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DECLARATION FOR A PATENT APPLICATION

INSTRUCTIONS (a) Insert "Convention" if applicable (b) Insert FULL name(s) of applicant(s)

In support of the (a) CONVENTION application made by (b) ESSEX SPECIALTY PRODUCTS, INC. 1135 Broad Street Clifton, New Jersey 07015, U.S.A. (hereinafter called "applicant(s)") for a patent (c) for an invention entitled (d)

(c) Insert "of addition" if applicable (d) Insert TITLE of invention

PRIMER COMPOSITION FOR IMPROVING THE BONDING OF A URETHANE ADHESIVE

(e) Insert FULL name(s) AND address(es) of declarant(s) (See headnote\*)

I/We (e) Richard G. Waterman, General Patent Counsel of THE DOW CHEMICAL COMPANY 2030 Dow Center, Abbott Road Midland, Michigan 48640, U.S.A.

do solemnly and sincerely declare as follows:

- 1. I am/We are the applicant(s) (or, in the case of an application by a body corporate) 1. I am/We are authorized to make this declaration on behalf of the applicant(s). 2. I am/We are the actual inventor(s) of the invention. (or, where the applicant(s) is/are not the actual inventor(s)) 2. (f)

(f) Insert FULL name(s) AND address(es) of actual inventor(s)

Harry W. S. Hsieh, 8 Melissa Court, Edison, New Jersey 08820, United States of America

(g) Recite how applicant(s) derive(s) title from actual inventor(s) (See headnote\*\*)

is/are the actual inventor(s) of the invention and the facts upon which the applicant(s) is/are entitled to make the application are as follows:

- (g) The applicant Company is the assignee of the said invention from the said actual inventor(s).

(Note: Paragraphs 3 and 4 apply only to Convention applications)

(h) Insert country, filing date, and basic applicant(s) for the/ or EACH basic application

- 3. The basic application(s) for patent or similar protection on which the application is based is/are identified by country, filing date, and basic applicant(s) as follows: (h)

United States of America filed on February 6, 1990, in the name of Harry W. S. Hsieh

- 4. The basic application(s) referred to in paragraph 3 hereof was/were the first application(s) made in a Convention country in respect of the invention the subject of the application.

(i) Insert PLACE of signing

(j) Insert DATE of signing

(k) Signature(s) of declarant(s)

CORP. SEAL

Declared at (k) Midland, Michigan 48640, U.S.A.

Dated (l) 10 January 1991

ESSEX SPECIALTY PRODUCTS, INC.

By: [Signature] RICHARD G. WATERMAN

RICHARD G. WATERMAN, General Patent Counsel, The Dow Chemical Company, authorized to act for an on behalf of ESSEX SPECIALTY PRODUCTS, INC. by virtue of a Power of Attorney dated January 3, 1991.

To: The Commissioner of Patents

Agent: Phillips, Ormonde & Fitzpatrick



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- (56) Prior Art Documents  
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- (57) Claim

1. A primer which includes a solution of:

(a) a polyester resin of a carboxylic acid and a glycol;

(b) a polymethylene poly(phenyl isocyanate), diphenylmethane diisocyanate, or mixture thereof;

in a volatile solvent, wherein the weight ratio of (a):(b) is in the range of from about 0.25:1.0 to 1.5:1.0.

4. A primer according to any one of Claims 1 to 3 wherein the average number of isocyanate groups per molecule of polyisocyanate is in the range of from 2.4 to 5.0.

5. A primer which includes a solution of:

- (a) 5 to 10 weight percent of a polyester resin of a carboxylic acid and a glycol; and
- (b) 6 to 17 weight percent of a polymethylene poly(phenyl isocyanate), diphenylmethane diisocyanate, or mixture thereof;

in a volatile solvent.

9. A composite including a painted metal substrate bonded to a glass substrate, by means of a cured layer of a primer and a urethane adhesive, wherein the primer includes a solution of:

- (a) a polyester resin of a carboxylic acid and a glycol;
- (b) a polymethylene poly(phenyl isocyanate), diphenylmethane diisocyanate, or mixture thereof;

in a volatile solvent, wherein the weight ratio of (a):(b) is in the range of from 0.25:1.0 to 1.5:1.0.

10. A composite including a painted metal substrate bonded to a glass substrate, by means of a cured layer of a primer and a urethane adhesive, wherein the primer includes a solution of:

- (a) 5 to 10 weight percent of a polyester resin of a carboxylic acid and a glycol; and
- (b) 6 to 17 weight percent of a polymethylene poly(phenyl isocyanate), diphenylmethane diisocyanate, or mixture thereof;

in a volatile solvent.



PRIMER COMPOSITION FOR IMPROVING  
THE BONDING OF A URETHANE ADHESIVE

5 This invention relates to a primer composition for priming a substrate surface to increase the adhesion of a sealant composition to such a surface. More particularly, this invention relates to a primer composition for priming a substrate surface which has been coated with a coating or paint to increase the adhesion of a sealant composition to such a surface.

10 Urethane sealants and adhesives are known to provide high tensile strengths and tear strengths when used to bond materials. Such sealants and adhesives are especially suitable for use in automobile manufacture for the bonding of a windshield to an auto body, wherein the firm bonding imparts additional structural integrity to the automobile body. However, some urethane sealants do not bond glass to painted metal sufficiently without the use of a primer to prime the metal substrate.

20 Primers for use in improving the bonding of glass to painted surfaces are known and are described. for example, in U.S. Patent 4,525,511 which describes a primer comprising a film-forming resin and a strong acid. U.S. Patent 4,643,794 describes a primer for bonding to both  
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5 glass and metal surfaces which comprises 10 to 20 parts polyester resin, 4 to 5 parts polyisocyanate cross-linking agent, 3 to 9 parts carbon black, and 66 to 83 parts volatile solvent. However, although such a primer is adapted for use on both glass and painted surfaces, it is often preferable to use different primers for priming the metal substrate and the glass which have optimum adhesion characteristics for their particular use in order to meet stringent federal motor vehicle safety standards when such a primer is used to bond windshields in automobiles. Further, it is not especially cumbersome to use multiple primer products during a glass installation process since separate applications of primer to glass and primer to paint are still necessary when a paint primer is used. Therefore, paint primers with improved adhesion characteristics for adhesion to painted surfaces are desirable.

20 In one aspect, this invention is a primer which includes ~~comprises~~ a solution of:

- 25 (a) a polyester resin of a carboxylic acid and a glycol; and  
(b) a polymethylene poly(phenyl isocyanate), diphenylmethane diisocyanate, or mixture thereof;

30 in a volatile solvent, wherein the weight ratio of (a):(b) is in the range of from 0.25:1.0 to ~~2.0:1.0~~ <sup>1.5:1.0</sup>.

In a second aspect, this invention is a primer which ~~comprises~~ <sup>include</sup> a solution of:



(a) 5 to 10 weight percent of a polyester resin of a carboxylic acid and a glycol; and

(b) 6 to 17 weight percent of a polymethylene poly(phenyl isocyanate), diphenylmethane diisocyanate, or mixture thereof;

in a volatile solvent.

In a third aspect, this invention is a composite including a painted metal substrate bonded to a glass substrate, by means of a cured layer of a primer and a urethane adhesive, wherein the primer includes a solution of:

(a) a polyester resin of a carboxylic acid and a glycol;

(b) a polymethylene poly(phenyl isocyanate), diphenylmethane diisocyanate, or mixture thereof;

in a volatile solvent, wherein the weight ratio of (a):(b) is in the range of from 0.25:1.0 to 1.5:1.0.

In a fourth aspect, this invention is a composite including a painted metal substrate bonded to a glass substrate, by means of a cured layer of a primer and a urethane adhesive, wherein the primer includes a solution of:

(a) 5 to 10 weight percent of a polyester resin of a carboxylic acid and a glycol; and



(b) 6 to 17 weight percent of a polymethylene poly(phenyl isocyanate), diphenylmethane diisocyanate, or mixture thereof;  
in a volatile solvent.

5

It has been discovered that the primer of the invention advantageously provides improved adhesion characteristics of metal-to-glass bonding when used to prime paint-coated metal substrates before the application of a urethane adhesive, particularly when used with a "fast cure" adhesive comprised of an isocyanate-functional prepolymer and dimorpholinediethyl ether. However, the primer of the invention may also be used to prime other types of surfaces for use with other types of adhesives. These and other advantages of this invention are apparent from the following description.

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The primer of the invention is a liquid mixture, which preferably has a density of about 8 lb/gal before application. After application, the mixture forms a tenacious coating upon solvent evaporation, and completely cures upon exposure to atmospheric moisture.

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The polyester resin of a carboxylic acid and a glycol component of the primer (hereafter "polyester resin") is a polymer of a carboxylic acid and a glycol. The polyester resin preferably has a molecular weight of from 15,000 to 25,000 and has a glass transition temperature which is preferably in the range of from 65°C to 70°C. This polyester resin is preferably a polymer of at least one aromatic dicarboxylic acid or alkyl ester thereof, and at least one glycol compound. The preparation of these polyester resins is described,

for example, in U.S. Patent 3,459,584, column 2, line 40 to column 4, line 3; and U.S. Patents 4,020,049 and 4,418,183. Preferred aromatic dicarboxylic acids include 1,3-benzenedicarboxylic acid and 1,4-benzenedicarboxylic acid. Preferred glycols include 1,2-ethanediol. Especially preferred is Vitel™ PE-200, a polyester resin with a molecular weight of about 20,000 sold by the Goodyear Tire and Rubber Co.

The polymethylene poly(phenyl isocyanate), diphenylmethane diisocyanate, or mixture thereof (hereafter "polyisocyanate") is a polyisocyanate which preferably has an NCO equivalent weight of at least about 130, more preferably at least about 133, and most preferably at least about 140; and is preferably no greater than about 500, more preferably no greater than about 300, and most preferably no greater than about 150. The average number of isocyanate groups per molecule of polyisocyanate is preferably at least about 2.4, more preferably at least about 2.7, and most preferably at least about 3.0; and is preferably no greater than about 5.0, more preferably no greater than about 4.0, and most preferably no greater than about 3.5. Preferably, the polyisocyanate comprises a mixture of polymethylene poly(phenyl isocyanate) and diphenylmethane diisocyanate. More preferably, the polymethylene poly(phenyl isocyanate) is present in an amount of at least about 10 percent of the polyisocyanate mixture, on a weight basis. Examples of suitable polyisocyanates include PAPI™ 20, PAPI™ 27, and PAPI™ 580, sold by The Dow Chemical Company, Lupranate™ M200, sold by BASF Corporation Chemicals Division, and PBA-2257 and PBA-2262, sold by ICI.

In addition, derivatives of 4,4'-diphenylmethane diisocyanate which are liquid at room temperature such as, for example, polyisocyanates which have carbodiimide groups in their backbone or mixtures thereof may also be used. The preparation of these materials is disclosed in U.S. Patent 3,152,162. An example of a commercial material of this type is Isonate™ 143L Isocyanate, a product of The Dow Chemical Company.

The polyester resin and the polyisocyanate are combined in a manner such that the weight ratio of (a):(b) is preferably at least about 0.25:1.0, more preferably at least about 0.33:1.0, and most preferably at least about 0.5:1.0; and is preferably no greater than about 2.0:1.0, more preferably no greater than about 1.5:1.0, and most preferably no greater than about 1.0:1.0.

In the primer of the second aspect of the invention, the polyester resin preferably comprises at least about 5 weight percent, more preferably at least about 7 weight percent, and most preferably at least about 8 weight percent; and is preferably no greater than about 18 weight percent, more preferably no greater than about 13 weight percent, and most preferably no greater than about 10 weight percent of the total primer. The polyisocyanate preferably comprises at least about 6 weight percent, more preferably at least about 8 weight percent, and most preferably at least about 10 weight percent; and is preferably no greater than about 17 weight percent, more preferably no greater than about 15 weight percent, and most preferably no greater than about 13 weight percent of the total primer.

The volatile solvent component of the primer of the invention may be any solvent, which is preferably anhydrous in order to prevent the isocyanate from reacting with any water present, which will dissolve the polyester resin at a temperature in the range of from about 20°C to 25°C. Examples of such solvents include xylene, methylene chloride, benzene, monochlorobenzene, trichloroethylene, ethylene chloride, toluene, acetone, and methyl ethyl ketone, and mixtures thereof, and is preferably acetone or methyl ethyl ketone, or a mixture thereof. More preferably, the solvent is a mixture of acetone and methyl ethyl ketone. The solvent is preferably used in an amount of at least about 50 percent, more preferably at least about 55 percent, and most preferably at least about 60 percent; and is preferably no greater than about 90 percent, more preferably no greater than about 85 percent, and most preferably no greater than about 80 percent, based on the weight of the total primer.

Catalysts which promote the reaction of the polyisocyanate with atmospheric moisture and with active hydrogen groups present on the substrate which is primed may also be included in the primer of the invention and include, for example, a stannous or stannic compound, such as a stannous salt of a carboxylic acid (e.g., stannous octoate, stannous oleate, stannous acetate, and stannous laurate), a trialkyltin oxide, a dialkyltin dicarboxylate (e.g., dibutyltin dilaurate, dibutyltin diacetate, diethyltin diacetate, and dihexyltin diacetate), a dialkyltin dihalide, or a dialkyltin oxide, such as di-2-ethylhexyltin oxide or dioctyltin dioxide, a tertiary amine, or a tin mercaptide. Tertiary amine

5 catalysts include trialkylamines (e.g., trimethylamine, triethylamine), heterocyclic amines, such as N-alkylmorpholines (e.g., N-methylmorpholine, N-ethylmorpholine, dimethyldiaminodiethyl ether, etc.), 1,4-dimethylpiperazine, triethylenediamine, etc., and aliphatic polyamines, such as N,N,N',N'-tetramethyl-1,3-butanediamine. Preferably, the catalyst is a mixture of an organic salt of a tertiary amine and a tin compound in an organic solvent. Such a catalyst is sold by Air Products and Chemicals, Inc. under the tradename Dabco™ DC-2.

10 Carbon black may also be added to the primer of the invention to modify the rheological properties of the primer, such as viscosity, sag resistance, and flow rate. When carbon black is employed, it is preferably used in an amount of at least about 0.5 percent, more preferably at least about 1.0 percent, and most preferably at least about 2.0 percent; and is preferably no greater than about 5.0 percent, more preferably no greater than about 4.0 percent, and most preferably no greater than about 3.0 percent, based on the weight of the total primer formulation.

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30 Other fillers and additives which may also be used to modify the rheological properties of the primer include, for example, surface-treated fumed silicas, titanium dioxide, calcium carbonate, talc, defoaming agents, mica, aluminum oxide, clays, and glass phenolic, or aluminum oxide bubbles. Such fillers and additives are preferably anhydrous, or dried before use in order to prevent the reaction of any moisture present with the isocyanate. When talc is added it is preferably used in an amount of at least about 3 percent, and more preferably at least about 5 percent; and is preferably no

greater than about 9 percent, and more preferably no greater than about 7 percent, based on the weight of the total primer formulation.

5 Additives which stabilize the free isocyanate groups present in the primer are also preferably employed. Such additives include, for example, diethyl malonate, which is preferably employed in an amount of at least about 0.02 percent, more preferably at least about 0.10 percent, and most preferably at least about 10 0.50 percent; and is preferably no greater than about 5.0 percent, more preferably no greater than about 2.5 percent, and most preferably no greater than about 1.5 percent, based in the weight of the total primer 15 formulation.

In the preparation and storage of the primer, it is preferable to minimize the moisture content of the primer, so that the free isocyanate groups will not react with the water. Additives which may be employed to reduce the free water content of the primer include, for example, molecular sieves which preferably have a pore diameter of about 3Å. These molecular sieves are preferably added in an amount of at least about 0.01 percent, and more preferably at least about 0.03 percent; and is preferably no greater than about 1.0 percent, and more preferably no greater than about 0.1 percent, based on the weight of the total primer formula- 20 tion. 25 30

The primer of the invention may be used to prime a substrate for use with any one-component or two-component adhesive by applying at least one coat of the primer to the substrate prior to the application of an

adhesive. The primer of the invention is especially well adapted for use with a urethane adhesive, particularly a moisture-curable urethane adhesive, and more particularly a "fast cure" urethane adhesive comprised of an isocyanate-functional prepolymer and dimorpholinediethyl ether, of the type which is described, for example, in U.S. Patents 4,758,648 and 4,780,520. Other urethane adhesives which may be used with the primer of the invention include, for example, sealants of the type described in U.S. Patents 3,707,521, 3,779,794, 4,624,996, 4,625,012, 4,758,648, and 4,719,267. The primer of the invention may be used to prime any type of substrate, but is especially well adapted for use with a painted substrate such as, for example, a metal substrate painted with a paint system comprising a base coat of an enamel paint coated with a clear coat of a polyurethane or acrylic melamine, or a monocoat of acrylic melamine high solids enamel.

The composites of the invention may be prepared by bonding a painted metal substrate to a glass substrate, by means of a cured layer of a primer and a urethane adhesive, wherein the primer comprises a solution of:

(a) a polyester resin of a carboxylic acid and a glycol;

(b) a polymethylene poly(phenyl isocyanate), diphenylmethane diisocyanate, or mixture thereof;

in a volatile solvent, wherein the weight ratio of (a):(b) is in the range of from 0.25:1.0 to 2.0:1.0;

or, wherein the primer comprises a solution of:

(a) 5 to 18 weight percent of a polyester resin of a carboxylic acid and a glycol; and

5 (b) 6 to 17 weight percent of a polymethylene poly(phenyl isocyanate), diphenylmethane diisocyanate, or mixture thereof;

in a volatile solvent.

10 Preferably, the primer is first applied to a surface of the metal substrate and the solvent therein is allowed to evaporate. The urethane adhesive is then applied on top of the dried primer. A surface of the  
15 glass substrate is then brought into contact with the urethane adhesive before the urethane adhesive reaches a tack-free state. The urethane adhesive is then allowed to cure. Any of the urethane adhesives and primers described above may be used to prepare the composites of  
20 the invention.

The following examples are given to illustrate the invention and should not be interpreted as limiting it in any way. Unless stated otherwise, all parts and  
25 percentages are given by weight.

Example 1

30 Vitel™ PE-200 polyester resin (34.8 g) and 119.2 g of anhydrous methyl ethyl ketone (MEK) are charged into a ball mill which is rolled on a roller for about 30 minutes, or until the polyester resin is completely dissolved in the MEK. Dried talc (32.7 g), dried carbon black (8.2 g), and a 3Å molecular sieve

powder (0.2 g) are added to the ball mill and ground for about 16 hours. PAPI™ 20 polyisocyanate (59.3 g), anhydrous acetone (91.6 g), diethyl malonate (2.0 g), methyl ethyl ketone (101.0 g), and Dabco™ DC-2 urethane catalyst (1.8 g) are added to the ball mill and ground for 1 hour.

Example 2

Using the procedure of Example 1, primers are prepared using the following amounts of components, and are used to prime a painted metal substrate before the application of a urethane adhesive:

8 291 70240

TABLE I

	<u>2A</u>	<u>2B</u>	<u>2C</u>	<u>2D</u>	<u>2E</u>
methyl ethyl ketone, g	220.2	220.2	220.2	220.2	220.2
Vitel™ PE-200 polyester resin, g	72.7	59.2	47.1	34.8	21.4
talc, g	32.7	32.7	32.7	32.7	32.7
carbon black, g	8.2	8.2	8.2	8.2	8.2
3Å molecular sieves, g	0.2	0.2	0.2	0.2	0.2
PAPI™ 20 polyisocyanate, g	21.4	34.9	47.1	59.3	72.7
acetone, g	91.6	91.6	91.6	91.6	91.6
diethyl malonate, g	2.1	2.1	2.1	2.1	2.1
Dabco™ urethane catalyst, g	0.9	0.9	0.9	0.9	0.9
Weight ratio of Vitel™ PE-200/PAPI™ 20	3.4:1.0	1.7:1.0	1.0:1.0	0.59:1.0	0.29:1.0

Lap shear testing is performed as follows: a plate glass is washed with a mild soap and warm water solution, rinsed thoroughly, and dried with a clean towel. The glass is then rinsed with acetone and dried with a clean towel. Painted panels are primed with freshly shaken primer which is applied with a clean paint dauber and dried for at least 30 minutes. The glass is wiped with a silane primer, which is then wiped off again 10 seconds after application. A glass primer is then applied and allowed to dry for at least 30 minutes. The painted panels are attached to a lap shear board, and a bead of a urethane sealant comprising a prepolymer and dimorpholinediethyl ether, sold as Essex Specialty Products' 573.02 sealant, approximately 1/4 inch wide by 5/16 inch high is run along the width of the glass and approximately 1/4 inch to 1/2 inch from the primed end. The primed panel is immediately placed on the sealant and the sample is allowed to cure in an environmental chamber at 25°C and 50 percent relative humidity for 5 days. The samples are lap shear tested on an Instron™ machine at a crosshead speed of 1.0 in/min. The remaining bead width of the samples is measured at five different places and the results averaged. The average lap shear is calculated by dividing the test load by the average cross section of the remaining sealant. The average results for three samples is shown below.

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TABLE II

polyester resin/ PAPI™ 20 ratio	Lap Shear, psi / mode of failure (%)	
	Paint Sample #1*	Paint Sample #2*
5		
3.4:1.0	524/20% CF 40% PF 40% PTL	880/97% CF 3% PF
1.7:1.0	768/100% CF	837/60% CF 40% PF
1.0:1.0	608/25% CF 75% PTL	656/100% CF
10		
0.59:1.0	875/97% CF 3% PTL	755/97% CF 3% PTL
0.29:1.0	869/100% CF	542/100% PF

\* Paint Sample #1 is a metal substrate painted with a paint system comprising a base coat of an enamel paint coated with a clear coat of a polyurethane or acrylic melamine, which is manufactured by BASF. Paint Sample #2 is a metal substrate painted with a similar paint system manufactured by DuPont.

PF - Paint Primer Failure

CF - Cohesive Failure within the sealant

PTL - Paint Lifting - failure occurs within substrate

Example 3

Using the procedure of Example 1, primers are prepared using the following amounts of components, and are used to prime a painted metal substrate before the application of a urethane adhesive.

TABLE III

	<u>3A</u>	<u>3B</u>	<u>3C</u>	<u>3D</u>	<u>3E</u>	<u>3F</u>
methyl ethyl ketone, g	220.2	220.2	220.2	220.2	220.2	220.2
Vitel™ PE-200 polyester resin, g	34.8	34.8	59.2	47.1	34.8	34.8
talc, g	32.7	32.7	32.7	32.7	32.7	32.7
carbon black, g	8.2	8.2	8.2	8.2	8.2	8.2
3Å molecular sieves, g	0.2	0.2	0.2	0.2	0.2	0.2
polyisocyanate*, g	59.3	59.3	34.9	47.1	59.3	59.3
Acetone, g	91.6	91.6	91.6	91.6	91.6	91.6
diethyl malonate, g	2.1	2.1	2.1	2.1	2.1	2.1
Dabco™ urethane catalyst, g	1.8	-	-	-	1.8	1.8

\* Ex. 3A - PAPI™ 27 - NCO functionality - 2.7  
 Ex. 3B - PAPI™ 20 - NCO functionality - 3.0  
 Ex. 3C - PAPI™ 20  
 Ex. 3D - PAPI™ 20  
 Ex. 3E - PBA 2262 - NCO functionality - 2.7  
 Ex. 3F - Lupranate™ M-200 - NCO functionality - 3.0

The claims defining the invention are as follows:

1. A primer which includes a solution of:

5 (a) a polyester resin of a carboxylic acid and a glycol;

(b) a polymethylene poly(phenyl isocyanate), diphenylmethane diisocyanate, or mixture thereof;

10 in a volatile solvent, wherein the weight ratio of (a):(b) is in the range of from about 0.25:1.0 to 1.5:1.0.

2. A primer according to Claim 1 wherein the weight ratio of (a):(b) is at least about 0.33:1.0.

15 3. A primer according to either Claim 1 or 2 wherein component (b) includes at least one diphenylmethane diisocyanate.

20 4. A primer according to any one of Claims 1 to 3 wherein the average number of isocyanate groups per molecule of polyisocyanate is in the range of from 2.4 to 5.0.

25 5. A primer which includes a solution of:

(a) 5 to 10 weight percent of a polyester resin of a carboxylic acid and a glycol; and

(b) 6 to 17 weight percent of a polymethylene poly(phenyl isocyanate), diphenylmethane diisocyanate, or mixture thereof;

30 in a volatile solvent.

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6. A primer according to Claim 5 wherein the weight percent of component (b) is at least about 8 weight percent.

5 7. A primer according to either Claim 5 or 6 wherein component (b) includes at least one diphenylmethane diisocyanate.

10 8. A primer according to any one of Claims 5 to 7 wherein the average number of isocyanate groups per molecule of polyisocyanate is in the range of from 2.4 to 5.0.

15 9. A composite including a painted metal substrate bonded to a glass substrate, by means of a cured layer of a primer and a urethane adhesive, wherein the primer includes a solution of:

(a) a polyester resin of a carboxylic acid and a glycol;

20 (b) a polymethylene poly(phenyl isocyanate), diphenylmethane diisocyanate, or mixture thereof;

25 in a volatile solvent, wherein the weight ratio of (a):(b) is in the range of from 0.25:1.0 to 1.5:1.0.

30 10. A composite including a painted metal substrate bonded to a glass substrate, by means of a cured layer of a primer and a urethane adhesive, wherein the primer includes a solution of:

(a) 5 to 10 weight percent of a polyester resin of a carboxylic acid and a glycol; and

35 (b) 6 to 17 weight percent of a polymethylene poly(phenyl isocyanate), diphenylmethane diisocyanate, or mixture thereof;

in a volatile solvent.



11. A primer substantially as described herein with reference to any one of the non-comparative examples.

5 12. A composite substantially as described herein with reference to any one of the non-comparative examples.

DATED: 27 October 1993

PHILLIPS ORMONDE & FITZPATRICK

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