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(54) Title: ACTIVE ENERGY RAY-CURABLE AQUEOUS RESIN COMPOSITION, ACTIVE ENERGY RAY-CURABLE AQUEOUS COATING MATERIAL, AND ARTICLE COATED WITH THE COATING MATERIAL

(57) Abstract: An active energy ray-curable aqueous resin composition includes a reaction product (X) of a hydroxyl group-having acrylic polymer (A) and an isocyanate group-having urethane (meth) acrylate (B), and an aqueous medium (Y), the urethane (meth) acrylate (B) having a carboxyl group and two or more (meth) acryloyl groups. The active energy ray-curable aqueous resin composition is useful for an active energy ray-curable aqueous coating film which can form a cured coating film having excellent adhesion, warm-water resistance, and chemical resistance, and the coating material can be coated on various articles.



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## [DESCRIPTION]

**ACTIVE ENERGY RAY-CURABLE AQUEOUS RESIN COMPOSITION, ACTIVE ENERGY RAY-CURABLE AQUEOUS COATING MATERIAL, AND ARTICLE COATED WITH THE COATING MATERIAL**

[Technical Field]

[0001]

The present invention relates to an active energy ray-curable aqueous resin composition, an active energy ray-curable aqueous coating material, and an article coated with the coating material.

[Background Art]

[0002]

An active energy ray-curable composition is used as a hard coating agent for plastic substrates of home electric appliances, cellular phones, and the like in view of the characteristics of little heat history to coating substrates and excellent hardness and scratch properties of coating films. An example of the active energy ray-curable composition is an active energy ray-curable composition (solvent-type active energy ray-curable composition) containing a polymer having a polymerizable unsaturated double bond, such as acryl acrylate or the like, a polymer not having an unsaturated double bond, such as a polymerizable acrylic resin or the like, a polymerizable monomer, and an organic solvent serving as a diluent. For example, when the active energy ray-curable composition is used as a coating material for spray coating, the coating material is required to contain as large as 50 to 90% by mass of the organic solvent. Therefore, when a cured coating film is formed on a substrate surface such as a plastic or the like by using an active energy ray-curable coating material containing the resin composition, there is a problem

of worsening the working environment due to the volatilization of the organic solvent in the coating material. The volatilized organic solvent also causes atmospheric pollution.

[0003]

Under the circumstances, a production method is proposed, which includes neutralizing a specific polyurethane acrylate-modified polyacrylate resin by adding an alkali solution, producing an anionic ultraviolet-curable resin (for example, refer to PTL 1). However, a cured coating film of the resin produced by the production method has unsatisfactory adhesion, warm-water resistance, and chemical resistance.

[0004]

Therefore, there is required an active energy ray-curable aqueous resin composition which can produce a cured coating film having excellent adhesion, warm-water resistance, and chemical resistance.

[Citation List]

[Patent Literature]

[0005]

[PTL 1]

Chinese Patent Application Publication No. CN109942772A

[Summary of Invention]

[Technical Problem]

[0006]

An object to be solved by the present invention is to provide an active energy ray-curable aqueous resin composition which can produce a cured coating film having excellent adhesion, warm-water resistance, and chemical resistance, an active energy ray-curable aqueous coating material containing the composition, and an article coated with the coating material.

[Solution to Problem]

[0007]

As a result of repeated earnest investigations for solving the problem, the inventors of the present invention found that the problem is solved by an active energy ray-curable aqueous resin

composition containing a reaction product of a hydroxyl group-having acrylic polymer and a specific isocyanate group-having urethane acrylate, and an aqueous medium, leading to completion of the present invention.

[0008]

That is, the present invention relates to an active energy ray-curable aqueous resin composition containing a reaction product (X) of a hydroxyl group-having acrylic polymer (A) and an isocyanate group-having urethane (meth)acrylate (B), and an aqueous medium (Y), the urethane (meth)acrylate (B) having a carboxyl group and two or more (meth)acryloyl groups, and also relates to an active energy ray-curable aqueous coating material containing the composition and an article coated with the coating material.

[Advantageous Effects of Invention]

[0009]

An active energy ray-curable aqueous resin composition of the present invention is useful for an active energy ray-curable aqueous coating material which can form a cured coating film having excellent adhesion, warm-water resistance, and chemical resistance, and various articles can be coated with the coating material. Therefore, the active energy ray-curable aqueous resin composition of the present invention can be preferably used for a coating material for coating articles such as bodies of home electric appliances such as a refrigerator, a television, an air conditioner, and the like, casings of information terminals such as a cellular phone, a smartphone, a personal computer, and the like, containers of automotive interior member cosmetics, packaging materials with high designability, and the like.

[Description of Embodiments]

[0010]

An active energy ray-curable aqueous resin composition of the present invention contains a reaction product (X) of a hydroxyl group-having acrylic polymer (A) and an isocyanate group-having

urethane (meth)acrylate (B), and an aqueous medium, the urethane (meth)acrylate (B) having a carboxyl group and two or more (meth)acryloyl groups.

[0011]

First, the acrylic polymer (A) is described. The acrylic polymer (A) is produced by copolymerizing a hydroxyl group-having acrylic monomer (a1) with an unsaturated monomer (a2) other than the acrylic monomer (a1).

[0012]

The acrylic monomer (a1) is a compound having a hydroxyl group and a (meth)acryloyl group. Examples of the acrylic monomer (a1) include 2-hydroxyethyl (meth)acrylate, 3-hydroxypropyl (meth)acrylate, 4-hydroxy-n-butyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, 2-hydroxy-n-butyl (meth)acrylate, 3-hydroxy-n-butyl (meth)acrylate, 1,4-cyclohexanedimethanol mono(meth)acrylate, N-(2-hydroxyethyl) (meth)acrylamide, glycerin mono(meth)acrylate, polyethylene glycol mono(meth)acrylate, polypropylene glycol mono(meth)acrylate, 2-hydroxy-3-phenoxypropyl (meth)acrylate, 2-(meth)acryloyloxyethyl-2-hydroxyethyl phthalate, a lactone-modified (meth)acrylate having a hydroxyl group at a terminal, and the like. These acrylic monomers (a1) can be used alone or in combination of two or more.

[0013]

Examples of the unsaturated monomer (a2) include methyl (meth)acrylate, ethyl (meth)acrylate, n-propyl (meth)acrylate, isopropyl (meth)acrylate, n-butyl (meth)acrylate, isobutyl (meth)acrylate, n-pentyl (meth)acrylate, n-hexyl (meth)acrylate, n-heptyl (meth)acrylate, n-octyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, nonyl (meth)acrylate, decyl (meth)acrylate, dodecyl (meth)acrylate, cetyl (meth)acrylate, stearyl (meth)acrylate, behenyl (meth)acrylate, cyclohexyl (meth)acrylate, 4-tert-butylcyclohexyl (meth)acrylate, isobornyl (meth)acrylate, dicyclopentanyl (meth)acrylate, benzyl

(meth)acrylate, methoxypolyethylene glycol (meth)acrylate, ethoxypolyethylene glycol (meth)acrylate, phenoxypolyethylene glycol (meth)acrylate, (meth)acrylic acid, (meth)acrylamide, N,N-dimethyl (meth)acrylamide, (meth)acrylonitrile, 3-(meth)acryloylpropyl trimethoxysilane, N,N-dimethylaminoethyl (meth)acrylate, glycidyl (meth)acrylate, aromatic vinyl monomers such as styrene,  $\alpha$ -methylstyrene, p-methylstyrene, p-methoxystyrene, and the like. These unsaturated monomers (a2) can be used alone or in combination of two or more.

[0014]

From the viewpoint of reaction points with urethane acrylate, the amount of the acrylic monomer (a1) used is preferably 5% to 70% by mass and more preferably 10% to 50% by mass in the monomer components used as raw materials of the acrylic polymer (A). The amount of the unsaturated monomer (a2) used is the residue obtained by subtracting the ratio of the acrylic monomer (a1) used from a total of 100% by mass of the monomer components used as raw materials of the acrylic polymer (A).

[0015]

A method for producing the acrylic polymer (A) is, for example, a method of copolymerizing the acrylic monomer (a1) with the unsaturated monomer (a2) using a polymerization initiator in an organic solvent. The organic solvent used is preferably an alcohol compound, a ketone compound, an ester compound, an ether compound, an amide compound, a sulfoxide compound, or a hydrocarbon compound. Examples thereof include methanol, ethanol, propanol, n-butanol, iso-butanol, tert-butanol, 3-methoxybutanol, acetone, methyl ethyl ketone, methyl isobutyl ketone, cyclohexanone, ethyl acetate, butyl acetate, propylene glycol monomethyl ether acetate, diisopropyl ether, ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol monobutyl ether, ethylene glycol dimethyl ether, diethylene glycol dimethyl ether, diethylene glycol diethyl ether, diethylene glycol dibutyl ether, propylene glycol monomethyl ether, propylene glycol monopropyl

ether, propylene glycol monobutyl ether, propylene glycol dimethyl ether, dipropylene glycol monomethyl ether, dipropylene glycol dimethyl ether, dimethyl formamide, dimethyl acetamide, N-methyl pyrrolidone, dimethyl sulfoxide, tetrahydrofuran, dioxane, toluene, xylene, and the like. Among these, from the viewpoint of improving storage stability of the resultant active energy ray-curable aqueous resin composition, dialkylene glycol dialkyl ethers such as ethylene glycol dimethyl ether, diethylene glycol diethyl ether, dipropylene glycol dimethyl ether, and the like are more preferred.

[0016]

Examples of the polymerization initiator include organic peroxides: ketone peroxide compounds such as cyclohexanone peroxide, 3,3,5-trimethylcyclohexanone peroxide, methylcyclohexanone peroxide, and the like; peroxyketal compounds such as

1,1-bis(tert-butylperoxy)-3,3,5-trimethylcyclohexane, 1,1-bis(tert-butylperoxy)cyclohexane, n-butyl-4,4-bis(tert-butylperoxy)valerate, 2,2-bis(4,4-di-tert-butylperoxycyclohexyl)propane, 2,2-bis(4,4-di-tert-amylperoxycyclohexyl)propane, 2,2-bis(4,4-di-tert-hexylperoxycyclohexyl)propane, 2,2-bis(4,4-di-tert-octylperoxycyclohexyl)propane, 2,2-bis(4,4-dicumylperoxycyclohexyl)propane, and the like; hydroperoxides such as cumene hydroperoxide, 2,5-dimethylhexane-2,5-dihydroperoxide, and the like; dialkyl peroxide compounds such as 1,3-bis(tert-butylperoxy-m-isopropyl)benzene, 2,5-dimethyl-2,5-di(tert-butylperoxy)hexane, diisopropylbenzene peroxide, tert-butylcumyl peroxide, and the like; diacyl peroxide compounds such as decanoyl peroxide, lauroyl peroxide, benzoyl peroxide, 2,4-dichlorobenzoyl peroxide, and the like; peroxy carbonate compounds such as bis(tert-butylcyclohexyl) peroxy carbonate and the like; and peroxyester compounds such as tert-butylperoxy-2-ethyl

hexanoate, tert-butyl peroxybenzoate, 2,5-dimethyl-2,5-di(benzoylperoxy)hexane, and the like; and azo compounds such as 2,2'-azobisisobutyronitrile, 1,1'-azobis(cyclohexane-1-carbonitrile) and the like.

[0017]

In addition, when the acrylic polymer (A) is produced, if required, a chain transfer agent, such as lauryl mercaptan, 2-mercaptoethanol, thioglycerol, ethylthioglycolic acid, octylthioglycolic acid, or the like, may be used.

[0018]

In view of improvement in water dispersibility and water resistance of a coating film, the hydroxyl value of the acrylic polymer (A) is preferably 20 to 300 mgKOH/g and more preferably 40 to 200 mgKOH/g.

[0019]

In view of improvement in dispersibility in water and improvement in storage stability of the resultant active energy ray-curable aqueous resin composition, the weight-average molecular weight (Mw) of the acrylic polymer (A) is preferably within a range of 2,000 to 50,000, more preferably within a range of 3,000 to 30,000, and still more preferably within a range of 3,000 to 20,000. The weight-average molecular weight (Mw) is the value in terms of polystyrene based on gel permeation chromatography (abbreviated as "GPC" hereinafter) measurement.

[0020]

The isocyanate group-containing urethane (meth)acrylate (B) has an isocyanate group, a carboxyl group, and two or more (meth)acryloyl groups.

[0021]

The urethane (meth)acrylate (B) can be produced by, for example, urethane reaction of a polyisocyanate (b1), a carboxyl group-containing polyol (b2), and a hydroxyl group-containing polyfunctional acrylate (b3), which are used as essential raw materials.

[0022]



Examples of the polyisocyanate (b1) include aromatic diisocyanate compounds such as tolylene diisocyanate, diphenylmethane diisocyanate, m-xylylene diisocyanate, m-phenylenebis(dimethylmethylen) diisocyanate, and the like; aliphatic or alicyclic diisocyanate compounds such as hexamethylene diisocyanate, lysine diisocyanate, 1,3-bis(isocyanatomethyl)cyclohexane, 2-methyl-1,3-diisocyanatocyclohexane, 2-methyl-1,5-diisocyanatocyclohexane, 4,4'-dicyclohexylmethane diisocyanate, isophorone diisocyanate, and the like; and the like. Among these, because of excellent yellowing resistance, the aliphatic or alicyclic diisocyanate compounds are preferred.

[0023]

Other usable examples of the polyisocyanate (b1) include isocyanate group-having prepolymers produced by addition reaction of the diisocyanate compounds described above with a polyhydric alcohol; isocyanurate ring-having compounds produced by cyclization trimerization of the diisocyanate compounds described above; urea bond or biuret bond-having polyisocyanate compounds produced by reaction of the diisocyanate compounds described above with water; homopolymers of isocyanate group-having acrylic monomers such as 2-isocyanatoethyl (meth)acrylate, 3-isopropenyl- $\alpha,\alpha$ -dimethylbenzyl isocyanate, (meth)acryloyl isocyanate, and the like; isocyanate group-having copolymers produced by copolymerizing the isocyanate group-having acrylic monomers with another acrylic monomer, a vinyl ester compound, a vinyl ether compound, an aromatic vinyl monomer, fluoroolefin, or the like; and the like.

[0024]

The polyisocyanate (b1) can be used alone or in combination of two or more.

[0025]

Examples of the carboxyl group-having polyol (b2) include 2,2-dimethylolpropionic acid, 2,2-dimethylolbutanoic acid,

2,2-dimethylolvaleric acid, and the like. Among these, from the viewpoint of reaction with isocyanate, 2,2-dimethylolpropionic acid and 2,2-dimethylolbutanoic acid are preferred. Also, carboxyl group-having polyester polyols produced by the carboxyl group-having glycol with various polycarboxylic acids can be used.

[0026]

The carboxyl group-having polyols (b2) can be used alone or in combination of two or more.

[0027]

Examples of the hydroxyl group-having polyfunctional (meth)acrylate (b3) include trimethylolpropane di(meth)acrylate, pentaerythritol tri(meth)acrylate, dipentaerythritol penta(meth)acrylate, isocyanuric acid EO-modified diacrylate, and the like. From the viewpoint of satisfying both warm-water resistance of a coating film and water dispersibility, pentaerythritol tri(meth)acrylate is preferred.

[0028]

The hydroxyl group-having polyfunctional (meth)acrylates (b3) can be used alone or in combination of two or more.

[0029]

If required, a polyol not having the carboxyl group and a monofunctional (meth)acrylate can also be used as raw materials for the urethane (meth)acrylate (B).

[0030]

Examples of a method for reacting the polyisocyanate (b1), the carboxyl group-having polyol (b2), and the hydroxyl group-having polyfunctional acrylate (b3) include a method of simultaneously reacting the polyisocyanate (b1), the carboxyl group-having polyol (b2), and the hydroxyl group-having polyfunctional acrylate (b3), a method of reacting the polyisocyanate (b1) with the carboxyl group-having polyol (b2), and then reacting the hydroxyl group-having polyfunctional acrylate (b3), a method of reacting the polyisocyanate (b1) with the hydroxyl group-having polyfunctional acrylate (b3), and

then reacting the carboxyl group-containing polyol (b2), and the like.

[0031]

In the present invention, urethane reaction can be performed without a catalyst but can be performed in the presence of a urethanization catalyst in order to promoting the proceeding of the reaction. Examples of the urethanization catalyst include amine compounds such as pyridine, pyrrole, triethylamine, diethylamine, dibutylamine, and the like; phosphine compounds such as triphenylphosphine, triethylphosphine, and the like; organic tin compounds such as dibutyltin dilaurate, octyltin trilaurate, octyltin diacetate, dibutyltin diacetate, tin octylate, and the like; organic metal compounds such as zinc octylate and the like; and the like.

[0032]

From the viewpoint of warm-water resistance of the resultant coating film, the isocyanate group content of the urethane (meth)acrylate (B) is preferably 1% to 5% by mass.

[0033]

The weight-average molecular weight of the urethane (meth)acrylate (B) is preferably 1,000 to 10,000.

[0034]

The reaction product (X) can be produced by urethane reaction of the hydroxyl group-containing acrylic polymer (A) with the isocyanate group-containing urethane (meth)acrylate (B).

[0035]

The mass ratio (A/B) of the acrylic polymer (A) to the urethane (meth)acrylate (B) is preferably within a range of 0.25 to 4.0 and more preferably within a range of 0.5 to 3.0 in view of improvement in dispersibility in water and improvement in storage stability of the resultant active energy ray-curable aqueous resin composition.

[0036]

The molar ratio (A/B) of hydroxyl groups possessed by the acrylic polymer (A) to isocyanate groups possessed by the urethane (meth)acrylate is preferably within a range of 0.8 to

1.2 and more preferably within a range of 0.9 to 1.1 in view of improvement in dispersibility in water and improvement in storage stability of the resultant active energy ray-curable aqueous resin composition.

[0037]

In view of more improvement in water dispersibility, the acid value of the reaction product (X) is preferably 10 to 60 mgKOH/g.

[0038]

The reaction product (X) is a reaction product of the acrylic polymer (A) and the urethane (meth)acrylate (B), but in view of more improvement in adhesion, preferably the reaction product (X) is a reaction product containing polycarbonate diol (P) as an essential raw material.

[0039]

The polycarbonate diol (P) is, for example, obtained by reaction of diol with a carbonate ester or phosgene.

[0040]

Examples of the diol, 1,3-propanediol, 1,2-propanediol, 2-methyl-1,3-propanediol, 2,2-dimethyl-1,3-propanediol, 2-butyl-2-ethyl-1,3-propanediol, 1,2-butanediol, 1,3-butanediol, 1,4-butanediol, 1,5-pentanediol, 2,4-pentanediol, 2-methyl-1,3-pentanediol, 3-Methyl-1,5-pentanediol, 1,6-hexanediol, 1,5-hexanediol, 2-ethyl-1,3-hexanediol, and the like. In view of more improvement in adhesion, 1,4-butanediol or 1,5-pentanediol are preferred.

[0041]

In view of more improvement in water dispersibility, the number-average molecular weight of the polycarbonate diol (P) is preferably 500 to 3,000 and more preferably 500 to 2,000.

[0042]

In view of more improvement in adhesion, the amount of the polycarbonate diol (P) used is preferably 5% to 20% by mass and more preferably 5% to 10% by mass in the reaction product (X).

[0043]

Examples of the reaction methods of the acrylic polymer (A),

the urethane (meth)acrylate (B), and the polycarbonate diol (P) include a method of simultaneously reacting the acrylic polymer (A), the urethane (meth)acrylate (B), and the polycarbonate diol (P), a method of reacting the polyisocyanate (b1) with the polycarbonate diol (P) and then the carboxyl group-containing polyol (b2) and the hydroxyl group-containing polyfunctional acrylate (b3), a method of reacting the polyisocyanate (b1) with the hydroxyl group-containing polyfunctional acrylate (b3) and the polycarbonate diol (P), and then reacting the carboxyl group-containing polyol (b2), and the like.

[0044]

The active energy ray-curable aqueous resin composition of the present invention contains the reaction product (X) produced by reacting the acrylic polymer (A) with the urethane (meth)acrylate (B), but in view of more improvement in chemical resistance, the composition preferably contains a polyfunctional (meth)acrylate (C) in addition to the reaction product (X). Examples of the polyfunctional (meth)acrylate (C) include ethylene glycol di(meth)acrylate, diethylene glycol di(meth)acrylate, triethylene glycol di(meth)acrylate, polyethylene glycol di(meth)acrylate, propylene glycol di(meth)acrylate, dipropylene glycol di(meth)acrylate, tripropylene glycol di(meth)acrylate, polypropylene glycol di(meth)acrylate, neopentyl glycol di(meth)acrylate, 1,3-butanediol di(meth)acrylate, 1,4-butanediol di(meth)acrylate, 1,6-hexanediol di(meth)acrylate, hydroxyisobutyric acid ester neopentyl glycol di(meth)acrylate, bisphenol A-di(meth)acrylate, bisphenol A-EO-modified di(meth)acrylate, isocyanuric acid EO-modified diacrylate, isocyanuric acid EO-modified triacrylate, trimethylolpropane tri(meth)acrylate, trimethylolpropane EO-modified tri(meth)acrylate, pentaerythritol tetra(meth)acrylate, ditrimethylolpropane tetraacrylate, dipentaerythritol hexa(meth)acrylate, and the like. From the viewpoint of water dispersibility of a resin and warm-water resistance of a coating film, trimethylolpropane EO-modified tri(meth)acrylate is

preferred.

[0045]

The polyfunctional (meth)acrylates (C) can be used alone or in combination of two or more.

[0046]

Examples of the aqueous medium (Y) include water, a hydrophilic organic solvent, and a mixture thereof. The hydrophilic organic solvent is preferably a water-miscible organic solvent miscible with water without being separated from water, and particularly preferably an organic solvent having a water solubility (the number of grams of an organic solvent dissolved in 100 g of water) at 25°C of 3 g or more. Examples of the water-miscible organic solvent include alcohol solvents such as methanol, ethanol, propanol, butanol, 3-methoxybutanol, 3-methyl-3-methoxybutanol, and the like; ketone solvents such as acetone, methyl ether ketone, and the like; glycol ether solvents such as ethylene glycol monomethyl ether, ethylene glycol dimethyl ether, ethylene glycol monoethyl ether, ethylene glycol diethyl ether, ethylene glycol monopropyl ether, ethylene glycol monoisopropyl ether, monobutyl ether, diethylene glycol monomethyl ether, diethylene glycol dimethyl ether, diethylene glycol monoethyl ether, diethylene glycol diethyl ether, diethylene glycol monoisopropyl ether, diethylene glycol monobutyl ether, triethylene glycol monomethyl ether, triethylene glycol dimethyl ether, propylene glycol monomethyl ether, propylene glycol dimethyl ether, propylene glycol monopropyl ether, propylene glycol monobutyl ether, dipropylene glycol monomethyl ether, dipropylene glycol dimethyl ether, and the like; and the like. These water-miscible organic solvents may be used alone or in combination of two or more.

[0047]

The active energy ray-curable aqueous resin composition of the present invention contains the reaction product (X) and the aqueous medium (Y), and the reaction product (X) is preferably dissolved or dispersed in the aqueous medium (Y) and is more

preferably a dispersion.

[0048]

A method for dissolving or dispersing the reaction product (X) in the aqueous medium (Y) is preferably a method of neutralizing the acid group possessed by the reaction product (X) with a basic compound and then mixing with the aqueous medium (Y).

[0049]

Examples of the basic compound include organic amines such as methylamine, dimethylamine, trimethylamine, ethylamine, diethylamine, triethylamine, butylamine, dibutylamine, tributylamine, monoalkanol amine such as N,N-dimethylethanol amine, 2-aminoethanol, and the like, diethanolamine, diisopropanolamine, dibutanolamine, and the like; inorganic basic compounds such as ammonia, sodium hydroxide, potassium hydroxide, and the like; quaternary ammonium hydroxides such as tetramethylammonium hydroxide, tetra-n-butylammonium hydroxide, trimethylbenzylammonium hydroxide, and the like; and the like. Among these, an organic amine and ammonia (may be ammonia water) are preferably used. These basic compounds can be used alone or in combination of two or more.

[0050]

In view of improving the storage stability of the active energy ray-curable aqueous resin composition, the amount of the basic compound used is preferably such an amount that the neutralization ratio of carboxyl groups in the reaction product (X) is within a range of 50% to 100%.

[0051]

An active energy ray-curable aqueous coating material of the present invention contains the active energy ray-curable aqueous resin composition of the present invention, and other usable compounds include additives such as an antistatic agent, an anti-foaming agent, a viscosity adjuster, a light-resistant stabilizer, a weather-resistant stabilizer, a heat-resistant stabilizer, an ultraviolet absorber, an antioxidant, a leveling agent, a pigment dispersant, and the like.

[0052]

Also, a cured coating film can be formed by applying the active energy ray-curable aqueous coating material of the present invention to a substrate and then irradiating the coating material with active energy rays. The term "active energy rays" represents ultraviolet light or ionizing radiation such as electron beams,  $\alpha$ -rays,  $\beta$ -rays,  $\gamma$ -rays, or the like. When a cured coating film is formed by irradiation with ultraviolet light as the active energy rays, curability is preferably improved by adding a photopolymerization initiator (D) to the active energy ray-curable aqueous coating material of the present invention. If required, curability can also be improved by further adding a photosensitizer. While when ionizing radiation such as electron beams,  $\alpha$ -rays,  $\beta$ -rays,  $\gamma$ -rays, or the like is used, curing rapidly proceeds without using the photopolymerization initiator and the photosensitizer, and thus the photopolymerization initiator (D) and the photosensitizer particularly need not be added. [0053]

Examples of the photopolymerization initiator (D) include an intramolecular cleavage-type photopolymerization initiator and a hydrogen abstraction-type photopolymerization initiator. Examples of the intramolecular cleavage-type photopolymerization initiator include acetophenone-based compounds such as diethoxyacetophenone, 2-hydroxy-2-methyl-1-phenylpropan-1-one, benzyl dimethylketal, 1-(4-isopropylphenyl)-2-hydroxy-2-methylpropan-1-one, 4-(2-hydroxyethoxy)phenyl-(2-hydroxy-2-propyl) ketone, 1-hydroxycyclohexyl-phenyl ketone, 2-methyl-2-morpholino(4-tiomethylphenyl)propan-1-one, 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)-butanone, and the like; benzolins such as benzoin, benzoin methyl ether, benzoin isopropyl ether, and the like; acylphosphine oxide-based compounds such as 2,4,6-trimethylbenzoin diphenylphosphine oxide, bis(2,4,6-trimethylbenzoyl)-phenyl phosphine oxide, and the like; benzyl; methylphenyl



glyoxyester; and the like.

[0054]

On the other hand, examples of the hydrogen abstraction-type photopolymerization initiator include benzophenone-based compounds such as benzophenone, methyl-4-phenylbenzophenone o-benzoylbenzoate, 4,4'-dichlorobenzophenone, hydroxybenzophenone, 4-benzoyl-4'-methyl-diphenyl sulfide, acrylated benzophenone, 3,3',4,4'-tetra(tert-butylperoxycarbonyl)benzophenone, 3,3'-dimethyl-4-methoxybenzophenone, and the like; thioxanthone-based compounds such as 2-isopropyl thioxanthone, 2,4-dimethyl thioxanthone, 2,4-diethyl thioxanthone, 2,4-dichlorothioxanthone, and the like; aminobenzophenone-based compounds such as Michler ketone, 4,4'-diethyl aminobenzophenone, and the like; 10-butyl-2-chloroacridone, 2-ethyl anthraquinone, 9,10-phenanthrenequinone, camphorquinone; and the like. These photopolymerization initiators (D) can be used alone or in combination of two or more.

[0055]

Examples of the photosensitizer include amines such as aliphatic amines, aromatic amines, and the like; ureas such as o-tolylthiourea and the like; sulfur compounds such as sodium diethyl dithiophosphate, s-benzylisothiuronium-p-toluene sulfonate, and the like.

[0056]

The amount of each of the photopolymerization initiator and photosensitizer used is preferably 0.05 to 20 parts by mass and more preferably 0.5 to 10 parts by mass relative to 100 parts by mass of the nonvolatile components in the active energy ray-curable aqueous coating material of the present invention.

[0057]

In addition, the active energy ray-curable aqueous coating material can be used as a coating material for coating various articles. Examples of articles which can be coated with the active energy ray-curable aqueous coating material of the

present invention include bodies of home electric appliances such as a refrigerator, a television, an air conditioner, and the like; casings of information terminals of a cellular phone, a smartphone, a personal computer, and the like; containers of automobile interior member cosmetics, packaging materials with high designability; and the like.

[0058]

A coating method for the active energy ray-curable aqueous coating material of the present invention depends on applications, and examples thereof include methods of a gravure coater, a roll coater, a comma coater, a knife coater, an air knife coater, a curtain coater, a kiss coater, a shower coater, a wheeler coater, a spin coater, dipping, screen printing, a spray, an applicator, a bar coater, and the like.

[0059]

As described above, examples of the active energy ray for curing the active energy ray-curable aqueous coating material of the present invention include ultraviolet light and ionizing radiation such as electron beams,  $\alpha$ -rays,  $\beta$ -rays,  $\gamma$ -rays, and the like. Specific examples of an energy source or curing device include a sterilizing lamp, a fluorescent lamp for ultraviolet light, a carbon arc, a xenon lamp, a high-pressure mercury lamp for copying, a medium-pressure or high-pressure mercury lamp, an ultrahigh-pressure mercury lamp, an electrodeless lamp, a metal halide lamp, ultraviolet light from a light source such as natural light or the like, an electron beam from a scanning-type or curtain-type electron beam accelerator, and the like.

[EXAMPLES]

[0060]

The present invention is described in further detail below by giving examples. In addition, the weight-average molecular weight (Mw) of a polymer was measured under the following GPC measurement conditions.

[0061]

[GPC measurement condition]

Measurement apparatus: high-speed GPC apparatus

("HLC-8220GPC" manufactured by Tosoh Corporation)

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

"TSKgel G5000" (7.8 mm I. D. × 30 cm) × 1

"TSKgel G4000" (7.8 mm I. D. × 30 cm) × 1

"TSKgel G3000" (7.8 mm I. D. × 30 cm) × 1

"TSKgel G2000" (7.8 mm I. D. × 30 cm) × 1

Detector: RI (differential refractometer)

Column Temperature: 40°C

Eluent: tetrahydrofuran (THF)

Flow rate: 1.0 mL/min

Injection amount: 100 µL (tetrahydrofuran solution at a sample concentration of 4 mg/mL)

Standard sample: A calibration curve was formed by using the following monodisperse polystyrene.

[0062]

[Monodisperse polystyrene]

"TSKgel standard polystyrene A-500" manufactured by Tosoh Corporation

"TSKgel standard polystyrene A-1000" manufactured by Tosoh Corporation

"TSKgel standard polystyrene A-2500" manufactured by Tosoh Corporation

"TSKgel standard polystyrene A-5000" manufactured by Tosoh Corporation

"TSKgel standard polystyrene F-1" manufactured by Tosoh Corporation

"TSKgel standard polystyrene F-2" manufactured by Tosoh Corporation

"TSKgel standard polystyrene F-4" manufactured by Tosoh Corporation

"TSKgel standard polystyrene F-10" manufactured by Tosoh Corporation

"TSKgel standard polystyrene F-20" manufactured by Tosoh Corporation

Corporation

"TSKgel standard polystyrene F-40" manufactured by Tosoh Corporation

"TSKgel standard polystyrene F-80" manufactured by Tosoh Corporation

"TSKgel standard polystyrene F-128" manufactured by Tosoh Corporation

"TSKgel standard polystyrene F-288" manufactured by Tosoh Corporation

"TSKgel standard polystyrene F-550" manufactured by Tosoh Corporation

[0063]

(SYNTHESIS EXAMPLE 1: Synthesis of acrylic polymer (A-1))

In a reactor provided with a stirrer, a thermometer, an inert gas inlet tube, a dropping funnel, and a reflux tube, 291 parts by mass of diethylene glycol dimethyl ether as an initial solvent was charged and heated to 130°C. Then, there were dropped over 3 hours, a monomer mixture composed of 355.2 parts by mass of methyl methacrylate, 231.6 parts by mass of n-butyl methacrylate, 42.2 parts by mass of styrene, 90.0 parts by mass of 2-hydroxyethyl methacrylate, and 8.4 parts by mass of methoxypolyethylene glycol acrylate ("AM-130G" manufactured by Shin-Nakamura Chemical Co., Ltd.), and a initiator solution composed of 33.7 parts by mass of tert-butylperhydroxy 2-ethyl hexanoate and 33.7 parts by mass of diethylene glycol dimethyl ether. The resultant mixture was held for 3 hours and then the temperature was decreased, producing a solution of acrylic polymer (A-1) with a nonvolatile content of 70.1% by mass.

[0064]

(SYNTHESIS EXAMPLES 2 and 3: Synthesis of acrylic polymers (A-2) and (A-3))

Acrylic polymers (A-2) and (A-3) were produced by the same method as in Synthesis Example 1 except that 2-hydroxyethyl methacrylate used in Synthesis Example 1 was changed as shown in Table 1.

[0065]

Table 1 shows the compositions of the acrylic polymers produced in Synthesis Examples 1 to 3.

[0066]

[Table 1]

Table 1		Synthesis Example 1	Synthesis Example 2	Synthesis Example 3	
Acrylic polymer		(A-1)	(A-2)	(A-3)	
Composition (parts by mass)	Acrylic monomer (a1)	HEMA	90	86.9	
		FM3		11.1	
	Unsaturated monomer (a2)	MMA	355.2	355.2	355.2
		BMA	231.6	231.6	231.6
		ST	42.2	42.2	42.2
		AM-130G	8.4	8.4	8.4
Solid content hydroxyl value (mgKOH/g)		53	53	40	
Number-average molecular weight		4500	4400	4500	
Weight-average molecular weight		8600	8500	8800	
Nonvolatile content of acrylic polymer solution (% by mass)		70.1	69.9	75.0	

[0067]

Abbreviations in Table 1 are as follows.

HEMA: hydroxyethyl methacrylate

FM3: 3-mole caprolactone adduct of hydroxyethyl methacrylate (manufactured by Daicel Corporation)

MMA: methyl methacrylate

BMA: butyl methacrylate

ST: styrene

AM-130G: methoxypolyethylene glycol acrylate (manufactured by Shin-Nakamura Chemical Co., Ltd.)

[0068]

(SYNTHESIS EXAMPLE 4: Synthesis of urethane (meth)acrylate (B-1))

In a reactor provided with a stirrer, a thermometer, an inert gas inlet tube, and a reflux tube, 416.7 parts by mass of isophorone diisocyanate, 485.5 parts by mass of pentaerythritol triacrylate, 3.1 parts by mass of dibutylhydroxytoluene, and

0.3 parts by mass of methoquinone were charged, heated to 80°C, and reacted for 2 hours. Then, 125.7 parts by mass of dimethylolpropionic acid was added and further reacted for 2 hours, producing urethane (meth)acrylate (B-1) having a carboxyl group and two or more (meth)acryloyl groups.

[0069]

(SYNTHESIS EXAMPLE 5: Synthesis of urethane (meth)acrylate (B-2))

In a reactor provided with a stirrer, a thermometer, an inert gas inlet tube, and a reflux tube, 416.7 parts by mass of isophorone diisocyanate, 410.5 parts by mass of pentaerythritol triacrylate, 150 parts by mass of polycarbonate diol ("DURANOL T5651" manufactured by Asahi Kasei Chemicals Corporation; hereinafter abbreviated as "polycarbonate diol (P-1)"), 3.1 parts by mass of dibutylhydroxytoluene, and 0.3 parts by mass of methoquinone were charged, heated to 80°C, and reacted for 2 hours. Then, 125.7 parts by mass of dimethylolpropionic acid was added and further reacted for 2 hours, producing urethane (meth)acrylate (B-2) having a carboxyl group and two or more (meth)acryloyl groups.

[0070]

(SYNTHESIS EXAMPLE 6: Synthesis of urethane (meth)acrylate (B-3))

In a reactor provided with a stirrer, a thermometer, an inert gas inlet tube, and a reflux tube, 416.7 parts by mass of isophorone diisocyanate, 485.5 parts by mass of isocyanuric acid EO-modified diacrylate, 3.1 parts by mass of dibutylhydroxytoluene, and 0.3 parts by mass of methoquinone were charged, heated to 80°C, and reacted for 2 hours. Then, 125.7 parts by mass of dimethylolpropionic acid was added and further reacted for 2 hours, producing urethane (meth)acrylate (B-3) having a carboxyl group and two or more (meth)acryloyl groups.

[0071]

(SYNTHESIS EXAMPLE 7: Synthesis of urethane (meth)acrylate (RB-1))

Urethane (meth)acrylate (RB-1) was produced by the same method as in Synthesis Example 4 except that 485.5 parts by mass of pentaerythritol triacrylate used in Synthesis Example 4 was changed to 119.1 parts by mass of 2-hydroxyethyl acrylate.

[0072]

(EXAMPLE 1: Synthesis of active energy ray-curable aqueous resin composition (1))

In a reactor provided with a stirrer, a thermometer, an inert gas inlet tube, and a reflux tube, 1085.8 parts by mass of the acrylic polymer (A-1) produced in Synthesis Example 1, 1031.3 parts by mass of the urethane (meth)acrylate (B-1), and 228.0 parts by mass of ethylene oxide adduct of trimethylolpropane triacrylate were charged, heated to 80°C, and reacted for 2 hours, producing a reaction product (X-1) having a carboxyl group and two or more (meth)acryloyl groups.

Next, 75.7 parts by mass of triethylamine was charged, and 2219.1 parts by mass of water was further charged, producing an active energy ray-curable aqueous resin composition (1).

[0073]

(EXAMPLES 2 and 3: Synthesis of active energy ray-curable aqueous resin compositions (2) and (3))

Active energy ray-curable aqueous resin compositions (2) and (3) were produced by the same method as in Example 1 except that the acrylic polymer (A-1) used in Example 1 was changed to the acrylic polymer (A-2) or (A-3).

[0074]

(EXAMPLE 4: Synthesis of active energy ray-curable aqueous resin composition (4))

In a reactor provided with a stirrer, a thermometer, an inert gas inlet tube, and a reflux tube, 1085.8 parts by mass of the acrylic polymer (A-1) produced in Synthesis Example 1, 1031.3 parts by mass of the urethane (meth)acrylate (B-1), 150 parts by mass of the polycarbonate diol (P-1) and 228.0 parts by mass of ethylene oxide adduct of trimethylolpropane triacrylate were charged, heated to 80°C, and reacted for 2 hours, producing a reaction product (X-1) having a carboxyl group and two or more

(meth)acryloyl groups.

Next, 75.7 parts by mass of triethylamine was charged, and 2219.1 parts by mass of water was further charged, producing an active energy ray-curable aqueous resin composition (4).

[0075]

(EXAMPLES 5 and 6: Synthesis of active energy ray-curable aqueous resin compositions (5) and (6))

Active energy ray-curable aqueous resin compositions (5) and (6) were produced by the same method as in Example 2 except that the urethane (meth)acrylate (B-1) used in Example 2 was changed to the urethane (meth)acrylate (B-2) or (B-3).

[0076]

(EXAMPLE 7: Synthesis of active energy ray-curable aqueous resin composition (7))

In a reactor provided with a stirrer, a thermometer, an inert gas inlet tube, and a reflux tube, 1093.8 parts by mass of the acrylic polymer (A-2) and 1031.3 parts by mass of the urethane (meth)acrylate (B-1) were charged, heated to 80°C, and reacted for 2 hours, producing a reaction product (X-7) having a carboxyl group and two or more (meth)acryloyl groups.

Next, 75.7 parts by mass of triethylamine was charged, and 2219.1 parts by mass of water was further charged, producing an active energy ray-curable aqueous resin composition (7).

[0077]

(COMPARATIVE EXAMPLE 1: Synthesis of active energy ray-curable aqueous resin composition (R1))

An active energy ray-curable aqueous resin composition (R1) was produced by the same method as in Example 1 except that the urethane (meth)acrylate (B-1) used in Example 1 was changed to the urethane (meth)acrylate (RB-1).

[0078]

(COMPARATIVE EXAMPLE 2: Synthesis of active energy ray-curable aqueous resin composition (R2))

An active energy ray-curable aqueous resin composition (R2) was produced by the same method as in Example 1 except that the urethane (meth)acrylate (B-1) used in Example 1 was changed to



the urethane (meth)acrylate (RB-1), and the ethylene oxide adduct of trimethylolpropane triacrylate was not used.

[0079]

[Preparation of active energy ray-curable aqueous coating material]

The active energy ray-curable aqueous resin composition produced as described above was mixed with a photopolymerization initiator ("Irgacure 500" manufactured by BASF Japan Ltd., eutectic mixture of 1-hydroxycyclohexyl phenyl ketone and benzophenone at a molar ratio of 1:1) at 5% by mass per solid content of the active energy ray-curable aqueous resin composition, thereby preparing an intended active energy ray-curable aqueous coating material.

[0080]

[Formation of cured coating film for evaluation]

An ABS (acrylonitrile-butadiene-styrene copolymer) plate and a PC (polycarbonate) plate were coated by spraying the active energy ray-curable aqueous coating material so that the film thickness after drying was 10  $\mu\text{m}$ , pre-dried for 10 minutes at a temperature of 60°C in a dryer, and then irradiated with ultraviolet light with an irradiation amount of 0.8 J/cm<sup>2</sup> by using a high-pressure mercury lamp with an output of 80 W/cm, forming a cured coating film for evaluation.

[0081]

[Evaluation of adhesion of coating film]

The coating film on the ABS plate or PC plate was cut with a cutter to make 10 × 10 1-mm square cuts, and a peeling test with a cellophane tape was performed to evaluate coating film adhesion based on the number of remaining squares according to the following criteria.

A: 95 to 100

B: 60 to 94

C: 59 or less

[0082]

[Evaluation of warm-water resistance]

The cured coating film on the ABS plate was immersed together

with the ABS plate as a substrate in warm water of 80°C for 2 hours, then taken out, and dried at 25°C for 2 hours. Then, the same peeling test with a cellophane tape as described above was performed to evaluate coating film adhesion after immersion in warm water based on the number of remaining squares according to the following criteria.

A: 95 to 100

B: 60 to 94

C: 59 or less

[0083]

[Evaluation of chemical resistance]

The cured coating film on the ABS plate was immersed together with the ABS plate as a substrate in an aqueous NaOH solution of 60°C with pH 9 for 1 hour, then taken out, and dried at 25°C for 1 hour. Then, the same peeling test with a cellophane tape as described above was performed to evaluate chemical resistance based on the number of remaining squares according to the following criteria.

A: 95 to 100

B: 60 to 94

C: 59 or less

[0084]

Table 2 shows the evaluation results of Examples 1 to 4. [0085]

[Table 2]

Table 2	Example 1	Example 2	Example 3	Example 4
Active energy ray-curable aqueous resin composition	(1)	(2)	(3)	(4)
Acrylic polymer (A)	A-1	A-2	A-3	A-2
Urethane (meth)acrylate (B)	B-1	B-1	B-1	B-1
Polycarbonatediol (P)				P-1
Polyfunctional (meth)acrylate (C)	EOTMPTA	EOTMPTA	EOTMPTA	
Mass ratio (A/B)	0.7	0.7	0.6	0.7
Acid value of reaction product (X) (mgKOH/g)	27	26	24	30
Nonvolatile content (% by mass)	40.4	40.5	42.8	35.5
Viscosity (millipascal seconds)	260	250	190	200
pH	7.0	7.0	7.0	7.0
Coating film adhesion (ABS)	A	A	A	A
Coating film adhesion (PC)	B	B	B	A
Warm-water resistance	A	A	A	A
Chemical resistance	A	A	A	B

[0086]

Table 3 shows the evaluation results of Examples 5 to 7 and Comparative Examples 1 and 2.

Table 2	Example 5	Example 6	Example 7	Comparative Example 1	Comparative Example 2
Active energy ray-curable aqueous resin composition	(5)	(6)	(7)	(R1)	(R2)
Acrylic polymer (A)	A-2	A-2	A-2	A-1	A-1
Urethane (meth)acrylate (B)	B-2	B-3	B-1	RB-1	RB-1
Polyfunctional (meth)acrylate (C)	EOTMPTA	EOTMPTA		EOTMPTA	
Mass ratio (A/B)	0.7	0.7	0.7	1.1	1.1
Acid value of reaction product (X) (mgKOH/g)	25	26	26	33	33
Nonvolatile content (% by mass)	44.1	43.2	43.2	38.2	38.2
Viscosity (millipascal seconds)	280	290	200	180	165
pH	7.0	7.0	7.0	7.0	7.0
Coating film adhesion (ABS)	A	A	A	B	C
Coating film adhesion (PC)	A	B	B	C	C
Warm-water resistance	A	A	A	C	C
Chemical resistance	A	A	B	B	C

[0087]

Abbreviations in Table 2 are as follows.

EOTEMPA: ethylene oxide adduct (about 1-mole ethylene oxide adduct per acrylate) of trimethylolpropane triacrylate

[0088]

It was confirmed that the coating film formed from the active energy ray-curable aqueous resin composition of the present invention has excellent coating film adhesion, warm-water resistance, and chemical resistance.

[0089]

On the other hand, in Comparative Examples 1 and 2 not using the urethane (meth)acrylate (B) having a carboxyl group and two or more (meth)acryloyl groups, which was an essential component of the present invention, it was confirmed that the resultant coating film has unsatisfactory coating film adhesion, warm-water resistance, and chemical resistance.

## [CLAIMS]

[Claim 1]

An active energy ray-curable aqueous resin composition comprising:

a reaction product (X) of a hydroxyl group-having acrylic polymer (A) and an isocyanate group-having urethane (meth)acrylate (B); and

an aqueous medium (Y),

wherein the urethane (meth)acrylate (B) has a carboxyl group and two or more (meth)acryloyl groups.

[Claim 2]

The active energy ray-curable aqueous resin composition according to Claim 1, wherein the urethane (meth)acrylate (B) is a reaction product of a polyisocyanate (b1), a carboxyl group-having polyol (b2), and a hydroxyl group-having polyfunctional (meth)acrylate (b3).

[Claim 3]

The active energy ray-curable aqueous resin composition according to Claim 1 or 2, further comprising polyfunctional (meth)acrylate (C).

[Claim 4]

The active energy ray-curable aqueous resin composition according to any one of Claims 1 to 3, wherein the reaction product (X) is a reaction product containing polycarbonate diol (P) as an essential raw material.

[Claim 5]

An active energy ray-curable aqueous coating material comprising the active energy ray-curable aqueous resin composition according to any one of Claims 1 to 4.

[Claim 6]

An article comprising the active energy ray-curable aqueous coating material according to Claim 5 coated thereon.

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2020/124346

<b>A. CLASSIFICATION OF SUBJECT MATTER</b>		
C08G 18/06(2006.01)i; C08G 18/67(2006.01)i; C08F 290/06(2006.01)i; C08F 299/06(2006.01)i; C08G 18/50(2006.01)i; C08F 283/00(2006.01)i; C09D 175/14(2006.01)i; C09D 133/14(2006.01)i; C09D 4/02(2006.01)i		
According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b>		
Minimum documentation searched (classification system followed by classification symbols) C08G, C08F, C09D		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) CNABS; SIPOABS; DWPI; CNKI; WEB OF SCIENCE: hydroxyl, aqueous, composition, acrylic, acrylate, isocyanate, urethane, acryloyl		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
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<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input checked="" type="checkbox"/> See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search <b>19 July 2021</b>		Date of mailing of the international search report <b>27 July 2021</b>
Name and mailing address of the ISA/CN <b>National Intellectual Property Administration, PRC 6, Xitucheng Rd., Jimen Bridge, Haidian District, Beijing 100088 China</b>		Authorized officer <b>YAN,Laiyan</b>
Facsimile No. (86-10)62019451		Telephone No. 86-010-62084471

**INTERNATIONAL SEARCH REPORT**

International application No.

**PCT/CN2020/124346**

<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
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**Information on patent family members**

International application No.

**PCT/CN2020/124346**

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