line with preferred embodiments thereof.

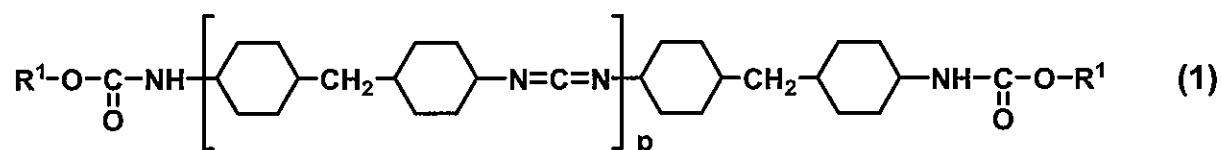
[0016] The two-package aqueous coating composition of the present invention contains:

(A) an aqueous acrylic resin having a carboxyl group, and

(B) a carbodiimide compound represented by the general formula (1):

[0017]

[Chemical formula 4]



[0018] In the present invention, as a resin for forming a coating film, an aqueous acrylic resin having a carboxyl group (A) is suitably used, and this is an acrylic resin obtained by copolymerizing an α,β -ethylenically unsaturated monomer having a carboxyl group and a different α,β -ethylenically unsaturated monomer. As the aqueous acrylic resin having a carboxyl group (A), a water dispersion of an acrylic resin having a carboxyl group is more suitably used. As one method of obtaining the water dispersion of an acrylic resin having a carboxyl group, there is an acrylic emulsion, and the acrylic emulsion can be prepared by performing emulsion polymerization in an aqueous medium.

[0019] Examples of the α,β -ethylenically unsaturated monomer having a

carboxyl group include acrylic acid, methacrylic acid, an acrylic acid dimer, crotonic acid, 2-acryloyloxyethylphthalic acid, 2-acryloyloxyethylsuccinic acid, ω -carboxy-polycaprolactone mono(meth)acrylate, isocrotonic acid, α -hydro- ω -((1-oxo-2-propenyl)oxy) poly(oxy(1-oxo-1,6-hexanediyl)), maleic acid, fumaric acid and itaconic acid. Among these, acrylic acid and methacrylic acid are preferred. In the present specification, "(meth)acryl" refers to both acryl and methacryl.

[0020] Examples of the different α,β -ethylenically unsaturated monomer include (meth)acrylic acid esters (e.g., methyl (meth)acrylate, ethyl (meth)acrylate, n-

propyl (meth)acrylate, n-butyl (meth)acrylate, isobutyl (meth)acrylate, t-butyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, lauryl methacrylate, phenyl acrylate, isobornyl (meth)acrylate, cyclohexyl methacrylate, t-butylcyclohexyl (meth)acrylate, dicyclopentadienyl (meth)acrylate, dihydrodicyclopentadienyl (meth)acrylate and the like), polymerizable amide compounds (e.g., (meth)acrylamide, N-methylol (meth)acrylamide, N-butoxymethyl (meth)acrylamide, N,N-dimethyl (meth)acrylamide, N,N-dibutyl (meth)acrylamide, N,N-dioctyl (meth)acrylamide, N-monobutyl (meth)acrylamide, N-monooctyl (meth)acrylamide, 2,4-dihydroxy-4'-vinylbenzophenone, N-(2-hydroxyethyl)acrylamide, N-(2-hydroxyethyl)methacrylamide and the like), polymerizable aromatic compounds (e.g., styrene, α -methylstyrene, vinyl ketone, t-butylstyrene, parachlorostyrene, vinylnaphthalene and the like), polymerizable nitriles (e.g., acrylonitrile, methacrylonitrile and the like), α -olefins (e.g., ethylene, propylene and the like), vinyl esters (e.g., vinyl acetate, vinyl propionate and the like), dienes (e.g., butadiene, isoprene and the like), polymerizable aromatic compounds, polymerizable nitriles, α -olefins, vinyl esters and dienes. These may be selected according to the intended use.

[0021] In the preparation of the aqueous acrylic resin having a carboxyl group (A), an α,β -ethylenically unsaturated monomer having a hydroxyl group may be further used as necessary. Examples of the α,β -ethylenically unsaturated monomer having a hydroxyl group include hydroxyethyl (meth)acrylate, hydroxypropyl (meth)acrylate, hydroxybutyl (meth)acrylate, allyl alcohol, methacryl alcohol, and an adduct of hydroxyethyl (meth)acrylate with ϵ -caprolactone. Among these, hydroxyethyl (meth)acrylate, hydroxybutyl (meth)acrylate, and an adduct of hydroxyethyl (meth)acrylate with ϵ -

caprolactone are preferred.

[0022] In the case where an acrylic emulsion having a carboxyl group is prepared by emulsion polymerization, a crosslinkable monomer can be used as the different α,β -ethylenically unsaturated monomer. The crosslinkable monomer is a compound having two or more radical polymerizable ethylenically unsaturated groups in a molecule, examples of which include divinyl compounds such as divinylbenzene, ethylene glycol di(meth)acrylate, hexanediol di(meth)acrylate, polyethylene glycol di(meth)acrylate, allyl (meth)acrylate, 1,4-butanediol di(meth)acrylate, 1,6-hexane di(meth)acrylate, neopentyl glycol di(meth)acrylate and pentaerythritol di(meth)acrylate, and also triallyl cyanurate, pentaerythritol tri(meth)acrylate, trimethylolpropane tri(meth)acrylate and dipentaerythritol hexa(meth)acrylate. The crosslinkable monomer may be a combination of the above-mentioned monomers. Allyl (meth)acrylate, ethylene glycol di(meth)acrylate and divinylbenzene which can be handled relatively easily are preferred.

[0023] The emulsion polymerization in an aqueous medium in preparation of the acrylic emulsion having a carboxyl group can be performed, for example, by dissolving an emulsifier in water, or an aqueous medium containing, as necessary, a hydrophilic organic solvent such as an alcohol, a glycol or the like, and adding dropwise a mixture of α,β -ethylenically unsaturated monomers to be used as a starting material, and a polymerization initiator under heating and stirring. The mixture of α,β -ethylenically unsaturated monomers to be used as a starting material may be emulsified using an emulsifier and water in advance.

[0024] Examples of the polymerization initiator which can be suitably used for emulsion polymerization include azo-based oily compounds (e.g.,

azobisisobutyronitrile, 2,2'-azobis(2-methylbutyronitrile), 2,2'-azobis(2,4-dimethyl valeronitrile) and the like) and aqueous compounds (e.g., anionic 4,4'-azobis(4-cyanovaleric acid), 2,2'-azobis(N-(2-carboxyethyl)-2-methylpropionamidine and cationic 2,2'-azobis(2-methylpropionamidine)); and
5 redox-type oily peroxides (e.g., benzoyl peroxide, parachlorobenzoyl peroxide, lauroyl peroxide, t-butyl perbenzoate and the like) and aqueous peroxides (e.g., potassium persulfate, ammonium persulfate and the like).

[0025] As the emulsifier, an emulsifier which is usually used by a person skilled in the art can be used. As the emulsifier to be used, a reactive emulsifier, for
10 example, Antox MS-60 (manufactured by NIPPON NYUKAZAI CO., LTD.), Eleminol JS-2 (manufactured by Sanyo Chemical Industries, Ltd.), ADEKA Reasoap NE-20 (manufactured by ADEKA Corporation), Aqualon HS 10 (manufactured by DAI-ICHI KOGYO SEIYAKU CO., LTD.) and the like are particularly preferable. In order to regulate a molecular weight, a chain transfer
15 agent such as mercaptan including lauryl mercaptan, α -methylstyrene dimer and the like can be used as necessary.

[0026] The reaction temperature is determined by an initiator, and is for example 60 to 90°C in an azo-based initiator, and it is preferable to perform a reaction at 30 to 70°C in a redox system. Generally, the reaction time is 1 to 8
20 hours. An amount of the initiator based on the total amount of the monomer mixture is generally 0.1 to 5% by mass, preferably 0.2 to 2% by mass. The emulsion polymerization can be performed in multiple-stages, and can be performed, for example, in two-stages. That is, first, a part of the mixture of α,β -ethylenically unsaturated monomers to be used as a starting material is
25 subjected to emulsion polymerization, the remainder of the α,β -ethylenically

unsaturated monomer mixture is further added thereto, and emulsion polymerization is performed.

[0027] An acrylic emulsion which can be thus obtained can be suitably used as the aqueous acrylic resin having a carboxyl group (A). It is preferable that a

5 volume average particle size of the emulsion is in the range of 0.01 to 1.0 μm .

When the volume average particle size is less than 0.01 μm , there is a possibility that workability is reduced, and when the volume average particle size exceeds 1.0 μm , there is a possibility that an appearance of the resulting coating film is deteriorated. It is possible to regulate this volume average

10 particle size by adjusting, for example, monomer composition or emulsion polymerization conditions. The volume average particle size can be measured by a laser light scattering method.

[0028] From the viewpoint of storage stabilities, the emulsion can be used at pH 5 to 10 by neutralizing with a basic compound. Examples of the basic

15 compound include ammonia, methylamine, ethylamine, dimethylamine, diethylamine, trimethylamine, triethylamine, dimethyl ethanolamine, diethanolamine, diethylaminoethanol, triethanolamine, tetraethylammonium hydroxide, propylamine, dipropylamine, tripropylamine, butylamine, dibutylamine, tributylamine and the like. The neutralization is preferably
20 performed before or after the emulsion polymerization by adding the basic compound to the system.

[0029] As a method of obtaining a water dispersion of an acrylic resin other than the acrylic emulsion, there is a method of performing solution polymerization to obtain an acrylic resin, and thereafter, obtaining a resin dispersion (acrylic
25 dispersion) in water. The acrylic dispersion can be obtained by first performing

solution polymerization of an α,β -ethylenically unsaturated monomer having an acid group described for the α,β -ethylenically unsaturated monomer mixture as an essential component, together with the different α,β -ethylenically unsaturated monomer, and neutralizing the resultant with a basic compound.

5 [0030] As the solution polymerization, a method in which the mixture of α,β -ethylenically unsaturated monomers to be used as a starting material, together with a polymerization initiator, are added dropwise to a solvent under heating condition while stirring is generally used. In the conditions upon solution polymerization, for example, the polymerization temperature is 60 to 160°C, and
10 the addition dropwise time is 0.5 to 10 hours. It is also possible to polymerize the α,β -ethylenically unsaturated monomers to be used as a starting material by dividing into two-stages. In this case, it is enough that the α,β -ethylenically unsaturated monomers to be used a starting material as a whole satisfy the requirement concerning a carboxyl group.

15 [0031] The polymerization initiator is not particularly limited as far as it is used in normal polymerization, and examples thereof include an azo-based compound and a peroxide. Generally, an amount of the polymerization initiator based on 100 parts by mass of the monomer mixture is 0.1 to 18 parts by mass, and preferably 0.3 to 12 parts by mass.

20 [0032] A solvent which can be used herein is not particularly limited as far as it does not adversely affect on the reaction, and examples thereof include an alcohol, a ketone, an ether and a hydrocarbon-based solvents and the like. Further, In order to regulate a molecular weight, a chain transfer agent such as mercaptan including lauryl mercaptan, α -methylstyrene dimer and the like can
25 be used as necessary.

[0033] It is preferable that a number average molecular weight of the acrylic resin thus obtained by solution polymerization is 4,000 to 20,000. As used herein, the number average molecular weight of the acrylic resin obtained by solution polymerization can be measured by gel permeation chromatography (GPC) using a polystyrene standard sample.

[0034] By removing the solvent from the acrylic resin obtained by solution polymerization as necessary, and adding a basic compound to neutralize the acrylic resin, thereby making the acrylic resin into an aqueous state, the aqueous acrylic resin having a carboxyl group (A) is obtained. Examples of the basic compound include the basic compounds exemplified previously. An addition amount of the basic compound is preferably such that a neutralization ratio of the carboxyl group in the acrylic resin obtained by solution polymerization is 60 to 100%. When the neutralization ratio is less than 60%, there is a possibility that the acrylic resin is not sufficiently made into an aqueous state, and storage stabilities are inferior.

[0035] The thus obtained acrylic resin can be used as a water dispersion of an acrylic resin. It is preferable that a volume average particle size of the water dispersion of an acrylic resin is in the range of 0.01 to 1 μm . When the volume average particle size falls within the above range, there are advantages that a stability of the water dispersion becomes good, and further, an appearance of the resulting coating film becomes good.

[0036] In the water dispersion of an acrylic resin having a carboxyl group, an acid value of the resin solid content is preferably 3 to 30 mg/KOH, and more preferably 5 to 25 mg/KOH. When the acid value of the resin solid content is higher than 30 mg/KOH, water resistances of a coating film are reduced, and

when the acid value is lower than 3 mg/KOH, a mechanical stability of the water dispersion of a resin is reduced.

[0037] The aqueous acrylic resin having a carboxyl group (A) may further contain a water-soluble acrylic resin in order to increase gloss. This water-soluble acrylic resin can be obtained by performing solution polymerization of the α,β -ethylenically unsaturated monomer having an acid group described for the α,β -ethylenically unsaturated monomer mixture as an essential component, together with the different α,β -ethylenically unsaturated monomer.

[0038] The water-soluble acrylic resin can be used, for example, by neutralizing the resin with a basic compound, for example, an organic amine such as monomethylamine, dimethylamine, trimethylamine, triethylamine, diisopropylamine, monoethanolamine, diethanolamine and dimethylethanolamine, and dissolving the resin in water.

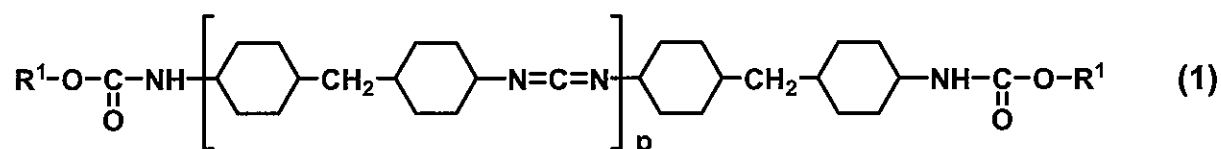
[0039] In the water-soluble acrylic resin, an acid value of the resin solid content is preferably 35 to 100 mg/KOH, and more preferably 40 to 80 mg/KOH. When the acid value of the resin solid content is higher than 100 mg/KOH, water resistances of a coating film are reduced, and when the acid value is lower than 35 mg/KOH, water-solubilization of the resin becomes insufficient. A number average molecular weight thereof is preferably 4,000 to 20,000. When the number average molecular weight is larger than 20,000, viscosity of a coating material becomes too high, and when the number average molecular weight is smaller than 4,000, water-resistances of a coating film are reduced.

[0040] A mass ratio of the resin solid content of the aqueous acrylic resin contained in a coating material (water dispersion : water soluble) is preferably 2:1 to 10:1 from the viewpoint of further improvement in coating film gloss.

[0041] In the present invention, a compound which can be suitably used as the carbodiimide compound represented by the general formula (1):

[0042]

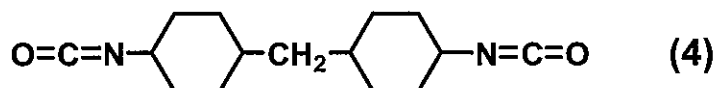
[Chemical formula 5]



and which is a curing agent can be produced by performing a condensation reaction accompanied with decarboxylation of 4,4-dicyclohexylmethane diisocyanate represented by the general formula (4):

[0043]

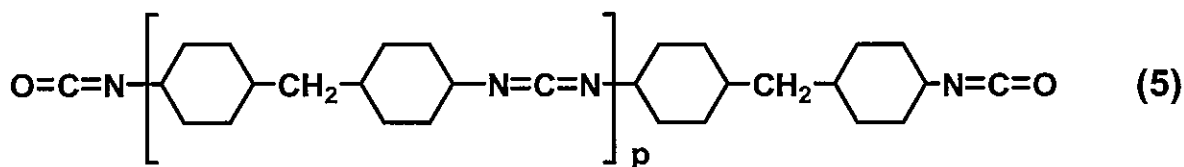
[Chemical formula 6]



in order to synthesize isocyanate-terminated dicyclohexylmethane carbodiimide represented by the general formula (5):

[0044]

[Chemical formula 7]



(wherein p represents an integer of 1 to 5) and, further, reacting this isocyanate-terminated dicyclohexylmethane carbodiimide with a mixture of polyethylene glycol monoalkyl ether and polypropylene glycol monoalkyl ether.

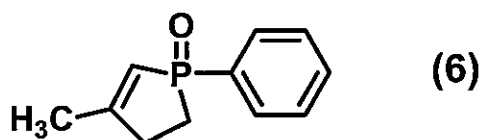
[0045] Production of the isocyanate-terminated dicyclohexylmethane

carbodiimide can be performed fundamentally according to a previous method of producing a carbodiimide (see US Patent No. 2,941,956 and JP-B No. 47-33279, J. Org. Chem., 28, 2069-2076 (1963), Chemical Review 1981, vol. 81, No. 4,619-4,621).

[0046] The condensation reaction accompanied with decarboxylation of dicyclohexylmethane diisocyanate progresses in the presence of a carbodiimidated catalyst, and as this catalyst, for example, phospholene oxide such as 1-phenyl-2-phospholene-1-oxide, 3-methyl-2-phospholene-1-oxide, 1-ethyl-2-phospholene-1-oxide, 1-ethyl-3-methyl-2-phospholene-1-oxide, 3-methyl-1-phenyl-2-phospholene-1-oxide or a 3-phospholene isomer thereof can be used, and from the viewpoint of reactivity, 3-methyl-1-phenyl-2-phospholene-1-oxide represented by the general formula (6):

[0047]

[Chemical formula 8]



is suitable.

[0048] It is preferable that the reaction temperature in the condensation reaction is in the range of 80 to 180°C, and when the reaction temperature is below this range, the reaction time becomes extremely long, and when the reaction temperature exceeds the range, a side reaction occurs, and it becomes impossible to obtain a carbodiimide having a good quality, and both cases are not preferable.

[0049] Further, the degree of condensation is preferably 1 to 5. When the

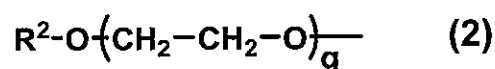
degree of condensation exceeds 5, dispersibility upon addition of aqueous dicyclohexylmethane carbodiimide to an aqueous resin is reduced, and further when the aqueous dicyclohexylmethane carbodiimide is formulated into an aqueous solution or an aqueous dispersion in advance, since the dispersibility is low, a good aqueous solution or aqueous dispersion is not obtained. In order to rapidly complete the reaction, it is preferable that the reaction of 4,4'-dicyclohexylmethane diisocyanate is performed under a stream of an inert gas such as nitrogen.

[0050] The aqueous dicyclohexylmethane carbodiimide of the present invention can be isolated from the reaction system according to a usual method, and the fact that a structure thereof is represented by the general formula (1) is supported by an infrared absorption (IR) spectrum and a nuclear magnetic resonance absorption (NMR) spectrum.

[0051] Two R¹s in the general formula (1) of the carbodiimide compound of the present invention are independently a PEG portion represented by the general formula (2):

[0052]

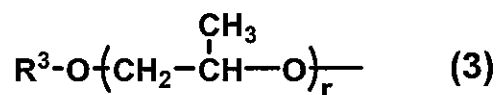
[Chemical formula 9]



(wherein a number average repetition number q of EG units is in the range of 6 to 40, and R² represents an alkyl group having 1 to 8 carbon atoms, or a phenyl group) and/or a PPG portion represented by the general formula (3):

[0053]

[Chemical formula 10]



(wherein a number average repetition number r of PG units is in the range of 4 to 14, and R^3 represents an alkyl group having 1 to 8 carbon atoms, or a phenyl group). That is, the carbodiimide compound of the present invention includes

the case where two R^1 's in the general formula (1) are a residue represented by the general formula (2) and a residue represented by the general formula (3),

respectively, and the case where both of two R^1 's are each a residue represented by the general formula (2) or the general formula (3). Specifically, the carbodiimide compound of the present invention includes the following

carbodiimide compounds (1A) to (1C) in such a range that PEG portion : PPG portion as a whole satisfies the range described later;

(1A) a compound in which one of two R^1 's in the general formula (1) is a residue represented by the general formula (2), and the other is a residue represented by the general formula (3);

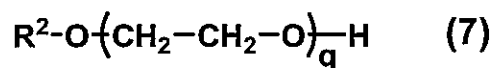
(1B) a compound in which both of two R^1 's in the general formula (1) are each a residue represented by the general formula (2); and

(1C) a compound in which both of two R^1 's in the general formula (1) are each a residue represented by the general formula (3).

[0054] The polyethylene glycol monoalkyl ether which can be used for forming the residue represented by the general formula (2) which is the PEG portion of the carbodiimide compound of the present invention is represented by the general formula (7):

[0055]

[Chemical formula 11]



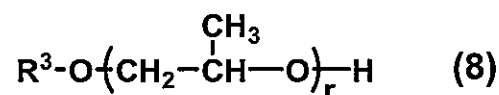
(wherein a number average repetition number q is in the range of 6 to 40, and R^2 represents an alkyl group having 1 to 8 carbon atoms, or a phenyl group), and specific examples thereof include poly(ethylene glycol) monomethyl ether, poly(ethylene glycol) monoethyl ether, poly(ethylene glycol) monopropyl ether, poly(ethylene glycol) monobutyl ether, and poly(ethylene glycol) monophenyl ether, and particularly, poly(ethylene glycol) monomethyl ether is suitable.

[0056] The number average repetition number q of the EG units in the PEG portion is preferably in the range of 6 to 40, and more preferably in the range of 10 to 35. When q is less than 6, hydrophilicity cannot be imparted, and water dispersibility is inferior. On the other hand, when q is more than 40, water resistances are inferior.

[0057] The polypropylene glycol monoalkyl ether which can be used for forming the residue represented by the general formula (3) which is the PPG portion of the carbodiimide compound of the present invention is represented by the general formula (8):

[0058]

[Chemical formula 12]



(wherein a number average repetition number r is the range of 4 to 14, and R^3 represents an alkyl group having 1 to 8 carbon atoms, or a phenyl group), and specific examples thereof include poly(propylene glycol) monomethyl ether, poly(propylene glycol) monoethyl ether, poly(propylene glycol) monopropyl

ether, poly(propylene glycol) monobutyl ether, poly(propylene glycol) mono-2-ethyl hexyl ether, and poly(propylene glycol) monophenyl ether, and particularly, poly(propylene glycol) monobutyl ether is suitable.

[0059] The number average repetition number r of the PG units in the PPG

5 portion is 4 to 14, preferably 4 to 12, more preferably 4 to 10, and most preferably 4 to 8. A carbodiimide group in the carbodiimide curing agent may react with water to generate a urea group during storage. When the

carbodiimide groups are reduced by the reaction with water, the crosslinking density of a coating film is reduced, and the sufficient performance of the

10 coating film cannot be exerted. When the repetition number r is in the aforementioned range, PPG having high hydrophobicity is present at a large amount in the vicinity of the carbodiimide group, and the carbodiimide group is protected from water, and thus generation of a urea group is suppressed, and a coating film having a rapid curing rate and a high crosslinking density is

15 obtained. Since the coating film contains a PPG group having high hydrophobicity at a large amount, water repellency is imparted to the coating film, and water resistances are improved. When the repetition number r is less than 4, PPG having high hydrophobicity is present only at a small amount in the vicinity of the carbodiimide group, and thus a curing rate is slow, and a coating

20 film having a high crosslinking density is not obtained. Further, since sufficient water repellency cannot be imparted to the coating film, water resistances are reduced. When the repetition number r exceeds 14, since hydrophobicity of a water dispersion of the carbodiimide becomes too large, there is a possibility that a particle size of the water dispersion becomes large so that gloss of the

25 coating film is reduced, or a water dispersion is not formed and oil and water

are separated.

[0060] In the carbodiimide compound (B) used in the present invention, a molar ratio of the PEG portion and the PPG portion is 1:1 to 1:15, preferably 1:2 to 1:15, more preferably 1:2 to 1:9, further preferably 1:3 to 1:8, and most preferably 1:4 to 1:6. When a molar ratio of the PEG portion is large, water resistances are inferior. A carbodiimide group in the carbodiimide curing agent, although slightly, reacts with water to generate a urea group. In order to suppress this reaction, it is preferable that the periphery of the carbodiimide group is hydrophobic as much as possible, and the contact with a water molecule is low. When a molar ratio of the PPG portion is large, since hydrophobicity is manifested too much, water dispersibility is inferior, and stabilities are not good. The molar ratio of the PEG portion and the PPG portion is based on a formulation molar ratio of PEG and PPG which are used at the production of the carbodiimide compound (B).

[0061] The reaction temperature for an addition reaction of the isocyanate-terminated dicyclohexylmethane carbodiimide with the mixture of polyethylene glycol monoalkyl ether and polypropylene glycol monoalkyl ether is in the range of 60 to 180°C, and preferably in the range of 100 to 160°C. When the reaction temperature is below this range, the reaction time becomes extremely long, and conversely when the reaction temperature exceeds the range, a side reaction occurs, and it becomes impossible to obtain the carbodiimide compound of the present invention, and both cases are not preferable.

[0062] In the aqueous coating composition of the present invention, a mixing ratio of the aqueous acrylic resin having a carboxyl group (A) and the carbodiimide compound represented by the general formula (1) (B) is such that

the aqueous acrylic resin (A) is 99 to 60% by mass, and preferably 95 to 80% by mass, and the carbodiimide compound (B) is 1 to 40% by mass, and preferably 5 to 20% by mass, as expressed by the resin solid content ratio.

When expressed by the molar ratio, a carboxyl group of the aqueous acrylic resin (A) : a carbodiimide group of the carbodiimide compound (B) is 0.8: 1 to 1.2 to 1.

[0063] Since the two-package aqueous coating composition of the present invention uses an acrylic resin, it has a good weather resistance, and can be used as a two-package topcoat coating material. In the present invention, the two-package coating means such a coating material that when a main agent and a curing agent are mixed, a curing reaction proceeds at ambient temperature, and thus the coating material cannot be stored as one component, and the two packages are stored separately, and the main agent and the curing agent are mixed immediately before use.

[0064] The two-package aqueous coating composition of the present invention can contain an organic solvent which dissolves in water. Specific examples of the organic solvent include ethylene glycol, propylene glycol, ethylene glycol monobutyl ether, propylene glycol monobutyl ether, diethylene glycol, dipropylene glycol, and diethylene glycol monobutyl ether. From the viewpoint of reducing use of VOC as much as possible, it is preferable that an amount of the organic solvent is as small as possible.

[0065] The two-package aqueous coating composition of the present invention can contain a pigment. Specific examples of the pigment include coloring pigments such as titanium oxide, yellow iron oxide, red iron oxide, carbon black, phthalocyanine blue, phthalocyanine green, azo red, quinacridone red, and

benzimidazolone yellow; extender pigments such as calcium carbonate, barium sulfate, kaolin, clay, and talc; and rust preventive pigments. A concentration of the pigment in the aqueous coating composition is preferably 10 to 50% by mass.

5 [0066] The two-package aqueous coating composition of the present invention can contain an additive. Specific examples of the additive include a dispersant, a viscosity adjusting agent, a curing catalyst, a surface conditioning agent, an antifoaming agent, a plasticizer, a film forming aid, an ultraviolet absorbing agent, an antioxidant, and a curing agent.

10 [0067] The two-package aqueous coating composition of the present invention can be coated onto an arbitrarily appropriate substrate. Examples of the substrate include metals, timber, plastics, rubber, stone materials, slates, concrete, mortar, fibers, paper, glass, porcelain, earthenware, films, and composites thereof. For example, when the substrate is an inorganic substrate
15 such as a slate or concrete, a sealer may be applied onto a surface thereof in advance. When properties are taken into consideration, preferably, the composition is applied to a metal. Examples of the metal include iron, copper, tin, zinc, aluminum, and stainless.

[0068] Examples of an article to be coated which has a metal on a surface
20 (outer surface and inner surface) include ships, vehicles (e.g., railroad vehicles, heavy vehicles), aircrafts, bridges, marine structures, plants, tanks (e.g., petroleum tank), pipes, steel pipes, and cast iron pipes. In addition, the aqueous coating composition can be also applied to a building and a civil engineering structure.

25 [0069] Examples of the coating method include, representatively, a method of

coating the aqueous coating composition on an article to be coated (substrate), followed by drying. As an application method, an arbitrarily appropriate method can be adopted depending on a kind of the article to be coated (substrate).

Examples thereof include an application with a brush, a roller, an air spray, an
5 airless spray or a trowel, and immersion.

[0070] As the drying method, an arbitrarily appropriate method can be adopted. Preferred is natural drying or heating drying. In the case of natural drying, the drying time is preferably 2 hours or longer, and further preferably 24 hours or longer.

10 [0071] The thickness of a coating film formed by coating the aqueous coating composition is preferably 10 to 100 μm , and further preferably 20 to 100 μm . When the thickness is more than 100 μm , there is a possibility that a disadvantage such as occurrence of dribble at coating or the like occurs.

[0072] When a water absorption ratio of a coating film obtained by applying and
15 drying the aqueous coating composition of present invention at room temperature is too large, a blister is generated on the coating film by rainfall immediately after execution, and a cracking may be generated in the coating film depending on the temperature at execution.

[0073] Before formation of a coating film by coating the aqueous coating
20 composition, in order to improve adherence and anticorrosion properties, an undercoat layer with an undercoat coating material can be formed, and an intermediate coat layer with an intermediate coating material can be formed on the undercoat layer.

[0074] As the undercoat coating material, an arbitrarily appropriate coating
25 material can be adopted. Examples thereof include an epoxy/Michael curing

coating material, an epoxy/amine-based coating material, an epoxy dispersion coating material, and a two-package urethane curing coating material. As the intermediate coating material, an arbitrarily appropriate coating material can be adopted. Examples thereof include an epoxy/amine-based coating material and
5 a two-package urethane curing coating material.

[0075] An organic or inorganic zinc-rich coating material may be coated before coating the undercoat coating material to form a zinc-rich layer. By forming the zinc-rich layer, anticorrosion properties are more excellent, and in the case where high anticorrosion properties are required, such as a bridge, a plant and
10 a tank, this can sufficiently correspond thereto.

[0076] The undercoat coating material, the intermediate coating material and the zinc-rich coating material can contain a pigment, an additive and the like. Examples of the pigment and the additive include the pigments and the additives described above. The number, kind and amount of the pigment and
15 additive to be added can be appropriately selected depending on the intended use.

[0077] As an application method and drying method of the undercoat coating material, the intermediate coating material and the zinc-rich coating material, arbitrarily appropriate methods can be adopted depending on a kind of the
20 coating material to be used. Examples of the application method and drying method of the undercoat coating material, the intermediate coating material and the zinc-rich coating material include the same methods as the application method and drying method of the aqueous coating composition described above.

EXAMPLES

[0078] The present invention will be specifically described below based on Examples and Comparative Examples, but the present invention is not limited to the following Examples. When simply “%” is described in the present Examples, it means “% by mass”, and when simply “part” is described, it means “part by mass”.

[0079] Production Example 1: Production of a carbodiimide compound having isocyanate groups on both ends

To 2500 parts of 4,4-dicyclohexylmethane diisocyanate was added 25 parts of 3-methyl-1-phenyl-2-phospholene-1-oxide serving as a carbodiimiding catalyst, and the materials were allowed to react at 170°C until an isocyanate equivalent was 436, to prepare a carbodiimide compound 1 having isocyanate groups on both ends. The carbodiimide compound 1 had 2.8 carbodiimide groups per one molecule.

[0080] Production Example 2: Production of a water dispersion of a carbodiimide compound

As shown in Table 1, to 872 parts of the carbodiimide compound 1 prepared in Production Example 1 were added 567 parts of Newpol LB-65 (polypropylene glycol monobutyl ether, manufactured by Sanyo Chemical Industries, Ltd.; number average repetition number 5) and 225 parts of MPG-081 (polyethylene glycol monomethyl ether, manufactured by NIPPON NYUKAZAI CO., LTD.; number average repetition number 15), and the materials were allowed to react at 160°C until absorption derived from an isocyanate group disappeared as measured by IR. Further, the reaction was cooled to 60°C, and 2496 parts of deionized water was gradually added to be

emulsified, and thus a milky-white carbodiimide water dispersion 1 having 40% of a solid content was obtained.

[0081] Production Example 3: Production of a water dispersion of a carbodiimide compound

5 A milky-white carbodiimide dispersion 2 having 40% of a solid content was obtained by using formulation shown on Table 1 in the same manner as that in Production Example 2.

[0082] Production Example 4: Production of a water dispersion of a carbodiimide compound

10 A milky-white carbodiimide dispersion 3 having 40% of a solid content was obtained by using formulation shown in Table 1 in the same manner as that in Production Example 2.

[0083] Comparative Production Example 1: Production of a water dispersion of a carbodiimide compound

15 A milky-white carbodiimide dispersion 4 having 40% of a solid content was obtained by using formulation shown on Table 1 in the same manner as that in Production Example 2.

[0084] Comparative Production Example 2: Production of a water dispersion of a carbodiimide compound

20 A milky-white carbodiimide dispersion 5 having 40% of a solid content was obtained by using formulation shown on Table 1 in the same manner as that in Production Example 2.

[0085] Comparative Production Example 3: Production of a water dispersion of a carbodiimide compound

25 A milky-white carbodiimide dispersion 6 having 40% of a solid content

was obtained by using formulation shown on Table 1 in the same manner as that in Production Example 2.

[0086] Comparative Production Example 4: Production of a water dispersion of a carbodiimide compound

5 A milky-white carbodiimide dispersion 7 having 40% of a solid content was obtained by using formulation shown on Table 1 in the same manner as that in Production Example 2.

[0087] Comparative Production Example 5: Production of a water dispersion of a carbodiimide compound

10 As shown in Table 1, to 872 parts of the carbodiimide compound 1 prepared in Production Example 1 were added 648 parts of polypropylene glycol monobutyl ether (number average repetition number 19) and 64 parts of polyethylene glycol monomethyl ether (number average repetition number 15), and the materials were allowed to react at 160°C until absorption of NCO
15 disappeared as measured by IR. Further, the reaction was cooled to 60°C and deionized water was gradually added, but a uniform water dispersion was not obtained.

[0088] Comparative Production Example 6: Production of a water dispersion of a carbodiimide compound

20 A milky-white carbodiimide dispersion 8 having 40% of a solid content was obtained by using formulation shown on Table 1 in the same manner as that in Production Example 2.

[0089]

[Table 1]

		Production Example 2	Production Example 3	Production Example 4	Comparative Production Example 1	Comparative Production Example 2	Comparative Production Example 3	Comparative Production Example 4	Comparative Production Example 5	Comparative Production Example 6
Carbodiimide compound 1	Degree of polymerization	2.8	2.8	2.8	2.8	2.8	2.8	2.8	2.8	2.8
	Amount (parts by mass)	872	872	872	872	872	872	872	872	872
Polyethylene glycol monoalkyl ether compound (PEG portion)	Trade name	MPG-081	MPG-041	MPG-081	MPG-081	MPG-081	MPG-081	MPG-081	MPG-081	MPG-081
	Hydroxyl value Measured value	83	41	83	83	83	83	83	83	83
	Ethylene glycol Calculated value of number average repetition number	15	30	15	15	15	15	15	15	15
	Monoalkyl portion	Methyl	Methyl	Methyl	Methyl	Methyl	Methyl	Methyl	Methyl	Methyl
	Amount (parts by mass)	225	304	338	225	135	225	901	64	338
	Amount (molar ratio)	0.33	0.22	0.5	0.33	0.2	0.33	1.33	0.1	0.5
Polypropylene glycol monoalkyl ether compound (PPG portion)	Trade name	Newpol LB-65	Newpol LB-65	Unilube MB-7	BFTG	MFTG	BFG	Newpol LB-65	Newpol LB-65	Unilube MB-11
	Hydroxyl value Measured value	165	165	73	226	272	425	165	165	53
	Propylene glycol Calculated value of number average repetition number	5	5	12	3	3	1	5	5	17
	Monoalkyl portion	Butyl	Butyl	Butyl	Butyl	Methyl	Butyl	Butyl	Butyl	Butyl
	Amount (parts by mass)	567	604	1155	413	371	220	227	648	1590
	Amount (molar ratio)	1.67	1.78	1.5	1.67	1.8	1.67	0.67	1.9	1.5
PEG portion : PPG portion		1:5	1:8	1:3	1:5	1:9	1:5	2:1	1:20	1:3
Deionized water	Amount (parts by mass)	2497	2670	3548	2266	2067	1976	3001	2377	4200
Form of carbodiimide compound		Water dispersion ₁	Water dispersion ₂	Water dispersion ₃	Water dispersion ₄	Water dispersion ₅	Water dispersion ₆	Water dispersion ₇	No emulsified	Water dispersion ₈

The molar ratio is a molar ratio of an amount (mole) of each compound based on an amount (mole) of a carbodiimide compound.

[0090] In the table, MPG-081, MPG-041, BFTG, MFTG and BFG are products manufactured by NIPPON NYUKAZAI CO., LTD.

Newpol LB-65 is a product manufactured by Sanyo Chemical Industries, Ltd.

5 Unilube MB-7 and Unilube MB-11 are products manufactured by NOF Corporation.

[0091] Production Example A1: Production of a water dispersion of an acrylic resin (acrylic emulsion) having a carboxyl group

10 A reaction vessel equipped with a stirrer, a nitrogen introducing tube, a temperature controlling device, a condenser and a dropping funnel was charged with 200.0 parts of deionized water, and the temperature was raised to 80°C while stirring under a nitrogen atmosphere.

15 To 579.4 parts of deionized water were added 236.3 parts of 2-ethylhexyl acrylate, 538.0 parts of methyl methacrylate, 200.0 parts of styrene, 25.7 parts of acrylic acid, and 100 parts of LATEMUL PD-104 (20% aqueous solution, manufactured by Kao Corporation) as an emulsifier, to thereby obtain an emulsified pre-emulsion, and then the pre-emulsion together with an aqueous initiator solution obtained by dissolving 3 parts of ammonium persulfate in 150 parts of deionized water were added dropwise for 2 hours.

20 After completion of the dropwise addition, the reaction was further continued at 80°C for 1 hour, the reaction was cooled, and 8.2 parts of N,N-dimethylaminoethanol was added to obtain an acrylic emulsion having 50% by mass of a resin solid content. An acid value of the resin solid content of this acrylic emulsion calculated from the monomer composition was 20 mgKOH/g, and the Tg was 40°C.

25

[0092] Production Example A2: Production of a water dispersion of an acrylic resin (acrylic emulsion) having a carboxyl group

A reaction vessel equipped with a stirrer, a nitrogen introducing tube, a temperature controlling device, a condenser and a dripping funnel was charged with 200.0 parts of deionized water, and the temperature was raised to 80°C while stirring under a nitrogen atmosphere.

To 579.4 parts of deionized water were added 237.0 parts of 2-ethylhexyl acrylate, 550.1 parts of methyl methacrylate, 200.0 parts of styrene, 12.8 parts of acrylic acid, and 100 parts of LATEMUL PD-104 (20% aqueous solution, manufactured by Kao Corporation) as an emulsifier, to thereby obtain an emulsified pre-emulsion, and then the pre-emulsion together with an aqueous initiator solution obtained by dissolving 3 parts of ammonium persulfate in 150 parts of deionized water were added dropwise for 2 hours.

After completion of the dropwise addition, the reaction was further continued at 80°C for 1 hour, the reaction was cooled, and 8.2 parts of N,N-dimethylaminoethanol was added to obtain an acrylic emulsion having 50% by mass of a resin solid content. An acid value of the resin solid content of this acrylic emulsion calculated from the monomer composition was 10 mgKOH/g, and the T_g was 40°C.

[0093] Production Example A3: Production of a water-soluble acrylic resin having a carboxyl group

A reaction vessel equipped with a stirrer, a nitrogen introducing tube, a temperature controlling device, a condenser and a dripping funnel was charged with 259.0 parts of 2-methoxy-1-propanol, and the temperature was raised to 120°C while stirring under a nitrogen atmosphere.

A monomer mixture of 35.0 parts of styrene, 19.8 parts of methyl methacrylate, 155.2 parts of n-butyl acrylate, 19.0 parts of ethyl acrylate, 137.2 parts of 2-ethylhexyl acrylate and 33.8 parts of methacrylic acid, together with an initiator solution obtained by dissolving 16.0 parts of Kayaester O (tert-butylperoxy-2-ethyl hexanoate, manufactured by Kayaku Akzo Co., Ltd.) in 25.0 parts of 2-methoxy-1-propanol were added dropwise for 3 hours.

After completion of the dropwise addition, the temperature was retained at 120°C for 0.5 hours, and then, an initiator solution obtained by dissolving 1.6 parts of Kayaester O in 16.0 parts of 2-methoxy-1-propanol was added dropwise for 0.5 hours, and further, the mixture was stirred at 120°C for 1 hour. Then, the reaction mixture was cooled to 60°C, and neutralized with 35.0 parts of N,N-dimethylethanolamine, and thereafter 287.4 parts of deionized water was added to make the resultant into a water-soluble state, and thus a water-soluble resin having 40% by mass of a resin solid content was obtained. An acid value of the resin solid content of this acrylic water-soluble resin calculated from the monomer composition was 55 mgKOH/g, and the Tg was -35°C.

[0094] Production Example A4: Production of a water-soluble acrylic resin having a carboxyl group

A reaction vessel equipped with a stirrer, a nitrogen introducing tube, a temperature controlling device, a condenser and a dropping funnel was charged with 259.0 parts of 2-methoxy-1-propanol, and the temperature was raised to 120°C while stirring under a nitrogen atmosphere.

A monomer mixture of 35.0 parts of styrene, 8.7 parts of methyl methacrylate, 155.2 parts of n-butyl acrylate, 19.0 parts of ethyl acrylate, 139.1 parts of 2-ethylhexyl acrylate, and 43.0 parts of methacrylic acid, together with

an initiator solution obtained by dissolving 16.0 parts of Kayaester O (tert-butylperoxy-2-ethyl hexanoate, manufactured by Kayaku Akzo Co., Ltd.) in 25.0 parts of 2-methoxy-1-propanol were added dropwise for 3 hours.

After completion of the dropwise addition, the temperature was retained at 120°C for 0.5 hours, and then, an initiator solution obtained by dissolving 1.6 parts of Kayaester O in 16.0 parts of 2-methoxy-1-propanol was added dropwise for 0.5 hours, and further, the mixture was stirred at 120°C for 1 hour. Then, the reaction mixture was cooled to 60°C, and neutralized with 44.5 parts of N,N-dimethylethanolamine, and thereafter 277.9 parts of deionized water was added to make the resultant into a water-soluble state, and thus a water-soluble resin having 40% by mass of a resin solid content was obtained. An acid value of the resin solid content of this acrylic water-soluble resin calculated from the monomer composition was 70 mgKOH/g, and the Tg was -35°C.

[0095] Production Example B1: Preparation of white enamel coating material (main agent)

By using a sand mill, 61.6 parts of deionized water, 30.0 parts of DISPERBYK-190 (dispersant, manufactured by BYK-Chemie), 1.0 part of Aqualen 810 (antifoaming agent, manufactured by Tego), and 285.6 parts of TipureR-706 (titanium oxide, manufactured by DuPont) were dispersed to obtain a dispersion paste of titanium oxide.

To 378.2 parts of the resulting dispersion paste were further added 25.4 parts of deionized water, 460.0 parts of the acrylic emulsion obtained in Production Example A1, 123.0 parts of the water-soluble acrylic resin obtained in Production Example A3, 54.0 parts of CS-12 (film forming aid, manufactured by CHISSO CORPORATION), 6.6 parts of ADEKANOL UH-550 (viscosity

increasing agent, manufactured by ADEKA CORPORATION), 4.0 parts of SN thickener 617 (viscosity increasing agent, manufactured by SAN NOPCO LIMITED), and 1.5 parts of 8610ADDITIVE (antifoaming agent, manufactured by Dow Corning) to obtain a white enamel coating material 1 (main agent).

5 [0096] Production Example B2: Preparation of a white enamel coating material (main agent)

By using a sand mill, 61.6 parts of deionized water, 30.0 parts of DISPERBYK-190 (dispersant, manufactured by BYK-Chemie), 1.0 part of Aqualen 810 (antifoaming agent, manufactured by Tego), and 285.6 parts of
10 TipureR-706 (titanium oxide, manufactured by DuPont) were dispersed to obtain a dispersion paste of titanium oxide.

To 378.2 parts of the resulting dispersion paste were further added 25.4 parts of deionized water, 559.1 parts of the acrylic emulsion obtained in Production Example A1, 65.6 parts of CS-12 (film forming aid, manufactured by
15 CHISSO CORPORATION), 6.6 parts of ADEKANOL UH-550 (viscosity increasing agent, manufactured by ADEKA CORPORATION), 4.0 parts of SN thickener 617 (viscosity increasing agent, manufactured by SAN NOPCO LIMITED), and 1.5 parts of 8610ADDITIVE (antifoaming agent, manufactured by Dow Corning) to obtain a white enamel coating material 2 (main agent).

20 [0097] Production Example B3: Preparation of a white enamel coating material (main agent)

By using a sand mill, 61.6 parts of deionized water, 30.0 parts of DISPERBYK-190 (dispersant, manufactured by BYK-Chemie), 1.0 part of Aqualen 810 (antifoaming agent, manufactured by Tego), and 285.6 parts of
25 TipureR-706 (titanium oxide, manufactured by DuPont) were dispersed to

obtain a dispersion paste of titanium oxide.

To 378.2 parts of the resulting dispersion paste were further added 25.4 parts of deionized water, 420.0 parts of the acrylic emulsion obtained in Production Example A2, 175.0 parts of the water-soluble acrylic resin obtained in Production Example A4, 54.0 parts of CS-12 (film forming aid, manufactured by CHISSO CORPORATION), 6.6 parts of ADEKANOL UH-550 (viscosity increasing agent, manufactured by ADEKA CORPORATION), 4.0 parts of SN thickener 617 (viscosity increasing agent, manufactured by SAN NOPCO LIMITED), and 1.5 parts of 8610ADDITIVE (antifoaming agent, manufactured by Dow Corning) to obtain a white enamel coating material 3 (main agent).

[0098] Production Example B4: Preparation of a white enamel coating material (main agent)

By using a sand mill, 61.6 parts of deionized water, 30.0 parts of DISPERBYK-190 (dispersant, manufactured by BYK-Chemie), 1.0 part of Aqualen 810 (antifoaming agent, manufactured by Tego), and 285.6 parts of TipureR-706 (titanium oxide, manufactured by DuPont) were dispersed to obtain a dispersion paste of titanium oxide.

To 378.2 parts of the resulting dispersion paste were further added 25.4 parts of deionized water, 497.0 parts of the acrylic emulsion obtained in Production Example A1, 77.8 parts of the water-soluble acrylic resin obtained in Production Example A3, 54.0 parts of CS-12 (film forming aid, manufactured by CHISSO CORPORATION), 6.6 parts of ADEKANOL UH-550 (viscosity increasing agent, manufactured by ADEKA CORPORATION), 4.0 parts of SN thickener 617 (viscosity increasing agent, manufactured by SAN NOPCO LIMITED), and 1.5 parts of 8610ADDITIVE (antifoaming agent, manufactured

by Dow Corning) to obtain a white enamel coating material 4 (main agent).

[0099] Examples 1 to 3

The white enamel coating material 1 obtained in Production Example B1 as a main agent, and each of the water dispersions 1 to 3 of the carbodiimide compounds obtained in Production Examples 2 to 4 as a curing agent were
5 mixed at a ratio shown in Table 2 to obtain coating materials 1 to 3.

[0100] Example 4

The white enamel coating material 2 obtained in Production Example B2 as a main agent, and the water dispersion 1 of the carbodiimide compound
10 obtained in Production Example 2 as a curing agent were mixed at a ratio shown in Table 2 to obtain a coating material 4.

[0101] Example 5

The white enamel coating material 3 obtained in Production Example B3 as a main agent, and the water dispersion 1 of the carbodiimide compound
15 obtained in Production Example 2 as a curing agent were mixed at a ratio shown in Table 2 to obtain a coating material 5.

[0102] Example 6

The white enamel coating material 4 obtained in Production Example B4 as a main agent, and the water dispersion 1 of the carbodiimide compound
20 obtained in Production Example 2 as a curing agent were mixed at a ratio shown in Table 2 to obtain a coating material 6.

[0103] Comparative Examples 1 to 5

The white enamel coating material 1 obtained in Production Example B1 as a main agent, and each of the water dispersions 4 to 8 of the carbodiimide
25 compounds obtained in Comparative Production Examples 1 to 4 and 6 as a

curing agent were mixed at a ratio shown in Table 3 to obtain coating materials 7 to 11.

[0104] A test for curing storage stabilities of a curing agent, as well as a test for water resistances of a coating film and measurement of gloss of a coating film were performed.

[0105] [Test for curing storage stabilities of a curing agent]

Immediately after preparation of the water dispersions 1 to 8 by the Production Examples and Comparative Production Examples, and after storage at 50°C for 1 month, 2 months and 3 months from the preparation, coating materials 1 to 11 were prepared by the respective Examples and Comparative Examples.

Each coating material was applied onto a glass plate with a 6 mil applicator, and this was dried at room temperature for one week. The prepared coating film was subjected to a rubbing treatment with acetone, and the rubbing times until a base glass was exposed were recorded, determining a reciprocation to be one time.

[0106] [Test for water resistances of a coating film]

(1) A test for water resistance after drying at 20°C for one hour

Each of the coating materials 1 to 11 was coated on a steel plate coated with a solution-type epoxy-based primer by using a brush under 20°C environment so that an application amount (at drying) was 120 g/m², and was dried at 20°C for 1 hour. The prepared coating film was immersed in water at 20°C for 16 hours, and immediately after pulling up, a blister on a surface of the coating film was observed. A blister of the coating film was determined by the criteria based on JIS K5600-8-2. The determination results were shown

according to the following indication method.

“Blister 0” means that no blister is generated.

In “blister j (Sk)”, “j” is a value relating to the number per unit area (density) of a generated blister, and it means that as the value is larger, a blister is generated densely. Further, “k” is a value relating to an average dimension (size) of a generated blister, and it means that as the value is larger, a dimension per one blister is larger.

[0107] (2) A test for water resistance after drying at 20°C for one week

Each of the coating materials 1 to 11 was coated on a steel plate coated with a solution-type epoxy-based primer by using a brush under 20°C environment so that an application amount (at drying) was 120 g/m², and was dried at 20°C for one week. The prepared coating film was immersed in water at 20°C for 3 days, and immediately after pulling up, a blister on a surface of the coating film was observed. A blister of the coating film was determined by the criteria based on JIS K5600-8-2. The determination results were shown according to the same method as that in the aforementioned indication method.

[0108] (3) A test for measurement of water absorption ratio of a coating film after drying at 20°C for one hour

Each of the coating materials 1 to 11 was coated on a polypropylene plate by using a brush under 20°C environment so that an application amount was 120 g/m², and was dried at 20°C for 1 hour. After drying, the coating film was peeled off, and a weight thereof is measured. After measurement of the weight, the coating film was immersed in water at 20°C for 16 hours, and immediately after pulling up, water on a surface of the coating film was slightly wiped off, and then a weight thereof was measured. From these measurement

values, water absorption ratio of the coating film was obtained by the following equation.

$$\text{Water absorption ratio (\%)} = \frac{(\text{weight of coating film after immersion})}{(\text{weight of coating film before immersion})} \times 100 - 100$$

5 [0109] (4) A test for water resistance after drying at 5°C for three hours

Each of the coating materials 1 to 11 was coated on a steel plate coated with a solution-type epoxy-based primer by using a brush under 5°C environment so that an application amount was 120 g/m², and was dried at 5°C for 3 hours. The prepared coating film was immersed in water at 5°C for 16
10 hours, and immediately after pulling up, a cracking on a surface of the coating film was observed. A crack of the coating film was determined by the criteria based on JIS K5600-8-4. The determination results were shown according to the following indication method.

“Crack 0” means that no crack is generated.

15 In “Crack j (Sk) l”, “j” is a value relating to the number per unit area (density) of a generated crack, and it means that as the value is larger, a cracking is generated densely. Further, “k” is a value relating to an average dimension (size) of a generated crack, and it means that as the value is larger, a dimension per one crack is larger. Moreover, “l” is a grade (a to c) relating to
20 a depth of a generated crack, “a” represents a surface crack which does not penetrate topcoat, “b” represents that a crack penetrates topcoat, but there is no crack on an underlying coating film, and “c” represents a crack penetrating a whole coating film layer.

[0110] (5) A test for measurement of water absorption ratio of a coating film
25 after drying at 5°C for three hours

Each of the coating materials 1 to 11 was coated on a polypropylene plate by using a brush under 5°C environment so that an application amount (at drying) was 120 g/m², and was dried at 5°C for 3 hours. After drying, the coating film was peeled off, and a weight thereof was measured. After measurement of the weight, the coating film was immersed in water at 5°C for 16 hours, and immediately after pulling up, water on a surface of the coating film was slightly wiped off, and then a weight thereof was measured. From these measurement values, water absorption ratio of the coating film was obtained by the following equation.

$$\text{Water absorption ratio (\%)} = \frac{(\text{weight of coating film after immersion})}{(\text{weight of coating film before immersion})} \times 100 - 100$$

[0111] [Measurement of gloss of a coating film]

Each of the coating materials 1 to 11 was applied onto a glass plate with a 6 mil applicator, and this was dried at room temperature for one week. Sixty degree gloss of a surface of the prepared coating film was measured with a glossmeter (micro-TRI-gloss, manufactured by BYK-Gardner). A gloss value of 80 or more is the range having no practical problem, and a gloss value of 85 or more is preferable.

[0112]

[Table 2]

	Example 1	Example 2	Example 3	Example 4	Example 5	Example 6
	Coating material 1	Coating material 2	Coating material 3	Coating material 4	Coating material 5	Coating material 6
Main agent	White enamel coating material 1	White enamel coating material 1	White enamel coating material 1	White enamel coating material 2	White enamel coating material 3	White enamel coating material 4
	105	105	105	105	105	105
Curing agent	Water dispersion	Water dispersion 2	Water dispersion 3	Water dispersion 1	Water dispersion 1	Water dispersion 1
	Ethylene glycol Calculated value of number average repetition number	30	15	15	15	15
	Propylene glycol Calculated value of number average repetition number	4.6	12	4.6	4.6	4.6
	Propylene glycol Terminal alkyl portion	Butyl	Butyl	Butyl	Butyl	Butyl
	PEG portion / PPG portion	1/8	1/3	1/5	1/5	1/5
	Amount (parts by mass)	20.7	27.5	14.8	18.5	17.7
Test for curing storage stabilities of curing agent	Initial	50 times or more	50 times or more	50 times or more	50 times or more	50 times or more
	One month after	50 times or more	50 times or more	50 times or more	50 times or more	50 times or more
	Two months after	50 times or more	50 times or more	50 times or more	50 times or more	50 times or more
	Three months after	50 times or more	50 times or more	50 times or more	50 times or more	50 times or more
Water resistances of coating film at 20°C	One hour drying blister on coating film	Blister 0	Blister 0	Blister 0	Blister 0	Blister 0
	One hour drying Water absorption ratio	16%	16%	11%	15%	17%
	One week drying blister on coating film	Blister 0	Blister 0	Blister 0	Blister 0	Blister 0
	Three hours drying Crack on coating film	Crack 0	Crack 0	Crack 0	Crack 0	Crack 0
Water resistances of coating film at 5°C	Three hours drying Water absorption ratio of coating film	15%	17%	11%	16%	16%
	Coating film gloss	89	88	87	88	87

[0113]

[Table 3]

		Comparative Example 1		Comparative Example 2		Comparative Example 3		Comparative Example 4		Comparative Example 5	
		Coating material 7		Coating material 8		Coating material 9		Coating material 10		Coating material 11	
Main agent	White enamel coating material	White enamel coating material 1		White enamel coating material 1		White enamel coating material 1		White enamel coating material 1		White enamel coating material 1	
	Amount (parts by mass)	105		105		105		105		105	
Curing agent	Water dispersion	Water dispersion 4		Water dispersion 5		Water dispersion 6		Water dispersion 7		Water dispersion 8	
	Ethylene glycol Calculated value of number average repetition number	15		15		15		15		15	
	Propylene glycol Calculated value of number average repetition number	3		3		1		4.6		17	
	Propylene glycol Terminal alkyl portion	Butyl		Methyl		Butyl		Butyl		Butyl	
	PEG portion / PPG portion	1/5		1/9		1/5		2/1		1/3	
	Amount (parts by mass)	17.6		16.0		15.3		23.3		32.6	
	Initial	50 times or more		50 times or more		50 times or more		50 times or more		50 times or more	
Test for curing storage stabilities of curing agent	One month after	50 times or more		50 times or more		30 times		50 times or more		50 times or more	
	Two months after	35 times		35 times		10 times		30 times		50 times or more	
	Three months after	20 times		20 times		5 times		20 times		50 times or more	
	One hour drying blister on coating film	Blister 3(S3)		Blister 3(S3)		Blister 4(S3)		Blister 5(S4)		Blister 0	
Water resistances of coating film at 20°C	One hour drying Water absorption ratio	25%		23%		30%		35%		12%	
	One week drying blister on coating film	Blister 0		Blister 0		Blister 0		Blister 2(S2)		Blister 0	
	Three hours drying Crack on coating film	Crack 4(S3)b		Crack 4(S3)b		Crack 5(S4)b		Crack 5(S4)b		Crack 0	
Water resistances of coating film at 5°C	Three hours drying Water absorption ratio of coating film	28%		26%		32%		38%		11%	
	Coating film gloss	89		89		89		89		75	

[0114] [Description of results]

(1) Regarding storage stabilities for curing

In each of Examples 1 to 6, even when a curing agent which had been stored at 50°C for 3 months from the production was used, the basis material was not seen through at 50 times or more of rubbing treatment, and the result was good. On the other hand, in each of Comparative Examples 1 to 4, when a curing agent which had been stored for one month or two months was used, the basis material was seen through before 50 times of rubbing treatment. It was found out that a difference in stabilities of the curing agent itself is seen, depending on a number average repetition number of the PG units in the carbodiimide curing agent, or a ratio of PEG/PPG.

[0115]

(2) Regarding water resistance after drying at 20°C for one hour

In each of Examples 1 to 6, there was no blister in the test for water resistance at the initial stage of the coating film, and the result was good. On the other hand, in each of Comparative Examples 1 to 4, a blister was generated in a part or a whole of the coating film. Accompanying with this, it resulted in that the water absorption ratio of the coating film is about 10 to 25% higher in each of Comparative Examples 1 to 4 than that in each of Examples 1 to 6. It was found out that a difference in water resistance at the initial stage is seen, depending on a number average repetition number of the PG units in the carbodiimide curing agent, or a ratio of PEG/PPG.

[0116]

(3) Regarding water resistance after drying at 5°C for three hours

In each of Examples 1 to 6, there was no cracking in the test for water

resistance at the initial stage of the coating film, and the result was good. On the other hand, in each of Comparative Examples 1 to 4, a cracking was generated in a part or a whole of the coating film. Accompanying with this, it resulted in that the water absorption ratio of the coating film is about 10 to 30% higher in each of Comparative Examples 1 to 4 than that in each of Examples 1 to 6. It was found out that like at 20°C, also at 5°C, a difference in water resistance at the initial stage is seen, depending on a number average repetition number of the PG units in the carbodiimide curing agent, or a ratio of PEG/PPG.

[0117]

(4) Regarding gloss of a coating film

The gloss value of each coating film of Examples 1 to 6 was 80 or more, and it was good. Further, when the water dispersion of an acrylic resin having an acid value of the resin solid content of 3 to 30 mg/KOH and the water-soluble acrylic resin having an acid value of the resin solid content of 35 to 100 mg/KOH were used, the gloss values of the coating films were 85 or more, and these were the best results (Examples 1 to 3 and 5 to 6).

[0118] [Measurement method]

(1) Hydroxyl value

A hydroxyl value was measured based on JIS K 1557-1 (Method of testing plastic-polyurethane starting material polyol-Part 1: How to obtain hydroxyl value).

[0119]

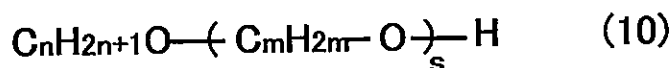
(2) Number average repetition numbers q and r

The number average repetition number q of ethylene glycol in

polyethylene glycol monoalkyl ether and the number average repetition number r of propylene glycol in polypropylene glycol monoalkyl ether correspond to a number average repetition number s of alkylene glycol in polyalkylene glycol monoalkyl ether represented by the following general formula (10). The number average repetition number s ($=q, r$) was obtained from the molecular weight and hydroxyl value of the relevant polymer based on the following mathematical expression.

[0120]

[Chemical formula 13]



[0121]

[Mathematical expression 1]

$$\text{Number average repetition number (s)} = \frac{(\text{molecular weight of polymer}) - (\text{sum of molecular weights of alkyl and hydrogen on both ends})}{(\text{unit molecular weight of ether portion})} = \frac{\frac{56100}{(\text{hydroxyl value})} - (14n + 18)}{14m + 16}$$

[0122] In the mathematical expression,

Unit molecular weight of ether portion $= 12m + 2m + 16 = 14m + 16$

Sum of molecular weights of alkyl and hydrogen on both ends $=$

$$12n + 2n + 1 + 16 + 1 = 14n + 18$$

[0123] [Industrial Applicability]

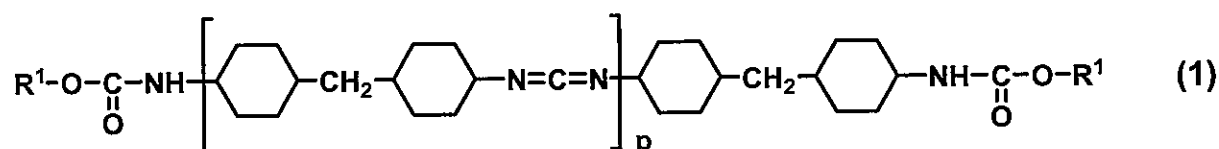
Since the two-package aqueous coating composition of the present invention uses a carbodiimide compound having a specific structure as a curing agent, it is excellent in curing properties at the initial stage, and further is also excellent in storage stabilities. Therefore, the coating composition can be used in the fields of a variety of coating materials for ambient temperature drying or

baking drying.

WHAT IS CLAIMED IS:

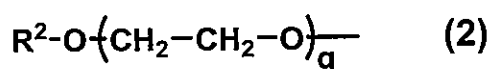
1. A two-package aqueous coating composition, comprising:
 (A) an aqueous acrylic resin having a carboxyl group, and
 (B) a carbodiimide compound represented by the general formula (1):

5 [Chemical formula 1]



wherein p represents an integer of 1 to 5, and two R¹s are independently a residue of polyethylene glycol monoalkyl ether represented by the general formula (2):

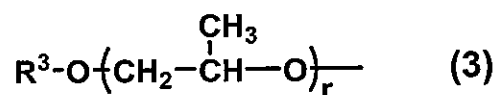
10 [Chemical formula 2]



wherein a number average repetition number q is in the range of 6 to 40, and R² represents an alkyl group having 1 to 8 carbon atoms, or a phenyl group,

15 and/or a residue of polypropylene glycol monoalkyl ether represented by the general formula (3):

[Chemical formula 3]



wherein a number average repetition number r is in the range of 4 to 14, and R³ represents an alkyl group having 1 to 8 carbon atoms, or a phenyl group,

20

wherein, in the R¹'s in the general formula (1), a molar ratio between the residue of polyethylene glycol monoalkyl ether represented by the general formula (2) and the residue of polypropylene glycol monoalkyl ether represented by the general formula (3) is 1:1 to 1:15.

5 2. The two-package aqueous coating composition according to claim 1, wherein the aqueous acrylic resin (A) comprises a water dispersion of an acrylic resin having an acid value of the resin solid content of 3 to 30 mg/KOH.

 3. The two-package aqueous coating composition according to claim 1, wherein the aqueous acrylic resin (A) comprises a water dispersion of an
10 acrylic resin having an acid value of the resin solid content of 3 to 30 mg/KOH and a water-soluble acrylic resin having an acid value of the resin solid content of 35 to 100 mg/KOH at a solid content mass ratio of 2:1 to 10:1.

 4. The two-package aqueous coating composition according to any one of claims 1 to 3, wherein the molar ratio between the residue of
15 polyethylene glycol monoalkyl ether and the residue of polypropylene glycol monoalkyl ether is 1:2 to 1:15.