

DESCRIPTION

WATER-BASED ADHESIVE AGENT COMPOSITION AND METHOD FOR PRODUCING SAME

5

TECHNICAL FIELD

[0001]

The present invention relates to a water-based pressure-sensitive adhesive composition and a method for
10 producing the same.

BACKGROUND ART

[0002]

Pressure-sensitive adhesives are classified to various
15 types and each type of pressure-sensitive adhesives that differ in performance (e.g., adhesion, holding power, heat resistance, moisture-heat resistance, and water resistance) has been known. In particular, an acrylic-based pressure-sensitive adhesive exhibits excellent adhesion, holding power, and the like, and
20 has been widely applied. The acrylic-based pressure-sensitive adhesive may be obtained by subjecting an acrylic-based monomer and the like to emulsion polymerization. A technique that incorporates a tackifier (tackifying resin) in the reaction system used for emulsion polymerization has been proposed in
25 order to further improve the adhesion of the acrylic-based pressure-sensitive adhesive (see Patent Documents 1 to 3, for example).

[0003]

:According to these disclosed techniques, the acrylic-based pressure-sensitive adhesive is obtained by a method that effects emulsion polymerization using a large amount of a polyoxyethylene rosin ester-based emulsifier, or a method that dissolves the tackifier in the monomers, and effects emulsion polymerization while finely dispersing the emulsified droplets using a high-pressure homogenizer (miniemulsion polymerization).

10 RELATED-ART DOCUMENT

PATENT DOCUMENT

[0004]

Patent Document 1: JP-A-8-301950

Patent Document 2: JP-A-2001-348551

15 Patent Document 3: JP-A-2003-327933

SUMMARY OF THE INVENTION

TECHNICAL PROBLEM

[0005]

20 However, the above techniques have a problem in that it is difficult to improve water resistance and adhesion in combination. Moreover, since a complex process that dissolves the tackifier in the monomers, and disperses the emulsified droplets is required to effect emulsion polymerization, a deterioration in productivity occurs.

[0006]

The present invention was conceived in view of the above

problems. An object of the present invention is to provide a technique that relates to a pressure-sensitive adhesive that exhibits high water resistance and high adhesion in combination.

5 SOLUTION TO PROBLEM

[0007]

The present invention provides the following water-based pressure-sensitive adhesive composition and method for producing the same.

10 [0008]

[1] A water-based pressure-sensitive adhesive composition including a copolymer dispersion obtained by subjecting 0.1 to 10 parts by mass of (a) an ethylenically unsaturated carboxylic acid monomer, 60 to 99 parts by mass of (b) an acrylate monomer that includes an alkyl group having 4 to 12 carbon atoms, and 15 0 to 39.9 parts by mass of (c) an ethylenically unsaturated monomer (provided that (a)+(b)+(c)=100 parts by mass) to emulsion polymerization in a reaction system that includes 0.1 to 10 parts by mass of a water-insoluble tackifier having an average particle size of 0.05 to 1.00 μm , particles included 20 in the copolymer dispersion having an average particle size of 0.3 to 10 μm , and the copolymer dispersion having a glass transition temperature of -70 to -30°C and a tetrahydrofuran-insoluble content of 70 mass% or less.

25 [0009]

[2] The water-based pressure-sensitive adhesive composition according to [1], further including a crosslinking agent.

[0010]

[3] A method for producing a water-based pressure-sensitive adhesive composition including effecting emulsion polymerization while adding 0.1 to 10 parts by mass of (a) an ethylenically unsaturated carboxylic acid monomer, 60 to 99 parts by mass of (b) an acrylate monomer that includes an alkyl group having 4 to 12 carbon atoms, and 0 to 39.9 parts by mass of (c) an ethylenically unsaturated monomer (provided that (a)+(b)+(c)=100 parts by mass) to a dispersion prepared by dispersing 0.1 to 10 parts by mass of a water-insoluble tackifier having an average particle size of 0.05 to 1.00 μm in a medium to obtain a copolymer dispersion.

[0011]

[4] A method for producing a water-based pressure-sensitive adhesive composition including adding 0.1 to 10 parts by mass of a water-insoluble tackifier having an average particle size of 0.05 to 1.00 μm to a pre-emulsion that includes 0.1 to 10 parts by mass of (a) an ethylenically unsaturated carboxylic acid monomer, 60 to 99 parts by mass of (b) an acrylate monomer that includes an alkyl group having 4 to 12 carbon atoms, 0 to 39.9 parts by mass of (c) an ethylenically unsaturated monomer (provided that (a)+(b)+(c)=100 parts by mass), a medium, and an emulsifier, and subjecting the pre-emulsion to emulsion polymerization to obtain a copolymer dispersion.

[0012]

[5] The method for producing a water-based pressure-sensitive adhesive composition according to [3] or [4], further including

adding a crosslinking agent to the copolymer dispersion.

ADVANTAGEOUS EFFECTS OF THE INVENTION

[0013]

The water-based pressure-sensitive adhesive composition
5 according to the present invention exhibits high water
resistance and high adhesion. The method for producing a
water-based pressure-sensitive adhesive composition according
to the present invention can produce a water-based
pressure-sensitive adhesive composition that exhibits high
10 water resistance and high adhesion through a simple process.

DESCRIPTION OF EMBODIMENTS

[0014]

Exemplary embodiments of the present invention are
15 described below. Note that the present invention is not limited
to the following exemplary embodiments. Various modifications,
revisions, and improvements may be made of the following
exemplary embodiments without departing from the scope of the
present invention.

20 [0015]

A water-based pressure-sensitive adhesive composition
according to the present invention includes a copolymer
dispersion obtained by subjecting 0.1 to 10 parts by mass of
(a) an ethylenically unsaturated carboxylic acid monomer
25 (hereinafter may be referred to as "component (a)"), 60 to 99
parts by mass of (b) an acrylate monomer that includes an alkyl
group having 4 to 12 carbon atoms (hereinafter may be referred

to as "component (b)"), and 0 to 39.9 parts by mass of (c) an ethylenically unsaturated monomer (hereinafter may be referred to as "component (c)") (provided that (a)+(b)+(c)=100 parts by mass) to emulsion polymerization in a reaction system that
5 includes 0.1 to 10 parts by mass of a water-insoluble tackifier having an average particle size of 0.05 to 1.00 μm . Furthermore, in the water-based pressure-sensitive adhesive composition according to the present invention, the copolymer dispersion included in the water-based pressure-sensitive adhesive
10 composition has a glass transition temperature of -70 to -30°C and a tetrahydrofuran-insoluble content of 70 mass% or less. Moreover, in the water-based pressure-sensitive adhesive composition according to the present invention, particles included in the copolymer dispersion included in the
15 water-based pressure-sensitive adhesive composition have an average particle size of 0.3 to 10 μm .

[0016]

The term "copolymer dispersion" used in this specification refers to a dispersion in which particles of an acrylic-based
20 copolymer obtained by copolymerizing the component (a), the component (b), and the component (c), particles of the water-insoluble tackifier, particles formed of the acrylic-based copolymer and the water-insoluble tackifier, and the like are dispersed in a medium (e.g., water).

25 [0017]

The term "average particle size" used herein in connection with the particles included in the copolymer dispersion refers

to the average particle size of all of the particles included in the copolymer dispersion including particles of the acrylic-based copolymer, particles of the water-insoluble tackifier, particles formed of the acrylic-based copolymer and the water-insoluble tackifier, and the like. The term "average particle size" used in this specification in connection with the particles included in the copolymer dispersion refers to a volume average particle size measured by a laser diffraction/scattering method.

10 [0018]

The water-based pressure-sensitive adhesive composition according to the present invention exhibits excellent stability and an excellent drying capability since the particles included in the copolymer dispersion have an average particle size of 0.3 to 10 μm . Specifically, in the water-based pressure-sensitive adhesive composition according to the present invention, it is preferable that the particles included in the copolymer dispersion included in the water-based pressure-sensitive adhesive composition have an average particle size of 0.5 to 5.0 μm , and more preferably 1.0 to 3.0 μm , from the viewpoint of ensuring that the water-based pressure-sensitive adhesive composition exhibits moderate viscosity and high water resistance. When the average particle size of the particles included in the copolymer dispersion is 0.3 μm or more, the viscosity of the copolymer dispersion does not increase to a large extent, and the solid content in the copolymer dispersion can be increased. When the average

particle size of the particles included in the copolymer dispersion is 10 μm or less, the viscosity of the copolymer dispersion does not decrease to a large extent (i.e., the copolymer dispersion exhibits moderate viscosity).

5 [0019]

Since the reaction system used for emulsion polymerization for obtaining the copolymer dispersion included in the water-based pressure-sensitive adhesive composition according to the present invention includes the water-insoluble tackifier
10 having an average particle size of 0.05 to 1.00 μm , the copolymerization reaction proceeds so that the particles of the water-insoluble tackifier serve as seeds.

[0020]

The water-based pressure-sensitive adhesive composition
15 according to the present invention exhibits high adhesion and high water resistance in combination as a result of producing the copolymer dispersion through emulsion polymerization in the reaction system that includes 0.1 to 10 parts by mass of the water-insoluble tackifier having an average particle size of
20 0.05 to 1.00 μm (provided that the total amount of the ethylenically unsaturated carboxylic acid monomer (a), the acrylate monomer (b) that includes an alkyl group having 4 to 12 carbon atoms, and the ethylenically unsaturated monomer (c) is 100 parts by mass).

25 [0021]

Especially, as shown in the water-based pressure-sensitive adhesive composition according to the

present invention, the water-based pressure-sensitive adhesive composition exhibits sufficiently high adhesion when the reaction system used for emulsion polymerization for obtaining the copolymer dispersion includes the

5 water-insoluble tackifier in an amount of 0.1 parts by mass or more. Also, as shown in the water-based pressure-sensitive adhesive composition according to the present invention, the water-based pressure-sensitive adhesive composition exhibits sufficiently high water resistance when the reaction system
10 used for emulsion polymerization for obtaining the copolymer dispersion includes the water-insoluble tackifier in an amount of 10 parts by mass or less.

[0022]

It is preferable that the reaction system used for emulsion
15 polymerization for obtaining the copolymer dispersion include 1.0 to 5.0 parts by mass of the water-insoluble tackifier (provided that the total amount of the ethylenically unsaturated carboxylic acid monomer (a), the acrylate monomer (b) that includes an alkyl group having 4 to 12 carbon atoms,
20 and the ethylenically unsaturated monomer (c) is 100 parts by mass) from the viewpoint of ensuring that the water-based pressure-sensitive adhesive composition according to the present invention exhibits improved adhesion and improved water resistance.

25 [0023]

In the water-based pressure-sensitive adhesive composition according to the present invention, since the

water-insoluble tackifier included in the reaction system used for emulsion polymerization for obtaining the copolymer dispersion has an average particle size of 0.05 to 1.00 μm , the water-insoluble tackifier is easily dispersed during emulsion polymerization. Therefore, even when the water-insoluble tackifier is included in the reaction system used for emulsion polymerization in an amount of 0.1 to 10 parts by mass, excellent stability is achieved during polymerization, and inhibition of the copolymerization reaction can be suppressed.

10 [0024]

When effecting emulsion polymerization for obtaining the copolymer dispersion, the water-insoluble tackifier may be dispersed in a medium (e.g., water) in advance, or may be added to a pre-emulsion that includes the monomers. The copolymer dispersion obtained by such emulsion polymerization provides the water-based pressure-sensitive adhesive composition according to the present invention with high tackiness and high water resistance.

[0025]

20 In the water-based pressure-sensitive adhesive composition according to the present invention, it is preferable that the water-insoluble tackifier included in the reaction system used for emulsion polymerization for obtaining the copolymer dispersion have an average particle size of 0.10 to 0.80 μm from the viewpoint of ensuring that the water-insoluble tackifier exhibits dispersion stability, and the acrylic-based copolymer has an appropriate average particle

size.

[0026]

The term "average particle size" used herein in connection with the water-insoluble tackifier in this specification refers to a volume average particle size measured by a laser diffraction/scattering method.

[0027]

The water-based pressure-sensitive adhesive composition according to the present invention exhibits sufficiently improved adhesion and sufficiently improved water resistance since the amount of the ethylenically unsaturated carboxylic acid monomer (a) is 0.1 to 10 parts by mass based on 100 parts by mass (in total) of the ethylenically unsaturated carboxylic acid monomer (a), the acrylate monomer (b) that includes an alkyl group having 4 to 12 carbon atoms, and the ethylenically unsaturated monomer (c) subjected to the copolymerization reaction for obtaining the copolymer dispersion.

[0028]

The water-based pressure-sensitive adhesive composition according to the present invention exhibits an improved anchor effect and improved adhesion since the copolymer dispersion has a glass transition temperature of -70 to -30°C.

[0029]

The ethylenically unsaturated carboxylic acid monomer (a) used to produce the water-based pressure-sensitive adhesive composition according to the present invention is an α,β -unsaturated carboxylic acid. Examples of the

ethylenically unsaturated carboxylic acid monomer (a) used to produce the water-based pressure-sensitive adhesive composition according to the present invention include acrylic acid, methacrylic acid, itaconic acid, maleic acid, fumaric acid, mono[2-(meth)acryloyloxyethyl] phthalate (half ester),
5 mono[2-(meth)acryloyloxyethyl] succinate, carboxyethyl acrylate, and the like. These ethylenically unsaturated carboxylic acid monomers may be used either alone or in combination. In the present invention, it is preferable to use
10 acrylic acid or methacrylic acid as the ethylenically unsaturated carboxylic acid monomer (a) since excellent stability can be achieved during polymerization, and water resistance can be improved.

[0030]

15 Examples of the acrylate monomer (b) that includes an alkyl group having 4 to 12 carbon atoms used to produce the water-based pressure-sensitive adhesive composition according to the present invention include n-butyl acrylate, i-butyl acrylate, t-butyl acrylate, 2-ethylhexyl acrylate, n-octyl acrylate,
20 isononyl acrylate, lauryl acrylate, and the like. It is preferable to use 2-ethylhexyl acrylate, n-octyl acrylate, or isononyl acrylate as the acrylate monomer (b) that includes an alkyl group having 4 to 12 carbon atoms since adhesion and water resistance can be improved.

25 [0031]

The ethylenically unsaturated monomer (c) used to produce the water-based pressure-sensitive adhesive composition

according to the present invention is a monomer that is copolymerizable with the ethylenically unsaturated carboxylic acid monomer (a) and the acrylate monomer (b) that includes an alkyl group having 4 to 12 carbon atoms.

5 [0032]

Examples of the ethylenically unsaturated monomer (c) used to produce the water-based pressure-sensitive adhesive composition according to the present invention include alkyl acrylates and alkyl methacrylates that include an alkyl group
10 having 3 or less carbon atoms, such as methyl acrylate, methyl methacrylate, ethyl acrylate, ethyl methacrylate, isopropyl acrylate, and isopropyl methacrylate; cyclic alkyl (meth)acrylates such as cyclohexyl (meth)acrylate; aromatic (meth)acrylates such as phenoxymethyl (meth)acrylate and
15 benzyl (meth)acrylate; aliphatic (meth)acrylates such as a hydroxyalkyl acrylate, a hydroxyalkyl methacrylate, polyoxyethylene (meth)acrylate, methoxyethyl acrylate, ethoxymethyl acrylate, glycidyl acrylate, and glycidyl methacrylate; (meth)acrylamides such as acrylamide,
20 methacrylamide, N-methylolacrylamide, N-methoxymethylacrylamide, and N-methoxybutylacrylamide; aldo group and/or keto group-containing radically polymerizable monomers such as vinyl methyl ketone, vinyl ethyl ketone, vinyl n-propyl ketone, vinyl i-propyl ketone, vinyl
25 n-butyl ketone, vinyl i-butyl ketone, vinyl t-butyl ketone, vinyl phenyl ketone, vinyl benzyl ketone, divinyl ketone, and diacetoneacrylamide; nitrile group-containing unsaturated

compounds such as (meth)acrylonitrile, crotonitrile,
2-cyanoethyl (meth)acrylate, 2-cyanopropyl (meth)acrylate,
and 3-cyanopropyl (meth)acrylate; monovinyl aromatic
compounds such as styrene, o-vinyltoluene, m-vinyltoluene,
5 p-vinyltoluene, p-ethylvinylstyrene, α -methylstyrene, and
 α -fluorostyrene; vinyl halides such as vinyl chloride and
vinylidene chloride; vinyl esters such as vinyl propionate; and
the like.

[0033]

10 Examples of an ethylenically unsaturated sulfonic acid
monomer that may be used as the ethylenically unsaturated
monomer (c) used to produce the water-based pressure-sensitive
adhesive composition according to the present invention include
isoprenesulfonic acid, styrene-3-sulfonic acid,
15 styrene-4-sulfonic acid, α -methylstyrene-3-sulfonic acid,
 α -methylstyrene-4-sulfonic acid,
2-acrylamide-2-methylpropanesulfonic acid,
allylalkylsulfonic acids, sulfates of polyoxyethylene alkyl
allyl ethers, sulfates of polyoxyethylene polyoxypropylene
20 alkyl allyl ethers, and the like. These ethylenically
unsaturated sulfonic acid monomers may be used either alone or
in combination.

[0034]

A salt (e.g., sodium salt, potassium salt, or ammonium
25 salt) of the above ethylenically unsaturated sulfonic acid
monomer may be used as the ethylenically unsaturated monomer
(c) used to produce the water-based pressure-sensitive adhesive

composition according to the present invention. These salts of the ethylenically unsaturated sulfonic acid monomer may be used in the present invention either alone or in combination.

[0035]

5 Still further examples of the ethylenically unsaturated monomer (c) used to produce the water-based pressure-sensitive adhesive composition according to the present invention include carbonyl group-containing unsaturated compounds such as caprolactone-modified acetoxy (meth)acrylate, and

10 commercially available products such as Placel ATFA1, Placel ATFA2, Placel ATFM1, and Placel ATFM2 (manufactured by Daicel Corporation.), γ -glycidoxypropyltrimethoxysilane,

γ -glycidoxypropyltriethoxysilane,

γ -methacryloxypropyltrimethoxysilane,

15 γ -methacryloxypropyltriethoxysilane,

γ -mercaptopropyltrimethoxysilane,

γ -mercaptopropyltriethoxysilane,

3,4-epoxycyclohexylethyltrimethoxysilane,

3,4-epoxycyclohexylethyltriethoxysilane,

20 vinyltrimethoxysilane, vinyltriethoxysilane, and the like.

Among the ethylenically unsaturated monomer, in the present invention, it is preferable to use methyl methacrylate, a hydroxyalkyl methacrylate, methoxyethyl acrylate,

ethoxymethyl acrylate, γ -methacryloxypropyltrimethoxysilane,

25 or γ -methacryloxypropyltriethoxysilane from the viewpoint of ensuring that excellent water resistance, adhesion, and holding power are obtained.

[0036]

Examples of the water-insoluble tackifier that is used to produce the water-based pressure-sensitive adhesive composition according to the present invention include natural
5 rosins such as gum rosin, tall oil rosin, and wood rosin, purified products thereof, polymerized rosins obtained by subjecting these rosins to disproportionation, hydrogenation, dehydration, dimerization, or the like, modified rosins such as a sulfonated rosin, addition reaction products of rosin and
10 maleic acid, maleic anhydride, fumaric acid, acrylic acid, or the like, esters, partial esters, or partial amidation products thereof, terpene phenol, and the like. These water-insoluble tackifiers may be used either alone or in combination. In the present invention, it is preferable to use an aqueous dispersion
15 of terpene phenol or a polymerized rosin as the water-insoluble tackifier from the viewpoint of adhesion.

[0037]

The water-based pressure-sensitive adhesive composition according to the present invention may include a crosslinking
20 agent. In particular, it is preferable that the reaction system used for emulsion polymerization for obtaining the copolymer dispersion include 0.1 to 1.0 parts by mass of the water-insoluble tackifier having an average particle size of 0.05 to 1.00 μm , and the water-based pressure-sensitive
25 adhesive composition according to the present invention include a crosslinking agent before application. The anchor effect and the holding power can be improved when it includes the

crosslinking agent before application.

[0038]

Examples of the crosslinking agent that may be used for the water-based pressure-sensitive adhesive composition according to the present invention include normal crosslinking agents such as a polyfunctional isocyanate-based crosslinking agent, an epoxy-based crosslinking agent, an oxazoline-based crosslinking agent, an aziridine-based crosslinking agent, a metal chelate-based crosslinking agent, and a dihydrazide compound (e.g., adipic acid dihydrazide). These crosslinking agents may be either oil-soluble or water-soluble. These crosslinking agents may be used in the present invention either alone or in combination. In particular, a polyglycidyl compound that includes two or more epoxy groups (i.e., epoxy-based crosslinking agent) (e.g., ethylene glycol diglycidyl ether, polyethylene glycol diglycidyl ether, propylene glycol diglycidyl ether, polypropylene glycol diglycidyl ether, neopentyl glycol diglycidyl ether, 1,6-hexanediol diglycidyl ether, dibromoneopentyl glycol diglycidyl ether, o-phthalic acid diglycidyl ester, glycerol polyglycidyl ether, trimethylolpropane polyglycidyl ether, diglycerol polyglycidyl ether, polyglycerol polyglycidyl ether, sorbitol polyglycidyl ether, N,N,N',N'-tetraglycidyl-m-xylylenediamine, N,N,N',N'-pentaglycidyl diethylenetriamine, and N,N,N',N'-tetraglycidylethylenediamine) may be used in the present invention as the crosslinking agent. Among these, it

is preferable to use in the present invention polyglycerol polyglycidyl ether or polyethylene glycol diglycidyl ether since miscibility and adhesion can be improved.

[0039]

5 The water-based pressure-sensitive adhesive composition according to the present invention may include various additives used for a normal water-based pressure-sensitive adhesive composition, such as a white pigment, a thickener, a wetting agent, an alkaline chemical, a stabilizer, an
10 emulsifier, a tackifier other than the above water-insoluble tackifier, a preservative, and an anti-mold agent.

[0040]

When forming a pressure-sensitive adhesive layer of a pressure-sensitive adhesive label, sheet, or tape using the
15 water-based pressure-sensitive adhesive composition according to the present invention, paper, cloth, polyvinyl chloride, polypropylene, a polyester, a polyimide, a foam, a metal foil, or the like may be used as the substrate of the pressure-sensitive adhesive label, sheet, or tape. Examples
20 of an adherend for the pressure-sensitive adhesive label, sheet, or tape include a plastic, a metal, paper, glass, silicone, a ceramic, a skin, and the like.

[0041]

The water-based pressure-sensitive adhesive composition
25 according to the present invention may be produced by the following method, for example.

[0042]

The copolymer dispersion included in the water-based pressure-sensitive adhesive composition according to the present invention may be obtained by subjecting a mixture of the ethylenically unsaturated carboxylic acid monomer (a), the
5 acrylate monomer (b) that includes an alkyl group having 4 to 12 carbon atoms, and the ethylenically unsaturated monomer (c) (hereinafter referred to as "monomer mixture") to emulsion polymerization.

[0043]

10 More specifically, in the present invention the monomer mixture and water are emulsified using an emulsifier to prepare a pre-emulsion, the water-insoluble tackifier, an initiator, and a molecular weight modifier are added to the pre-emulsion, and the mixture is normally subjected to polymerization in an
15 inert atmosphere. A copolymer dispersion is thus obtained that includes particles of the acrylic-based copolymer, particles of the water-insoluble tackifier, and particles formed of the acrylic-based copolymer and the water-insoluble tackifier.

[0044]

20 Alternatively, in the present invention a dispersion in which the water-insoluble tackifier is dispersed in a medium (e.g., water) may be prepared in advance, and emulsion polymerization may be effected while adding the monomer mixture and an emulsifier to the dispersion (see the examples for
25 details).

[0045]

The above two types of emulsion polymerization can be

advantageously implemented without grinding and dissolving the tackifier in the monomers, or dispersing emulsified droplets using a high-pressure homogenizer or the like. Specifically, in the present invention emulsion polymerization can be easily
5 implemented.

[0046]

In the present invention, the monomer mixture may be polymerized while continuously or intermittently supplying the pre-emulsion and the initiator to the reaction system.

10 [0047]

In the present invention, a persulfate or a redox initiator may be used as the initiator. The redox initiator is an initiator that includes an oxidizing agent and a reducing agent in combination. The redox initiator may include only one type
15 of oxidizing agent, or may include different types of oxidizing agent. The redox initiator may include only one type of reducing agent, or may include different types of reducing agent.

[0048]

20 Examples of the oxidizing agent used for the redox initiator include persulfates such as potassium persulfate, sodium persulfate, and ammonium persulfate; peroxides such as hydrogen peroxide, t-butyl hydroperoxide, t-butylperoxymaleic acid, succinic peroxide, benzoyl peroxide, cumene
25 hydroperoxide, diisopropyl peroxydicarbonate, cumyl peroxyneodecanoate, cumyl peroxyoctoate, diisopropylbenzene hydroperoxide, p-menthane hydroperoxide, and

2,2-bis(4,4-di-t-butylperoxycyclohexyl)propane; and the like.

[0049]

On the other hand, examples of the reducing agent used for the redox initiator include sodium hydrogen sulfite, sodium dithionite, sodium thiosulfate, rongalite, ascorbic acid, reducing sugars such as fructose, iron salts such as ferrous sulfate and ferric sulfate, and the like. A chelating agent such as sodium ethylenediaminetetraacetate may optionally be used in combination with the reducing agent.

[0050]

When obtaining the copolymer dispersion included in the water-based pressure-sensitive adhesive composition according to the present invention using the redox initiator, the following combinations A to C are preferable as the combination of the oxidizing agent, the reducing agent, and the chelating agent, for example.

Combination A: persulfate, sodium hydrogen sulfite, and ferrous sulfate

Combination B: t-butyl hydroperoxide, sodium hydrogen sulfite, and ferrous sulfate

Combination C: p-menthane hydroperoxide, ferrous sulfate, sodium ethylenediaminetetraacetate, and sodium formaldehyde sulfoxylate

[0051]

In the present invention, the redox initiator is preferably used in an amount of 0.01 to 5.0 parts by mass, more

preferably 0.05 to 3.0 parts by mass, and still more preferably 0.1 to 1.0 part by mass, based on 100 parts by mass (in total) of the ethylenically unsaturated carboxylic acid monomer (a), the acrylate monomer (b) that includes an alkyl group having 4 to 12 carbon atoms, and the ethylenically unsaturated monomer (c). When using only a persulfate as the oxidizing agent used for the redox initiator, the redox initiator is preferably used in an amount of 0.1 to 1.0 part by mass based on 100 parts by mass (in total) of the ethylenically unsaturated carboxylic acid monomer (a), the acrylate monomer (b) that includes an alkyl group having 4 to 12 carbon atoms, and the ethylenically unsaturated monomer (c).

[0052]

Examples of the emulsifier that may be used when obtaining the copolymer dispersion included in the water-based pressure-sensitive adhesive composition according to the present invention include surfactants such as a polyoxyethylene alkyl ether, a polyoxyethylene alkyl sulfate salt, a polyoxyethylene polycyclic phenyl ether sulfate salt, a sodium polyoxyethylene alkylsuccinate, sodium laurylsulfate, and sodium dodecylbenzenesulfonate. Specific examples of the emulsifier include reactive emulsifiers such as Latemul S-180A and Latemul PD-104 (manufactured by Kao Corporation); Eleminol JS-2 (manufactured by Sanyo Chemical Industries, Ltd.); Aqualon KH-10 (manufactured by Dai-ichi Kogyo Seiyaku Co., Ltd.); Adeka Reasoap SE-10N and Adeka Reasoap SR-10N (manufactured by Adeka Corporation); Antox MS-60 (manufactured by Nippon Nyukazai Co.,

Ltd.); and Surfmer FP-120 (manufactured by Toho Chemical Industry Co., Ltd.).

[0053]

The emulsifier is preferably used in an amount of 0.2 to 7.0 parts by mass, more preferably 0.5 to 5.0 parts by mass, and still more preferably 0.7 to 3.0 parts by mass, based on 100 parts by mass (in total) of the ethylenically unsaturated carboxylic acid monomer (a), the acrylate monomer (b) that includes an alkyl group having 4 to 12 carbon atoms, and the ethylenically unsaturated monomer (c).

[0054]

Examples of the molecular weight modifier that may be used when obtaining the copolymer dispersion included in the water-based pressure-sensitive adhesive composition according to the present invention include butylmercaptan, dodecylmercaptan, octyl thioglycolate, isopropyl alcohol, methanol, carbon tetrachloride, and the like.

[0055]

In the present invention, the molecular weight modifier is preferably used in an amount of 0.001 to 0.50 parts by mass, more preferably 0.003 to 0.30 parts by mass, and still more preferably 0.005 to 0.20 parts by mass, based on 100 parts by mass (in total) of the ethylenically unsaturated carboxylic acid monomer (a), the acrylate monomer (b) that includes an alkyl group having 4 to 12 carbon atoms, and the ethylenically unsaturated monomer (c).

[0056]

In the present invention, a copolymer dispersion in which particles of the acrylic-based copolymer having the desired weight average molecular weight (Mw) and the desired tetrahydrofuran-insoluble content (THF-insoluble content) are dispersed can be obtained by appropriately selecting the type and the amount of the molecular weight modifier.

[0057]

The water-based pressure-sensitive adhesive composition according to the present invention exhibits sufficient adhesion and sufficient water resistance, and exhibits high cohesive force due to interaction between the carboxyl groups included in the particles of the acrylic-based copolymer. As a result, the water-based pressure-sensitive adhesive composition according to the present invention exhibits excellent holding power. Since the water-based pressure-sensitive adhesive composition according to the present invention has a tetrahydrofuran-insoluble content (THF-insoluble content) of 70% or less, the water-based pressure-sensitive adhesive composition easily penetrates a substrate when forming a pressure-sensitive adhesive layer, and an excellent anchor effect can be obtained. The above method for producing a water-based pressure-sensitive adhesive composition can produce a water-based pressure-sensitive adhesive composition that exhibits excellent water resistance and excellent adhesion with high productivity.

EXAMPLES

[0058]

The present invention is further described below by way of examples. Note that the present invention is not limited to the following examples.

5 [0059]

(1) Raw material

The following raw materials were used in the examples and comparative examples.

[0060]

10 (1-1) Monomer:

Component (a) (ethylenically unsaturated carboxylic acid monomer):

Acrylic acid (manufactured by Toagosei Co., Ltd.)

Methacrylic acid (manufactured by Kuraray Co., Ltd.)

15 [0061]

Component (b) (acrylate monomer):

2-Ethylhexyl acrylate (manufactured by Toagosei Co., Ltd.)

Butyl acrylate (manufactured by Toagosei Co., Ltd.)

[0062]

20 Component (c) (ethylenically unsaturated monomer):

Methyl methacrylate (manufactured by Mitsubishi Rayon Co., Ltd.)

Styrene (manufactured by Mitsubishi Chemical Corporation)

Methoxyethyl acrylate (manufactured by Osaka Organic Chemical

25 Industry Ltd.)

γ -Methacryloxypropyltrimethoxysilane (manufactured by Shin-Etsu Silicone Co., Ltd.)

2-Hydroxyethyl methacrylate (manufactured by Osaka Organic Chemical Industry Ltd.)

[0063]

(1-2) Water-insoluble tackifier:

5 Terpenephenol E200-NT (manufactured by Arakawa Chemical Industries, Ltd., average particle size: 0.66 μm)

Polymerized rosin E865-NT (manufactured by Arakawa Chemical Industries, Ltd., average particle size: 0.66 μm)

[0064]

10 (1-3) Water-soluble rosin-based emulsifier for emulsion polymerization:

EO-addition rosin ester DRA-1500 (manufactured by Toho Chemical Industry Co., Ltd., aqueous solution (average particle size could not be measured))

15 [0065]

(1-4) Emulsifier:

Non-reactive emulsifier: Newcol 707SF (manufactured by Nippon Nyukazai Co., Ltd.)

Reactive emulsifier: KH-1025 (manufactured by Dai-ichi Kogyo Seiyaku Co., Ltd.)

[0066]

(1-5) Other:

Thickener: UH-420 (manufactured by Adeka Corporation)

25 Wetting agent: Surflon S234 (manufactured by AGC Seimi Chemical Co., Ltd.)

[0067]

(2) Copolymerization reaction

Examples 1 to 3 and Comparative Examples 1 to 4

In Examples 1 to 3 and Comparative Examples 1 to 4, the components (a) to (c) (monomers) and the water-insoluble tackifier were mixed and reacted in the ratio shown in Table

1. Note that the amount (unit: parts by mass) of each component shown in Table 1 is based on 100 parts by mass of the components (a) to (c) (monomers) in total. The amount (unit: parts by mass) of each component shown below is also based on 100 parts by mass of the components (a) to (c) (monomers) in total unless

otherwise indicated. Specifically, a reaction vessel was charged with water and the water-insoluble tackifier dispersed in water in advance, and the mixture was stirred under a nitrogen stream to prepare a dispersion A. After heating the dispersion A to 70°C, a solution of the components (a) to (c) (monomers), 40 parts by mass of water, and 1 part by mass of the emulsifier "Newcol 707SF" were added to the dispersion A, and the mixture was stirred to effect pre-emulsification. A catalyst aqueous solution (0.1% ammonium persulfate aqueous solution) prepared in advance was added dropwise to the reaction vessel at 80°C over about 3 hours in parallel with the monomers, and the mixture was held at 80°C for about 1 hour. After cooling the mixture, 1.4 parts by mass of 25% aqueous ammonia was added to the mixture. The viscosity of the mixture was adjusted to about 25,000 mPa·s by gradually adding the thickener "UH-420", and 0.35 parts by mass of the wetting agent "Surflon S234" was added to the mixture to obtain a water-based pressure-sensitive adhesive composition.

[0068]

Example 4

In Example 4, emulsion polymerization was effected in the same manner as in Example 1, except that the components (a) to
5 (c) (monomers) and the water-insoluble tackifier were used in the ratio shown in Table 1, and 0.5 part by mass of the emulsifier "Newcol 707SF" and 0.5 part by mass of the emulsifier "KH-1025" were used.

[0069]

10 Comparative Examples 5 and 6

In Comparative Examples 5 and 6, emulsion polymerization was effected in the same manner as in Example 1, except that the components (a) to (c) (monomers) were used in the ratio shown in Table 1, and the dispersion A was prepared by dissolving the
15 water-soluble rosin-based emulsifier (EO-addition rosin ester DRA-1500) in water in the ratio shown in Table 1 instead of the water-insoluble tackifier.

[0070]

Comparative Example 7

20 In Comparative Example 7, emulsion polymerization was effected in the same manner as in Example 1, except that the raw materials were used in the ratio shown in Table 1, and the water-insoluble tackifier was dried at 100°C, ground using a mortar, and dissolved directly in the solution of the components
25 (a) to (c) (monomers) instead of using the dispersion A prepared by dispersing the water-insoluble tackifier in water.

[0071]

Comparative Example 8

In Comparative Example 8, emulsion polymerization was effected in the same manner as in Example 7, except that the raw materials were used in the ratio shown in Table 1. Note
5 that emulsion polymerization was effected without adding a powder of the water-insoluble tackifier, and a powder of the water-insoluble tackifier was added before application.

[0072]

A water-based pressure-sensitive adhesive composition
10 could be obtained in Examples 1 to 4 and Comparative Examples 1 to 4, 6, and 8. In Comparative Examples 5 and 7, a water-based pressure-sensitive adhesive composition could not be obtained since a large amount of aggregates were produced during emulsion polymerization.

[0073]

TABLE 1

Copolymerization reaction	Monomer component	Component (a)	Component (b)	Component (c)	Example 1	Example 2	Example 3	Example 4
					2.00	4.00	2.50	2.00
Properties	Adhesion performance (N/25 mm)	Acrylic acid	Methacrylic acid	2-Ethylhexyl acrylate	0.50	0.00	0.00	0.50
					77.00	77.00	79.80	77.00
					3.00	3.00	0.00	3.00
					12.00	12.00	12.50	12.00
					3.50	2.00	0.00	3.50
					0.00	0.00	3.00	0.00
					0.00	0.00	0.20	0.00
					2.00	2.00	2.00	2.00
					3.00	3.00	0.00	3.00
					0.00	0.00	3.00	3.00
					0.00	0.00	0.00	0.00
					99.9	99.8	99.8	99.5
					39	42	38	41
					-49	-49	-52	-51
					2.2	2.3	2.1	1.6
Properties	Adhesion performance (N/25 mm)	SUS 305	Polypropylene	Average particle size (μm)	12.3	11.3	10.9	13.1
					4.8	4.0	5.5	6.2
					Good	Excellent	Excellent	Good
					Good	Good	Excellent	Good
					Excellent	Good	Excellent	Excellent
	Water-whitening resistance	Holding power	Anchor effect	Water-whitening resistance	Reaction ratio (%)	THF-insoluble content (mass%)	Glass transition temperature (°C)	Average particle size (μm)

TABLE 1 (continued)

Copolymerization reaction	Monomer component	Component	Comp. Example 1	Comp. Example 2	Comp. Example 3	Comp. Example 4	Comp. Example 5	Comp. Example 6	Comp. Example 7	Comp. Example 8
	Monomer component	Component (a)	Acrylic acid							
			Methacrylic acid							
		Component (b)	2-Ethylhexyl acrylate							
			Butyl acrylate							
		Component (c)	Methyl methacrylate							
			Styrene							
			Methoxyethyl acrylate							
			γ -Methacryloxy-propyltrimethoxysilane							
			2-Hydroxyethyl methacrylate							
			Terpene phenol E200-NT							
	Water-insoluble tackifier		Polymersized rosin E865-NT							
			EO-addition rosin ester DRA-1500							
	Properties	Rosin-based emulsifier	0.00							
			99.8							
		Reaction ratio (%)	44							
			-49							
		THF-insoluble content (mass%)	97.3							
			30							
		Glass transition temperature (°C)	-49							
			-49							
		Average particle size (µm)	0.32							
			1.40							
	Adhesion performance	Adhesion (N/25 mm)	7.3							
			12.9							
	Holding power	Polypropylene	1.6							
			5.7							
	Water-whitening resistance	Anchor effect	Poor							
			Good							
			Good							
			Good							
			Good							
			Good							

*1: The water-insoluble tackifier was added directly to the monomer mixture (not emulsified).

*2: Emulsion polymerization was effected in the reaction system that did not include the water-insoluble tackifier, and the water-insoluble tackifier was added before application.

[0074]

The water-based pressure-sensitive adhesive compositions obtained in Examples 1 to 4 and Comparative Examples 1 to 4, 6, and 8 were evaluated as described below (see (3) to (10)).

5 [0075]

(3) Measurement of glass transition temperature

The glass transition temperature was measured in accordance with JIS K 7121. The results are shown in Table 1.

[0076]

10 (4) Measurement of average particle size

The average particle size was measured using a particle size analyzer "Microtrac MT3000" (manufactured by Nikkiso Co., Ltd.). The results are shown in Table 1.

[0077]

15 (5) Measurement of tetrahydrofuran-insoluble content
(THF-insoluble content)

The tetrahydrofuran-insoluble content (THF-insoluble content) was measured as described below. Specifically, 0.15 g of a dry film of the water-based pressure-sensitive adhesive composition was added to 50 mL of tetrahydrofuran, and dissolved
20 for 16 hours with stirring. After filtering the solution using a class 2 filter paper specified in JIS P 3801, 10 mL of the filtrate was collected, and dried. The tetrahydrofuran-insoluble content (gel fraction) was
25 calculated from the mass remaining after evaporation to dryness. The results are shown in Table 1 (see "THF-insoluble content (mass%)" in Table 1).

[0078]

(6) Preparation of specimen

The water-based pressure-sensitive adhesive composition was applied (application amount: DRY 20 to 25 μm) to a release
5 paper ("Separator EN78P" manufactured by Lintec Corporation) using an applicator under the following conditions to form a pressure-sensitive adhesive layer to prepare a specimen.

Drying conditions: 115°C×90 sec (using hot-air drier)

Substrate: PET film (50 μm)

10 Curing: 40°C×3 days

[0079]

(7) Measurement of adhesion

The adhesion was measured in accordance with JIS Z 0237. The measurement conditions are listed below. The results are
15 shown in Table 1.

Peel: 180° peel (peel speed: 300 mm/min)

Adherend: SUS 305 or polypropylene

Width of specimen: 25 mm

Compression bonding: A 2 kg roller was caused to make one round
20 trip on each adherend at 23°C and 50%RH.

Timing of tensile test: The tensile test was performed when 1 day had elapsed after bonding.

[0080]

(8) Measurement of holding power

25 A load of 500 g was applied at a temperature of 40°C and a humidity of 65%, and the shift amount (change in position) was measured when 24 hours had elapsed. A case where the shift

amount was 1 mm or less was evaluated as "Excellent", a case where the shift amount was more than 1 mm and 3 mm or less was evaluated as "Good", and a case where the shift amount was more than 3 mm, or a fall was observed, was evaluated as "Poor". The results are shown in Table 1.

[0081]

(9) Evaluation of water-whitening resistance

The specimen was dipped in ion-exchanged water (23°C), and the degree of whitening of the pressure-sensitive adhesive layer of the specimen was observed with the naked eye when 3 hours had elapsed. A case where whitening was not observed, or the pressure-sensitive adhesive layer was transparent in spite of slight bluish coloring, was evaluated as "Excellent", a case where the pressure-sensitive adhesive layer was transparent in spite of slight whitening was evaluated as "Good", and a case where whitening was observed, or the pressure-sensitive adhesive layer was not transparent, was evaluated as "Poor". The results are shown in Table 1.

[0082]

(10) Evaluation of anchor effect

An operation that bends the specimen to effect autohesion, and an operation that cancels the autohesion were repeated to measure the operation count at which the pressure-sensitive adhesive layer was removed from the substrate. A case where the operation count was 10 or more was evaluated as "Excellent", a case where the operation count was 5 to 9 was evaluated as "Good", and a case where the operation count was 4 or less was

evaluated as "Poor". The results are shown in Table 1.

[0083]

The water-based pressure-sensitive adhesive compositions of Examples 1 to 4 exhibited sufficient adhesion, a sufficient
5 anchor effect, and excellent water resistance.

[0084]

In contrast, the water-based pressure-sensitive adhesive compositions of Comparative Examples 1 to 8 exhibited poor properties.

10 [0085]

Specifically, the water-based pressure-sensitive adhesive composition of Comparative Example 1 exhibited insufficient adhesion and holding power since the water-insoluble tackifier was not used.

15 [0086]

The water-based pressure-sensitive adhesive composition of Comparative Example 2 exhibited insufficient water resistance since the amount of the water-insoluble tackifier was outside the range according to the present invention.

20 [0087]

The water-based pressure-sensitive adhesive composition of Comparative Example 3 exhibited insufficient water resistance and adhesion to a polyolefin since the amount of the component (a) was outside the range according to the present
25 invention.

[0088]

The water-based pressure-sensitive adhesive composition

of Comparative Example 4 exhibited an insufficient anchor effect and adhesion to a polyolefin since the THF-insoluble content was outside the range according to the present invention.

5 [0089]

It was confirmed from Comparative Examples 5 and 6 (in which the water-soluble rosin-based emulsifier for emulsion polymerization (EO-addition rosin ester DRA-1500) was used instead of the water-insoluble tackifier according to the present invention) that the water-based pressure-sensitive adhesive composition cannot be obtained if the amount of the rosin-based emulsifier for emulsion polymerization is small. It was confirmed from Comparative Example 6 that the water-based pressure-sensitive adhesive composition obtained using a large amount of the water-soluble rosin-based emulsifier for emulsion polymerization (EO-addition rosin ester DRA-1500) exhibited poor holding power and water resistance.

[0090]

In Comparative Example 7 in which seed polymerization was not performed, a water-based pressure-sensitive adhesive composition could be obtained.

[0091]

The mixing ratio of the raw materials in Comparative Example 8 was the same as that of Example 3. It was confirmed from the comparison between Comparative Example 8 and Example 3 that the water-based pressure-sensitive adhesive composition exhibited poor adhesion, holding power, and water-whitening

resistance when the water-insoluble tackifier was added
(post-addition) before application after emulsion
polymerization was effected in a state in which the
water-insoluble tackifier was not included in the reaction
5 system. Specifically, it was confirmed that the adhesion, the
holding power, and the water-whitening resistance could be
improved by effecting seed polymerization in the presence of
the water-insoluble tackifier.

10 INDUSTRIAL APPLICABILITY

[0092]

The present invention can thus be used to implement a
water-based pressure-sensitive adhesive composition and a
method for producing the same.

15

CLAIMS

1. A water-based pressure-sensitive adhesive composition comprising a copolymer dispersion obtained by subjecting 0.1
5 to 10 parts by mass of (a) an ethylenically unsaturated carboxylic acid monomer, 60 to 99 parts by mass of (b) an acrylate monomer that includes an alkyl group having 4 to 12 carbon atoms, and 0 to 39.9 parts by mass of (c) an ethylenically unsaturated monomer (provided that (a)+(b)+(c)=100 parts by mass) to
10 emulsion polymerization in a reaction system that includes 0.1 to 10 parts by mass of a water-insoluble tackifier having an average particle size of 0.05 to 1.00 μm ,

particles included in the copolymer dispersion having an average particle size of 0.3 to 10 μm , and

15 the copolymer dispersion having a glass transition temperature of -70 to -30°C and a tetrahydrofuran-insoluble content of 70 mass% or less.

2. The water-based pressure-sensitive adhesive composition
20 according to claim 1, further comprising a crosslinking agent.

3. A method for producing a water-based pressure-sensitive adhesive composition comprising effecting emulsion
polymerization while adding 0.1 to 10 parts by mass of (a) an
25 ethylenically unsaturated carboxylic acid monomer, 60 to 99 parts by mass of (b) an acrylate monomer that includes an alkyl group having 4 to 12 carbon atoms, and 0 to 39.9 parts by mass

of (c) an ethylenically unsaturated monomer (provided that
(a)+(b)+(c)=100 parts by mass) to a dispersion prepared by
dispersing 0.1 to 10 parts by mass of a water-insoluble
tackifier having an average particle size of 0.05 to 1.00 μm
5 in a medium to obtain a copolymer dispersion.

4. A method for producing a water-based pressure-sensitive
adhesive composition comprising adding 0.1 to 10 parts by mass
of a water-insoluble tackifier having an average particle size
10 of 0.05 to 1.00 μm to a pre-emulsion that includes 0.1 to 10
parts by mass of (a) an ethylenically unsaturated carboxylic
acid monomer, 60 to 99 parts by mass of (b) an acrylate monomer
that includes an alkyl group having 4 to 12 carbon atoms, 0 to
39.9 parts by mass of (c) an ethylenically unsaturated monomer
15 (provided that (a)+(b)+(c)=100 parts by mass), a medium, and
an emulsifier, and subjecting the pre-emulsion to emulsion
polymerization to obtain a copolymer dispersion.

5. The method for producing a water-based pressure-sensitive
20 adhesive composition according to claim 3 or 4, further
comprising adding a crosslinking agent to the copolymer
dispersion.