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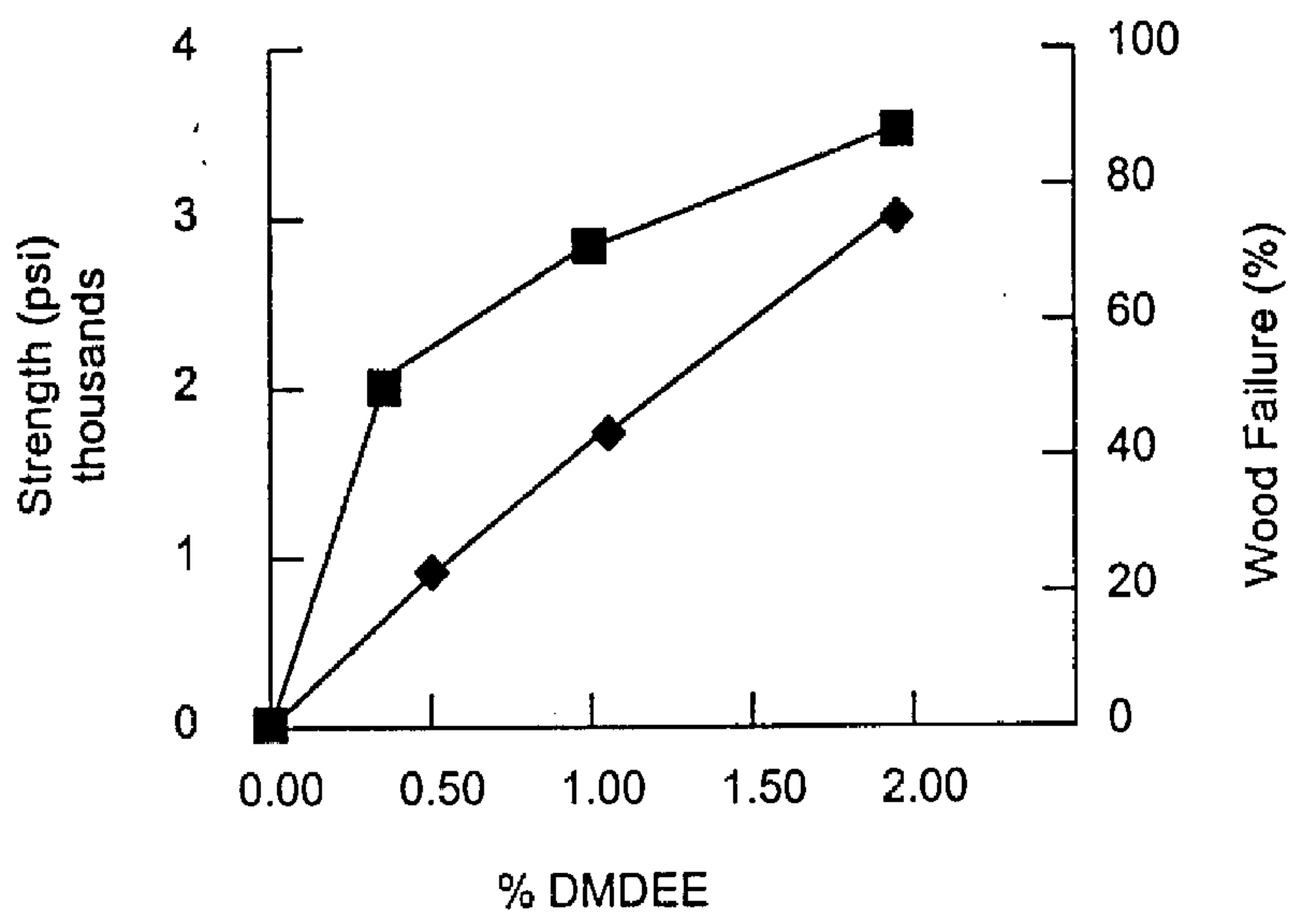
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(54) **ADHESIF POLYURETHANE POUR LE BOIS, A UN COMPOSANT ET A RETICULATION PAR L'HUMIDITE**

(54) **MOISTURE-CURING ONE-PART POLYURETHANE ADHESIVE FOR WOOD**



(57) A moisture curing one-part polyurethane adhesive of the invention having good bonding to wood comprises an isocyanate-terminated prepolymer having an isocyanate content of from about 10 % to about 20 % by weight, dimorpholinodiethyl ether in an amount of from about 0.1% by weight to about 3.0 % by weight as a catalyst, and from about 0.1 % by weight to about 2.0 % by weight of fumed silica. In another embodiment, a curable polyurethane adhesive is provided that has good bonding to wood and comprises an isocyanate-terminated prepolymer having an isocyanate content of from about 10 % to about 20 % by weight, and dimorpholinodiethyl ether in an amount of from about 0.4 % by weight to about 3.0 % by weight as a catalyst.

ABSTRACT OF THE DISCLOSURE

A moisture curing one-part polyurethane adhesive of the invention having good bonding to wood comprises an isocyanate-terminated prepolymer having an isocyanate content of from about 10 % to about 20 % by weight, dimorpholinodiethyl ether in an amount of from about 0.1% by weight to about 3.0 % by weight as a catalyst, and from about 0.1 % by weight to about 2.0 % by weight of fumed silica. In another embodiment, a curable polyurethane adhesive is provided that has good bonding to wood and comprises an isocyanate-terminated prepolymer having an isocyanate content of from about 10 % to about 20 % by weight, and dimorpholinodiethyl ether in an amount of from about 0.4 % by weight to about 3.0 % by weight as a catalyst.

TITLE: MOISTURE-CURING ONE-PART POLYURETHANE ADHESIVE FOR WOOD

BACKGROUND OF THE INVENTION

Field of the invention:

This invention relates to moisture-curing polyurethane adhesives and more particularly to such adhesives that have good bonding properties to wood substrates.

Brief description of the prior art:

Assembly of the constituent parts of wooden articles such as furniture, window frames, and the like, has long been accomplished using adhesives. Although the use of natural resins such as animal-derived glues for this purpose is ancient, current practice, especially in industrial applications, almost universally uses modern industrial glues based on synthetic resins. Adhesive formulations that require the mixing of two or more ingredients, e.g., casein glues and resorcinol-based glues, have enjoyed some utility in manufacturing wooden products. However, the greater convenience of one-part formulations has promoted the use of such materials. Such adhesives can be

supplied in closed containers and can be applied merely by removing the curable composition from the container and applying it to the surfaces to be joined.

Typical of one-part adhesive formulations are those based on polyvinyl acetate (PVAc) emulsions which cure by evaporation of the water vehicle and subsequent hardening, and moisture-curing polyurethane adhesives, which are cured by reaction with atmospheric moisture.

In a typical process currently used in the wood bonding industry, a formulated PVAc-based emulsion adhesive (water-based) is applied to the surfaces to be joined, and the surfaces are then approximated and clamped together under ambient plant conditions for 45 minutes to one hour. Although the clamping pressure can be then released, joints so prepared must be seasoned by being allowed to equilibrate for an additional 18-24 hours. This allows excess water to leave the glue line. If unseasoned parts are machined immediately, there is a risk of sunken glue lines due to subsequent evaporation of water from the adhesive.

One-part moisture-curing polyurethane adhesives, because they are essentially 100 % solids, do not require an equilibration or seasoning time. Consequently, the glued products can be machined as soon as the clamps are released after

the adhesive has cured. However, the adhesive performance of polyurethane adhesives has typically been somewhat inferior to that of traditional PVAc adhesives. The difference in performance is most noticeable in the adhesion between the adhesive and the wood substrate. When a satisfactory glued joint having at least one wooden substrate is tested to failure, the joint fails by fracture within the wood itself, rather than at the line of contact between wood and adhesive. Typically, joints made with PVAc adhesives have exhibited an adhesion to the wood substrate, as manifested in wood failure under test, that is superior to that of polyurethane adhesives. Furthermore, although polyurethane adhesives require no post-cure seasoning, the curing period itself, during which the joint must be clamped, is typically longer for a polyurethane adhesive using conventional tin-based catalysts than for a PVAc adhesive. Consequently, the time during which the assembly jigs and fixtures are occupied has tended to be greater for polyurethane adhesives than for PVAc adhesives.

Accordingly, a need has continued to exist for a moisture-curing polyurethane adhesive that has a rapid cure and good strength and adhesion, particularly to wood substrates.

SUMMARY OF THE INVENTION

This problem has now been alleviated by the moisture curing one-part polyurethane adhesive of the invention comprising

an isocyanate-terminated prepolymer having an isocyanate content of from about 12 % to about 20 % by weight;

as a catalyst, dimorpholinodiethyl ether in an amount of from about 0.1% by weight to about 2.7 % by weight; and

from about 0.1 % by weight to about 2.0 % by weight of fumed silica.

In another embodiment, the invention is an isocyanate-terminated prepolymer having an isocyanate content of from about 12 % to about 20 % by weight;

as a catalyst, dimorpholinodiethyl ether in an amount of from about 0.4 % by weight to about 3.0 % by weight.

Accordingly, it is an object of the invention to provide a moisture curing one-part polyurethane adhesive.

A further object is to provide a polyurethane adhesive having strong bonding to a wood substrate.

A further object is to provide a polyurethane adhesive having good strength.

A further object is to provide a polyurethane adhesive having a having a high rate of cure.

Other objects of the invention will become apparent from the description of the invention which follows.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 shows a plot of the effect the percentage of dimorpholinodiethyl ether catalyst has on the strength and wood bonding of the composition of the invention.

Figure 2 shows a plot of the effect the percentage of fumed silica has on the strength and wood bonding of the composition of the invention containing 0.4 % of the dimorpholinodiethyl ether catalyst.

Figure 3 shows a comparison of the effect the additional fumed silica has on the strength and wood bonding of the invention Compositions containing a conventional tin-based catalyst and the dimorpholinodiethyl ether catalyst are described.

DETAILED DESCRIPTION OF THE INVENTION AND PREFERRED EMBODIMENTS

The moisture-curing polyurethane adhesive of the invention comprises a major proportion of an isocyanate terminated prepolymer having an isocyanate content of about 10 % by weight to about 20 % by weight, preferably from about 14 % by weight to about 18 % by weight, and more preferably about 16 % by weight.

Such prepolymers typically have a viscosity of less than about 10,000 centipoises and can be conveniently applied evenly to the surfaces of substrates to be fastened together.

The prepolymers are prepared by generally conventional procedures. Typically, an isocyanate component having an isocyanate functionality of from about 2.1 to about 2.8 is reacted in excess with a polyol component to form a prepolymer end-capped with isocyanate functional groups. The polyols are typically liquid polyethers or polyesters of relatively low molecular weight. The polyether polyols are polymers of ethylene oxide or propylene oxide terminated with hydroxy groups. The reaction of the isocyanate component with the polyol is conducted at temperatures near room temperature or slightly above, e.g. in a temperature range of about 30°C-65°C.

Isocyanate terminated prepolymers and their preparation are conventional in the art of curable polyurethane compositions. Suitable diisocyanates and polyols, as well as general methods of preparation of isocyanate-terminated prepolymers are disclosed; for example, in U.S. Patent 4,758,648, to Rizk et al., and U.S. Patent 5,558,941, to Stobbie IV et al. The entire disclosures of U.S. Patent 4,758,648 and U.S. Patent 5,558,941 are incorporated herein by reference.

The diisocyanate reactant used to prepare the polyurethane prepolymer may be any conventional diisocyanate. Such compounds include toluene diisocyanate, isophorone diisocyanate, bis(4-isocyanatocyclohexyl)methane, bis(4-isocyanatophenyl)methane, and the like. A preferred diisocyanate is bis(4-isocyanato-phenyl)methane (diphenylmethane-4,4'-diisocyanate, "polymeric MDI"). The diisocyanate component used in preparing the prepolymer of the invention preferably incorporates a proportion of polyfunctional isocyanates. The isocyanate functionality preferably is between about 2.1 and 2.8. Such "diisocyanate" components are commercially available, for example from Dow Chemical Co., Midland, Michigan, under the tradename PAPI®. The amount of diisocyanate component used to prepare the polyurethane prepolymer may range from about 50 % by weight to about 70 % by weight of the reactants used to prepare the polyurethane prepolymer, preferably from about 55 % by weight to about 65 % by weight.

Typically, the polyol oligomers are hydroxy-terminated polyesters or polyethers prepared by conventional techniques known to those skilled in the art. Such materials are commercially available. For example, polyester polyols are marketed by the Witco Corporation under the tradename Fomrez®, and polyether polyols are marketed by the Dow Chemical Company

under the tradename Voranol®. The amount of the polyol oligomer used is from about 30 % by weight to about 50 % by weight of the reactants used in preparing the polyurethane prepolymer. Preferably this is from about 34 % by weight to about 40 % by weight. A mixture of polyol oligomers may be used to adjust the viscosity of the prepolymer and to facilitate the mixing of the ingredients.

The polyurethane prepolymer of the invention is prepared by mixing at least part of the calculated amount of the liquid polyol oligomer and the liquid diisocyanate at room temperature or slightly above, e.g., about 35°C. The reaction is continued with agitation and progressive heating up to a temperature of about 55°C-65°C over a period of several hours, with addition of any remaining polyol. The percentage of isocyanate in the reaction mixture decreases as the reaction proceeds and is monitored periodically. The reaction is halted when the isocyanate content reaches the target value by cooling the reaction mixture, e.g., to a temperature of about 40°C. Thereupon the catalyst, dimorpholinodiethyl ether (DMDEE), is added to the mixture and thoroughly mixed therewith.

Throughout the preparation of the isocyanate-terminated prepolymer, and during its discharge from the reaction vessel

into sealed containers for storage and distribution, care is taken to exclude atmospheric moisture. This is done by conducting the process under vacuum or a blanket of inert gas, such as nitrogen, according to conventional procedures.

The target value of isocyanate content at which the reaction is terminated ranges from about 10 % by weight to about 20 % by weight, preferably from about 14 % by weight to about 18.5 % by weight, and more preferably from about 16 % by weight to about 18.5 % by weight. The isocyanate functionality of the urethane prepolymer may range from about 2.2 to about 2.5, preferably about 2.3.

If fumed silica is to be incorporated into the adhesive of the invention it is typically added to the polyol component before the isocyanate component is mixed therewith in order to facilitate the dispersion of the silica. The silica used can be any fumed silica, either untreated or surface-treated with a conventional silane surface treatment. It is preferred to use surface-treated silica. Such fumed silicas are commercially available, e.g., from the Cabot Corporation as Cab-O-Sil® in various grades.

The moisture-curable polyurethane adhesive of the invention may be prepared by the following general procedure:

Step 1: A liquid propylene oxide based diol having a molecular weight of about 1200 is charged to a reactor under anhydrous conditions. Fumed silica is added to the liquid diol with exclusion of atmospheric moisture, e.g., by continuous purge with dry nitrogen, and thoroughly mixed into the polymeric diol to form a uniform dispersion.

Step 2: Into a separate reactor the diisocyanate component is charged under anhydrous conditions. The diisocyanate component is then heated to 35°C and a quantity of a poly(propylene oxide)-based diol having a molecular weight of about 2200 is added with stirring until the ingredients are thoroughly mixed. The mixture is held at a temperature of 35°C for 60 minutes. One-half of the mixture of poly(propylene oxide) diol and fumed silica prepared in Step 1 is then added under anhydrous conditions and the mixture is heated with stirring to 50°C and held at that temperature for 60 minutes. The remainder of the diol-silica mixture is then added with stirring and the reaction mixture is heated to 55°C and held for 60 minutes. The reaction mixture is then heated to 65°C and held for 60 minutes. A sample is taken to determine the isocyanate content. When the isocyanate content has reached the target value, e.g., from about 16 % by weight to about 18.5 % by weight, the reaction mixture is cooled to 40°C and the catalyst, DMDEE, is added with thorough

mixing for 15 minutes. The finished adhesive is then cooled to room temperature and filled into packages under anhydrous conditions. Alternatively, the calculated amount of fumed silica may be mixed with a portion of the polymeric diol having a molecular weight of about 1200.

The adhesive of the invention is well-adapted to use in conventional assembly of wooden articles. The adhesive is typically applied in a thin layer on a surface of one of two wooden parts to be joined. The parts are assembled and clamped for a time sufficient for the adhesive to cure. The clamping pressure may vary from about 100 pounds per square inch to about 500 pounds per square inch. The pressure is adapted to the wood being joined. Low density woods, such as poplar, basswood, and spruce are typically clamped at 100-150 pounds per square inch. Medium-density woods, such as gum, soft maple, and cherry, are typically clamped at 150-200 pounds per square inch. High-density woods, such as birch, hard maple, and oak are typically clamped at 200-250 pounds per square inch. The clamping pressure is maintained until the adhesive has cured, typically about one hour. The clamping pressure is then released and the assembled article is ready for further processing. Although the adhesive of the invention is essentially cured after the prescribed clamping time, a slight increase in the strength of bonding to

the wood substrate can sometimes be detected after an assembled article has been allowed to age for several hours, e.g., overnight.

The invention will be further illustrated by the following examples, which are not intended to be limiting. All parts and percentages specified in the compositions of the examples are parts or percentages by weight.

EXAMPLE 1

This example illustrates the performance of an adhesive according to the invention incorporating DMDEE as a catalyst.

A series of four compositions were prepared by the procedure described above. A control composition contained no DMDEE catalyst, while three test compositions contained 0.4 % by weight, 1.0 % by weight, and 2.0 % by weight, respectively of DMDEE, balance polyurethane prepolymer.

Test samples comprising two hard maple wood blocks adhered with the compositions were prepared by applying the adhesive to a smooth surface of one block, applying a mating surface of the other block to the adhesive-coated surface, and clamping for 60 minutes at a pressure of 420 pounds per square inch (psi). The clamping pressure was then released and the samples were

immediately tested according to ASTM D-905 (block shear testing). In the block shear test samples 1.5 inches by 1.5 inches are subjected to shear force parallel to the glue line until the sample breaks. The failure may occur at the interface between the adhesive and the wood surface, or the wood itself may break within the body of the block (wood failure). The strength of the glued joint is recorded, together with the percentage of the area of the glued surface where the failure was within the wood itself. When dealing with a natural product such as wood, it is to be expected that there will be relatively large variations in the adhesive strength and percentage of wood failure from sample to sample. Accordingly, a number of samples are measured and the results are averaged to provide a measure of the strength of the glued joint. The results of the tests are summarized in Table 1 below and in Figure 1.

Table 1

Sample	% DMDEE	Strength (psi-thousands)	Wood Failure %
1	0.00	0.0	0
2	0.40	2.0	25
3	1.00	2.9	45
4	2.00	3.4	74

Control samples using the same prepolymer with a tin-based catalyst typically yield strengths in the range of 2800-3200 psi and wood failure values in the range of 10-25 % after 4 hours clamping time and 24 hours cure. The same control samples yield only 1600-2000 psi and 0-10% wood failure immediately out of the 4-hour clamp.

EXAMPLE 2

This example illustrates the enhancement of the adhesive properties of the invention with addition of fumed silica.

A series of four compositions of the invention were prepared by the procedure described above. Each of the compositions contained 0.4% by weight of DMDEE. A control composition contained no fumed silica, while three test compositions contained 0.25% by weight, 1.0% by weight, and 2.0% by weight, respectively, of fumed silica (Cab-O-Sil® TS-610). The balance of each of the compositions was the polyurethane prepolymer. The compositions were applied to smooth prepared wood surfaces, clamped during the cure period, and tested as in Example 1. The

results of the tests are summarized in Table 2 below and in Figure 2.

Table 2

Sample	% Fumed Silica	Strength (psi-thousands)	Wood Failure %
1	0.00	2.0	25
2	0.25	2.6	65
3	1.00	3.0	45
4	2.00	2.5	15

The results indicate that the addition of fumed silica produces an enhanced strength and improved wood bonding when added in a defined proportion within a relatively narrow range.

EXAMPLE 3

This example illustrates the effect of fumed silica addition in the DMDEE-catalyzed adhesive of the invention as compared with a formulation using a conventional organotin catalyst.

Four formulations were prepared by the general procedure described above. Each formulation comprised the same prepolymer of the invention. A first pair of the formulations contained 0.04% of dibutyltin dilaurate as the catalyst, while a second

pair contained 1% DMDEE as the catalyst. One member of each pair contained no fumed silica, while the other member contained 1% of fumed silica. Each of the formulations was used to fasten two wooden blocks together, by application, clamping, and curing. The glued samples were tested for strength and bonding to the wood by the procedure described in Example 1. (Note: 4 hr. clamp/24 hr. care for hour catalyzed formula.)

The results are presented in Figure 3. Formulations 1 and 2 used the organotin catalyst. Formula 2 contained 1% of fumed silica while Formula 1 had no fumed silica. The adhesive strength of Formulas 1 and 2 are very similar, while the bonding to wood is generally poor as indicated by the low wood failure (<10% for the formulation without silica). Formulas 3 and 4, using DMDEE as the catalyst, exhibit strength superior to that of Formulas 1 and 2, which use the tin-based catalyst. Addition of 1 % silica fume (Formula 4) has little effect on the strength of the glued joint in this test, but it substantially improves the bonding to wood (from about 45 % wood failure to about 60 % wood failure).

EXAMPLE 4

This example illustrates a preferred formulation of the adhesive of the invention.

A moisture-curing adhesive of the invention was prepared by the general procedure outlined above having the following composition, wherein the percentages given are by weight.

4,4'-diphenylmethane diisocyanate (PAPI® 2901 (Dow))	60.88
propylene oxide based diol (Mn ≈ 1020) (Voranol® 220-110N (Dow))	30.88
propylene oxide based diol (Mn ≈ 4200) (Voranol® 220-028 (Dow))	6.44
surface-treated fumed silica (Cab-O-Sil® TS-720)	1.00
dimorpholinyl diethyl ether (Jeffcat® DMDEE (Huntsman))	0.40
monomeric 4,4'-diphenylmethane diisocyanate (PTSI (Vanchem))	0.40

The polymerization procedure was continued until an NCO content of about 16.5% by weight was reached, with a viscosity of 8100 cps.

Test samples were prepared from pairs of maple blocks to which the adhesive was applied within the open working time of 20-25 minutes. The blocks were assembled, clamped for 45 minutes and allowed to cure for 4 hours, then tested according to ASTM D-905 as in Example 1. The strength of ten test samples varied

from 3022 psi to 4889 psi, with an average value of 3636 psi. The wood adhesion, as measured by wood failure for the ten samples, ranged from 0% to 100%, with an average of 71%.

EXAMPLE 5

This example illustrates another preferred formulation of the adhesive of the invention.

A moisture-curing adhesive of the invention was prepared by the general procedure outlined above having the following composition, wherein the percentages given are by weight.

4,4'-diphenylmethane diisocyanate (PAPI® 2901 (Dow))	60.55
propylene oxide based diol (Mn ≈ 1020) (Voranol® 220-110N (Dow))	30.88
propylene oxide based diol (Mn ≈ 2200) (Voranol® 220-028 (Dow))	6.58
surface treated fumed silica (Cab-O-Sil® TS-530)	0.99
dimorpholinyl diethyl ether (Jeffcat® DMDEE (Huntsman))	1.00

The polymerization procedure was continued until an NCO content of 16.17% by weight was reached.

Test samples were prepared and tested as in the previous example. When tested immediately after release of clamping pressure, the strength of five test samples varied from 3156 psi to 4444 psi, with an average value of 3636 psi. The wood adhesion, as measured by wood failure for the five samples, ranged from 25% to 80%, with an average of 54%. Five test samples were allowed to remain overnight at room temperature to assure a complete cure and then tested as described above. The strength of the five overnight test samples varied from 2889 psi to 4133 psi, with an average value of 3698 psi. The wood adhesion for the five overnight samples, as measured by wood failure, ranged from 35% to 100%, with an average of 86%. These results suggest that the strength of the adhesive joint in the fully cured samples does not change much from the strength measured in samples tested immediately after release of the clamping pressure, but that the adhesion to the wood surface is improved for the fully cured samples.

In order to test the effect of severe exposure to wet conditions, a boil test was conducted as follows. Fingerjointed Ponderosa Pine samples were prepared as above, clamped, and allowed to cure. Thereupon, the samples were subjected to boiling water for four hours, dried overnight, again subjected to a four-hour boiling water treatment, and tested while wet (ASTM

D-5572). Eighteen samples were measured yielding values of the bond strength from 370 psi to 920 psi with an average of 681 psi. The wood adhesion varied from 20% to 100%, with an average of 76%. These test results indicate that the adhesive of the invention has good water resistance.

EXAMPLE 6

This example illustrates another preferred formulation of the adhesive of the invention.

A moisture-curing adhesive of the invention was prepared by the general procedure outlined above having the following composition, wherein the percentages given are by weight.

4,4'-diphenylmethane diisocyanate (PAPI® 2901 (Dow))	65.85
propylene oxide based diol (Mn ≈ 1020) (Voranol® 220-110N (Dow))	27.02
propylene oxide based diol (Mn ≈ 2200) (Voranol® 220-028 (Dow))	5.75
surface treated fumed silica (Cab-O-Sil® TS-610)	0.88
dimorpholinyl diethyl ether (Jeffcat® DMDEE (Huntsman))	0.50

The polymerization procedure was continued until an NCO content of 18.05 % by weight was reached.

Test samples were prepared from pairs of maple blocks and tested as in Example 1. The blocks were assembled, clamped for 60 minutes at a pressure of 420 psi, then tested according to ASTM D-905. The immediate strength of five test samples varied from 2622 psi to 4222 psi, with an average value of 3407 psi. When five test samples were tested after aging overnight, the strength varied from 2622 psi to 4178 psi, with an average value of 3267 psi.

The invention having now been fully described, it should be understood that it may be embodied in other specific forms or variations without departing from its spirit or essential characteristics. Accordingly, the embodiments described above are to be considered in all respects as illustrative and not restrictive, the scope of the invention being indicated by the appended claims rather than by the foregoing description, and all changes which come within the meaning and range of equivalency of the claims are intended to be embraced therein.

I CLAIM:

1. A moisture-curable one-part polyurethane adhesive comprising

from about 95 % by weight to about 99.8 % by weight of an isocyanate-terminated prepolymer having an isocyanate content of from about 10 % to about 20 % by weight,

from about 0.1% by weight to about 2.7 % by weight of dimorpholinodiethyl ether; and

from about 0.1 % by weight to about 2.0 % by weight of fumed silica.

2. The composition of Claim 1 wherein said isocyanate content is from about 14 % by weight to about 18.5 % by weight.

3. The composition of Claim 1 wherein said isocyanate content is from about 16 % by weight to about 18.5 % by weight.

4. The composition of Claim 1 wherein said dimorpholinodiethyl ether is present in an amount of from about 0.25% by weight to about 2.0 % by weight.

5. The composition of Claim 1 wherein said dimorpholinodiethyl ether is present in an amount of from about 0.3% by weight to about 1.5 % by weight.

6. The composition of Claim 1 wherein said fumed silica is present in an amount of from about 0.15 % by weight to about 1.5 % by weight.

7. The composition of Claim 1 wherein said fumed silica is present in an amount of from about 0.2 % by weight to about 1.2 % by weight.

8. A method of bonding a wood surface to a substrate surface comprising

applying a layer of the curable adhesive of Claim 1 to at least one of a wood surface and a substrate surface in the presence of atmospheric moisture,

contacting said wood surface with said substrate, whereby a layer of the composition of Claim 1 is interposed between said wood surface and said substrate surface,

and maintaining said wood surface and said substrate surface in contact with said adhesive interposed therebetween for a period of time sufficient for said curable adhesive to cure.

9. The method of Claim 8 wherein said wood surface and said substrate surface are maintained in contact by clamping with a pressure of from about 100 pounds per square inch to about 500 pounds per square inch.

10. The method of Claim 8 wherein said wood surface and said substrate surface are maintained in contact for a period of from about one-half hour to about 2 hours.

11. A moisture-curable one-part polyurethane adhesive comprising

from about 97 % by weight to about 99.8 % by weight of an isocyanate-terminated prepolymer having an isocyanate content of from about 10 % to about 20 % by weight, and

from about 0.4% by weight to about 3.0 % by weight of dimorpholinodiethyl ether.

12. The composition of Claim 11 wherein said isocyanate content is from about 14 % by weight to about 18.5 % by weight.

13. The composition of Claim 11 wherein said isocyanate content is from about 16 % by weight to about 18.5 by weight.

14. The adhesive of Claim 11 wherein said catalyst is present in an amount of from about 1.0 % by weight to about 2.7 % by weight.

15. A method of bonding a wood surface to a substrate surface comprising

applying a layer of the curable adhesive of Claim 11 to at least one of a wood surface and a substrate surface in the presence of atmospheric moisture,

contacting said wood surface with said substrate, whereby a layer of the composition of Claim 11 is interposed between said wood surface and said substrate surface,

and maintaining said wood surface and said substrate surface in contact with said adhesive interposed therebetween for a period of time sufficient for said curable adhesive to cure.

16. The method of Claim 15 wherein said catalyst is present in amount of from about 1.0 % by weight to about 2.7 % by weight.

17. The method of Claim 15 wherein said wood surface and said substrate surface are maintained in contact by clamping with a pressure of from about 100 pounds per square inch to about 500 pounds per square inch.

18. The method of Claim 15 wherein said wood surface and said substrate surface are maintained in contact for a period of from about 10 minutes to about 2 hours.

19. The moisture-curable one-part polyurethane adhesive of Claim 1 having the composition

4,4'-diphenylmethane diisocyanate	60.88 % by weight
propylene oxide based diol (Mn ≈ 1020)	30.88 % by weight
propylene oxide based diol (Mn ≈ 4200)	6.44 % by weight
surface-treated fumed silica	1.00 % by weight
dimorpholinyl diethyl ether	0.40 % by weight
monomeric 4,4'-diphenylmethane diisocyanate	0.40 % by weight

20. The moisture-curable one-part polyurethane adhesive of Claim 1 having the composition

4,4'-diphenylmethane diisocyanate	60.55 % by weight
propylene oxide based diol (Mn ≈ 1020)	30.88 % by weight

propylene oxide based diol (Mn ≈ 4200)	6.58 % by weight
surface-treated fumed silica	0.99 % by weight
dimorpholinyl diethyl ether	1.00 % by weight

21. The moisture-curable one-part polyurethane adhesive of Claim 1 having the composition

4,4'-diphenylmethane diisocyanate	65.85 % by weight
propylene oxide based diol (Mn ≈ 1020)	27.02 % by weight
propylene oxide based diol (Mn ≈ 4200)	5.75 % by weight
surface-treated fumed silica	0.88 % by weight
dimorpholinyl diethyl ether	0.50 % by weight

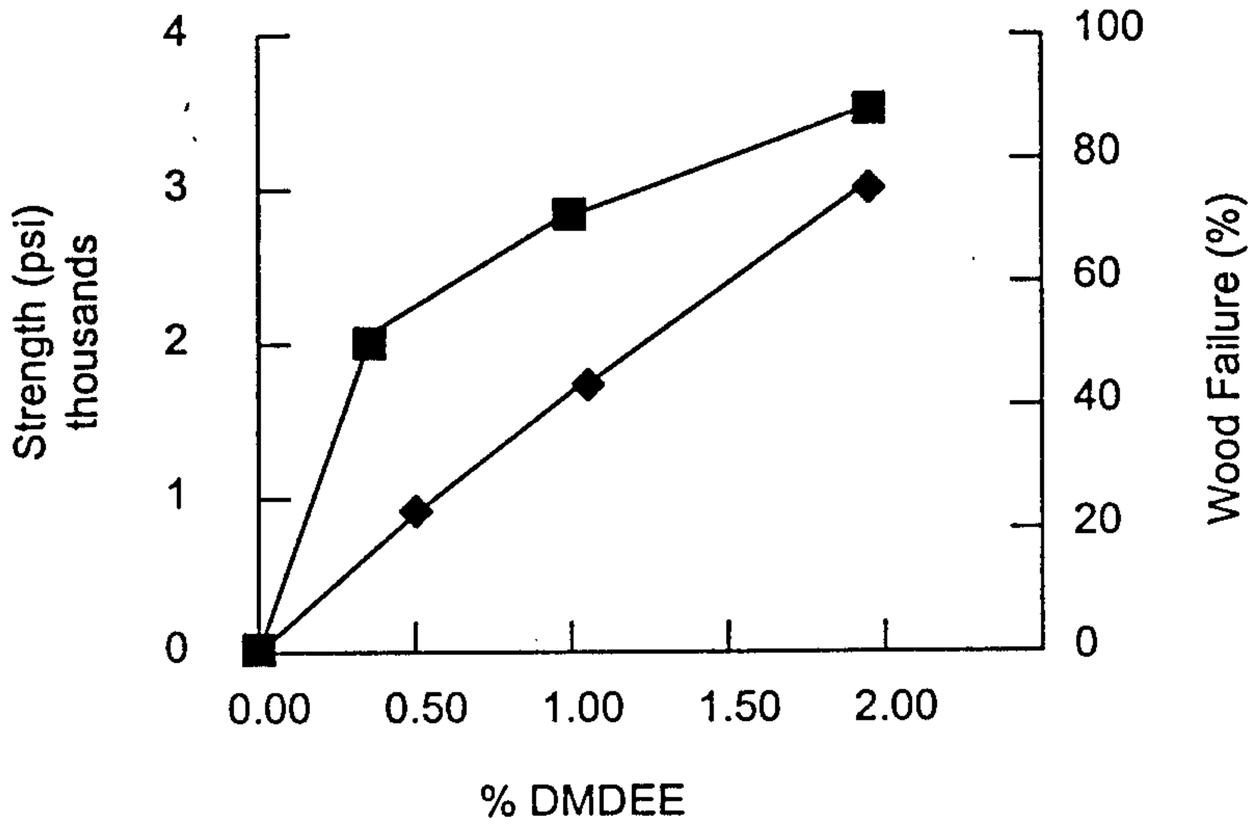

Strength (psi)
thousands
4
3
2
1
0
100
80
60
40
20
0
Wood Failure (%)
0.00
0.50
1.00
1.50
2.00
% DMDEE

Fig. 1

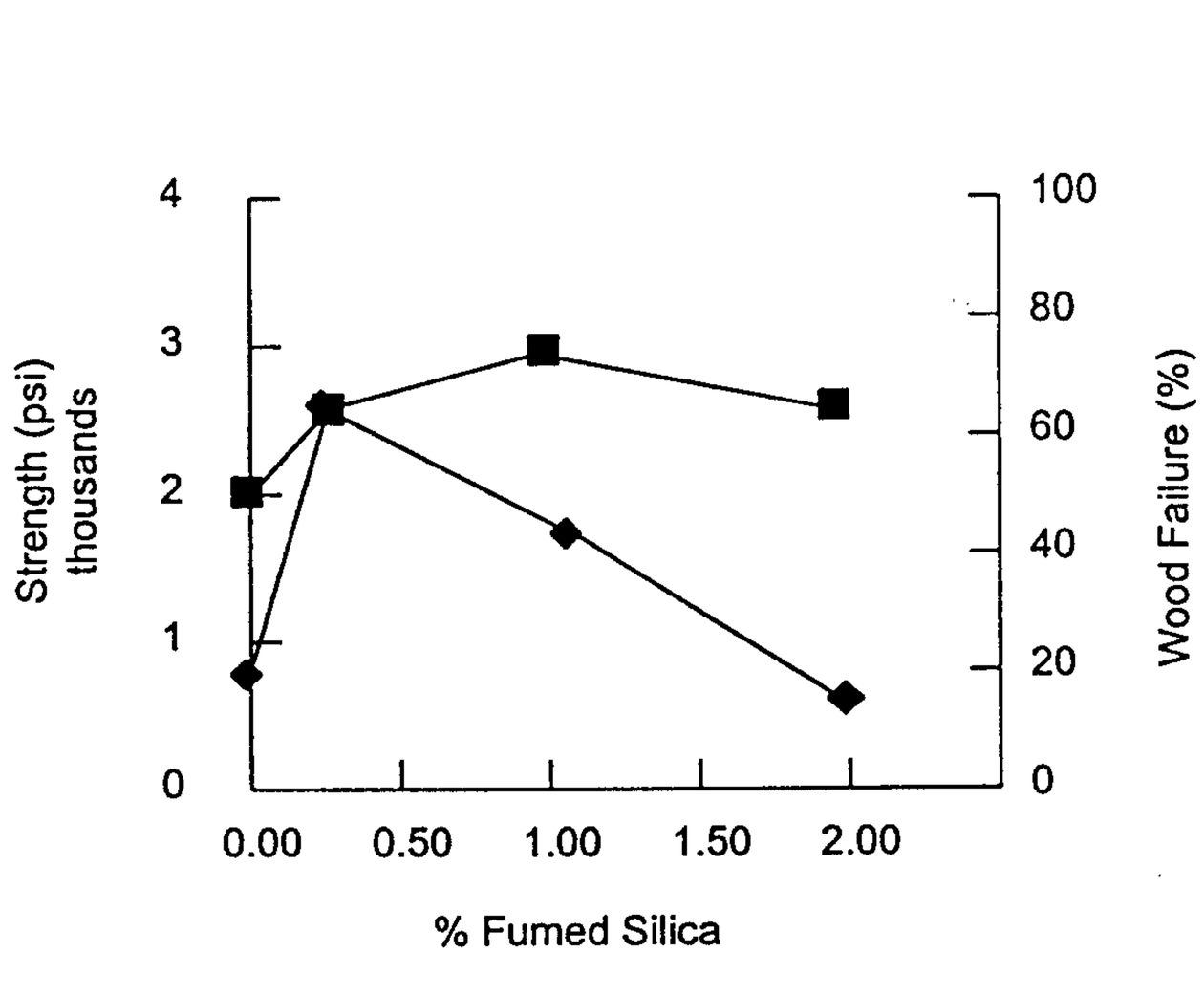

Strength (psi)
thousands
4
3
2
1
0
100
80
60
40
20
0
Wood Failure (%)
0.00
0.50
1.00
1.50
2.00
% Fumed Silica

Fig. 2

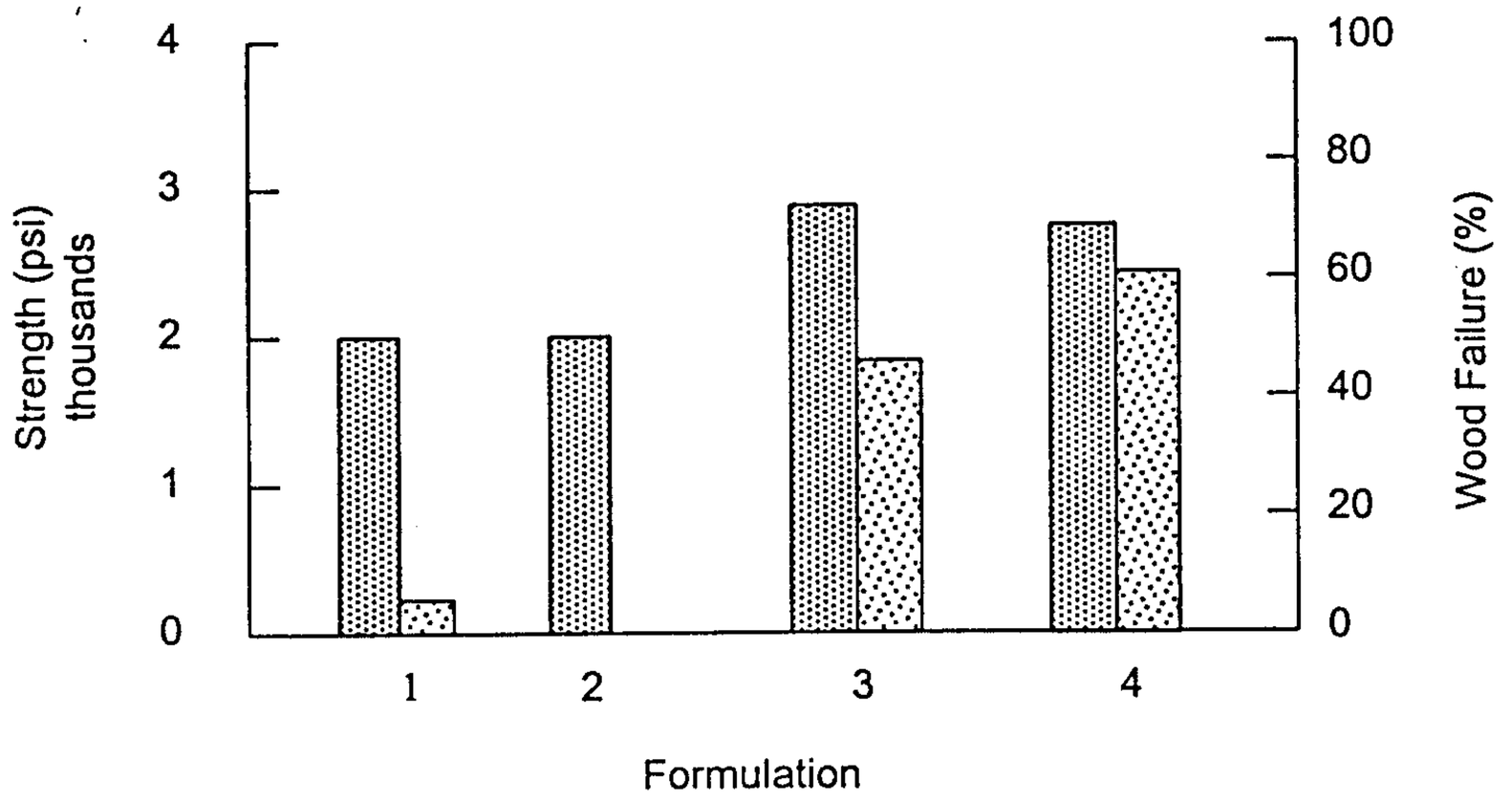

Strength (psi)
thousands
4
3
2
1
0
100
80
60
40
20
0
Wood Failure (%)
1
2
3
4
Formulation

Fig. 3