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(54) **ADHESIF SIMPLE A BASE D'URETHANNE A PRISE SOUS HUMIDITE**

(54) **ONE-PART MOISTURE-CURING URETHANE ADHESIVE**

(57) The present invention is directed to a one-part (one-pack) moisture-curing urethane adhesive comprising a urethane prepolymer having isocyanate groups (NCO) at the terminus, said urethane prepolymer being a reaction product of a polyol and an excess amount of a polyisocyanate. The improvement comprises adding 0.01 to 5 % by weight of a gelling agent based on the whole amount of the adhesive, and optionally adding a thermoplastic urethane multi-block copolymer resin and a thixotropic agent selected from the group consisting of a hydrophilic colloidal silica and a polysiloxane-polyoxyalkylene copolymer. The adhesive of the present invention can obviate float or glass slippage in the adhesive application of window glass of automobiles.

ABSTRACT

The present invention is directed to a one-part (one-pack) moisture-curing urethane adhesive comprising a urethane prepolymer having isocyanate groups (NCO) at the terminus, said urethane prepolymer being a reaction product of a polyol and an excess amount of a polyisocyanate. The improvement comprises adding 0.01 to 5 % by weight of a gelling agent based on the whole amount of the adhesive, and optionally adding a thermoplastic urethane multi-block copolymer resin and a thixotropic agent selected from the group consisting of a hydrophilic colloidal silica and a polysiloxane-polyoxyalkylene copolymer. The adhesive of the present invention can obviate float or glass slippage in the adhesive application of window glass of automobiles.

ONE-PART MOISTURE-CURING URETHANE ADHESIVE

The present invention relates to a one-part (one-pack) moisture-curing urethane adhesive, more particularly, to a one-part moisture-curing urethane adhesive which can be used for adhesion of, for example, automobile window glass, and can obviate float or glass slippage in automobile production lines due to improvement in an initial adhesive strength at a normal temperature.

For adhesion of automobile window glass, there has been used, for example, a one-part moisture-curing urethane adhesive comprising a urethane prepolymer having isocyanate groups at the terminus, said urethane prepolymer being a reaction product of a polyol and an excess amount of a polyisocyanate. After applying said adhesive to the periphery of the window glass, the window glass is then attached with pressure to a flange of an automobile body. However, said adhesive does not have a sufficient initial adhesive strength at a normal temperature, and hence, tends to cause float or glass slippage due to pressure applied when a door is opened or closed. This causes problems along the production line.

Under the circumstances, the present inventors have studied intensively in order to improve the initial adhesive strength of the above noted one-part moisture-curing urethane adhesive, and as a result, have found that desired initial adhesive strength can be obtained by adding a specific amount of a gelling agent to the adhesive so that a temperature-sensitive viscosity is enhanced and the adhesive is made the so-called "hot apply" type which is applied at a temperature of 50 to 100°C, and optionally adding a thermoplastic urethane multi-block copolymer resin which is prepared by reacting a polyfunctional ring-containing and active hydrogen-containing compound, and a diol or triol compound with an equivalent or excess amount of a polyisocyanate compound.

An object of the present invention is to provide in a one-part moisture-curing urethane adhesive comprising a urethane prepolymer having isocyanate (NCO) groups at the terminus, said urethane prepolymer being a reaction product of a polyol and an excess amount of a polyisocyanate, the improvement which comprises adding a gelling agent in an amount of 0.01 to 5 % by weight based on the total amount of the adhesive.

Another object of the present invention is to provide in a one-part moisture-curing urethane adhesive comprising a urethane prepolymer having isocyanate (NCO) groups at the terminus, said urethane prepolymer being a

reaction product of a polyol and an excess amount of a polyisocyanate, the improvement which comprises adding a gelling agent in an amount of 0.01 to 5 % by weight based on the total amount of the adhesive; and a thermoplastic urethane multi-block copolymer resin which is prepared by reacting a polyfunctional ring-containing and active hydrogen-containing compound, and a diol or triol compound with an equivalent or excess amount of a polyisocyanate compound.

Still another object of the present invention is to provide in a one-part moisture-curing urethane adhesive comprising a urethane prepolymer having isocyanate (NCO) groups at the terminus, said urethane prepolymer being a reaction product of a polyol and an excess amount of a polyisocyanate, the improvement which comprises adding a gelling agent in an amount of 0.01 to 5 % by weight based on the total amount of the adhesive; a thermoplastic urethane multi-block copolymer resin which is prepared by reacting a polyfunctional ring-containing and active hydrogen-containing compound, and a diol or triol compound with an equivalent or excess amount of a polyisocyanate compound; and a thixotropic agent selected from the group consisting of a hydrophilic colloidal silica and a polysiloxane-polyoxyalkylene copolymer.

These and other objects and advantages of the invention will be apparent to those skilled in the art from the following description.

In one aspect of the present invention there is provided, in a moisture-curing one-part urethane adhesive comprising a urethane prepolymer having isocyanate groups (NCO) at the terminus, said urethane prepolymer containing 1 to 10% by weight of NCO groups at the terminus and being a reaction product of a polyol and an excess amount of a polyisocyanate, the improvement which comprises adding N-lauroyl-L-glutamic acid-α,γ-di-n-butylamide as a gelling agent in an amount of 0.01 to 5% by weight based on the whole amount of the adhesive and optionally adding a thermoplastic urethane multi-block copolymer resin which is prepared by reacting a polyfunctional ring-containing and active hydrogen-containing compound, and a diol or triol compound with an equivalent or excess amount of a polyisocyanate compound and optionally adding a plasticizer, a filler, a curing catalyst, a colouring agent and a stabilizing agent, said plasticizer being contained in an amount of up to 30% by weight, said filler being contained in an amount of up to 60% by weight based on the whole amount of the adhesive, said curing catalyst, colouring agent and stabilizing agent being contained in an amount of up to 10% by weight based on the whole amount of the adhesive.

The polyol used for preparing the urethane prepolymer includes, for example, a polyether polyol, a

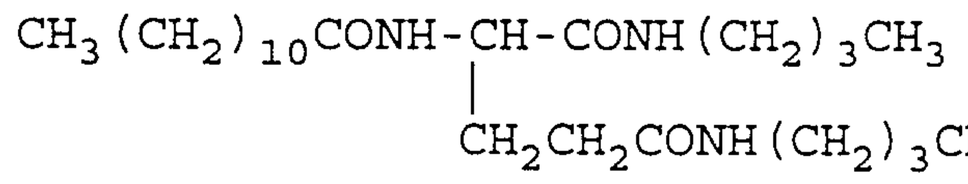
polyester polyol, a polybutadiene polyol, an isoprene polyol, a hydrogenated isoprene polyol, an acryl polyol, castor oil derivatives, tall oil derivative, and the like.

The polyisocyanate used for preparing the urethane prepolymer includes, for example, trimethylene diisocyanate, tetramethylene diisocyanate, hexamethylene diisocyanate, pentamethylene diisocyanate, 2,4,4- or 2,2,4-trimethylhexamethylene diisocyanate, dodecamethylene diisocyanate, 1,3-cyclopentane diisocyanate, 1,4-cyclohexane diisocyanate, 1,3-cyclohexane diisocyanate, 4,4''methylene bis(cyclohexyl isocyanate), methyl 2,4-cyclohexane diisocyanate, methyl 2,6-cyclohexane diisocyanate, 1,4-bis(isocyanate methyl) cyclohexane, 1,3-bis(isocyanate methyl) cyclohexane, m-phenylene

diisocyanate, p-phenylene diisocyanate, 4,4'-diphenyl diisocyanate, 1,5-naphthalene diisocyanate, 4,4'-diphenylmethane diisocyanate (MDI), crude diphenylmethane diisocyanate, 2,4- or 2,6-tolylene diisocyanate, 4,4'-toluidine diisocyanate, dianidine diisocyanate, 4,4'-diphenylether diisocyanate, 1,3- or 1,4-xylylene diisocyanate, ω,ω'-diisocyanate-1,4-diethylbenzene, and the like.

The reaction of the polyol with an excess amount of the polyisocyanate compound is carried out under usual conditions, for example,in the case where the polyether polyol is used as the polyol,by heating a mixture of the polyether polyol and the polyisocyanate at a temperature of 70 to 90°C for 0.5 to 5 hours.

The gelling agent used in the adhesive of the present invention may be any gelling agent in so far as it enhances the temperature-sensitive viscosity of the urethane prepolymer. A preferred gelling agent is N-lauroyl-L-glutamic acid-α,γ-di-n-butylamide having the formula:



This suitable gelling agent is commercially available, for example, from Ajinomoto Kabushiki Kaisha under the trade mark "GP-1".

The amount of the gelling agent used in the adhesive ranges from 0.01 to 5 %, preferably from 0.05 to 1.0 %, based

on the total amount of the adhesive. When the gelling agent is used in an amount of less than 0.01 %, the initial adhesive strength is not enhanced, and when the amount is over 5 %, storage stability decreases.

In another aspect of the present invention, the one-part moisture-curing urethane adhesive of the present invention comprises a urethane prepolymer as a main component supplemented with a gelling agent and a thermoplastic urethane multi-block copolymer resin. The thermoplastic urethane multi-block copolymer resin used in the adhesive of the present invention is prepared by reacting a polyfunctional ring-containing and active hydrogen-containing compound, and a diol or triol compound with an equivalent or excess amount of a polyisocyanate compound.

The polyfunctional ring-containing and active hydrogen-containing compound usually has a weight average molecular weight of 100 to 4,000, preferably 400 to 2,000, and includes, for example, bisphenol resins, terpene resins, coumarone resins, xylene resins, rosin resins, rosin ester resins, styrene resins, phenol resins, terpene phenol resins, polyester resins, and the like. The diol compound includes, for example, ethylene glycol, 1,4-butanediol, 1,6-hexanediol, 1,8-octanediol, polycarbonate diol, polytetramethylene glycol, hydrogenated butadienediol, polyacryldiol, polyoxyalkylene ether diol, polyoxyalkylene-adduct bisphenol, and other active

hydrogen-containing compounds. The triol compound includes, for example, trimethylolpropane, glycerin, triethylene triol, polyoxyalkylene ether triol, and the like. The polyisocyanate compound includes all the above-mentioned compounds, but from the viewpoint of increasing the aggregation energy of urethane and, in particular, from the viewpoint of safety and cost, MDI is the most preferred.

The thermoplastic urethane multi-block copolymer resins thus prepared are commercially available, for example, in the name of "Thermoplastic Resin Toyo Ace U-B*" manufactured by K.K. Toyo Chemical Research Institute, which has a melting point of 70 to 100°C.

The thermoplastic urethane multi-block copolymer resin is effective for exhibiting the initial adhesive strength of the adhesive. Besides, the copolymer has urethane bond and ring compound residue in the molecule, by which the aggregation energy is exhibited and can show thermoplastic properties. Moreover, since it has a polarity due to the ring compound residue and urethane bond, it can show good compatibility with the above urethane prepolymer.

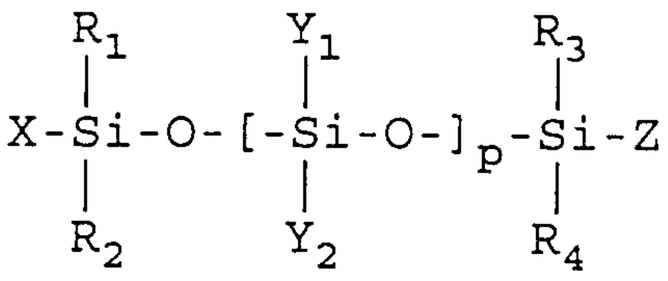
In still another embodiment of the present invention, the one-part moisture-curing urethane adhesive of the present invention comprises a urethane prepolymer as a main component supplemented with a gelling agent, a thermoplastic urethane multi-block copolymer resin and a thixotropic agent

*Trade mark

selected from the group consisting of a hydrophilic colloidal silica and a polysiloxane-polyoxyalkylene copolymer.

The hydrophilic colloidal silica used in the present invention excludes a hydrophobic product having a CH_3 group on the surface. The hydrophilic colloidal silica is commercially available, for example, under the name of U-200* and U-300* (both) manufactured by Nippon Aerosil Kabushiki Kaisha, Japan).

The polysiloxane-polyoxyalkylene copolymer is a known compound, for example, a compound of the formula:



wherein R_1, R_2, R_3 and R_4 are the same or different and are each methyl or phenyl;

p is an integer of 0 to 70, preferably 10 to 30;

either one of X and Z is a polyoxyalkylene-containing group of the formula:

$$-(CH_2)q-O-\{(C_3H_6O)_a(C_2H_4O)_b\}-R_5 \qquad [a]$$

wherein q is an integer of 1 to 4, preferably 2 or 3; a is an integer of 0 to 50, preferably 0 to 10; b is an integer of 10 to 100, preferably 20 to 50; and R_5 is a hydrogen atom, an alkyl having 1 to 8 carbon atoms (e.g. methyl, ethyl, propyl, butyl, pentyl, etc.), or an alkylcarbonyl having 1 to 18 carbon atoms (e.g. acetyl, propionyl, butyroyl,

*Trade mark

etc.); and when a is not less than 1, the group: C_3H_6O and the group: C_2H_4O may bind mutually in any order,

and another X and Z is methyl, phenyl, or a polyoxyalkylene-containing group of the above formula [a];

Y_1 and Y_2 are the same or different and are each methyl, phenyl, or a polyoxyalkylene-containing group of the above formula [a], and when p is 2 or more, these Y_1 and Y_2 groups may be different groups in each repeating unit.

The polysiloxane-polyoxyalkylene copolymer usually has a molecular weight of about 500 to 30,000, and is commercially available, for example, under the trade mark "Formate" (manufactured by Takeda Chemical Industries, Ltd., Japan).

In addition to the urethane prepolymer, the gelling agent and the thermoplastic urethane multi-block copolymer, the adhesive of the present invention may further optionally contain a plasticizer [e.g. dioctyl phthalate (DOP), trioctyl trimellitate (TOTM), dioctyl adipate, dibutyl sebacate, tris-chloroethyl phosphate, chloroparaffins, etc.]; a filler [e.g. carbon black, calcium carbonate, talc, barium sulfate, etc.]; a curing catalyst [e.g. dibutyl tin dilaurate (DBTDL), tin octoate, lead octoate, etc.]; a colouring agent; a thixotropic agent (e.g. fine powder silica, etc.); a stabilizing agent, and the like. In this case, the gelling agent is preferably dissolved in the plasticizer with heating at 60 to 120°C and

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the obtained solution (usually containing 0.2 to 5 % of the gelling agent) is added.

The plasticizer may be contained in an amount of up to 30 % by weight and the filler may be contained in an amount of up to 60 % by weight based on the total amount of the adhesive. Other additives such as the curing catalyst, the colouring agent, the stabilizing agent and the like may be included in an amount of up to 10 % by weight based on the total amount of the adhesive.

The adhesive of the present invention can be used as a hot apply type adhesive due to the addition of the gelling agent, i.e. the adhesive is applied at a temperature of 50 to 100°C and, with cooling of the adhesive, viscosity of the adhesive increases to give a desired initial adhesive strength. This allows for prevention of float or glass slippage in the adhesive application of automobile window glass.

The present invention is explained in more detail by means of the following Example and Reference Example but should not be construed to be limited thereto.

Example 1

(1) Preparation of a solution of a gelling agent:

To 30 parts (parts by weight, hereinafter the same) of DOP was added 0.6 parts of a gelling agent (GP-1) and the

mixture was stirred at 80 to 100°C for 30 minutes to give a solution of a gelling agent.

(2) Synthesis of a urethane prepolymer:

To a polyoxypropylene triol (MW: 7000; 3000 g) was added MDI (350 g) and the reaction was conducted under a nitrogen atmosphere at 80°C for 3 hours to give a urethane prepolymer having a free NCO content of 2.3 and a viscosity of 38,000 cps (20°C).

(3) Preparation of an adhesive:

To 100 parts of the urethane prepolymer prepared in the above process (2) were added 30.6 parts of the solution of a gelling agent prepared in (1), 20 parts of TOTM, 100 parts of a dry carbon black, 30 parts of calcium carbonate and 0.1 parts of DBTDL and the mixture was stirred under reduced pressure to give a one-part moisture-curing urethane adhesive (the amount of the gelling agent in the total amount of the adhesive is 0.21 %).

Example 2

To 100 parts of the urethane prepolymer prepared in the process (2) of Example 1 were added 30.6 parts of the solution of a gelling agent prepared in the process (1) of Example 1, 15 parts of a thermoplastic urethane multi-block copolymer resin (Thermoplastic Resin Toyo Ace U-B*), 20 parts of TOTM, 100 parts of a dry carbon black, 30 parts of calcium carbonate and 0.1 parts of DBTDL and the mixture was stirred

*Trade mark

under reduced pressure to give a one-part moisture-curing urethane adhesive.

Example 3

To 100 parts of the urethane prepolymer prepared in the process (2) of Example 1 were added 30.6 parts of the solution of a gelling agent prepared in the process (1) of Example 1, 15 parts of a thermoplastic urethane multi-block copolymer resin (Thermoplastic Resin Toyo Ace U-B*), 1.5 parts of a thixotropic agent (Formate ST*), 20 parts of TOTM, 100 parts of a dry carbon black, 30 parts of calcium carbonate and 0.1 parts of DBTDL and the mixture was stirred under reduced pressure to give a one-part moisture-curing urethane adhesive.

Reference Example 1

The procedures of Example 1 were repeated using the same components as in Example 1 except that the gelling agent (GP-1) (0.6 parts) was not used in this Example to give an adhesive.

Results of Experiment

A viscosity at 60°C, a tack free time (T.F.T.)(20°C, 65%RH) and an initial shearing adhesive strength (tensile speed: 50 mm/minute) measured for the adhesives of Examples 1 to 3 and Reference Example 1 are shown in the following Table 1.

*Trade mark

Table 1

		Ex. 1	Ex. 2	Ex. 3	Ref.Ex. 1
	Viscosity (60°C, poise)	900	1000	1000	700
	T.F.T.(minutes)	30	30	30	30
5	Initial shearing adhesive strength (kgf/cm^2)	0.2	0.3	0.3	0.1

CLAIMS:

1. In a moisture-curing one-part urethane adhesive comprising a urethane prepolymer having isocyanate groups (NCO) at the terminus, said urethane prepolymer containing 1 to 10% by weight of NCO groups at the terminus and being a reaction product of a polyol and an excess amount of a polyisocyanate, the improvement which comprises adding N-lauroyl-L-glutamic acid-α,γ-di-n-butylamide as a gelling agent in an amount of 0.01 to 5% by weight based on the whole amount of the adhesive and optionally adding a thermoplastic urethane multi-block copolymer resin which is prepared by reacting a polyfunctional ring-containing and active hydrogen-containing compound, and a diol or triol compound with an equivalent or excess amount of a polyisocyanate compound and optionally adding a plasticizer, a filler, a curing catalyst, a colouring agent and a stabilizing agent, said plasticizer being contained in an amount of up to 30% by weight, said filler being contained in an amount of up to 60% by weight based on the whole amount of the adhesive, said curing catalyst, colouring agent and stabilizing agent being contained in an amount of up to 10% by weight based on the whole amount of the adhesive.

2. The adhesive of claim 1 which comprises 20 to 60% by weight of the urethane prepolymer, 0.01 to 5% by weight of the gelling agent, and up to 20% by weight of the thermoplastic urethane multi-block copolymer resin.

3. The adhesive of claim 1 or 2 which further comprises a thixotropic agent.

4. The adhesive of claim 3 wherein said thixotropic agent is selected from the group consisting of a hydrophilic colloidal silica and a polysiloxane-polyoxyalkylene copolymer.

5. The adhesive of claim 3 or 4 which comprises said thixotropic agent in an amount of up to 5% by weight.