

## ADHESIVE COMPOSITION AND METHOD FOR PRODUCING THE SAME

### Field of the Invention

The present invention relates to an adhesive composition.

### Background of the Invention

As an adhesive composition having excellent normal-state adhesive property and thermal creep resistance, an adhesive composition composed of an aqueous emulsion containing vinyl acetate-ethylene copolymer, which is a kind of ethylene-vinyl esters, and a polyurethane containing aqueous emulsion is disclosed in Patent literatures 1 and 2. Also disclosed is that such adhesive composition is suitable for adhering a wood and a sheet of polyvinyl chloride and can adhere a sheet of polyolefin such as polyethylene and polypropylene with a wood.

[Patent literature 1] JP 60-163981 A [Claims]

[Patent literature 2] JP 9-194811 A [Claims]

### Summary of the Invention

According to the study of the present invention, it comes out that the adhesive composition obtained by mixing an neutral to weakly acidic ethylene-vinyl ester based copolymer containing aqueous emulsion with a alkaline polyurethane aqueous emulsion as it is sometimes coagulates itself and increases its viscosity after a long preservation. The study further shows that, when the neutral to weakly acidic ethylene-vinyl acetate based copolymer emulsion is mixed after

the pH value thereof is adjusted with aqueous ammonia to around the pH value of the alkaline polyurethane aqueous emulsion, the obtained adhesive composition hardly coagulates and never increases its viscosity after a long preservation. The study also shows, however, that the adhesive composition applied with aqueous ammonia decreases its pH value after a long preservation, resulting in deterioration of pH stability.

The object of the present invention is to provide an adhesive composition significantly decreasing coagulation and having excellent stabilities of viscosity and pH, and a method for producing the same.

The inventors have found that an adhesive composition having a kind of surfactant with a specific amount is excellent in stabilities of viscosity and pH even after a long preservation.

Namely, the invention provides the following aspects of [1] to [7]:

[1]. An adhesive composition comprising an ethylene-vinyl ester based copolymer containing aqueous emulsion (A), a polyurethane containing aqueous emulsion (B), and at least one selected from the group consisting of a polyoxyethylene alkylether (C) and a condensed polyoxyethylene polyoxypropylene compound (D), wherein a weight ratio of (A)/(B) of a solid content is from 52/48 to 98.5/1.5, and a total weight of a solid content of (C) and (D) is 0.05 to 0.75 parts by weight per 100 parts by weight

of the total weight of (A) and (B).

[2]. The adhesive composition according to [1], wherein the composition has pH of 4 to 7.

[3]. The adhesive composition according to [1] or [2], wherein an emulsifying agent applied for producing (A) is a protective colloid.

[4]. An adhesive comprising the adhesive composition according to any one of [1] to [3] and a hardening agent.

[5]. A laminate comprising laminating a water-absorbent material and a plastic material via the adhesive composition according to any one of [1] to [3].

[6]. A laminate comprising laminating a water-absorbent material and a plastic material via the adhesive according to [4].

[7]. A method for producing an adhesive composition comprising the steps of;

mixing an ethylene-vinyl ester based copolymer containing aqueous emulsion (A) with at least one selected from the group consisting of a polyoxyethylene alkyl ether (C) and a condensed polyoxyethylene polyoxypropylene compound (D) to obtain a mixture, and then

mixing the mixture with a polyurethane containing aqueous emulsion (B).

#### Detailed Description of the Invention

The present invention will be explained in detail as follows.

The ethylene-vinyl ester based copolymer containing aqueous emulsion (A) used in the present invention is an aqueous emulsion containing a copolymer having structural units derived from ethylene and vinyl ester. A content of the structural unit derived from ethylene of the copolymer is usually about 5% to about 70% by weight, and preferably about 10% to about 35% by weight.

It is preferable that, when the content of the structural unit derived from ethylene in the copolymer contained in (A) is 5% by weight or more, film forming ability of the obtained adhesive at a room temperature tends to improve and close adhesive property to hard-to-bond substrates such as polyolefin tends to enhance, when the content is 70% by weight or less, heat resistance and adhesive strength tend to enhance.

The vinyl ester used for (A) is a vinyl ester of mono carboxylic acid.

Examples of the vinyl ester include alkyl acid vinyl esters such as vinyl acetate, vinyl butyrate, vinyl propionate, vinyl pivalate, vinyl laurate, vinyl isononanate, and vinyl vassatate. Two or more kinds of vinyl esters may be used as a vinyl ester unit. Among the vinyl esters, vinyl acetate is preferably used.

A content of the structural unit derived from the vinyl ester in the copolymer contained in (A) is usually 95 to 30% by weight, and preferably 90 to 65% by weight. It is preferable that, when the content is 95% by weight or less, a film forming

ability of the aqueous emulsion at a room temperature tends to improve and close adhesive property to hard-to-bond substrates such as polyolefin tends to enhance. It is preferable that, on the other hand, when the content is 30% by weight or more, heat resistance and adhesive strength tend to enhance.

The monomer used for producing (A), besides ethylene and vinyl esters, a monomer (hereinafter, occasionally referred to "copolymerizable monomer") which can copolymerize with such monomers and which has one ethylenic double bond in the molecule may be used. Examples of the copolymerizable monomer include halogenated vinyls such as vinyl chloride and vinyl bromide; halogenated vinylidenes such as vinylidene chloride; vinyl compounds such as vinyl phosphonic acid, and vinyl sulfonic acid and salts thereof; aromatic vinyls such as styrene,  $\alpha$ -methylstyrene, and chlorostyrene; (meth)acrylic acids such as methacrylic acid and acrylic acid; (meth)acrylic esters such as methyl (meth)acrylate, butyl (meth)acrylate, and 2-ethylhexyl (meth)acrylate;  $\alpha$ ,  $\beta$ -unsaturated dicarboxylic acids such as maleic acid, maleic anhydride, succinic acid, and itaconic acid; nitriles such as (meth)acrylonitrile; acrylamides such as N-methylol acrylamide and N-butoxymethyl acrylamide; conjugated dienes such as butadiene and isoprene; and allyl compounds such as allyl sulfonate, diallylphtalate, triallylcyanulate, and triallylisocyanulate.

A content of the structural unit derived from the copolymerizable monomer of the copolymer contained in (A) is

usually 20% by weight or less, and preferably 10% by weight or less.

The (A) may further contain a copolymerizable crosslinking monomer having two or more ethylenic double bonds (hereinafter, occasionally referred to "crosslinking monomer") which is different from ethylene, vinyl esters, and copolymerizable monomers to generate a toluene insoluble. Examples of the crosslinking monomer include diallylphtalate, triallylcyanulate, triallylisocyanulate, ethyleneglycol diacrylate, allylmethacrylate, adipic acid diacrylate, and trimethylolpropane dimethacrylate.

A content of the structural unit derived from the crosslinking monomer of the copolymer contained in (A) is usually 5% by weight or less, and preferably 3% by weight or less. The (A) containing the structural unit derived from the crosslinking monomer tends to provide heat resistance to an adhesive to be obtained and to improve thermal creep resistance of the adhesive.

The (A) can be obtained with an emulsion polymerization. A protective colloid is suitably used as an emulsifying agent. The emulsifying agent consisting only of a protective colloid is particularly preferable. The protective colloid, for example, includes polyvinyl alcohols such as partially saponified polyvinyl alcohol, fully saponified polyvinyl alcohol, sulfonic acid-modified polyvinyl alcohol, carboxyl-modified

polyvinyl alcohol, and silanol group-modified polyvinyl alcohol; and cellulose derivatives such as hydroxyethylcellulose, methylcellulose, and carboxymethylcellulose. Among them, partially saponified polyvinyl alcohol and fully saponified polyvinyl alcohol are preferable, and polyvinyl alcohol saponified in a saponification degree of 80 to 100% by moles is suitable.

An average polymerization degree of the protective colloid is usually 200 to 3000, and the emulsion polymerization is preferably conducted using polyvinyl alcohols having the average polymerization degree of 250 to 2500 as the protective colloid.

A content of the solid such as ethylene-vinyl ester copolymer and protective colloid in (A) is usually 40 to 78% by weight, and preferably 43 to 75% by weight. It is preferable that, when the solid content is 40% by weight or more, generation of coagulation tends to suppress; and when the content is 78% by weight or less, gelation of the copolymer tends to suppress and the emulsion polymerization tends to facilitate.

The solid content in the present invention can be determined according to JIS K-6828-1.

Namely, a flat-bottom dish made of aluminum foil having a diameter of 50 mm is dried in a forced-circulation drier at 140°C for 30 minutes, left standing to cool to a room temperature, and then weighed with an accuracy of 1 mg.

A sample weighed in an amount of  $1.0 \pm 0.2$  g with an accuracy

of 1 mg is placed on the flat-bottom dish, and then spread uniformly. The sample on the flat-bottom dish is put in the forced-circulation drier at a temperature of 140°C, dried for 30 minutes, left standing to cool to a room temperature, and then weighed with an accuracy of 1 mg. The solid content is determined according to the following formula:

$$N = \frac{m_2 - m_0}{m_2 - m_1} \times 100$$

wherein N: Solid content (%),

$m_0$ : Mass (g) of flat-bottom dish,

$m_1$ : Mass (g) of flat-bottom dish and sample, and

$m_2$ : Mass (g) of flat-bottom dish and evaporated residue.

A hardened substance consisting only of (A) has usually a glass-transition temperature of -25 to +15°C, and preferably -20 to +10°C. When the glass-transition temperature is -25°C or more, heat resistance tends to enhance; and when the temperature is 15°C or less, film forming ability at a room temperature tends to enhance.

The (A) used in the present invention usually has pH of about 4 to about 7. The pH value of the fore-mentioned range results from the pH range originated from the (A) produced with the emulsion polymerization, and serves to easily produce an adhesive composition without adjusting the pH value to an alkaline domain as almost same as an alkalinity of the

polyurethane containing aqueous emulsion (B).

Moreover, it is preferable that adjusting the pH value of 7 or less tends to cause the ethylene vinyl ester based copolymer emulsion to stably exist with less pH change and to enhance preservation ability of the obtained adhesive composition.

The polyurethane containing aqueous emulsion (B) is an aqueous emulsion dispersing in water the polyurethane which is obtained by reacting a polyisocyanate compound and a polyol compound, and, if required, an other compound. A reaction method, for example, includes an acetone method, a prepolymer mixing method, a ketimine method, and a hot-melt dispersion method.

The polyisocyanate compound includes organic polyisocyanate compounds used for producing conventional polyurethanes. Examples of the polyisocyanate compound include aliphatic diisocyanates such as 1,4-tetramethylene diisocyanate, 1, 6-hexamethylene diisocyanate, 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, 1,3-bis(isocyanate)methylcyclohexane, tetra-methylxylylene diisocyanate, trans-cyclohexane-1,4-diisocyanate, and lysine diisocyanate;

aromatic diisocyanates such as 2, 4-toluylene diisocyanate, 2, 6-toluylene diisocyanate, diphenylmethane-4,4'-diisocyanate, 1,5'-naphthene diisocyanate, tolidine diisocyanate, diphenylmethyldiphenylmethane diisocyanate, tetra-alkyldiphenylmethane diisocyanate, 4,4'-dibenzyl diisocyanate, and 1,3-phenylene diisocyanate; and 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, an adduct of trimethylolpropane and toluylene diisocyanate, and an adduct of trimethylolpropane and 1,6-hexamethylene diisocyanate.

They may be used alone or a combination of two kinds or more thereof.

The polyol compound includes compounds of which molecule having two or more hydroxy groups, which are used for producing conventional polyurethanes, for example, polyhydric alcohols such as ethylene glycol, diethylene glycol, propylene glycol, 1,4-butanediol, 1,6-hexanediol, neopentylglycol, trimethylolpropane, and glycerol; polyether polyols such as polyethylene glycol, polypropylene glycol, and polytetramethylene ether glycol; polyester polyols obtained from a dicarboxylic acid and polyol compound, the dicarboxylic acid including 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, and azelaic acid, and the polyol compound including ethylene glycol, diethylene glycol, propylene glycol, 1,4-butanediol, 1,6-hexanediol, neopentylglycol, 1,2-propanediol, 1,3-propanediol, 1,9-nonanediol, 3-methyl-1,5-pentanediol, 1,3-propanediol, tripropylene glycol, trimethylolpropane, and glycerol;

polylactone based polyester polyols such as polycaprolactone polyol and poly- $\beta$ -methyl- $\delta$ -valerolactone; and polybutadiene polyol or its hydrogenated compound, polycarbonate polyol, polythioether polyol, and polyacrylic acid ester polyol.

Introducing a hydrophilic group in a molecule during producing the polyurethane is preferable to enhance the stability when the polyurethane contained in (B) is dispersed in water. The compound used for introducing the hydrophilic group, for example, includes a compound (hereinafter, occasionally referred to "hydrophilic group-containing compound") of which molecule has a nonionic hydrophilic group such as a structure unit derived from polyethylene glycol, and has one or more active hydrogen which are reactive with an isocyanate group, such as sulfonyl group, carboxyl group, hydroxyl group, primary amino group ( $-NH_2$ ), secondary amino group ( $=NH$ ), and the like.

Examples of the hydrophilic group containing compound include sulfonic acid containing compounds such as 3,4-diaminobutanesulfonic acid, 3,6-diamino-2-toluenesulfonic acid, 2,6-diaminobenzenesulfonic acid, and N-(2-aminoethyl)-2-aminoethylsulfonic acid; and carboxylic acid containing compounds such as 2,2-dimethylolactic acid, 2,2-dimethylolpropionic acid, and 2,2-dimethylolvaleric acid. The hydrophilic group containing compound may be used alone or a combination of two or more thereof.

As the (B) has a hydrophilic group in the molecule obtained by using such hydrophilic group containing compounds, the (B) contains an ionomer structure and has a surface active ability by itself. Therefore, (B) tends to be easily dispersible in water and enhance a water resistance of the aqueous emulsion obtained by further emulsion polymerizing the polyurethane aqueous emulsion with a monomer.

The hydrophilic group is preferably anionic groups such as sulfone group and carboxyl group, and particularly preferably sulfone group because of tendency to further enhance the water resistance of the aqueous emulsion obtained by emulsion polymerizing the monomer.

The anionic group is usually preferably neutralized with a neutralizing agent. The neutralizing agent includes tertiary amines such as triethylamine and triethalamine; inorganic alkali compounds such as sodium hydroxide; and ammonia.

When producing (B), if required, in order to elongate a chain length or control a molecular weight, may be co-used a compound which is different from the hydrophilic group containing compound and of which molecule has an active hydrogen reactive with an isocyanate group. Such compound, for example, includes polyamines such as ethylenediamine, 1,4-butanediamine, and 1,6-hexanediamine; tertiaryamine containing polyhydric alcohols such as triethanolamine; and monoalcohols such as methanol, ethanol, and butanol.

The commercial available polyurethane containing aqueous emulsions are used as it is.

Specifically included are HYDRAN ECOS3000, ADS-120, and ADS-110 manufactured by Dainippon Ink and Chemicals Inc., UPRENE UXA-3005 manufacture by Sanyo Chemical Industries, Ltd., and U-53, U-54, and U-56 manufactured by Sumika Bayer Urethane Co., Ltd.

In the adhesive composition of the invention, a weight ratio of a solid content of (A)/(B) is from 52/48 to 98.5/1.5, and preferably from 88/12 to 97/3. It is preferable that, when the weight ratio of (B) is 48 or less, a heat resistance of the obtained adhesive tends to enhance, and when the ratio of (B) is 1.5 or more, close adhesive property to hard-to-bond materials such as polyolefin tends to increase.

The adhesive composition of the present invention includes a polyoxyethylene alkylether (C) and/or condensed polyoxyethylene polyoxypropylene compound (D).

(C) is an alkylether of polyethylene glycol. It is preferable that, when using the polyoxyethylene alkylether of which structural unit ( $-\text{CH}_2-\text{CH}_2-\text{O}-$ ) derived from polyethylene glycol has the average polymerization number of 7 to 49 and of which alkyl portion has 10 to 18 carbon atoms, a coagulation of the adhesive composition tends to decrease when mixing (A) and (B).

Examples of commercially available (C) include Emulgen 1108, Emulgen 1118S-70, Emulgen 1135S-70, and Emulgen 1150S-70 manufactured by Kao Co. These commercial products may be used alone or a combination of two or more thereof.

(D) is a condensed polyoxyethylene polyoxypropylene compound. It is preferable that, when using the condensed polyoxyethylene polyoxypropylene compound (D) which has a molecular weight of 2000 to 27000 and contains a structural unit derived from ethylene oxide in an amount of 10 to 80% by weight, a coagulation of the adhesive composition tends to decrease when mixing (A) and (B).

Examples of commercially available (D) include Pluronic L-34, 44, and 64 manufactured by ADEKA CORPORATION; these commercial products may be used alone or a combination of two or more thereof.

Furthermore, (C) and (D) may be used in combination.

In the present adhesive composition, a total weight of (C) and (D) (of a solid content) is 0.05 to 0.75 parts by weight, and preferably 0.05 to 0.6 parts by weight, more preferably 0.08 to 0.3 parts by weight per 100 parts by weight of (A) and (B) (as the whole weight composing (A) and (B)). Here, the whole weight composing (A) and (B) means a whole weight of the aqueous emulsion composed of a solvent such as water and a solid content.

It is preferable that, when the total weight of (C) and (D) is 0.05 parts or more, a coagulation of the adhesive composition tends to decrease when mixing (A) and (B) and hydrolysis of the structure derived from vinyl ester contained in (A) tends to suppress, and eventually enhance the stability of pH; and when the total weight is 0.75 part or less, adhesive property tends to enhance.

The pH of the adhesive composition of the present invention is usually about 4 to about 7. It is preferable, when the pH value is in the above range, hydrolysis of the structure derived from vinyl ester contained in (A) tends to suppress, and eventually the stability of pH tends to enhance.

The adhesive composition of the present invention may be blended with, for example, thermosetting resins such as urea resins, melamine resins, and phenol resins; fillers such as clay, kaolin, talc, and calcium carbonate; antiseptics; corrosion inhibitors; defoaming agents; foaming agents; thickeners such

as polyacrylic acids, polyethers, methylcelluloses, carboxymethylcelluloses, polyvinyl alcohols, and starch; viscosity modifiers; flame retardants; pigments such as titanium oxide; high boiling- point solvents such as dibasic acid esters of dimethyl succinate and dimethyl adipate; and plasticizers.

Among them, the fillers is recommended to be used for improving flame resistance and coating ability during adhesion working; and its use amount is usually about 1 to about 500 parts by weight, and preferably about 5 to about 200 parts by weight, per 100 parts by weight of the solid content of the adhesive composition.

The adhesive composition of the present invention is preferably prepared by mixing (A) with (C) and/or (D) followed by mixing with (B) because the generation of a coagulation tends to significantly reduce in comparison with an order of mixing (B) with (C) and/or (D) followed by mixing (A), or an order of mixing (A) and (B) followed by mixing with (C) and/or (D).

The adhesive composition of the present invention may be used as it is as a one-component type adhesive, and suitably used as an adhesive composed of a mixture of the adhesive composition of the present invention and a hardening agent.

The hardening agent is an isocyanate based hardening agent, specifically including diphenylmethane-4,4'-diisocyanate (MDI), tolylene

diisocyanate (2,4-TDI, 2,6-TDI), hexamethylene diisocyanate (HDI), and m-xylylene diisocyanate (XDI) and oligomers thereof, and block types thereof. Commercially available hardening agents may be used as it is, specifically including Sumidur 44V20 and N3300 manufactured by Sumika Bayer Urethane Co., Ltd., and CR-60N manufactured by Dainippon Ink and Chemicals Inc.

The hardening agent is blended in the adhesive in an amount of usually 0.1 to 20 parts by weight, and preferably 1 to 10 parts by weight, per 100 parts by weight of the adhesive composition (the whole weight composing the adhesive composition). When the amount is 0.1 parts by weight or more, a thermal creep resistance and water resistance tend to enhance; and when the amount is 20 parts by weight or less, available time of the adhesive tends to extend.

Materials capable of being adhered with the adhesive composition or adhesive of the present invention are water-absorbent materials, and examples thereof include woody materials such as woods, plywoods, MDF(Medium Density Fiberboard), particle boards, and fiberboard; papery materials such as wallpapers and wrapping papers; cellulosic materials such as cotton clothes, hemp clothes, and rayons; and porous materials.

Furthermore, when a layer of the adhesive composition or adhesive adheres to a water-absorbent material on one side of the layer, the other side thereof may be adhered to a material including polyolefins such as polyethylenes, polypropylenes,

and polystyrenes; plastic materials such as polyesters, polyethers, and polyvinyl chlorides; glasses; and ceramic materials such as potteries.

Among of them, a laminate obtained by adhering a water-absorbent material and polyolefin via the adhesive composition or adhesive of the present invention is preferable, because this laminate has an excellent normal-state adhesive property as same as a laminate obtained by adhering via an adhesive composition composed of the conventional ethylene-vinyl acetate based copolymer aqueous emulsion and polyurethane aqueous emulsion, and tends to enhance a thermal creep resistance thereof.

The adhesive composition of the present invention hardly has a coagulation, and significantly suppresses the increase of viscosity and decrease of pH after a long preservation; furthermore, no process of pH adjustment is required before blending and can be produced easily in comparison with blending an ethylene-vinyl ester based copolymer emulsion with a polyurethane emulsion after adjusting the pH value of the copolymer emulsion with aqueous ammonia.

#### Examples

The present invention will be explained in more detail according to the following Examples, however, the invention should not be construed to be limited thereto. "Parts" and "%" represent ratios in terms of weight unless being specifically defined. The solid content was determined with a measurement

according to JIS K-6828 mentioned above. The viscosity was determined with a value measured with a Brookfield viscometer (manufactured by Toki Sangyo Co., Ltd.) at BL-60 rpm after adjusting a temperature in a water bath at 25°C.

#### Example 1

<Production Example of Ethylene-Vinyl ester based Copolymer containing Aqueous Emulsion (A)>

In a pressure-resistant vessel, charged was a solution previously dissolving, in 160 parts of water, 180 parts of vinyl acetate, 8 parts of polyvinyl alcohol "POVAL 217" (manufactured by KURARAY CO., LTD., saponification degree 88% by mole, average polymerization degree 1700) as a protective colloid, 2.3 parts of "POVAL 205" (manufactured by KURARAY CO., LTD., saponification degree 88% by mole, average polymerization degree 500) as a protective colloid, 0.005 parts of ferrous sulfate heptahydrate, and 0.4 parts of acetic acid. Thereafter, the atmosphere of the pressure-resistant vessel was replaced with nitrogen gas, the solution therein was heated up to 60°C, and then pressured with ethylene to 4.6 MPa. Thereafter, 0.1 parts of aqueous hydrogen peroxide solution and 0.6 parts of sodium erythorbate were diluted with water respectively, and then dropped. After confirming the increase of the solution temperature in the pressure-resistant vessel, a solution dissolving 0.19 parts of triallylisocyanulate with 10 parts of vinyl acetate was added over 3 hours. The temperature in the reaction vessel was maintained at 60°C during polymerization

by controlling a jacket temperature, the aqueous hydrogen peroxide solution was further added, and then the reaction solution was agitated until a vinyl acetate concentration reached to 1% or less, and then un-reacted ethylene gas was removed to obtain an ethylene-vinyl acetate polyfunctional monomer based copolymer aqueous emulsion (A).

The resin composition of the obtained aqueous emulsion (A), per 100 parts of the structural unit derived from vinyl acetate, contained 22 parts of the structural unit derived from ethylene, 0.1 parts of the structural unit derived from triallylisocyanulate, and 5.4 parts of the structural unit derived from polyvinyl alcohol. The solid content of the aqueous emulsion (A) was 55.0% and the viscosity thereof was 3000 mPa·s.

#### <Production Example of Adhesive composition>

In a vessel, mixed were 150 g of the (A) obtained in <Production Example of ethylene-vinyl ester based copolymer containing aqueous emulsion (A)> and 1.06 g of a solution, as polyoxyethylene alkylether (C), in which Emargen 1118S-70 manufactured by Kao Co. was adjusted to 20% concentration. Thereafter, in the vessel, mixed was 50 g of the polyurethane aqueous emulsion ECOS3000 manufactured by Dainippon Ink and Chemicals Inc., as polyurethane containing aqueous emulsion (B). The obtained adhesive composition had the pH value of 5.4 and the viscosity of 1500 mPa·s. After preserving the composition at a room temperature for 2 weeks, the pH value was 5.4 and the viscosity was 1760 mPa·s. After preserving the composition at

50 °C for 2 weeks, the pH value was 5.2 and the viscosity was 2450 mPa·s.

#### Comparative Example 1

Except for not using (C) and directly mixing (A) and (B) in Example 1, a composition was obtained in the same manner as in Example 1. The obtained composition had the pH value of 5.4 and the viscosity of 2430 mPa·s. After preserving the composition at a room temperature for 2 weeks, the pH value was 5.4 and the viscosity was 7800 mPa·s. After preserving the composition at 50 °C for 2 weeks, the pH value was 5.2 and the viscosity was 10000 mPa·s.

#### Examples 2 to 6

Except for using (C) listed in Table 1 in place of Emulgen 1118S-70, a pH and viscosity were measured in the same manner as in Example 1. The results are shown in Table 1 together with that of Example 1.

Table 1

| Example                                                                      | 1           | 2           | 3           | 4           | 5           | 6           |
|------------------------------------------------------------------------------|-------------|-------------|-------------|-------------|-------------|-------------|
| (A) (parts)                                                                  | 150         | 150         | 150         | 150         | 150         | 150         |
| (C)-1 (parts)                                                                | 1.06        |             |             |             |             |             |
| (C)-2 (parts)                                                                |             | 1.06        |             |             |             |             |
| (C)-3 (parts)                                                                |             |             | 1.06        |             |             |             |
| (C)-4 (parts)                                                                |             |             |             | 1.06        |             |             |
| (C)-5 (parts)                                                                |             |             |             |             | 1.06        |             |
| (C)-6 (parts)                                                                |             |             |             |             |             | 1.06        |
| (B) (parts)                                                                  | 50          | 50          | 50          | 50          | 50          | 50          |
| pH after<br>production,<br>Viscosity<br>(mPa·s)                              | 5.4<br>1500 | 5.4<br>1840 | 5.4<br>1740 | 5.4<br>1810 | 5.4<br>1720 | 5.4<br>2140 |
| pH after at a<br>room<br>temperature<br>for 2 weeks,<br>Viscosity<br>(mPa·s) | 5.4<br>1760 | 5.4<br>2000 | 5.4<br>2610 | 5.4<br>2600 | 5.4<br>2640 | 5.4<br>3350 |
| pH after at 50°C<br>for 2 weeks,<br>Viscosity<br>(mPa·s)                     | 5.2<br>2450 | 5.2<br>3100 | 5.2<br>3630 | 5.2<br>3670 | 5.2<br>4150 | 5.2<br>4830 |

(C)-1: 20% Emulgen 1118S-70, manufactured by Kao Co.,  
polyoxyethylene alkylether,

(C)-2: 20% Emulgen 1108, manufactured by Kao Co.,  
polyoxyethylene alkylether,

(C)-3: 20% Emulgen 1135S-70, manufactured by Kao Co.,  
polyoxyethylene alkylether,

(C)-4: 20% Emulgen 1150S-60, manufactured by Kao Co., polyoxyethylene alkylether,

(C)-5: 20% Pluronic L-64, manufactured by ADEKA CORPORATION, condensed polyoxyethylene-polyoxypropylene compound, and

(C)-6: 20% Pluronic L-44, manufactured by ADEKA CORPORATION, condensed polyoxyethylene-polyoxypropylene compound.

Viscosity: measured with BL-60.

#### Comparative Examples 2 to 4

Except for using the surfactants listed in Table 2 in place of Emulgen 1118S-70, a pH and viscosity were measured in the same manner as in Example 1. In the Comparative Example 4, the (A) of Example 1 was added with aqueous ammonia and agitated, and then, after adjusting the pH value to 8 or more, mixed with (B) without using a surfactant.

The results are shown in Table 2 together with that of Comparative Example 1.

Table 2

| Comparative Example                                                    | 1             | 2             | 3           | 4           |
|------------------------------------------------------------------------|---------------|---------------|-------------|-------------|
| (A) (parts)                                                            | 150           | 150           | 150         | 150         |
| (C')-1 (parts)                                                         |               | 1.06          |             |             |
| (C')-2 (parts)                                                         |               |               | 1.06        |             |
| (C')-3 (parts)                                                         |               |               |             | 0.2         |
| (B) (parts)                                                            | 50            | 50            | 50          | 50          |
| pH after production,<br>Viscosity (mPa·s)                              | 5.4<br>2430   | 6.1<br>2720   | 5.1<br>3360 | 8.9<br>4450 |
| pH after at a room<br>temperature for 2<br>weeks, Viscosity<br>(mPa·s) | 5.4<br>7800   | 5.9<br>>10000 | 5.0<br>7870 | 6.8<br>5120 |
| pH after at 50°C for 2<br>weeks, Viscosity<br>(mPa·s)                  | 5.2<br>>10000 | 5.2<br>>10000 | 4.8<br>8100 | 5.6<br>6930 |

(C')-1: 20% POIZE 520, manufactured by Kao Co., special carboxylic acid type polymer surfactant,

(C')-2: 20% DEMOL P, manufactured by Kao Co., special carboxylic acid type polymer surfactant, and

(C')-3: 25% aqueous ammonia.

#### <Production Example 1 of Adhesive>

An adhesive was obtained as follows: 100 parts of the adhesive composition (just after produced) of Example 1 was blended with 10 parts of DBE manufacture by INVISTA (Japan) K.K. (a mixture of dibasic acid esters (dimethyl succinate, dimethyl adipate, dimethyl glutarate)) as an organic solvent, and then

added with a 2-times diluent thickener (SN thickener A-812, SAN NOPCO LIMITED, registered trade name, urethane-modified polyether based, effective component 40%) to adjust the viscosity (measured with BH-10) to about 10000 mPa·s.

#### <Adhesive Property Test>

After coating an aqueous emulsion on JAS1 group water-resistance plywood in an amount of 110 g/m<sup>2</sup>, a non-polyvinyl chloride sheet WS-201E (polyolefin sheet, 0.16 mm thick) manufactured by Dai Nippon Printing Co., Ltd. was adhered, deaerated with a hand roller, left for 1 day under being pressed with  $5.4 \times 10^{-3}$  MPa, and then released from pressing and dried for further 6 days to obtain a laminate.

The normal-state peeling strength of the laminate was determined with the peeling rate of 200 mm/min. (Shimadzu autograph). The thermal creep resistance was determined as follows: after the temperature of the laminate was adjusted at 80°C, the laminate was peeled off under the conditions of the peeling angle of 90° and the load of 500 g/25mm to measure a peeled length after passing 24 hours. The results are shown in Table 3.

#### <Production Examples 2 to 6 of Adhesive, and Adhesive Property Test thereof>

Except for using the adhesive composition of Example 1 preserved at 50 °C for 2 weeks in place of the adhesive composition of Example 1 (just after production), Production

Example 2 obtained an adhesive in the same manner as in <Production Example 1 of Adhesive> and conducted adhesive property test in the same manner as in Example 1.

Except for using the adhesive composition of Example 5 (just after production) in place of the adhesive composition of Example 1 (just after production), Production Example 3 obtained an adhesive in the same manner as in <Production Example 1 of Adhesive> and conducted adhesive property test in the same manner as in Example 1.

Except for using the adhesive composition of Example 5 preserved at 50 °C for 2 weeks in place of the adhesive composition of Example 1 (just after production), Production Example 4 obtained an adhesive in the same manner as in <Production Example 1 of Adhesive> and conducted adhesive property test in the same manner as in Example 1.

Except for using the adhesive composition of Comparative Example 1 (just after production) in place of the adhesive composition of Example 1 (just after production), Production Example 5 obtained an adhesive in the same manner as in <Production Example 1 of Adhesive> and conducted adhesive property test in the same manner as in Example 1.

The evaluation results of the adhesive property test are shown in Table 3 together with that of Production Example 1.

Table 3

| Production Example | Adhesive composition  | Preservation Condition        | Normal-State Peeling Strength (N/25mm) | Thermal Creep Resistance (mm) |
|--------------------|-----------------------|-------------------------------|----------------------------------------|-------------------------------|
| 1                  | Example 1             | Just after production         | 45                                     | 4                             |
| 2                  | Example 1             | Preserved at 50°C for 2 weeks | 47                                     | 3                             |
| 3                  | Example 5             | Just after production         | 43                                     | 4                             |
| 4                  | Example 5             | Preserved at 50°C for 2 weeks | 40                                     | 5                             |
| 5                  | Comparative Example 1 | Just after production         | 41                                     | 5                             |
| 6                  | Comparative Example 1 | Preserved at 50°C for 2 weeks | No adhesibility test                   |                               |

(Production Example 6 was impossible to conduct the adhesive property test because the viscosity of the adhesive composition measured with BL-60 was larger than 10000 mPa·s, causing deterioration of blending the adhesive.)

As apparent from Table 3, the adhesive composition of the present invention can be easily prepared without adjusting pH of the ethylene-vinyl ester copolymer emulsion; furthermore, the adhesive composition is a less-change and stable blended aqueous emulsion of which viscosity hardly increases after a long preservation and of which pH hardly decreases; and the production method thereof. Moreover, the adhesive of the present invention is aqueous and can be used as a base emulsion of adhesive for overlay plywoods and the like.

#### Examples 7 to 10

Except for using Emulgen 1118S-70 ((C)-1) or Pluronic L-64 ((C)-5) in an amount listed in Table 4, a pH and viscosity were determined in the same manner as in Example 1. The results are shown in Table 4 together with that of Example 1.

#### Comparative Examples 5 to 8

Except for using Emulgen 1118S-70 ((C)-1) or Pluronic L-64 ((C)-5) in an amount listed in Table 4, a pH and viscosity were determined in the same manner as in Example 1. The results are shown in Table 4.

<Production Examples 7 to 10 of Adhesive, and Adhesive Property Test thereof>

Except for using the adhesive composition of Example 8 (just after production) in place of the adhesive composition of Example 1 (just after production), Production Example 7 obtained an adhesive in the same manner as in <Production Example 1 of Adhesive> and conducted adhesive property test in the same manner as in Example 1.

Except for using the adhesive composition of Example 8 preserved at 50 °C for 2 weeks in place of the adhesive composition of Example 1 (just after production), Production Example 8 obtained an adhesive in the same manner as in <Production Example 1 of Adhesive> and conducted adhesive property test in the same manner as in Example 1.

Except for using the adhesive composition of Comparative

Example 6 (just after production) in place of the adhesive composition of Example 1 (just after production), Production Example 9 obtained an adhesive in the same manner as in <Production Example 1 of Adhesive> and conducted adhesive property test in the same manner as in Example 1.

Except for using the adhesive composition of Comparative Example 6 preserved at 50°C for 2 weeks in place of the adhesive composition of Example 1 (just after production), Production Example 10 obtained an adhesive in the same manner as in <Production Example 1 of Adhesive> and conducted adhesive property test in the same manner as in Example 1.

#### <Adhesive Property Test>

After coating an aqueous emulsion on JAS1 group water-resistance plywood in an amount of 110 g/m<sup>2</sup>, a non-polyvinyl chloride sheet WS-201E (polyolefin sheet, 0.16 mm thick) manufactured by Dai Nippon Printing Co., Ltd. was adhered, deaerated with a hand roller, left for 1 day under being pressed with  $5.4 \times 10^{-3}$  MPa, and then released from pressing and dried for further 6 days to obtain a laminate.

The Water resistance peeling strength of the laminate was determined with the peeling rate of 200 mm/min. (Shimadzu autograph). The thermal creep resistance was determined as follows: after the temperature of the laminate was adjusted at 80°C, the laminate was peeled off under the conditions of the peeling angle of 90° and the load of 500 g/25mm to measure a peeled length after passing 24 hours. The result are shown in Table 5.

Table 4

|                                             | Example |      |      |      |      | Comparative Example |      |      |      |
|---------------------------------------------|---------|------|------|------|------|---------------------|------|------|------|
|                                             | 1       | 7    | 8    | 9    | 10   | 5                   | 6    | 7    | 8    |
| (A) (parts)                                 | 150     | 150  | 150  | 150  | 150  | 150                 | 150  | 150  | 150  |
| (C)-1 (parts)                               | 1.06    | 0.50 |      |      |      | 0.30                |      |      |      |
| (C)-1' (parts)                              |         |      | 1.43 |      |      |                     | 2.86 |      |      |
| (C)-5 (parts)                               |         |      |      | 0.50 |      |                     |      | 0.30 |      |
| (C)-5' (parts)                              |         |      |      |      | 1.00 |                     |      |      | 2.00 |
| (B) (parts)                                 | 50      | 50   | 50   | 50   | 50   | 50                  | 50   | 50   | 50   |
| pH after production,                        | 5.4     | 5.4  | 5.4  | 5.5  | 5.5  | 5.4                 | 5.4  | 5.5  | 5.5  |
| Viscosity (mPa·s)                           | 1500    | 2060 | 1140 | 2180 | 1070 | 2400                | 730  | 2540 | 890  |
| pH after at a room temperature for 2 weeks, | 5.4     | 5.4  | 5.4  | 5.5  | 5.5  | 5.2                 | 5.4  | 5.3  | 5.4  |
| Viscosity (mPa·s)                           | 1760    | 2350 | 1270 | 3200 | 1490 | 2940                | 820  | 3610 | 1130 |
| pH after at 50°C for 2 weeks,               | 5.2     | 5.1  | 5.4  | 5.1  | 5.4  | 4.7                 | 5.3  | 4.7  | 5.4  |
| Viscosity (mPa·s)                           | 2450    | 3680 | 1780 | 5660 | 2090 | 4790                | 1130 | 7130 | 1650 |

(C)-1': 70% Emulgen 1118S-70, manufactured by Kao Co.,  
polyoxyethylene alkylether,

(C)-5': 100% Pluronic L-64, manufactured by ADEKA CORPORATION,  
condensed polyoxyethylene-polyoxypropylene compound.

Table 5

| Production Example | Adhesive composition  | Preservation Condition        | Water Resistance Peeling Strength (N/25mm) | Thermal Creep Resistance (mm) |
|--------------------|-----------------------|-------------------------------|--------------------------------------------|-------------------------------|
| 1                  | Example 1             | Just after production         | 23                                         | 4                             |
| 7                  | Example 8             | Just after production         | 22                                         | 6                             |
| 8                  | Example 8             | Preserved at 50°C for 2 weeks | 20                                         | 8                             |
| 9                  | Comparative Example 6 | Just after production         | 13                                         | 8                             |
| 10                 | Comparative Example 6 | Preserved at 50°C for 2 weeks | 12                                         | 9                             |

### Industrial Applicability

According to the present invention, for applications to woodworks, paper processings, wallpapers, packings, (secondary) plywoods, construction fields, construction factories, laminations, fibers, home usage, civil engineering works, book-bindings, and the like, a one-pack type adhesive, a two-pack type co-used with a hardening agent, and a base emulsion for paints and the like can be provided.

What is claimed is:

1. An adhesive composition comprising an ethylene-vinyl ester based copolymer containing aqueous emulsion (A), a polyurethane containing aqueous emulsion (B), and at least one selected from the group consisting of a polyoxyethylene alkylether (C) and a condensed polyoxyethylene polyoxypropylene compound (D), wherein a weight ratio of (A)/(B) of a solid content is from 52/48 to 98.5/1.5, and a total weight of a solid content of (C) and (D) is 0.05 to 0.75 parts by weight per 100 parts by weight of the total weight of (A) and (B).

2. The adhesive composition according to Claim 1, wherein the composition has pH of 4 to 7.

3. The adhesive composition according to Claim 1 or 2, wherein an emulsifying agent applied for producing (A) is a protective colloid.

4. An adhesive comprising the adhesive composition according to any one of Claims 1 to 3 and a hardening agent.

5. A laminate comprising laminating a water-absorbent material and a plastic material via the adhesive composition according to any one of Claims 1 to 3.

6. A laminate comprising laminating a water-absorbent material and a plastic material via the adhesive according to Claim 4.

7. A method for producing an adhesive composition comprising the steps of;

    mixing an ethylene-vinyl ester based copolymer containing aqueous emulsion (A) with at least one selected from the group consisting of a polyoxyethylene alkyl ether (C) and a condensed polyoxyethylene polyoxypropylene compound (D) to obtain a mixture, and then

    mixing the mixture with a polyurethane containing aqueous emulsion (B).