

SPECIFICATION

AQUEOUS EMULSION AND METHOD OF PRODUCING THE SAME

Technical Field of the Invention

The present invention relates to an aqueous emulsion and a method of producing the same.

Background of the Invention

As an adhesive composition excellent in an adhesion property under normal conditions and heat resistant creep, an adhesive composition containing an ethylene-vinyl acetate-polyfunctional monomer-based copolymer aqueous emulsion and a polyurethane aqueous emulsion is known (Japanese Patent Application Laid-Open (JP-A) No. 9-194811, [Claims], [0017]) and there is disclosed an adhesive composition suitable for adhesive between a wood-based material and a polyvinyl chloride sheet.

From the standpoint of environmental problems, a polyvinyl chloride sheet is shifting to a polyolefin sheet, and also with respect to a polyolefin sheet, an adhesive composition excellent in an adhesion property under normal conditions and heat resistant creep which are equal to or more than those of a polyvinyl chloride sheet is required.

As an adhesive composition excellent in heat resistant creep

and an adhesion property under normal conditions for a polyolefin sheet, there is disclosed an adhesive composition obtained by emulsion-polymerizing ethylene and vinyl acetate with ammonium persulfate using a polyurethane aqueous emulsion as a seed (JP-A No. 2004-211037, [Claim 1], [0035]).

The present inventors have made an attempt to produce an aqueous emulsion obtained by further emulsion-polymerizing ethylene and vinyl acetate with ammonium persulfate as a catalyst using a polyurethane aqueous emulsion as a seed according to Example 1 of JP-A No. 2004-211037, however, the emulsion polymerization did not progress.

Disclosure of the Invention

An object of the present invention is to provide an aqueous emulsion giving an adhesive excellent in heat resistant creep, and a method of producing the same.

The present inventors have investigated to find an aqueous emulsion with few problems as described above, and resultantly found that an aqueous emulsion giving an adhesive excellent in heat resistant creep can be produced according to a method of producing an aqueous emulsion comprising emulsion-polymerizing a polyurethane aqueous emulsion with some kinds of monomers under a certain condition, and have completed the present invention.

That is, the present invention provides the following [1]

to [6].

[1] A method for producing a modified polyurethane aqueous emulsion comprising emulsion-polymerizing a polyurethane aqueous emulsion and monomers containing ethylene, vinyl ester and polyfunctional monomer with a redox catalyst containing a salt of a transition metal, erysorbic acids and/or ascorbic acids as a reducing agent.

[2] The method according to [1], wherein the redox catalyst contains hydrogen peroxide as an oxidizing agent.

[3] A modified polyurethane aqueous emulsion obtained by the method according to [1] or [2].

[4] An adhesive comprising the modified polyurethane aqueous emulsion according to [3].

[5] A laminate comprising an adhesive layer made of the adhesive according to [4], and a base material capable of absorbing water.

[6] The laminate according to [5], wherein a polyolefin layer is further laminated at the side of the adhesive layer.

[7] A method for producing a modified polyurethane aqueous emulsion comprising the steps of:

adding monomers containing ethylene, vinyl ester and polyfunctional monomer into a polyurethane aqueous emulsion in the presence of a redox catalyst containing a salt of a transition metal, erysorbic acids and/or ascorbic acids as a reducing agent, and

heating at the temperature of from about 20°C to about 80°C.

Mode for Carrying Out of the Invention

The present invention will be illustrated in detail below.

The polyurethane aqueous emulsion used in the present invention is an aqueous emulsion containing a polyurethane dispersed in water, the polyurethane being obtained by reacting a polyisocyanate compound with a polyol compound, further if necessary, with other compounds. As this reaction method, for example, an acetone method, prepolymer mixing method, ketimine method, hot melt dispersion method and the like are mentioned.

As the polyisocyanate compound, organic polyisocyanate compounds having two or more isocyanate compounds in the molecule used for usual polyurethane production are mentioned. Specific examples thereof include aliphatic diisocyanates such as 1,4-tetramethylene diisocyanate, 1,6-hexamethylene diisocyanate (HDI), 2,2,4-trimethylhexamethylene diisocyanate, 3-isocyanatemethyl-3,5,5-trimethylcyclohexyl isocyanate, dicyclohexylmethane-4,4'-diisocyanate, methylcyclohexyl-2,4-diisocyanate, methylcyclohexyl-2,6-diisocyanate, xylylene diisocyanate (XDI), 1,3-bis(isocyanate)methylcyclohexane, tetramethylxylylene diisocyanate, trans cyclohexane-1,4-diisocyanate, lysine diisocyanate and the like; aromatic diisocyanates such as 2,4-toluylene

diisocyanate (TDI), 2,6-toluylene diisocyanate (TDI), diphenylmethane-4,4'-diisocyanate (MDI), 1,5'-naphthene diisocyanate, tolidine diisocyanate, diphenylmethylethane diisocyanate, tetraalkyldiphenylmethane diisocyanate, 4,4'-dibenzyl diisocyanate, 1,3-phenylene diisocyanate and the like; triisocyanates such as lysine ester triisocyanate, triphenylmethane triisocyanate, 1,6,11-undecane triisocyanate, 1,8-isocyanate-4,4-isocyanate methyloctane, 1,3,6-hexamethylene triisocyanate, bicycloheptane triisocyanate, adduct of trimethylolpropane with toluylene diisocyanate, adduct of trimethylolpropane with 1,6-hexamethylene diisocyanate, and the like, and these may be used singly or in combination of two or more.

As the polyol compound, compounds having two or more hydroxyl groups in the molecule used for usual polyurethane production are mentioned, and specific examples thereof include polyhydric alcohols such as ethylene glycol, diethylene glycol, propylene glycol, 1,4-butanediol, 1,6-hexanediol, neopentyl glycol, trimethylolpropane, glycerin and the like; polyether polyols such as polyethylene glycol, polypropylene glycol, polytetramethylene ether glycol and the like; polyester polyols obtained from dicarboxylic acids such as adipic acid, sebacic acid, itaconic acid, maleic anhydride, terephthalic acid, isophthalic acid, fumaric acid, succinic acid, oxalic acid, malonic acid, glutaric acid, pimelic acid, suberic acid,

azelaic acid and the like and polyol compounds such as ethylene glycol, diethylene glycol, propylene glycol, 1,4-butanediol, 1,6-hexanediol, neopentyl glycol, 1,2-propanediol, 1,3-propanediol, 1,9-nonanediol, 3-methyl-1,5-pentanediol, 1,3-propanediol, tripropylene glycol, trimethylolpropane, glycerin and the like; polylactone-based polyester polyols such as polycaprolactone polyol, poly δ -methyl-d-valerolactone and the like; polybutadiene polyol or hydrogenated substances thereof, polycarbonate polyol, polythioether polyol, polyacrylate polyol and the like.

Introduction of a hydrophilic group into a molecule in producing a polyurethane aqueous emulsion is preferable since stability when dispersing a polyurethane aqueous emulsion in water can be improved. As a compound used for introduction of a hydrophilic group, there are mentioned, for example, compounds having a nonionic hydrophilic group such as a structural unit derived from polyethylene glycol in the molecule and having one or more active hydrogens having reactivity with an isocyanate group, such as a sulfonyl group, carboxyl group, hydroxyl group, primary amino group ($-NH_2$), secondary amino group ($=NH$) and the like (hereinafter, referred to as hydrophilic group-containing compound in some cases).

As the hydrophilic group-containing compound, for example, sulfonic acid-containing compounds such as 3,4-diaminobutanesulfonic acid,

3,6-diamino-2-toluenesulfonic acid,
2,6-diaminobenzenesulfonic acid,
N-(2-aminoethyl)-2-aminoethylsulfonic acid and the like;
carboxylic acid-containing compounds such as
2,2-dimethylolactic acid, 2,2-dimethylolpropionic acid,
2,2-dimethylolvaleric acid and the like. The hydrophilic
group-containing compounds may be used singly or in combination
of two or more.

A polyurethane aqueous emulsion containing in the molecule
a hydrophilic group obtained by using these hydrophilic
group-containing compounds is called ionomer structure, and
itself has a surface active ability. Therefore, it is easily
dispersed in water, and shows a preferable tendency of improving
water resistance of an aqueous emulsion obtained by further
emulsion-polymerizing a monomer with a polyurethane aqueous
emulsion.

As the hydrophilic group, anionic groups such as a sulfonyl
group, carboxyl group and the like are preferable, and
particularly, a sulfonyl group is preferable since it has a
tendency of further improving water resistance of an aqueous
emulsion obtained by emulsion polymerization of a monomer.

The anionic group is preferably neutralized usually with
a neutralizing agent. The neutralizing agent includes
tertiary amine compounds such as triethylamine,
triethanolamine and the like; inorganic alkali compounds such

as sodium hydroxide and the like; ammonia and the like.

In producing a polyurethane aqueous emulsion, a compound containing in the molecule active hydrogen capable of reacting with an isocyanate compound and which is different from the hydrophilic group-containing compound may be used, if necessary, for the purpose of chain extension and molecular weight control. Examples of such a compound include polyhydric amine compounds such as ethylenediamine, 1,4-butanediamine, 1,6-hexanediamine and the like; polyhydric alcohols containing a tertiary amine such as triethanolamine and the like, monoalcohols such as methanol, ethanol, butanol and the like.

As the polyurethane aqueous emulsion, commercially available polyurethane aqueous emulsions may be used as they are.

Specifically mentioned are HYDRAN ECOS-3000, ADS-120, ADS-110 manufactured by Dainippon Ink & Chemicals, Inc., UPRENE UXA-3005 manufactured by Sanyo chemical industries, Ltd., U-53, U-54, U-56 manufactured by Sumika Bayer Urethane Co., Ltd., and the like.

The method of producing a modified polyurethane aqueous emulsion of the present invention is a method for emulsion polymerization using ethylene, vinyl ester and polyfunctional monomer as monomers and using a polyurethane aqueous emulsion as a seed. Hereinafter, this process is referred to as a seed polymerization process.

As the vinyl ester used for the seed polymerization process, for example, alkylvinyl esters such as vinyl acetate, vinyl butyrate, vinyl propionate, vinyl pivalate, vinyl laurate, vinyl isononanoate, vinyl versatate, and the like are mentioned. As the vinyl ester, two or more vinyl esters may be used. Among vinyl ester, vinyl acetate is suitably used.

The use amount of the vinyl ester is about 60 to 95 parts by weight based on 100 parts by weight of the total amount of monomers used in the seed polymerization process.

The polyfunctional monomer means a monomer capable of feeding two or more ethylenic double bonds to a monomer such as ethylene, vinyl ester and the like. Specific examples of the polyfunctional monomer include triallyl cyanurate, triallyl isocyanurate, diallyl phthalate and the like.

The used amount of the polyfunctional monomer is about 0.01 to 1 part by weight, preferably about 0.05 to 0.5 parts by weight based on 100 parts by weight of a vinyl ester used in the seed polymerization process, and within this range, there is a preferable tendency of improving heat resistance creep.

The monomer used in the seed polymerization process is a monomer different from ethylene, vinyl ester and polyfunctional monomer, and monomers capable of feeding one ethylenic double bond (hereinafter, referred to as copolymerizable monomer in some cases) may be used, and specific examples thereof include vinyl halides such as vinyl chloride, vinyl bromide and the

like; vinylidene halides such as vinylidene chloride and the like; vinyl compound such as vinylphosphonic acid, vinylsulfonic acid and salts thereof and the like; aromatic vinyls such as styrene, α -methylstyrene, chlorostyrene and the like; (meth)acrylic acids such as methacrylic acid, acrylic acid and the like; (meth)acrylates such as methyl (meth)acrylate, butyl (meth)acrylate, 2-ethylhexyl (meth)acrylate and the like; α,β -unsaturated dicarboxylic acids such as maleic acid, maleic anhydride, succinic acid, itaconic acid and the like; nitriles such as (meth)acrylonitrile and the like; acrylamides such as N-methylolacrylamide, N-butoxymethylacrylamide and the like; allyl compounds such as allyl sulofnate and the like.

The use amount of the copolymerizable monomer is usually 20 parts by weight or less, preferably 10 parts by weight or less based on 100 parts by weight of the total amount of a monomer used in the seed polymerization process.

In the present invention, a redox-based catalyst is used in the seed polymerization process.

The redox-based catalyst means a catalyst system generating a radical by reaction of an oxidizing agent and a reducing agent. The redox-based catalyst can generate a radical even at lower temperatures of about 25°C.

The reaction is initiated by heat generation caused by mixing of an oxidizing agent and a reducing agent at one time

or in division. The method of adding to the polymerization system includes a method of adding both an oxidizing agent and a reducing agent simultaneously in a lump or in division by dropping and the like, a method of adding one of an oxidizing agent and a reducing agent previously to the polymerization system and adding another one in a lump or in division by dropping and the like.

As the reducing agent for the redox-based catalyst, erisorbic acids and/or ascorbic acids are used together with a salt of a transition metal.

As the salt of a transition metal, for example, chlorides, sulfates and the like of iron, copper, cobalt, titanium, nickel, chromium, zinc, manganese, vanadium, molybdenum, cerium and the like are mentioned. Of them, ferrous chloride, ferrous sulfate, copper sulfate and the like are preferably used.

The salt of a transition metal is usually about 0.001 to 0.05-fold by weight based on erisorbic acids and/or ascorbic acids as a reducing agent. When 0.001-fold by weight or more, there is a preferable tendency of improving the reaction speed of emulsion polymerization, and when 0.05-fold by weight or less, there is a preferable tendency of reducing coloration of the produced aqueous emulsion.

Examples of the erisorbic acids and/or ascorbic acids as a reducing agent include erisorbic acid and ascorbic acid, and additionally, alkali metal salts of them such as sodium salts,

potassium salts and the like. Of them, sodium salts are preferable, and particularly, sodium erisorbate is preferably used.

The reducing agent is used usually in an amount of 0.02 to 1 part by weight based on 100 parts by weight of a vinyl ester. When 0.02 parts by weight or more, there is a preferable tendency of improving the reaction speed of emulsion polymerization, and when 1 part by weight or less, there is a tendency of suppressing discoloration of the produced aqueous emulsion, and there is a preferable tendency of improving abilities of the resultant aqueous emulsion, for example, strength, water resistance and the like in the case of a film made of the aqueous emulsion.

Examples of the oxidizing agent for the redox-based catalyst include persulfates such as ammonium persulfate, potassium persulfate, sodium persulfate and the like; peroxides such as t-butyl peroxide, hydrogen peroxide and the like. Of them, hydrogen peroxide is preferable since handling thereof is simple and it shows a tendency of suppressing discoloration of the resultant aqueous emulsion.

One example of the method of producing a modified polyurethane aqueous emulsion (seed polymerization process) will be shown below.

A polyurethane aqueous emulsion, an emulsion dispersing agent, all or part of a vinyl ester, a salt of a transition metal, and if necessary, all or part of a copolymerizable monomer, all

or part of a polyfunctional monomer, and a neutralizing agent such as acetic acid and the like, are charged in a pressure-resistant vessel, purged with nitrogen, then, the temperature is increased usually to about 20 to 80°C, preferably about 40 to 70°C, then, subsequently, ethylene is pressurized so that partial pressure of ethylene is usually about 1 to 10 MPa, preferably about 3 to 8 MPa.

Next, an oxidizing agent such as hydrogen peroxide and the like and erisorbic acids and/or ascorbic acids are gradually mixed in the pressure-resistant vessel at about 20 to 80°C. The oxidizing agent and erisorbic acids and/or ascorbic acids may be diluted with water and the like so that production thereof is made easy.

Simultaneously, the remaining vinyl ester, copolymerizable monomer and polyfunctional monomer are gradually added into the pressure-resistant vessel while keeping the temperature, and the mixture is thermally insulated and stirred until the vinyl ester in the reaction solution in the pressure-resistant vessel decreases sufficiently.

When the vinyl ester does not decrease sufficiently, a redox-based catalyst such as an oxidizing agent and the like may be added.

The use amount of a polyurethane aqueous emulsion used in the seed polymerization process (non-volatile content) is usually about 3 to 50 parts by weight based on 100 parts by weight

of the non-volatile content of the aqueous emulsion produced by seed polymerization. When 3 parts by weight or more, there is a preferable tendency of improving an adhesion ability, and when 50 parts by weight or less, there is a preferable tendency of improving emulsion polymerization speed of ethylene, vinyl ester and the like.

In the seed polymerization process, an emulsifying agent may be used.

Examples of the emulsifying agent include protection colloids such as partially or completely saponified polyvinyl alcohol, hydroxyethylcellulose, methylcellulose, carboxymethylcellulose, starch, modified starch, oxidized starch, sodium alginate and the like, nonionic surfactants such as polyoxyethylene alkyl ether, polyoxyethylene alkylphenol ether, polyoxyethylene-polyoxypropylene block copolymer, polyoxyethylene fatty acid ester, polyoxyethylene sorbitan fatty acid ester and the like, anionic surfactants such as alkyl sulfates, alkylbenzene sulfonates, alkylsulfosuccinates, alkyl diphenyl ether disulfonates, polyoxyethylene alkylsulfates, polyoxyethylene alkylphosphates and the like.

Here, polyvinyl alcohol may be modified with a compound containing a carboxylic acid, sulfonic acid, siloxane and the like.

As the polyvinyl alcohol, particularly, those having an average polymerization degree of about 100 to 3000 and an

average saponification degree of about 80 to 98 mol% are suitable.

Regarding the use amount of the emulsion dispersing agent, the non-volatile content of the emulsion dispersing agent is usually about 3 to 12 parts by weight, preferably about 4 to 8 parts by weight based on 100 parts by weight of the total amount of monomers used in the seed polymerization process.

The content of a structural unit derived from ethylene in the produced aqueous emulsion is usually about 5 to 70 parts by weight based on 100 parts by weight of the total amount of monomers used in the seed polymerization process. Particularly, when a structural unit derived from ethylene is contained in an amount of 5 to 35 parts by weight, there is a preferable tendency of improving adhesion force even at lower temperatures of about 0 to 10°C.

When ethylene partial pressure in the seed polymerization process is 1 MPa or more, there are a tendency of improving the content of a structural unit derived from ethylene in the produced aqueous emulsion and a tendency of reducing reaction time. On the other hand, a partial pressure of 10 MPa or less is preferable from the standpoint of pressure resistance of a pressure-resistant vessel.

For enhancing the proportion of a structural unit derived from ethylene based on the total amount of structures derived from all monomers used in the seed polymerization process,

polymerization may be advantageously conducted while maintaining the vinyl ester content of a monomer in the reaction solution in the pressure-resistant vessel at low level, and specifically, the amount of a vinyl ester added initially or subsequently may be appropriately controlled.

The modified polyurethane aqueous emulsion to be produced has a non-volatile content of usually about 40 to 75 wt%, and if necessary, the emulsion can be diluted with water.

The aqueous emulsion can be used as it is, alternatively, the water content thereof is adjusted, and if necessary, compounding agents described later are added, and the resulting mixture can be used as an adhesive such as an adhesive for wood, adhesive for paper processing, adhesive for plastic, and the like, or used as a paint by coating on the surface of a base material.

As the compounding agent capable of being compounded in the adhesive, for example, thermosetting resins such as urea resins, melamine resins, phenol resins and the like, fillers such as clay, kaolin, talc, calcium carbonate and the like, preservatives, rust proof agents, de-foaming agents, foaming agents, thickening agents such as polyacrylic acids, polyethers and the like, viscosity controlling agents, flame retardants, pigments such as titanium oxide and the like, plasticizers such as dibasic acid esters, and the like are mentioned.

It is recommended to use a filler for improving flame

retardant and coatability in adhering, and the use amount thereof is usually about 1 to 500 parts by weight, preferably 5 to 200 parts by weight based on 100 parts by weight of the non-volatile content of the aqueous emulsion.

When the aqueous emulsion is used as an adhesive, it may be used as one pot type adhesive containing an aqueous emulsion as an effective ingredient, and when adhesion abilities such as heat resistant creep, water resistance and the like are required, it is preferable to use a hardener together.

As the hardener, an isocyanate-based hardener is effective, and for example, the above-mentioned MDI, TDI, HDI, XDI and oligomers and polymers thereof are mentioned. The compounding amount of the harder is usually 0.1 to 20 parts by weight, preferably 1 to 10 parts by weight based on 100 parts by weight of an aqueous emulsion. As commercially available products, for example, Sumidur 44V20, Sumidur N3300 and the like manufactured by Sumika Bayer Urethane Co.,Ltd. are mentioned.

As the base material which is adhered to the adhesive of the present invention, for example, wood-based materials such as wood, plywood, MDF (medium density fiber board), particle board, fiber board and the like; paper-based materials such as wall paper, wrapping paper and the like; cellulose-based materials such as cotton cloth, hemp cloth, rayon and the like; materials absorbing water such as porous materials and the like; materials capable of removing water such as non-woven fabric

and the like are mentioned.

When a part of the adhesive of the present invention is adhered to a material capable of removing water, other parts may be adhered to plastic materials such as polyolefins such as polyethylene, polypropylene, polystyrene and the like, polyesters, polyethers, polyvinyl chloride and the like, or ceramic materials such as glass, pottery and the like.

Particularly, a laminate obtained by laminating a material absorbing water and a polyolefin via an adhesive of the present invention has an adhesion property under normal conditions approximately equal to or more than that of a laminate obtained via an adhesive composition composed of an ethylene-vinyl acetate-based copolymer aqueous emulsion and a polyurethane aqueous emulsion, and is excellent remarkably in heat resistance creep.

According to the present invention, there can be produced an aqueous emulsion having an adhesion property under normal conditions approximately equal to or more than that of an adhesive obtained by separately producing an ethylene-vinyl acetate-based copolymer emulsion and a polyurethane aqueous emulsion and mixing them, additionally, having remarkably excellent heat resistance creep.

Further, according to the present invention, an aqueous emulsion excellent remarkably in heat resistance creep can be produced easily and with high reproducibility.

Examples

The present invention will be illustrated more in detail by the following examples, but it is needless to say that the present invention is not limited to these examples.

Parts and % are by weight unless otherwise stated. The non-volatile content was measured by a method according to JIS K-6828. The viscosity was measured by Brookfield viscometer (manufactured by Toki Sangyo Co., Ltd.) at 25°C.

Example 1

<Production Example of aqueous emulsion (B1)>

Into a pressure-resistant vessel was introduced a solution prepared by previously dissolving 160 parts of vinyl acetate, 7 parts of polyvinyl alcohol "PVA-217" (manufactured by Kuraray Corp., degree of saponification: 88 mol%, average degree of polymerization: 1700), 2 parts of "PVA-205" (manufactured by Kuraray Corp., degree of saponification: 88 mol%, average degree of polymerization: 500), 40 parts of a polyurethane aqueous emulsion (A1, anion type urethane emulsion "HYDRAN ECOS-3000" manufactured by Dainippon Ink & Chemicals, Inc., non-volatile content: 40%), 0.005 parts of ferrous sulfate hepta-hydrate and 0.4 parts of acetic acid in 150 parts of water. Then, an atmosphere in the pressure-resistant vessel was purged with a nitrogen gas, and the atmosphere in the vessel was heated up to 60°C, then, pressurized with ethylene up to 4.6 MPa. Next,

0.5 parts of 30% hydrogen peroxide-containing aqueous solution and 0.6 parts of sodium erisorbate were diluted with water, and dropping of them was initiated. Subsequently, increase of liquid temperature in the pressure-resistant vessel was confirmed, then, a solution prepared by dissolving 0.17 parts of triallyl isocyanurate in 10 parts of vinyl acetate was added over a period of 3 hours. The temperature in the reaction vessel was kept at 60°C by controlling the temperature of a jacket during the polymerization, further, an aqueous solution of hydrogen peroxide was added, and the mixture was stirred until the concentration of vinyl acetate in the reaction solution reached 1% or less, then, an un-reacted ethylene gas was removed, to obtain an aqueous emulsion (B1).

The resin composition of the resultant aqueous emulsion (B1) included 22 parts of a structural unit derived from ethylene, 0.1 part of a structural unit derived from triallyl isocyanurate, 9 parts of a resin component (non-volatile component) derived from the polyurethane aqueous emulsion (A) and 5.3 parts of a resin component (non-volatile component) derived from polyvinyl alcohol based on 100 parts of a structural unit derived from vinyl acetate. The aqueous emulsion (B1) had a non-volatile content of 52.5% and a viscosity of 1200 mPa·s.

<Production Example 1 of adhesive and laminate>

To 110 parts of the aqueous emulsion (B1) was compounded 5.3 parts of DBE (mixture of dibasic esters (dimethyl succinate,

dimethyl adipate, dimethyl glutarate)) manufactured by INVISTA JAPAN as a plasticizer, and 6 parts of a substance obtained by 2-fold diluting a thickener (SN thickener A-812, manufactured by SAN NOPCO LIMITED, registered trademark, urethane-modified polyether, effective ingredient: 40%) was compounded, and the product was used as an adhesive. Using this adhesive, an adhesion test was conducted as described below.

<Evaluation of adhesive force>

An aqueous emulsion was applied at 110 g/m² on a JAS 1 water resistant plywood, then, a non-vinyl chloride sheet WS-201E manufactured by Dai Nippon Printing Co., Ltd. (polyolefin sheet, thickness: 0.16 mm) was laminated and deaerated by a hand roller, then, allowed to stand still for 1 day while compressing under 50 kgf/900 cm², compression was released, further dried for 6 days to obtain a laminate.

The peeling strength under normal conditions was measured at a peeling speed of 200 mm/min by Autograph(manufactured by Shimadzu). For the heat resistance creep, the laminated was controlled at 80°C, then, peeled at a peeling angle of 90° and at a load of 500 gf/25 mm, and peeled length at each time was measured. The results are summarized in Table 1.

Example 2

<Production Example of aqueous emulsion (B2)>

The same procedure was conducted as in Example 1 except that 32 parts of a polyurethane aqueous emulsion (A2, ADS-120 (50%))

manufactured by Dainippon Ink & Chemicals, Inc.) was used instead of the polyurethane aqueous emulsion (A1, 40 parts of HYDRAN ECOS-3000 manufactured by Dainippon Ink & Chemicals, Inc.) in Example 1.

The resin composition of the resultant aqueous emulsion (B2) included 22 parts of a structural unit derived from ethylene, 0.1 part of a structural unit derived from triallyl isocyanurate, 9 parts of a resin component (non-volatile component) derived from the polyurethane aqueous emulsion (A) and 5.3 parts of a resin component (non-volatile component) derived from polyvinyl alcohol based on 100 parts of a structural unit derived from vinyl acetate. The aqueous emulsion (B2) had a non-volatile content of 53.1% and a viscosity of 7570 mPa·s.

To 110 parts of this aqueous emulsion (B2) was compounded 5.3 parts of DBE manufactured by INVISTA JAPAN, and 0.5 parts of a substance obtained by 2-fold diluting a thickener A-812 manufactured by SAN NOPCO LIMITED was compounded, and the product was used as an adhesive and an adhesion test was conducted as described in Example 1

Comparative Example 1

<Production Example of aqueous emulsion (C)>

The same procedure was conducted as in Example 1 except that "0.5 parts of sodium persulfate" was used instead of "0.5 parts of 30% hydrogen peroxide-containing aqueous solution and 0.6 parts of sodium erisorbate" in Example 1.

Vinyl acetate in the pressure-resistant vessel did not decrease, and no emulsion polymerization progressed.

Comparative Example 2

<Production Example of ethylene-vinyl acetate-polyfunctional monomer-based copolymer aqueous emulsion (D)>

Into a pressure-resistant vessel was introduced a solution prepared by previously dissolving 180 parts of vinyl acetate, 8 parts of polyvinyl alcohol "PVA-217" (manufactured by Kuraray Corp., degree of saponification: 88 mol%, average degree of polymerization: 1700), 2.3 parts of "PVA-205" (manufactured by Kuraray Corp., degree of saponification: 88 mol%, average degree of polymerization: 500), 0.005 parts of ferrous sulfate hepta-hydrate and 0.4 parts of acetic acid in 160 parts of water. Then, an atmosphere in the pressure-resistant vessel was purged with a nitrogen gas, and the atmosphere in the vessel was heated up to 60°C, then, pressurized with ethylene up to 4.6 MPa. Next, 0.33 parts of 30% hydrogen peroxide-containing aqueous solution and 0.6 parts of sodium erisorbate were diluted with water, and dropping of them was initiated. Subsequently, increase of liquid temperature in the pressure-resistant vessel was confirmed, then, a solution prepared by dissolving 0.19 parts of triallyl isocyanurate in 10 parts of vinyl acetate was added over a period of 3 hours. The temperature in the reaction vessel was kept at 60°C by controlling the temperature of a jacket during the polymerization, further, an aqueous solution of

hydrogen peroxide was added, and the mixture was stirred until the concentration of vinyl acetate in the reaction solution reached 1% or less, then, an un-reacted ethylene gas was removed, to obtain an ethylene-vinyl acetate-polyfunctional monomer-based copolymer aqueous emulsion (D).

The resin composition of the resultant aqueous emulsion (D) included 22 parts of a structural unit derived from ethylene, 0.1 part of a structural unit derived from triallyl isocyanurate, and 5.4 parts of a resin component derived from polyvinyl alcohol based on 100 parts of a structural unit derived from vinyl acetate. The aqueous emulsion (D) had a non-volatile content of 55.0% and a viscosity of 3000 mPa·s.

<Production Example of adhesive and laminate>

To 100 parts of the aqueous emulsion (D) was compounded 4.8 parts of DBE manufactured by INVISTA JAPAN, and 4 parts of a substance obtained by 2-fold diluting a thickener A-812 manufactured by SAN NOPCO LIMITED was compounded, and the product was used as an adhesive. Using this adhesive, an adhesion test was conducted as described in Example 1. The results are summarized in Table 1.

Comparative Example 3

<Production Example of adhesive composition composed of aqueous emulsion (D) and polyurethane aqueous emulsion>

100 parts of the aqueous emulsion (D) obtained in Comparative Example 2, 10.6 parts of an anion type urethane

emulsion "HYDRAN ECOS-3000" (manufactured by Dainippon Ink & Chemicals, Inc., non-volatile content: 40%) and 5.3 parts of DBE manufactured by INVISTA JAPAN were compounded, and pH thereof was adjusted to 8 to 9 with 0.2 parts of 25% ammonia, then, 4 parts of a substance obtained by 2-fold diluting a thickener A-812 manufactured by SAN NOPCO LIMITED was compounded, to obtain an adhesive. Using this adhesive, the same adhesion test was conducted as in Example 1. The results are summarized in Table 1.

Comparative Example 4

<Production Example of adhesive composition composed of ethylene-vinyl acetate-polyfunctional monomer-based copolymer aqueous emulsion (D) and polyurethane aqueous emulsion>

100 parts of the aqueous emulsion (D) obtained in Comparative Example 2, 8.5 parts of an anion type urethane emulsion "HYDRAN ADS-120" (manufactured by Dainippon Ink & Chemicals, Inc., non-volatile content: 50%) and 5.3 parts of DBE manufactured by INVISTAR JAPAN were compounded, and pH thereof was adjusted to 8 to 9 with 0.2 parts of 25% ammonia, then, 4 parts of a substance obtained by 2-fold diluting a thickener A-812 manufactured by SAN NOPCO LIMITED was compounded, to obtain an adhesive. Using this adhesive, the same adhesion test was conducted as in Example 1. The results are summarized in Table 1.

Comparative Example 5

<Production Example of aqueous emulsion (E)>

Into a pressure-resistant vessel was introduced a solution prepared by previously dissolving 170 parts of vinyl acetate, 2 parts of polyvinyl alcohol "PVA-217" (manufactured by Kuraray Corp., degree of saponification: 88 mol%, average degree of polymerization: 1700), 6 parts of "PVA-205" (manufactured by Kuraray Corp., degree of saponification: 88 mol%, average degree of polymerization: 500), 40 parts of a polyurethane aqueous emulsion (A)(polyester-based anion type urethane emulsion "HYDRAN ECOS-3000" manufactured by Dainippon Ink & Chemicals, Inc., non-volatile content: 40%), 0.005 parts of ferrous sulfate hepta-hydrate and 0.4 parts of acetic acid in 150 parts of water. Then, an atmosphere in the pressure-resistant vessel was purged with a nitrogen gas, and the atmosphere in the vessel was heated up to 60°C, then, pressurized with ethylene up to 4.6 MPa. Next, 0.5 parts of 30% hydrogen peroxide-containing aqueous solution and 0.6 parts of sodium erisorbate were diluted with water, and dropping of them was initiated. The temperature in the reaction vessel was kept at 60°C by controlling the temperature of a jacket during the polymerization, further, an aqueous solution of hydrogen peroxide was added, and the mixture was stirred until the concentration of vinyl acetate in the reaction solution reached 1% or less, then, an un-reacted ethylene gas was removed, to

obtain an aqueous emulsion (E).

The resin composition of the resultant aqueous emulsion (E) included 22 parts of a structural unit derived from ethylene, 9 parts of a resin component (non-volatile content) of the aqueous emulsion (A), and 4.7 parts of a resin component (non-volatile content) of polyvinyl alcohol based on 100 parts of a structural unit derived from vinyl acetate.

The aqueous emulsion (E) had a non-volatile content of 52.9% and a viscosity of 1890 mPa·s.

Into 110 parts of this emulsion (E) was compounded 5.3 parts of DBE manufactured by INVISTA JAPAN, and 6 parts of a substance obtained by 2-fold diluting a thickener A-812 manufactured by SAN NOPCO LIMITED was compounded, to obtain an adhesive, and using this adhesive, the same adhesion test was conducted as in Example 1. The results are summarized in Table 1.

Comparative Example 6

<Production Example of ethylene-vinyl acetate-based copolymer aqueous emulsion (F)>

Into a pressure-resistant vessel was introduced a solution prepared by previously dissolving 190 parts of vinyl acetate, 2.3 parts of polyvinyl alcohol "PVA-217" (manufactured by Kuraray Corp., degree of saponification: 88 mol%, average degree of polymerization: 1700), 7 parts of "PVA-205" (manufactured by Kuraray Corp., degree of saponification: 88 mol%, average degree of polymerization: 500), 0.005 parts of

ferrous sulfate hepta-hydrate and 0.4 parts of acetic acid in 160 parts of water. Then, an atmosphere in the pressure-resistant vessel was purged with a nitrogen gas, and the atmosphere in the vessel was heated up to 60°C, then, pressurized with ethylene up to 4.6 MPa. Next, 0.33 parts of 30% hydrogen peroxide-containing aqueous solution and 0.6 parts of sodium erisorbate were diluted with water, and dropping of them was initiated. The temperature in the reaction vessel was kept at 60°C by controlling the temperature of a jacket during the polymerization, further, an aqueous solution of hydrogen peroxide was added, and the mixture was stirred until the concentration of vinyl acetate in the reaction solution reached 1% or less, then, an un-reacted ethylene gas was removed, to obtain an ethylene-vinyl acetate-based copolymer aqueous emulsion (F).

The resin composition of the resultant aqueous emulsion (F) included 22 parts of a structural unit derived from ethylene, and 4.9 parts of a resin component (non-volatile content) of polyvinyl alcohol based on 100 parts of a structural unit derived from vinyl acetate. The aqueous emulsion (F) had a non-volatile content of 55.0% and a viscosity of 1200 mPa·s.

<Production Example of adhesive composition composed of aqueous emulsion (F) and polyurethane aqueous emulsion>

100 parts of the aqueous emulsion (F), 10.6 parts of an anion type urethane emulsion "HYDRAN ECOS-3000" (manufactured by

Dainippon Ink & Chemicals, Inc., non-volatile content: 40%) and 5.3 parts of DBE manufactured by INVISTA JAPAN were compounded, and pH thereof was adjusted to 8 to 9 with 0.2 parts of 25% ammonia, then, 6 parts of a substance obtained by 2-fold diluting a thickener A-812 manufactured by SAN NOPCO LIMITED was compounded, to obtain an adhesive. Using this adhesive, the same adhesion test was conducted as in Example 1. The results are summarized in Table 1.

Table 1

	Example 1	Example 2	Comparative Example 2	Comparative Example 3	Comparative Example 4	Comparative Example 5	Comparative Example 6
Aqueous emulsion (B1)	110						
Aqueous emulsion (B2)		110					
Aqueous emulsion (D)			100	100	100		
Aqueous emulsion (E)						110	
Aqueous emulsion (F)							100
ECOS-3000				10.6			10.6
ADS-120					8.5		
DBE	5.3	5.3	4.8	5.3	5.3	5.3	5.3
2-fold diluted A-812	6	0.5	4	4	2.5	6	6
25% ammonia water				0.2			0.2
Viscosity (BH-10 mPa·s)	10100	23200	12400	11600	10560	12600	11100
Adhesion test							
Strength under normal conditions (N/25mm)	47	49	39	45	49	44	45
Heat resistance creep, 80°C							
Peeled distance (mm)							
1 hour	1.5	1.5	8	3	5	105	7
3 hours	2	5	23	6	13	200<	21
5 hours	3	7	31	8	18	200<	29

ECOS-3000: HYDRAN ECOS-3000 manufactured by Dainippon Ink & Chemicals, Inc.

ADS-120: HYDRAN ADS-120 manufactured by Dainippon Ink & Chemicals, Inc.

DBE: DBE manufactured by INVISTA JAPAN

2-fold diluted A-812: obtained by 2-fold diluting A-812 manufactured by SAN NOPCO LIMITED

As apparent from Table 1, reproduction of JP-A No. 2004-211037 is difficult (Comparative Example 1), however, the production method of the present invention (Examples 1 and 2) was be performed easily. The adhesive of the present invention has strength under normal conditions approximately equal to that of the adhesive (Comparative Example 2) containing only an ethylene-vinyl acetate-polyfunctional monomer copolymer-containing aqueous emulsion as an effective ingredient, and those of adhesives (JP-A No. 9-194811, Comparative Examples 3, 4 and 6) containing the copolymer-containing aqueous emulsion and a polyurethane aqueous emulsion. However, the heat resistance creep of the adhesive of the present invention is more excellent even in a longer period of time.

Further, when a polyfunctional monomer is not used in seed polymerization (Comparative Example 5), heat resistance creep lowers remarkably.

Industrial Applicability

The modified polyurethane aqueous emulsion produced by the method of the present invention can be suitably used in one pot type adhesives such as those for carpentry, for paper processing, for wall paper, for wrapping, for (secondary) plywood, for building site, for building factory, for lamination, for fiber,

for domestic, for civil construction, for book binding and the like; two pot type adhesives using a hardener together; paints, and the like.

What is claimed is:

1. A method for producing a modified polyurethane aqueous emulsion comprising emulsion-polymerizing a polyurethane aqueous emulsion and monomers containing ethylene, vinyl ester and polyfunctional monomer with a redox catalyst containing a salt of a transition metal, erysorbic acids and/or ascorbic acids as a reducing agent.

2. The method according to Claim 1, wherein the redox catalyst contains hydrogen peroxide as an oxidizing agent.

3. A modified polyurethane aqueous emulsion obtained by the method according to Claim 1 or 2.

4. An adhesive comprising the modified polyurethane aqueous emulsion according to Claim 3.

5. A laminate comprising an adhesive layer made of the adhesive according to Claim 4, and a base material capable of absorbing water.

6. The laminate according to Claim 5, wherein a polyolefin layer is further laminated at the side of the adhesive layer.

7. A method for producing a modified polyurethane aqueous emulsion comprising the steps of:

adding monomers containing ethylene, vinyl ester and polyfunctional monomer into a polyurethane aqueous emulsion in the presence of a redox catalyst containing a salt of a transition metal, erysorbic acids and/or ascorbic acids as a

reducing agent, and

heating at the temperature of from about 20°C to about 80°C.