Claims

1. A moisture-curable polyurethane formulation capable of curing to form a reaction product, and comprising:
   a) at least one isocyanate-terminated prepolymer which is the product of an isocyanate reactive compound and at least one monomeric/polymeric isocyanate, wherein sufficient monomeric/polymeric isocyanate is present to provide an excess of free isocyanate in the prepolymer and/or formulation, wherein the NCO/OH mole ratio of the prepolymer is within the range of about 5 to about 20;
   b) optionally, additional monomeric/polymeric isocyanate;
   c) at least one of:
      i) a urea-based thixotropic additive in the presence of a carrier, wherein the additive comprises about 4% to about 15% of urea groups and the reaction product comprises at least about 1% to about 5% urea groups; or
      ii) a urea-based thixotropic additive compound produced by the in situ reaction of the excess of free isocyanate in the isocyanate-terminated prepolymer or the additional monomeric/polymeric isocyanate with an amine in the presence of a carrier in a NCO/NH_2 equivalent ratio of at least 3 to provide greater than 1% of urea groups in the reaction product; and
   d) at least one rheology modifier or filler;
   wherein the formulation is capable of being dispensed from a caulking gun and has sufficient green strength to adhesively bond a first substrate weighing at least 500 grams to a second substrate without the need for any holding instrument, wherein a contact surface between the first substrate and the second substrate is at least 18 $inch^2$.

2. The polyurethane formulation of claim 1 wherein the urea-based thixotropic additive comprises about 4% to about 6% of urea groups and the reaction product comprises at least about 1.8% to about 3% urea groups.

3. The polyurethane formulation of claim 1, wherein the urea-based thixotropic additive of component c(i) comprises a paste formed by dispersing the urea-based thixotropic additive in a plasticizer.

4. The polyurethane formulation of claim 3, wherein the urea-based thixotropic additive comprises a HAT paste comprising about 15% to about 35% of a urea thixotrope and about 65% to about 85% phthalate plasticizer.

5. The polyurethane formulation of claim 1, wherein the urea-based thixotropic additive comprises at least about 25% by weight of the reaction product.

6. The polyurethane formulation of claim 1, wherein the polyurethane formulation additionally comprises at least one of organic fillers, inorganic fillers, plasticizers, antioxidants, UV stabilizers, fungicides, mildewcides, biocides, fire retardants, surface additives, coloring agents, solvents, mineral oils, additional thixotropic agents, dispersing agents, adhesion promoters, catalysts, defoaming agents, drying agents or mixtures thereof.

7. The polyurethane formulation of claim 1, wherein the monomeric/polymeric isocyanate comprises at least one of toluene diisocyanates, methylene diphenyl diisocyanates, phenylene diisocyanate, xylylene diisocyanate, diphenylmethane diisocyanate, polyphenylmethane polyisocyanate (Polymeric MDI), naphthalene diisocyanate, triphenylmethane triisocyanate, diphenyl sulfone diisocyanate, cyclohexane diisocyanates, ethylene diisocyanate, propylene diisocyanate, tetramethylene diisocyanate, hexamethylene diisocyanates, isophorone diisocyanate, dimers and trimers of these diisocyanates or mixtures thereof.

8. The polyurethane formulation of claim 7, wherein the monomeric/polymeric isocyanate comprises at least one of toluene 2,4-diisocyanate, toluene 2,6-diisocyanate, naphthylene 1,5-diisocyanate, 4,4'-methylene diphenyl diisocyanate, 2,4'-methylene diphenyl diisocyanate, 1-methyl-2,4-diisocyanatocyclohexane, 1-methyl-2,6-diisocyanatocyclohexane, 4,4'-dicyclohexylmethane diisocyanate, urethodione diisocyanate, isocyanurate trisocyanate, cyclohexane-1,4-diisocyanate, 1-methoxyphenyl-2,4-diisocyanate, 4,4'-biphenylene diisocyanate, 3,3'-dimethoxy-4,4' biphenyl diisocyanate, 3,3'-dimethyl-4,4'-biphenyl diisocyanate, and 3,3' dimethyldiphenylmethane-4,4'-diisocyanate, or mixtures thereof.

9. The polyurethane formulation of claim 1 wherein the isocyanate reactive compound comprises at least one of acrylic polyols, polyester polyols, polyoxyalkylene polyols, urethane polyols, epoxy polyols and polycarbonate polyols, having at least two hydroxyl groups in the molecule, or combinations thereof.

10. The polyurethane formulation of claim 1, wherein the amine comprises at least one of primary amines, secondary amines, saturated aliphatic amines, unsaturated aliphatic amines, alkoxy alkyl amines, alicyclic amines, aralkyl amines, aromatic amines, or mixtures thereof.

11. The polyurethane formulation of claim 1, wherein the amine comprises at least one of methylamine, ethylamine, propylamine, isopropylamine, butylamine, amylamine, hexylamine, dimethylamine, diethylamine, dipropylamine, diisopropylamine,

dibutylamine, allylamine, diallylamine; cyclopropylamine, cyclobutylamine, cyclopentylamine, cyclohexylamine, aniline, diphenylamine, methylaniline, ethylaniline, toludine, xylidine, benzylamine, or naphthylamine.

12. The polyurethane formulation of claim 1 wherein the carrier comprises at least one of plasticizer or polyol.

13. The polyurethane formulation of claims 3 or 12 wherein the plasticizer comprises at least one of C4-C12 alkyl phthalate, adipate, azelainate, sebacate, sulfonate, trimellitate, phosphate, fumarate, or maleate ester or diester, or mixtures thereof.

14. The polyurethane formulation of claim 13 comprising at least one of diisooctyl phthalate, diisodecyl phthalate, dioctyl phthalate, 2-ethylhexyl phthalate, diisononyl phtalate, dibutyl phthalate, diheptyl phthalate, dioctyl adipate, 2-ethylhexyl adipate, diisononyl adipate, or diisodecyl adipate, di(2-ethylhexyl)azelainate, di(2-ethylhexyl)sebacate, phenyl alkylsulfonates, tri(2-ethylhexyl)trimellitate, triphenyl phosphate, tricresyl phosphate, trixylenyl phosphate, cresyl diphenyl phosphate, xylenyl diphenyl phosphate, butyl fumarate, bis(2-methylpropyl) fumarate, diisobutyl fumarate, or bis(2-ethylhexyl) fumarate, dimethyl maleate or diethyl maleate, or mixtures thereof.

15. The polyurethane formulation of claim 12 wherein the polyol comprises at least one of acrylic polyols, polyester polyols, polyoxyalkylene polyols, urethane polyols, epoxy polyols and polycarbonate polyols, having at least two hydroxyl groups in the molecule, or combinations thereof.

16. The polyurethane formulation of claims 9 or 15 wherein the at least one polyoxyalkylene polyol comprises at least one of polyethylene glycol; polypropylene glycol; polytetramethylene glycol; or polyether prepared by the copolymerization of a cyclic ether comprising at least one of ethylene oxide, propylene oxide, trimethylene oxide, tetrahydrofuran, or mixtures thereof with at least one aliphatic polyol comprising ethylene glycol, 1,3-butanediol, diethylene glycol, dipropylene glycol, 1,2-propylene glycol, 1,3-propylene glycol, 1,4-butylene glycol, or mixtures thereof.

17. The polyurethane formulation of claims 9 or 15 wherein the at least one polyester polyol is prepared by (a) the reaction of a dicarboxylic acid or anhydride with an excess of a diol; (b) the reaction of a lactone with a diol; or (c) the esterification of a dicarboxylic acid comprising at least one of phthalic acid, isophthalic acid or terephthalic acid or mixtures thereof with polyol initiators comprising at least one of ethylene glycol, diethylene glycol,

propylene glycol, dipropylene glycol, butanediol, polyethylene glycol, glycerin, pentanetriol, or mixtures thereof.

18. The polyurethane formulation of claim 1 wherein the rheology modifier comprises at least one of polyureas, fumed silica, hydroxyethyl cellulose, hydroxypropyl cellulose, polyamide waxes, modified castor oil, clay intercalated with organic cations, or mixtures thereof.

19. The polyurethane formulation of claim 1 wherein the filler comprises at least one of organic fibers, inorganic fibers, rubber particles, cork particles, carbon black, titanium dioxide, glass, crushed glass, glass spheres, iron particles, quartz, silica, amorphous precipitated silica, hydrophilic fumed silica, hydrophobic fumed silica, kaolin, mica, diatomaceous earth, talc, zeolites, clays, aluminum hydroxide, sulfates, aluminum sulfate, barium sulfate, calcium carbonate, dolomite, calcium sulfate, barites, limestone, wollastonite, perlite, flint powder, kryolite, alumina, alumina trihydrate, polymer granules, polymer powders, granulated or micronized polyethylene granulated or micronized polypropylene, melamine, polypropylene fibers, nylon fibers, zinc oxide, or mixtures thereof.

20. The polyurethane formulation of claim 1 wherein the urea-based thixotropic additive comprises the product of:
polyisocyanates comprising at least one of toluene-2,4-diisocyanate, toluene-2,6-diisocyanate, 4,4'-methylene diphenyl diisocyanate, 2,4'-methylene diphenyl diisocyanate, 4,4'-dicyclohexylmethane diisocyanate, isophorone diisocyanate, or hexamethylene diisocyanate; allophanate, biuret, uretdione, isocyanurate or carbodiimide derivatives thereof, or mixtures thereof; and
primary alkyl monoamines comprising at least one of linear or branched C_{4-10} alkyl monoamines, or linear or branched C_{1-4} alkoxy C_{3-6} alkyl monoamines.

21. The polyurethane formulation of claim 1 wherein the formulation provides a green lap shear strength in excess of about 0.13 lbs/in^2 or greater.

22. A method for making a moisture-curable polyurethane formulation capable of curing to form a reaction product, comprising:
providing components:
a) at least one isocyanate-terminated prepolymer having an NCO/OH mole ratio within the range of about 5 to about 20;
b) optionally additional monomeric/polymeric isocyanate;
c) a thixotropic component comprising at least one of

(i) a urea based thixotropic additive in the presence of a carrier, where the additive comprises at least about 4% of urea groups; or,

(ii) a urea-based thixotropic additive compound produced by the in situ reaction of the excess of free isocyanate in the isocyanate-terminated prepolymer or the additional monomeric/polymeric isocyanate with an aliphatic amine in the presence of a carrier in a NCO/NH_2 equivalent ratio of at least 3 to provide greater than 1% of urea groups in a polyurethane reaction product; and,

d) at least one rheology modifier or filler;

wherein the formulation is capable of being dispensed from a caulking gun; and reacting the components a, optionally b, c(i) or c(ii) and d to form the reaction product comprising greater than 1% of urea groups;

wherein the reaction product has sufficient green strength to adhesively bond a first substrate weighing at least 500 grams to a second substrate without the need for any holding instrument, wherein a contact surface between the first substrate and the second substrate is at least 18 $inch^2$.

23. The method of claim 22, wherein the formulation provides a green lap shear strength in excess of about 0.13 lbs/in^2 or greater.

24. A method of adhering a first substrate to a second substrate comprising applying the polyurethane formulation of claim 1 to a first substrate and contacting the polyurethane formulation-applied first substrate surface with the second substrate.

25. The method of claim 24, wherein applying comprises dispensing the polyurethane formulation from a caulking gun.

26. The method of claim 24, wherein the first and second substrates comprise at least one of concrete, stone, metal, ceramic, glass, plastic, wood, asphalt, rubber or composite materials.

27. A method for bonding materials together which comprises applying the polyurethane formulation of claim 1 to a first substrate, bringing a second substrate in contact with the formulation applied to the first substrate, and subjecting the applied formulation to moisture which will allow the formulation to cure to an irreversible solid form.

Claims

1. A moisture-curable polyurethane formulation capable of curing to form a reaction product, and comprising:

a) at least one isocyanate-terminated prepolymer which is the product of an isocyanate reactive compound and at least one monomeric/polymeric isocyanate;

b) optionally, additional monomeric/polymeric isocyanate;

c) at least one of:

i) a urea-based thixotropic additive in the presence of a carrier;

or

ii) a urea-based thixotropic additive compound produced by the *in situ* reaction of the excess of free isocyanate in the isocyanate-terminated prepolymer or the additional monomeric/polymeric isocyanate with an amine in the presence of a carrier; and

d) at least one rheology modifier or filler;

characterized in that:

sufficient monomeric/polymeric isocyanate is present to provide an excess of free isocyanate in the prepolymer and/or formulation, wherein the NCO/OH mole ratio of the prepolymer is within the range of 5 to 20;

the urea-based thixotropic additive comprises 4% to 15% of urea groups and the reaction product comprises at least 1% to 5% urea groups;

or

the urea-based thixotropic additive compound is produced by the *in situ* reaction of the excess of free isocyanate in the isocyanate-terminated prepolymer or the additional monomeric/polymeric isocyanate with an amine in the presence of a carrier in a NCO/NH_2 equivalent ratio of at least 3 to provide greater than 1% of urea groups in the reaction product; and

wherein the formulation is capable of being dispensed from a caulking gun and has sufficient green strength to adhesively bond a first substrate weighing at least 500 grams to a second substrate without the need for any holding instrument, wherein a contact surface between the first substrate and the second substrate is at least 116 cm^2(18 $inch^2$).

2. The polyurethane formulation of claim 1 wherein the urea-based thixotropic additive comprises 4% to 6% of urea groups and the reaction product comprises at least 1.8% to 3% urea groups.

3. The polyurethane formulation of claim 1, wherein the urea-based thixotropic additive of component c(i) comprises a paste formed by dispersing the urea-based thixotropic additive in a plasticizer.

4. The polyurethane formulation of claim 3, wherein the urea-based thixotropic additive comprises a HAT paste comprising 15% by weight to 35% by weight of a urea thixotrope and 65% by weight to 85% by weight phthalate plasticizer.

5. The polyurethane formulation of claim 1, wherein the polyurethane formulation additionally comprises at least one of organic fillers, inorganic fillers, plasticizers, antioxidants. UV stabilizers, fungicides, mildewcides, biocides, fire retardants, surface additives, coloring agents. solvents, mineral oils, additional thixotropic agents, dispersing agents. adhesion promoters, catalysts, defoaming agents. drying agents or mixtures thereof.

6. The polyurethane formulation of claim 1, wherein the monomeric/polymeric isocyanate comprises at least one of toluene diisocyanates, methylene diphenyl diisocyanates, phenylene diisocyanate. xylylene diisocyanate, diphenylmethane diisocyanate, polyphenylmethane polyisocyanate (Polymeric MDI), naphthalene diisocyanate, triphenylmethane triisocyanate, diphenyl sulfone diisocyanate, cyclohexane diisocyanates, ethylene diisocyanate, propylene diisocyanate, tetramethylene diisocyanate, hexamethylene diisocyanates, isophorone diisocyanate, dimers and trimers of these diisocyanates or mixtures thereof.

7. The polyurethane formulation of claim 1 wherein the isocyanate reactive compound comprises at least one of acrylic polyols, polyester polyols, polyoxyalkylene polyols, urethane polyols, epoxy polyols and polycarbonate polyols, having at least two hydroxyl groups in the molecule, or combinations thereof.

8. The polyurethane formulation of claim 1. wherein the amine comprises at least one of primary amines, secondary amines, saturated aliphatic amines, unsaturated aliphatic amines, alkoxy alkyl amines, alicyclic amines, aralkyl amines, aromatic amines, or mixtures thereof.

9. The polyurethane formulation of claim 1 wherein the carrier comprises at least one of plasticizer or polyol.

10. The polyurethane formulation of claim 1 wherein the rheology modifier comprises at least one of polyureas, fumed silica, hydroxyethyl cellulose, hydroxypropyl cellulose, polyamide waxes, modified castor oil, clay intercalated with organic cations, or mixtures thereof.

11. The polyurethane formulation of claim 1 wherein the filler comprises at least one of organic fibers, inorganic fibers, rubber particles, cork particles, carbon black, titanium dioxide, glass, crushed glass, glass spheres, iron particles, quartz, silica, amorphous

precipitated silica, hydrophilic fumed silica, hydrophobic fumed silica, kaolin, mica, diatomaceous earth, talc, zeolites, clays, aluminum hydroxide, sulfates, aluminum sulfate, barium sulfate, calcium carbonate, dolomite, calcium sulfate, barites, limestone, wollastonite, perlite, flint powder, kryolite, alumina, alumina trihydrate, polymer granules, polymer powders, granulated or micronized polyethylene granulated or micronized polypropylene, melamine, polypropylene fibers, nylon fibers, zinc oxide, or mixtures thereof.

12. The polyurethane formulation of claim 1 wherein the urea-based thixotropic additive comprises the product of:
polyisocyanates comprising at least one of toluene-2,4-diisocyanate, toluene-2,6diisocyanate, 4,4'-methylene diphenyl diisocyanate, 2,4'-methylene diphenyl diisocyanate, 4,4'-dicyclohexylmethane diisocyanate, isophorone diisocyanate, or hexamethylene diisocyanate; allophanate, biuret, uretdione, isocyanurate or carbodiimide derivatives thereof, or mixtures thereof; and
primary alkyl monoamines comprising at least one of linear or branched C_{4-10} alkyl monoamines, or linear or branched C_{1-4} alkoxy C_{3-6} alkyl monoamines.

13. The polyurethane formulation of claim 1 wherein the formulation provides a green lap shear strength in excess of 896 Pa (0.13 lbs/in^2) or greater.

14. A method for making a moisture-curable polyurethane formulation capable of curing to form a reaction product, comprising:
providing components:
a) at least one isocyanate-terminated prepolymer;
b) optionally additional monomeric/polymeric isocyanate;
c) a thixotropic component comprising at least one of
(i) a urea based thixotropic additive in the presence of a carrier; or,
(ii) a urea-based thixotropic additive compound produced by the *in situ* reaction of the excess of free isocyanate in the isocyanate-terminated prepolymer or the additional monomeric/polymeric isocyanate with an aliphatic amine in the presence of a carrier; and,
d) at least one rheology modifier or filler;
characterized in that
the at least one isocyanate-terminated prepolymer has an NCO/OH mole ratio within the range of 5 to 20;
the urea based thixotropic additive comprises at least 4% of urea groups; or,
the urea-based thixotropic additive compound is produced by the *in situ* reaction of the excess of free isocyanate in the isocyanate-terminated prepolymer or the additional monomeric/polymeric isocyanate with an aliphatic amine in the presence of a carrier in a

NCO/NH2 equivalent ratio of at least 3 to provide greater than 1% of urea groups in the polyurethane reaction product;
wherein the formulation is capable of being dispensed from a caulking gun; and
reacting the components a, optionally b, c(i) or c(ii) and d to form the reaction product comprising greater than 1% of urea groups;
wherein the reaction product has sufficient green strength to adhesively bond a first substrate weighing at least 500 grams to a second substrate without the need for any holding instrument, wherein a contact surface between the first substrate and the second substrate is at least 116 cm^2 (18 $inch^2$).

15. A method for bonding materials together which comprises applying the polyurethane formulation of claim 1 to a first substrate, bringing a second substrate in contact with the formulation applied to the first substrate, and subjecting the applied formulation to moisture which will allow the formulation to cure to an irreversible solid form.