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1POLYURETHANE ADHESIVE COMPOSITIONS

This invention relates to novel adhesive compositions, and is particularly concerned with polyurethane adhesive compositions which are useful as an adhesive for metals, plastics, rubber, etc.

5 Recently, as packaging materials for foodstuffs, etc., there have been developed and put into wide use multi-ply composite films comprising two, three or four layers and consisting of films of plastics, such as polyethylene, polypropylene, nylon, polyester and
10 polyvinyl chloride, laminated to metal foils, such as aluminium foil.

For bonding together these plastic films or metal foils, it has been known to use an adhesive composition containing a linear saturated polyester glycol, an
15 epoxy resin having not less than 2 hydroxyl groups, a polyisocyanate compound and an ester of phosphoric acid. However, this composition suffers from the defects that the resultant bond does not always exhibit adequate adhesive strength and is inferior in heat resistance or
20 resistance to chemicals, such as acids and alkalis.

For example, there is encountered the disadvantage that the resulting composite film, when heat-sterilized by high-temperature hot water of not less than 120°C after highly acid food containing free fatty acids is packaged
25 therein, not only shows a reduction in adhesive strength

between the metal foil and the plastic films but also exhibits reduced strength as a packaging material and, in extreme cases, develops complete delamination, with the resultant induction of pinholes through the metal foil, reducing the air-barrier properties inherent to metals and hence, constituting a serious hindrance to achievement of the object of preserving foodstuffs for a long period of time.

After extensive investigations conducted with a specific view to eliminating these defects we have found that the incorporation of a silane coupling agent in the said composition can produce adhesive compositions having an adhesive strength superior to those obtained using the previously known compositions and thus can yield coating films having outstandingly excellent heat- and chemical resistance. Further investigations have culminated in the development of the present adhesive composition. Accordingly, based on these investigations, the present invention provides a polyurethane adhesive composition, wherein the composition comprises an organic polyisocyanate, a polyol, an oxyacid of phosphorus or a derivative thereof, an epoxy resin and a silane coupling agent, and wherein some or all of the ingredients may be present in the form of a reaction product.

Examples of suitable organic polyisocyanates which are useful in the present composition include polyisocyanates monomers, such as aliphatic diisocyanates

exemplified by trimethylene diisocyanate, tetramethylene diisocyanate, hexamethylene diisocyanate, pentamethylene diisocyanate, 1,2-propylene diisocyanate, 1,2-butylene diisocyanate, 2,3-butylene diisocyanate, 1,3-butylene diisocyanate, 2,4,4- or 2,2,4-trimethylhexamethylene diisocyanate, 2,6-diisocyanatomethyl caproate, etc.; alicyclic diisocyanates exemplified by 1,3-cyclopentane-diisocyanate, 1,4-cyclohexanediisocyanate, 1,3-cyclohexane-diisocyanate, 3-isocyanatomethyl-3,5,5-trimethylcyclohexyl isocyanate, 4,4'-methylenebis(cyclohexylisocyanate), methyl-2,4-cyclohexanediisocyanate, methyl-2,6-cyclohexane-diisocyanate, 1,4-bis(isocyanatomethyl)cyclohexane, 1,3-bis(isocyanatomethyl)cyclohexane, etc.; aromatic diisocyanates exemplified by m-phenylene diisocyanate, p-phenylene diisocyanate, 4,4'-diphenyl diisocyanate, 1,5-naphthalenediisocyanate, 4,4'-diphenylmethanediisocyanate, 2,4- or 2,6-tolylene diisocyanate or mixtures thereof, 4,4'-toluidinediisocyanate, dianisidinediisocyanate, 4,4'-diphenyl ether diisocyanate, etc.; aralkyl diisocyanates exemplified by 1,3- or 1,4-xylylene diisocyanate or mixture thereof, ω,ω' -diisocyanato-1,4-diethylbenzene and the like; organic triisocyanates exemplified by triphenylmethane-4,4'-4"-triisocyanate, 1,3,5-triisocyanatobenzene, 2,4,6-triisocyanatotoluene, etc.; and organic tetraisocyanates exemplified by

4,4'-diphenyldimethylmethane-2,2'-5,5'-tetraisocyanate and the like; dimers, trimers, biurets and allophanates derived from the above polyisocyanate monomers; polyisocyanates having a 2,4,6-oxidiazinetriene ring
5 obtained from carbon dioxide and the above polyisocyanate monomers; adducts formed with low-molecular-weight polyols having a molecular weight of not more than 200 such as ethylene glycol, propylene glycol, butylene glycol, hexylene glycol, neopentyl glycol, cyclohexanedi-
10 methanol, diethylene glycol, triethylene glycol, dipropylene glycol, glycerol, trimethylolpropane, pentaerythritol and sorbitol; or adducts formed with those having a molecular weight of about 200 to 10,000 to be described hereinafter such as polyester polyols, polyether polyols, polyether
15 ester polyols, polyester amide polyols, acrylic polyols, polyhydroxyalkanes and castor oil.

Examples of the polyols which are useful in this invention include compounds having from 2 to 6, preferably 2 to 4, functional groups and a molecular weight of 200
20 to 10,000, preferably about 300 to 5,000. Particularly preferred are polyester polyols, polyether polyols, polyether ester polyols, polyester amide polyols, acrylic polyols, polyhydroxyalkenes, castor oil, polyurethane polyols or mixtures thereof.

25 Examples of such polyester polyols include polyester

polyols obtained by reacting dibasic acids, such as terephthalic acid, isophthalic acid, adipic acid and sebacic acid, their dialkyl esters or mixtures thereof with glycols such as ethylene glycol, propylene glycol, 5 diethylene glycol, butylene glycol and neopentyl glycol or mixtures thereof.

Examples of suitable polyether polyols include polyether polyols obtained by polymerizing oxirane compounds such as ethylene oxide, propylene oxide, butylene oxide 10 and tetrahydrofuran with the use of a low molecular weight polyol, such as water, ethylene glycol, propylene glycol, trimethylolpropane and glycerol, as an initiator.

Examples of suitable polyester amide polyols include those obtained by the combined use of starting 15 materials having amino groups such as ethylenediamine, propylenediamine and hexamethylene diamine in the above esterification reaction.

Examples of suitable acrylic polyols include those obtained by copolymerizing monomers having not 20 less than one hydroxyl group in the molecule, such as hydroxyethyl acrylate, hydroxypropyl acrylate, hydroxybutyl acrylate, etc., or their corresponding methacrylic acid derivatives, with acrylic acid, methacrylic acid or their esters.

25 Examples of suitable polyhydroxyalkenes include

polybutadiene polyols obtained by polymerizing butadiene or copolymerizing butadiene with acrylamide, etc.

The polyurethane polyols which may be used are polyols having a urethane linkage in the molecule and are
5 for example obtained by reacting polyether polyols, polyester polyols or polyether ester polyols having a molecular weight of about 200 to 5,000 with the above-mentioned organic polyisocyanates in a ratio of NCO/OH of less than about 1, preferably not more than about 0.8.

10 Besides the polyols described above, further, low molecular weight polyols having a molecular weight of 62 to 200 may be included in the composition in order to adjust the average molecular weight of the polyol component. Examples of these low molecular weight
15 polyols include ethylene glycol, propylene glycol, butylene glycol, diethylene glycol, dipropylene glycol, hexylene glycol, neopentyl glycol, cyclohexanedi-methanol, glycerol, trimethylolpropane and the like.

With reference to the oxyacids of phosphorus or
20 derivatives thereof which are useful in this invention, examples of suitable oxyacids of phosphorus include hypophosphorous acid, phosphorous acid, orthophosphoric acid and hypophosphoric acid, and condensed phosphoric acids, such as metaphosphoric acid,
25 pyrophosphoric acid, tripolyphosphoric acid, polyphosphoric

acid and ultraphosphoric acid; examples of the derivatives of the oxyacids of phosphorus mentioned above include salts of phosphoric acid and condensed phosphoric acids with sodium, potassium, etc., monoesters of oxyacids of phosphorus such as monomethyl orthophosphate, monoethyl orthophosphate, monopropyl orthophosphate, monobutyl orthophosphate, mono-2-ethylhexyl orthophosphate, monophenyl orthophosphate, monoethyl phosphite, monoethyl phosphite, monopropyl phosphite, monobutyl phosphite, mono-2-ethylhexyl phosphite and monophenyl phosphite, di- and triesters of oxyacids of phosphorus such as di-2-ethylhexyl orthophosphate, diphenyl orthophosphate, trimethyl orthophosphate, triethyl orthophosphate, tripropyl orthophosphate, tributyl orthophosphate, tri-2-ethylhexyl orthophosphate, triphenyl orthophosphate, dimethyl phosphite, diethyl phosphite, dipropyl phosphite, dibutyl phosphite, di-2-ethylhexyl phosphite, diphenyl phosphite, trimethyl phosphite, triethyl phosphite, tripropyl phosphite, tributyl phosphite, tri-2-ethylhexylphosphite and triphenyl phosphite, and mono-, di- and tri-esterified products of condensed phosphoric acids with alcohols, such as adducts obtained by adding epoxy compounds such as ethylene oxide and propylene oxide to the above oxyacids of phosphorus.

The oxyacids of phosphorus or derivatives thereof as mentioned above may be used singly or in the form of a

mixture of two or more thereof.

Among the above compounds, those having not less than one free oxyacid group are particularly preferred, and orthophosphoric acid, polyphosphoric acid or partial
5 adducts of orthophosphoric acid or polyphosphoric acid with epoxy compounds are favourable. The oxyacid of phosphorus or derivative thereof is capable of forming an ionic or covalent bond with metals, and can also react with the epoxy resin and isocyanate groups to be described
10 hereinafter, with the result that the oxyacid of phosphorus or derivative thereof plays a very important role in enhancing adhesion of the composition to metals and also in improving the acid and alkali resistance of the composition. The amount of oxyacid or derivative to be added may be in
15 the range of from 0.01 to 10 weight percent based on the weight of the total adhesive composition, preferably about 0.05 to 5 weight percent, more preferably about 0.1 to 1 weight percent.

Epoxy resins which are useful in this invention
20 include, for example, reaction products between polyhydric phenols, such as bisphenol A and tetrahydroxydiphenylethane, and polyfunctional halohydrins, such as epichlorohydrin, which reaction products have a molecular weight of about 320 to 5,000, preferably about 320 to 4,000 and an
25 epoxy equivalent of about 140 to 3,500, preferably 450 to 1,000. The amount of the epoxy resin present in the

composition may be in the range of about 1 to 50 weight percent, preferably about 5 to 30 weight percent, based on the weight of the total adhesive composition.

Examples of silane coupling agents which are
5 useful in this invention include compounds having the structural formula $R-Si(X)_3$ or $R-Si(R')(X)_2$ (where R is an organic vinyl, epoxy, amino, imino or mercapto radical; R' is an alkyl radical having 1 to 8 carbon atoms; X is a methoxy, ethoxy or β -methoxy ethoxy radical or a chlorine atom). Such
10 silane coupling agents are exemplified by chlorosilanes, such as vinyltrichlorosilane etc.; imino- or aminosilanes, such as N-(dimethoxymethylsilylpropyl)-ethylenediamine and N-(triethoxysilylpropyl)ethylenediamine, γ -aminopropyl-triethoxysilane etc.; epoxysilanes, such as γ -glycidoxy-
15 propyltrimethoxysilane and β -(3,4-epoxy-cyclohexyl)ethyl-trimethoxysilane etc.; vinyl silanes, such as vinyltriethoxy-silane, vinyl tris(β -methoxyethoxy)silane etc.; and mercaptosilanes such as γ -mercaptopropyltrimethoxysilane etc. The amount of the silane coupling agent to be added
20 is preferably in the range of about 0.05 to 20 weight percent based on the weight of the total adhesive composition, preferably about 0.1 to 5 weight percent. In addition to the silane coupling agent, it is possible to include in the composition, if necessary, conventional
25 additives such as antioxidants, ultraviolet absorbers,

hydrolysis stabilizers, antifungal or antibacterial agents, thickening agents, plasticizers, pigments and fillers. Also, known catalysts, additives, etc., can be used for the regulation of the curing reaction.

5 The present polyurethane adhesive composition may be obtained by mixing the above-mentioned organic polyisocyanate, polyol, oxyacid of phosphorus or derivative thereof, the epoxy resin and the silane coupling agent.

10 The NCO/H ratio, i.e., the ratio of the number of the NCO groups of the organic polyisocyanate / the number of the active hydrogen atoms (H) of the polyol, the oxyacid of phosphorus or the derivative thereof and the epoxy resin is preferably chosen to be in the
15 range of about 0.4 to 20.

 The present polyurethane adhesive composition can be used either as a one-can type (one-component) or two-can type (two-component) adhesive according to the intended object.

20 Thus, the one-can type adhesive is obtained by reacting a uniformly mixed solution of a polyol, an oxyacid of phosphorus or derivative thereof, an epoxy resin and a silane coupling agent with an organic polyisocyanate in the presence of an excess of isocyanate
25 groups. This type of adhesive is cured by reaction with

water or moisture in the air. In producing the one-can type adhesive, it is convenient to select the isocyanate groups (NCO) with the active hydrogen atoms (H) of the polyol and oxyacid of phosphorus or derivative thereof and the epoxy resin so as to result in an NCO/H ratio of about 1.5 to 20, preferably about 2 to 10. An NCO/H ratio of less than 1.5 results in an excessive increase in the viscosity of the resultant composition, and leads in some instance to its gelation. When NCO/H ratio is in excess of 20, curing characteristics are impaired and a composition with an adequate adhesive strength cannot in some instances, be obtained. The reaction is carried out normally at 30° to 100°C, whereby the organic metal catalyst, tertiary amine catalyst, etc., if desired, may be added.

Another embodiment of the present composition is the so-called two-can type, in which the resultant adhesive composition is obtained by mixing a polyol as the principal component with a curing agent of an organic polyisocyanate immediately before use. The oxyacid of phosphorus or derivative thereof and the silane coupling agent are respectively added to either the polyisocyanate or the polyol, but it is preferred to add either or both of them in advance to the polyol or to a mixture thereof with the epoxy resin. In the case of the two-can type, the

proportion in which the curing agent is mixed with the principal component is preferably such that the NCO/H ratio is about 0.4 to 10, preferably about 0.5 to 2.0. As is the case with the one-can type, it is possible in 5 the case of the two-can type to use catalysts such as organic metal and tertiary amine catalysts.

Normally, the two-can type of composition exhibits a faster curing rate and better adhesive performance than the one-can type, and therefore finds 10 wider application. Though the two-can type of composition shows a shorter pot life, it can be used without difficulty by employing a device which is adapted automatically to deliver a principal component and a curing agent through separate stream lines in the 15 determined weight ratio and only in the minimal weights required for a coating application, and to mix the streams immediately before use.

The adhesive composition of this invention, when it has a viscosity of about 100 to 10,000 cps., preferably 20 about 100 to 5,000 cps., at normal temperature to 140°C., preferably normal temperature to 100°C., can be used as a solvent-free type of composition.

When the viscosity exceeds the above range, the adhesive composition may be diluted with an organic 25 solvent, whether it be used as a one-can type or two-can

type. The organic solvent, is conveniently any solvent which is inert to the isocyanate group, and the solvent may be an ester exemplified by ethyl acetate, butyl acetate, 2-ethoxyethyl acetate, etc., a ketone 5 exemplified by methyl ethyl ketone, methyl isobutyl ketone etc., an aromatic exemplified by toluene, xylene, etc.; or an ether exemplified by tetrahydrofuran, dioxane etc.

The polyurethane adhesive composition of this 10 invention may be used, for example, by applying the adhesive composition to the surface of a film by means of a solvent type or solvent-free type laminator, joining the mating surfaces either after the solvent has evaporated in the case where the composition is of the solvent type 15 or directly in the case where the composition is solvent-free, and curing the composition at normal temperature or under heat.

Normally, it is preferred to apply the adhesive composition in an amount within the range of about 1.0 to 20 2.0 g/m^2 in the case of the solvent-free type and about 2.0 to 4.0 g/m^2 in the case of the solvent type.

As compared with the conventional solvent type of adhesive composition, a solvent-free type adhesive composition of the present invention permits the saving 25 of energy and does not require solvent recovery facilities,

thus enabling the overhead expense to be reduced down to not more than the half of those for the conventional solvent type.

As compared with the conventional solvent-free
5 type urethane adhesives, the present adhesive composition exhibits faster curing characteristics and better adhesive performance, and in particular exhibits excellent adhesive strength, heat resistance, water resistance and chemical resistance when applied to films of plastics
10 such as polyethylene terephthalate, nylon, polyethylene, polypropylene and polyvinyl chloride as well as metals such as aluminium, stainless steel, iron, copper and lead. On the other hand, a solvent type adhesive composition of this invention is superior in adhesive
15 strength, heat resistance and chemical resistance to the conventional solvent type adhesives. In particular this is due to the fact that the epoxy rings in the resin are opened by the oxyacid of phosphorus or derivative thereof, thus yielding coating films having excellent
20 chemical resistance.

The present polyurethane adhesive composition, when used for example as an adhesive for packaging materials for food, provides a bond having outstandingly excellent adhesive strength, heat resistance and hot-water resistance
25 between metal foil, such as aluminium foil, and films of

plastics such as polyethylene, polypropylene, nylon and polyethylene terephthalate etc. The packaging materials thus prepared, when they are filled with foods and sealed, and are then subjected to a high-temperature, 5 hot-water sterilization treatment at a temperature of not less than 120°C, are entirely free from delamination between the metal foil and the plastics film, and can therefore be used advantageously as a packaging material which shows improved tolerance to foodstuffs and ensures 10 the prolonged shelf lives of foodstuffs.

The invention will now be more particularly described and illustrated by the following Examples and Reference Examples in which all percentages are percentages by weight.

Example 1

15 A mixture of 500 g. of polyoxypropylene glycol (mol. weight 1,000), 1.8 g. of polyphosphoric acid composed mainly of tetrapolyphosphoric acid and 4.6 g. of N-(diethoxymethylsilyl-propyl)ethylenediamine was heated at 90°C, and 50 g. of an epoxy resin (mol. weight 20 1,060; epoxy equivalent 650; "Epicote" 1002; produced by Shell Chemical Co.; "Epicote" is a registered Trade Mark, were added to it and dissolved uniformly. Then, the temperature of the solution was lowered to 70°C, and 360 g. of diphenylmethane diisocyanate were added and a reaction 25 was conducted at 70°C for 3 hours.

By the above procedure, there was obtained an adhesive composition having an NCO group content of 7.5% and a viscosity of 1,000 cps at 90°C. (Composition 1).

5 By means of a solventless laminator, Composition 1 was applied at a temperature of 90°C to a polyester (PET) film having a thickness of 12 μ , at an application rate of 1.5 g/m², whereafter the film was joined to an aluminium foil (Al) having a thickness of 9 μ . Then,
10 Composition 1 was applied to the face of the foil at an application rate of 1.5 g/m², and a film of cast polypropylene (CPP) having a thickness of 60 μ and a corona-treated surface, was laid over it to form a three-ply laminated film. The adhesive composition thus
15 applied was allowed to cure at 40°C for 3 days.

The adhesive strength between the Al and the CPP as measured was 900 g/15 mm. (tensile speed of 300 mm./min., T-peel strength). From the multiple laminated film thus prepared, a pouch was fabricated of which the inner
20 surface was CPP, and a 2% aqueous acetic acid solution was filled into it. After the sealed pouch had been subjected to hot-water sterilization at 120°C and under a pressure of 2 kg./cm² for 30 min., investigation was conducted on the degree of delamination and change in
25 the adhesive strength. The results are as shown below:

Adhesive strength : 920 g./15 mm.
The degree of delamination : The same as before
hot-water
sterilization.

5

Example 2

A solution consisting of a mixture of 500 g. of polyethylenebutylene adipate (mol. weight 2,000, ethylene glycol/1,4-butylene glycol, molar ratio 1/1), 26.5 g. of diethylene glycol and 1.3 g. of an adduct of
10 pyrophosphoric acid and propylene oxide (molar ratio 1/1.6) was heated at 90°C. and 50 g. of an epoxy resin (mol. weight 900, epoxy equivalent 450; "Epicote" 1001; produced by Shell Chemical Co.), were added and dissolved uniformly therein. Then, the temperature of the
15 mixture was lowered to 70°C, and 417.8 g. of xylylene diisocyanate were added, and a reaction was conducted at 70°C. for 4 hours. The reaction mixture was freed of the unreacted isocyanate monomer by thin-layer distillation at 180°C/1 mmHg, and there was obtained
20 760 g. of a residue, which was then mixed uniformly with 7.6 g. of γ -glycidoxypropyltrimethoxysilane, thus yielding an adhesive composition having an NCO group content of 4.8% and a viscosity of 1,500 cps., at 90°C. (Composition 2).

25

By the same procedure as in Example 1,

5 Adhesive strength; 1,100 g./15 mm.

Adhesive strength after hot-water sterilization;

1,200 g./15 mm.

The degree of delamination after hot-water
sterilization; the same as before the sterilization.

Example 3

A solution consisting of a mixture of 500 g. of polyoxypropylene glycol (mol. weight 1,000), 40 g. of dipropylene glycol and 18 g. of trimethylolpropane was heated at 70°C, and 1,000 g. of diphenylmethane diisocyanate were added to it. The reaction was conducted at 70°C. for 3 hours, thus yielding a polyurethane polyisocyanate (curing agent) having an NCO group content of 16% and a viscosity at 40°C. of 1,300 cps.

20 A mixture of 500 g. of polyoxypropylene glycol (mol. weight 1,000) and 2 g. of a 1 : 1 (weight ratio) mixture of pyrophosphoric acid and sodium pyrophosphate was heated at 90°C and 58 g. of the epoxy resin as used in Example 2 was added. After the mixture had been

25 cooled to 70°C. 42.4 g. of diphenylmethane diisocyanate

and 6 g. of γ -glycidoxypropyltrimethoxysilane were added, and the reaction was conducted at 70°C for 3 hours, thus yielding a polyurethane polyol (principal component) having a hydroxyl value of 72 mg KOH/g and a viscosity of 5 2,500 cps. at 40°C.

100 g. of the curing agent and 300 g. of the principal component were mixed uniformly at 40°C. and there was obtained Composition 3, which had a viscosity of 2,100 cps. at 40°C. Immediately, Composition 3 was used 10 for preparing a three-ply laminated film of PET/Al/CPP, and an adhesive test on the bond between the Al and the CPP was conducted. The results are as shown below:

Adhesive strength; 1,050 g./15 mm.

Adhesive strength after hot-water sterilization;

15 1,000 g./15 mm.

The degree of delamination after hot-water sterilization; the same as before the sterilization.

Example 4

20 A mixture of 411 g. of a polyester glycol (mol. weight 600) prepared from a 1:1 mixture of isophthalic acid and adipic acid and diethylene glycol, and 1.0 g. of an adduct of polyphosphoric acid (PPA) composed mainly of tetrapolyphosphoric acid and propylene oxide 25 (PO) (PPA/PO: molar ratio 1/3) was heated at 90°C. and

82.2 g. of the epoxy resin used in Example 1 and 2.5 g. of γ -glycidoxypropyltrimethoxysilane were added and dissolved uniformly, thus yielding a polyol component (principal component) having a viscosity of 4,300 cps. at 60°C. and 5 a hydroxyl value of 172 mg. KOH/g.

230 g. of the principal component were uniformly mixed with a curing agent comprising 100 g. of a liquid diphenylmethane diisocyanate having an NCO group content of 29.4% ("Isonate" 143L; produced by Kasei Upjohn 10 Co., "Isonate" is a registered Trade Mark) at 60°C., yielding Composition 4 having a viscosity of 1,500 cps. at 60°C.

In the same manner as in Example 1, Composition 4 was immediately used to prepare a three-ply laminated 15 film of PET/Al/CPP at 60°C., and an adhesive test on the bond between the Al and the CPP was conducted. The results are as shown below:

Adhesive strength; 1,300 g./15 mm.

Adhesive strength after hot-water sterilization;

20 1,250 g./15 mm.

The degree of delamination after hot-water sterilization; the same as before the sterilization.

Example 5

25 A mixture of 900 g. of a polyester glycol (mol. weight 650) having the composition of isophthalic acid/

adipic acid, molar ratio 3/1, and ethylene glycol/
neopentyl glycol, molar ratio 2/1, and 2.0 g. of
polyphosphoric acid composed mainly of tetrapolyphosphoric
acid was heated at 90°C, and 90 g. of the epoxy resin
5 used in Example 1 and 10 g. of vinyltriethoxysilane
were added and dissolved uniformly, thus yielding a
polyol component (principal component) having a
viscosity of 4,300 cps., at 70°C. and a hydroxyl value
of 170 mg. KOH/g.

10 188.2 g. of xylylene diisocyanate were heated
at 90°C. and 44.7 g. of trimethylolpropane were
gradually added to it. The reaction was carried out for
2 hours. Then, 232.9 g. of the biuret derivative of
hexamethylene diisocyanate (having an NCO group content
15 of 22.8%) were mixed uniformly with the mixture, thus
yielding a polyurethane polyisocyanate (curing agent)
having a viscosity of 1,120 cps. at 70°C and an NCO
group content of 20.0%.

100 g. of the curing agent were uniformly
20 mixed with 200 g. of the principal component, and there
was obtained Composition 5, which had a viscosity of 3,500
cps. at 70°C. In the same manner as in Example 1,
Composition 5 was immediately used to prepare a three-ply
laminated film of PET/Al/CPP, and an adhesive test on the
25 bond between the Al and the CPP was conducted. The

results are as shown below:

Adhesive strength; 1,350 g./15 mm.

Adhesive strength after hot-water sterilization;
1,200 g./15 mm.

- 5 The degree of delamination after hot-water
sterilization; the same as before the
sterilization.

Reference Example 1

A mixture of 500 g. of polyoxypropylene glycol
10 (mol. weight 1,000) and 4.6 g. of N-(diethoxymethylsilyl-
propyl)-ethylenediamine was heated at 90°C, and 50 g. of
the epoxy resin used in Example 1 was added and
dissolved uniformly. Then, the temperature of the
solution was lowered to 70°C, and 360 g. of
15 diphenylmethane-diisocyanate were added. The reaction
was conducted at 70°C for 3 hours, yielding an adhesive
composition having NCO group content of 7.6% and a
viscosity of 800 cps. at 90°C. In the same manner as in
Example 1, the adhesive composition was used to prepare
20 a three-ply laminated film of PET/Al/CPP at 90°C, and
an adhesive test on the bond between the Al and the CPP
was conducted. The results are as shown below:

Adhesive strength; 700 g./15 mm.

Adhesive strength after hot-water sterilization;

- 25 None

The degree of delamination after hot-water sterilization; Completely delaminated.

Reference Example 2

A 411 g. portion of the polyester glycol with a
5 molecular weight of 600 used in Example 4 was mixed
uniformly with 2.5 g. of γ -glycidoxypropyltrimethoxysilane
at 60°C, and there was obtained a polyol component
(principal component) having a viscosity of 2,500 cps.
at 60°C. and a hydroxyl value of 182 mg. KOH/g. 230 g.
10 of the principal component were mixed uniformly at 60°C.
with 100 g. of the liquid diphenylmethane diisocyanate
employed in Example 4 as a curing agent, and there was
obtained a composition having a viscosity of 1,000 cps.
at 60°C. In the same manner as in Example 1, the
15 composition was immediately used to prepare a three-ply
laminated film of PET/Al/CPP, and an adhesive test on the
bond between the Al and the CPP was conducted. The
results are as shown below:

Adhesive strength; 950 g./15 mm.

20 Adhesive strength after hot-water sterilization;
350 g./15 mm.

The degree of delamination after hot-water
sterilization; Partially delaminated.

Example 6

25 A solution consisting of a mixture of 100 g. of a

polyester glycol (mol. weight 2,000) having the composition isophthalic acid/sebacic acid molar ratio 1/1 and ethylene glycol/neopentyl glycol molar ratio 1/1, 8.7 g. of tolylene diisocyanate (2,4/2,6-isomer = 5 80/20), 109.0 g. of ethyl acetate and 0.03 g. of dibutyltin dilaurate was allowed to react at 60°C for 5 hours, and 1.0 g. of ethylene glycol, 33 g. of the epoxy resin used in Example 1, 1 g. of vinyltriethoxysilane, 34 g. of ethyl acetate and 0.4 g. of monoethyl 10 orthophosphate were added to the solution. The reaction was carried out for a further hour, and there was obtained a polyurethane polyol (principal component) having a solids content of 50%, a hydroxyl value of 25 mg. KOH/g. and a viscosity of 1,200 cps. at 25°C.

15 A solution consisting of a mixture of 174.2 g. of tolylene diisocyanate, 44.7 g. of trimethylolpropane and 73.0 g. of ethyl acetate was allowed to react at 65°C. for 3 hours, and there was obtained a polyurethane polyisocyanate (curing agent) having a solids content 20 of 75%, an NCO group content of 14.4% and a viscosity of 1,000 cps. at 25°C.

100 g. of the principal component and 10 g. of the curing agent were mixed and diluted with ethyl acetate to a solids content of 25%. By means of a laminator, the 25 solution was applied at an application rate of 3.0 g./m²

Adhesive strength; 1,400 g./15 mm.

Adhesive strength after hot-water sterilization;
1,400 g./15 mm.

10 Example 7

100 g. of the principal component were mixed with 10 g. of the curing agent used in Example 6, and the mixture was diluted with ethyl acetate to a solids content of 25%. By means of a dry laminator, the solution was applied at an application rate of 3.0 g./m² for the lamination of a

three-ply laminated film of PET/Al/PPP. The adhesive thus applied was allowed to cure at 40°C for 3 days, and the adhesive test described in Example 1 was conducted.

The results are as shown below:

5 Adhesive strength; 1,500 g./15 mm.

Adhesive strength after hot-water sterilization;
1,450 g./15 mm.

The degree of delamination after hot-water
sterilization; the same as before the
10 sterilization.

Reference Example 3

Using the principal component of Example 6 without the addition of orthophosphoric acid and the curing agent, the adhesive test was conducted by the same procedure as
15 in Example 6. The results are as shown below:

Adhesive strength; 1,000 g./15 mm.

Adhesive strength after hot-water sterilization;
400 g./15 mm.

The degree of delamination after hot-water
sterilization; partially delaminated.
20

Example 8

A solution consisting of a mixture of 100 g. of the polyester glycol with a molecular weight of 2,000 used in Example 6, 11.1 g. of 3-isocyanatomethyl-3,5,5-
25 trimethylcyclohexylisocyanate, 111.1 g. of ethyl acetate

and 0.03 g. of dibutyltin dilaurate was allowed to react at 65°C for 7 hours, and 2.1 g. of diethylene glycol, 22.2 g. of an epoxy resin (mol. weight 1,600, epoxy equivalent 925; "Epicote" 1004; produced by 5 Shell Chemical Co.), 1.1 g. of vinyltrichlorosilane, 0.2 g. of phosphoric acid and 25.6 g. of ethyl acetate were added to the solution. The reaction was carried out for a further hour, and there was obtained a polyurethane polyol (principal component) having a solids content 10 of 50%, a hydroxyl value of 19 mg. KOH/g. and a viscosity of 1,500 cps. at 25°C.

A solution consisting of a mixture of 111.2 g. of 3-isocyanatomethyl-3,5,5-trimethylcyclohexylisocyanate, 22.3 g. of trimethylolpropane, 44.5 g. of ethyl acetate 15 and 0.03 g. of dibutyltin dilaurate was allowed to react at 65°C for 4 hours, and there was obtained a polyurethane polyisocyanate (curing agent) having a solids of 75%, an NCO group content of 11.8% and a viscosity of 3,000 cps. at 25°C.

20 100 g. of the principal component were mixed with 15 g. of the curing agent, and the mixture was diluted with ethyl acetate to a solids content of 25%. By means of a dry laminator, the solution was applied at an application rate of 3.0 g./m² for the lamination of a three-ply 25 laminated film of PET/Al/PPP. The adhesive thus applied

was allowed to cure at 40°C. for 3 days, and the adhesive test as described in Example 1 was conducted. The results are as shown below:

Adhesive strength; 1,200 g./15 mm.

5 Adhesive strength after hot-water sterilization;
1,300 g./15 mm.

The degree of delamination after hot-water sterilization; the same as before the sterilization.

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Example 9

A solution consisting of a mixture of 500 g. of polyethylenebutylene adipate (mol. weight 2,000, ethylene glycol/1,4-butyleneglycol, molar ratio 1/1, 26.5 g. of diethylene glycol and 1.3 g. of an adduct of pyrophosphoric
15 acid and propylene oxide molar ratio 1/1.6 was heated at 90°C, and 50 g. of an epoxy resin (mol. weight 900, epoxy equivalent 450; "Epicote" 1001, produced by Shell Chemical Co.) and 7.6 g. of γ -mercaptopropyltrimethoxysilane were added to it and dissolved uniformly. Then, the
20 temperature of the solution was lowered to 70°C, and 417.8 g. of xylylene diisocyanate were added. The reaction was conducted at 70°C for 4 hours. The reaction solution was freed of the unreacted isocyanate monomer by thin-layer distillation at 180°C. under a vacuum of
25 1 mmHg, and there were obtained 764 g. of a residue, thus

yielding an adhesive composition having an NCO content of 4.7% and a viscosity of 2,000 cps. at 90°C.

By the same procedure as described in Example 1, the composition was used to prepare a three-ply laminated 5 film of PET/Al/CPP, and an adhesive test on the bond between the Al and the CPP was conducted. The results are as shown below:

Adhesive strength; 1,300 g./15 mm.

Adhesive strength after hot-water sterilization;

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1,350 g./15 mm.

The degree of delamination after hot-water sterilization; the same as before the sterilization.

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Claims:

1. A polyurethane adhesive composition, wherein the composition comprises an organic polyisocyanate, a polyol, an oxyacid of phosphorus or a derivative thereof, an epoxy resin and a silane coupling agent, and wherein some or all of the ingredients may be present in the form of a reaction product.
2. A polyurethane adhesive composition as claimed in Claim 1, wherein the composition has been obtained by reacting a mixture in solution of the polyol, the oxyacid of phosphorus or the derivative thereof, the epoxy resin and the silane coupling agent with the organic polyisocyanate, and wherein the ratio of the number of the NCO groups of the organic polyisocyanate/(the number of the active hydrogen atoms (H) of the polyol, the oxyacid of phosphorus or the derivative thereof and the epoxy resin) is 1.5 to 20.
3. A polyurethane adhesive composition as claimed in Claim 1, wherein a mixture of the polyol, the oxyacid of phosphorus or the derivative thereof, the epoxy resin and the silane coupling agent constitutes a principal component and the organic polyisocyanate is a curing agent, the ratio of the number of the NCO groups of the organic polyisocyanate/(the active hydrogen atoms (H) of the polyol, the oxyacid of phosphorus or the derivative thereof and the epoxy resin) being 0.4 to 10.



- 31 -

4. A polyurethane adhesive composition as claimed in any one of Claims 1 to 3, wherein the amount of the oxyacid of phosphorus or the derivative thereof is in the range of 0.01 to 10 weight percent based on the weight of the total adhesive composition.
5. A polyurethane adhesive composition as claimed in any one of Claims 1 to 4, wherein the amount of the epoxy resin is in the range of 1 to 50 weight percent based on the weight of the total adhesive composition.
- 10 6. A polyurethane adhesive composition as claimed in any one of Claims 1 to 5, wherein the amount of the silane coupling agent is in the range of 0.05 to 20 weight percent based on the weight of the total adhesive composition.
7. A polyurethane adhesive composition as claimed in any
15 one of Claims 1 to 6, wherein the silane coupling agent is a compound having the structural formula:
- $$R-Si(X)_3 \text{ or } R-Si(R')(X)_2$$
- (wherein R is an organic vinyl, epoxy, amino, imino or mercapto radical; R' is an alkyl radical having 1 to 8
20 carbon atoms; X is a methoxy, ethoxy or β -methoxy ethoxy radical or a chlorine atom).
8. A polyurethane adhesive composition as claimed in Claim 7, wherein the silane coupling agent is N-(diethoxymethylsilylpropyl)ethylenediamine.
- 25 9. A polyurethane adhesive composition as claimed in Claim 7, wherein the silane coupling agent is



γ -glycidoxypropyltrimethoxysilane.

10. A polyurethane adhesive composition as claimed in Claim 7, wherein the silane coupling agent is vinyltriethoxysilane.

5 11. A polyurethane adhesive composition as claimed in Claim 7, wherein the silane coupling agent is vinyltrichlorosilane.

12. A polyurethane adhesive composition as claimed in Claim 7, wherein the silane coupling agent is

10 γ -mercaptopropyltrimethoxysilane.

13. A polyurethane adhesive composition substantially as hereinbefore described in any one of Examples 1 to 9 of the foregoing Examples.

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