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(54) Title: UNSATURATED POLYMER POLYURETHANE STRUCTURAL ADHESIVE		
(57) Abstract <p>This invention is a structural adhesive and a laminate of untreated substrates adhered together with a structural adhesive which combines a two part polyurethane adhesive with a two part free radical curing adhesive. The adhesive is especially useful in the manufacture of personal watercraft built to withstand rough waves and made of fiberglass reinforced plastic.</p>		

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UNSATURATED POLYMER POLYURETHANE STRUCTURAL ADHESIVE

This invention relates to adhesives useful on fiberglass reinforced polyester (FRP) substrates used to make personal watercraft which must
5 withstand rough treatment by waves.

Background of The Invention

Commercially available polyurethane has been used to adhere FRP structural adhesives on personal watercraft substrates but only if the surface
10 to be bonded is pretreated, such as by sanding or priming with a solvent before applying the adhesive to the substrate. As watercraft manufacturers become more aware of the labor intensity and the environmental problems caused by such surface treatments, new adhesives are needed to bond these structures together without any surface treatment.

15

Detailed Description of The Invention

Personal watercraft are made by hand laying glass mats or glass fibers on a mold or form. The glass is then bonded together with a resin, usually unsaturated polyesters cured at room temperature by free radical chemistry
20 initiated by peroxides. Typically, such parts are cured in the open air, although sometimes they are compressed briefly to control thickness uniformity. In either process, air in the surrounding atmosphere inhibits the

crosslinking reaction resulting in a partially uncured top surface. It is well known that such an inadequately cured surface is difficult to adhere without some surface treatment, such as a solvent wipe or sanding.

It was discovered that if the adhesive contains unsaturation
5 functionality, hereafter referred to as an "unsaturated polymer", it can be cured by free radical chemistry initiated by peroxide and used to bond watercraft parts without any surface treatment. However, the unsaturated polymer / peroxide cured adhesive is very brittle, since there is no strength
10 reinforcement in the adhesive such as the glass fibers used to build the watercraft itself. It was discovered that such peroxide cured adhesives can be toughened or flexibilized by a cocuring polyurethane adhesive.

In addition to adhesion, this very flexible unsaturated polymer / polyurethane adhesive for watercraft showed excellent sag resistance, fast green strength development and a tack free surface. Retention of adhesion
15 was also demonstrated by exposing the bonds in 100% relative humidity environment at 100°F (38°C) for eight weeks. Testing of bond strength after such exposure typically showed greater than 230 psi.

Examples of unsaturated polymers for such adhesives include the same type of unsaturated polyesters used to construct watercraft as well as
20 unsaturated polyurethanes. Typical unsaturated polyesters are the reaction product of a glycol and an unsaturated carboxylic acid or anhydride and dicyclopentadiene or styrene. The unsaturated polyurethane is typically

prepared by endcapping a polymeric polyol with a polyisocyanate to prepare a prepolymer. Then, the isocyanate end groups are converted to unsaturation by reaction of the isocyanate with the hydroxyl group of an unsaturated alcohol, such as hydroxylethyl acrylate or hydroxyethyl methacrylate (HEMA). U.S. Patents 4,480,079, 5,126,396 and 5,250,608 describe the preparation of unsaturated polyurethane.

To reduce the viscosity of the unsaturated polyurethane product, one commonly adds more isocyanate to the prepolymer to prepare a low molecular weight adduct of HEMA-capped polyisocyanate simultaneously with the prepolymer preparation step. Also very effective in viscosity reduction is the addition of low molecular weight reactive diluents such as styrene, acrylates or methacrylates. These diluents also cocure with the unsaturated polymer when exposed to a free radical initiator such as a peroxide.

Alternatively, the prepolymer step of such unsaturated polyurethane may be bypassed by simply reacting HEMA, polyol and polyisocyanate in one step to form an unsaturated polyurethane.

A room temperature curing adhesive for bonding personal watercraft without surface preparation is formed by combining the unsaturated polymer with a polyurethane. Exemplary polyurethane adhesives are described in U.S. Patents 4,923,756, 5,002,806 and 5,548,056. Examples of such combination include 1) having polyisocyanate and peroxide as Part A and

polyol/polyamine and unsaturated polymer as Part B or 2) having polyol and peroxide as Part A and polyisocyanate and unsaturated polymer as Part B. Interpenetrating network structural adhesives are prepared by mixing Part A and Part B using a propeller type mechanical mixer or a mix machine such as Model 200 from EMC², Sterling Heights, Michigan. To facilitate room temperature curing, a peroxide such as benzoyl peroxide to initiate free radical formation at room temperature and conventional catalysts such as tertiary amine, organotin, and organocobalt may be used.

Alternatively, since many commercial peroxides are available for the initiation of peroxide formation above room temperature, a peroxide other than benzoyl peroxide may be used for the adhesives of this invention, if the curing at elevated temperatures is desired. In such cases, the formulator has the option of combining all the ingredients into a single mixture, instead of Part A and Part B. When the adhesive is ready to be cured heat is applied to initiate free radical formation and thus crosslinking.

Among the fiberglass reinforced polyester substrates useful in the practice of this invention are those hand layup and cold press substrates provided by Arctic Cat, Inc, Thief River Falls, MN (formerly known as Arctco) or Mercury Marine, Hartford, WI.

The unsaturated polymer polyurethane adhesive of this invention is made by combining a polyisocyanate, a component reactive toward polyisocyanate, an unsaturated polymer and a free radical initiator. Among the polyisocyanates useful in this invention are:

diphenylmethane diisocyanate,

toluene diisocyanate,

1,4-phenylene diisocyanate,

3,3'-dimethoxy-4,4'-biphenyl diisocyanate,

5 3,3'-dimethyl-4,4'-diisocyanatobiphenyl,

3,3' dimethyl-4,4'-diisocyanato diphenyl methane,

or their polymerized versions or mixtures thereof. The most preferred isocyanate in the practice of this invention is polymeric Rubinate 9310 available from ICI, Sterling Heights, Michigan or Isonate 143 L

10 polyisocyanate from Dow Chemical, Midland, Michigan.

Alternatively, the polyisocyanate useful in this invention may also be derived from the reaction product of a polyisocyanate and a polyol of 1.8-6 functionality. The polyols useful for the preparation of such prepolymers may be 700 to 10,000 molecular weight polypropylene oxide ether diol,

15 polyethylene oxide polypropylene oxide ether diol, polytetramethylene ether glycol, polythioether diol, polyester diol, polyepsilon caprolactone diol, polycarbonate diol, polybutadiene diol or mixtures of these diols. The preferred polyol is a polypropylene oxide ether diol of 1000 or 2000 molecular weight available from Olin Chemicals, New Haven, Connecticut as Poly G 20-
20 112 or Poly G 20-56, respectively.

The component selected to cure the polyisocyanate in the unsaturated polymer polyurethane adhesive of this invention includes the polyols used to make the prepolymer and polyamines. Other polyols include polyester and polyether polyols which have a functionality of 1.8 to 6.0 and a hydroxyl
25 number from 100 to 1200. A hydroxyl number range of 200 to 700 and a functionality range of 3 to 5 are preferred. Suitable active hydrogen containing materials include diols, triols and tetrols, having primary, secondary and/or tertiary alcohol groups. Among the preferred polyether

polyols are: Pluracol PeP 550 polyol, a propoxylated derivative of pentaerythritol having four secondary hydroxyl groups, a hydroxyl number of 450, and a molecular weight of 500 available from BASF Wyandotte Corporation, Parsippany, N.J.; Arcol F3220, an ethoxylated / propoxylated
5 derivative of glycerin having three secondary hydroxyl groups, a hydroxyl number of 52 and a molecular weight of about 3200 available from ARCO Chemical Company, Newtown Square, PA; Fomrez ET3500, a propoxylated derivative of glycerin having three secondary hydroxyl groups, a hydroxyl number of 48 and a molecular weight of about 3500, available from Witco
10 Corporation, Organic Division, Houston, Texas; Pluracol P-355 polyol, an ethoxylated/propoxylated derivative of ethylene diamine having about 80% of its hydroxyl groups as primary and having a hydroxyl number of 450, also available from BASF Wyandotte Corporation; Thanol R470X polyol, available from Texaco Chemical Co., Bellaire, Tex., a propoxylated derivative of
15 diethanolamine with a functionality of about 4 and a hydroxy number of 500; Thanol SF-265 polyol, also available from Texaco Chemical Co., a propoxylated derivative of triethanolamine with a functionality of about 3 and a hydroxyl number of 600; Voranol 230-660 polyol, a polyether triol of 85.4 equivalent weight based on the propoxylation of glycerin, available from Dow
20 Chemical Co., Midland, Mich.; and Dianol 2210 polyol, an ethoxylated derivative of bisphenol-A with a functionality of 2 and a hydroxyl number of 280, available from Akzo Chemie America, Chicago, Ill.

Among the numerous diamines useful for curing the unsaturated polymer polyurethane adhesive of this invention are the following aromatic
25 diamines:

- toluene diamine
- 1-methyl-3,5-diethyl-2,4-diaminobenzene
- 1-methyl-3,5-diethyl-2,6-diaminobenzene (also known as DETDA or diethyl toluene diamine)
- 30 di(methylthio) toluene diamine

- 1,3,5-triethyl-2,6-diaminobenzene
 toluene diamine derivatives containing halogen groups, cyano groups,
 alkoxy, alkylthio, alkenyl or carbonylic moieties
 m-phenylene diamine
 5 p-phenylene diamine
 4,4'-methylenedianiline
 4,4'-diaminodiphenyl sulfone
 2,6-diamino-pyridine
 4,4'-methylene bis(3-chloroaniline)
 10 4,4'-methylene bis(3-chloro-2,6-diethylaniline)
 4,4'-methylene bis (3-chloro-2,5-diethylaniline)
 3,3'-di-isopropyl-4,4'-diaminodiphenylmethane
 3,5,3', 5'-tetraethyl-4,4'-diaminodiphenylmethane
 propylene-di-4-aminobenzoate
 15 isobutyl 4-chloro-3,5-diaminobenzoate
 bis (2-aminophenyl) disulfide
 bis (4-aminophenyl) disulfide
 di (alkylated amino) benzene secondary diamine
 bis (alkylated aminophenyl) methane secondary diamine
 20 3,3'-carbomethoxy-4,4'-diamino diphenylmethane

and mixtures thereof. The most preferred diamine for the adhesive of this invention is diethyl toluene diamine (Ethacure 100, from Albemarle Corporation, Orangeburg, SC), which also contributes to the sag resistance of the adhesive because of its high reactivity.

- 25 Another ingredient in the formulation of the adhesive of this invention is an optional catalyst to facilitate the crosslinking reaction of the adhesive between amines and isocyanates, and between polyols and isocyanates. Suitable tertiary amine catalysts include N, N', N''-dimethylaminopropylhexahydrotriazine (Polycat 41) and 1,4-
 30 diazabicyclooctane, and suitable organo metallic catalysts such as those

derived from zinc, potassium, bismuth and tin including dibutyltin dilaurate, dibutyltin diacetate, ferric acetyl acetonate, nickel acetylacetonate, dibutyltin dialkyl acid, stannous octoate, dibutyltin diiso-octyl mercapto acetate, dibutyltin diisooctyl maleate, and mixtures of these catalysts. The preferred organo
5 metallic catalyst is the dibutyltin diacetate known as DABCO T1 available from Air Products, Allentown, Pa. The preferred tertiary amine catalyst is dimethyl aniline.

Other optional ingredients in the formulation of the adhesive of this invention include thickening, coloring, odor control agents and drying agents.
10 The preferred optional thickening agents are: aluminum silicates, carbon black, talcs (magnesium silicates), calcium carbonate, calcium silicates, barium sulfates, graphite, or mixtures of fillers. The preferred filler ingredient is Aerosil 200 or Aerosil R972 fumed silica from Degussa Inc., New York, N.Y.; and Cabosil TS 720 fumed silica from Cabot Corporation, Cab-O-Sil
15 Division, Tuscola, IL.

Small amounts of other optional materials may also be added to the adhesive formulation. These include coloring agents, for example, Stanton HCCC. 6783 green coloring agent from Harwick Chemical Company, Akron, Ohio, which is a blend of C.I. Pigment Green #7 and C.I. Pigment Black #7
20 dispersed in a polyoxypropylene polyol at 17.8 parts of pigment to 82.2 parts polyol.

It may be desirable also to use from 0.5 to 15.0 percent of a drying agent such as a Molecular Sieve powder of the 5 Angstrom size available from Union Carbide or anhydrous aluminum sulfate powder from Geo Specialty
25 Chemicals, Inc, Little Rock, Arkansas.

The customer combines Part A and Part B in the desired ratio, usually 1 weight part Part A is blended with 1-10 weight parts Part B. Unsaturated polymer polyurethane structural adhesives are prepared by mixing Part A and Part B typically using a mix machine Model 200 from EMC², Sterling Heights,
30 Michigan. The adhesive is applied to the first substrate by conventional

means. The second substrate is then laminated over the first adhesive coated substrate. The adhesive is typically cured at room temperature, although other energy sources such as microwave, radio frequency or dielectric energy or electromagnetic energy maybe used to accelerate the
5 cure of the adhesive.

Crosspeel adhesion samples were prepared using room temperature cured hand layup fiberglass reinforced polyester plaques, prepared from dicyclopentadiene, vinyl esters, or the reaction product of unsaturated dicarboxylic acid and glycol. Representative types of theses substrates are
10 the Arctco FRP or Arctco Cold Press or Mercury Marine FRP constructions used to manufacture personal watercrafts. A fiberglass reinforced polyester plaque was cut into 1 inch by 3 inch strips. Adhesive was applied onto the center 1 inch by 1 inch area with no surface pretreatment. A few glass beads of 30 mils diameter was spinkled onto the adhesive to control the bondline
15 thickness when the center of a second 1 inch by 3 inch fiberglass polyester plaque was mated onto the first strip with the adhesive. After curing the adhesive at room temperature, the crosspeel samples were pulled on a Monsanto Tensometer 10 tester fitted with a jig to hold the four unadhered ends of the crosspeel samples. The upper strip of the crosspeel was pulled
20 until it is separated from the bottom strip. Adhesion strength values over 600 psi were observed with failure occurring by tearing apart the cured polyester resin from the fiberglass used to reinforce the substrate. This is referred to in the industry as "fiber tear" or "FT" and is a very desirable result. The performance of an adhesive is rated on the amount of fiber tear based on the

percentage of the adhered one square inch. The data is recorded as pounds per square inch (psi) followed by a parenthesis which contains a first % of fiber tear and a second of cohesive failure. When the summation of the percentage values in the parenthesis does not equal to 100 the remainder is understood to be adhesive failure. Cohesive failure is designated to be a failure leaving adhesive on both pieces of plaque forming the crosspeel adhesion sample. Adhesive failure is designated to be a failure with separation of the adhesive from the substrate without exposure of the glassfiber reinforcing the substrate.

Green strength development of an adhesive is evaluated by testing adhesion crosspeel samples after they are cured at different intervals of time at room temperature, typically at 20 and 30 minutes. An adhesion strength of about 50 psi is considered adequate for handling the weight of personal watercraft parts in the production assembly line. Fiber tear accompanying failure of the crosspeel sample is considered superior performance of the adhesive.

The nature and advantage of this invention can be more readily seen and appreciated by reference to the following representative examples, where all components are expressed in parts by weight (pbw). All patents mentioned herein are expressly incorporated by reference.

EXAMPLE 1

This example one describes the preparation of a polyisocyanate / peroxide Part A to be cured by a polyol / polyamine / unsaturated polymer Part B.

5 **Formulation:**

Polyisocyanate 4495

	Rubinate 9310 polydiphenylmethane diisocyanate	11.92pbw
10	Moisture scavenger Molecular Sieves 5A powder	0.18
	Cabosil TS720 treated fumed silica	0.88
	Luperco ATC 50% Benzoyl Peroxide	<u>5.29</u>
		18.27

15 **Procedure**

Rubinate 9310 was charged into a 22-liter flask. With an efficient, high shearing stirrer and under a nitrogen blanket, Molecular sieves 5A powder was added, followed by Cabosil TS720. Then, Luperco ATC was added to
20 the resulting very viscous mixture. Mixing of the peroxide was initiated by handmixing with a paddle. Final thorough mixing was achieved by low shearing with a mechanical mixer for 15 minutes. Degassing of the final

mixture was initiated by slowly opening the vacuum line. When full vacuum was achieved the product was degassed for 30 minutes before discharge. The product was stored under a nitrogen blanket.

5

EXAMPLE 2

This example 2 describes the preparation of another polyisocyanate / peroxide Part A, a polyol is reacted with the polyisocyanate before the addition of peroxide.

10 **Formulation:****Polyisocyanate 4627**

	PolyG 20-112 ethylene oxide capped polypropylene ether glycol (MW 1000)	
15		50.00pbw
	Moisture scavenger Molecular Sieves 5A powder	3.86
	Rubinate 9310 polydiphenylmethane diisocyanate	158.40
	Mistron RCS Talc	46.31
	Aerosil R972 hydrophobic fumed silica	11.58
	Lupercos ATC 50% Benzoyl peroxide	<u>115.78</u>
		385.93

Procedure

Polypropylene ether glycol (PPG) (MW 1000), PolyG 20-112 was dehydrated in a vessel at 100-105°C and at a vacuum of less than 1 mm Hg, or until the moisture content was less than 0.05%. The dried PPG was cooled to 85°C before adding Molecular Sieves 5A and Rubinate 9310. Degassing was resumed and the polyol and polyisocyanate reacted at 85-95°C for an hour or until the isocyanate content reached the theoretical value of 19.79%. The mixture was cooled to 50°C and the vacuum was broken. A nitrogen blanket was introduced before the addition of Mistron RCS and then Aerosil R972. When the addition of the filler was complete Luperco ATC was added. Mixing of the resulting viscous mixture was initiated by handmixing with a paddle. Final thorough mixing was achieved by low shearing with a mechanical mixer for 15 minutes. The final mixture was degassed. When full vacuum was achieved degassing was continued for 30 minutes before discharge. The product was stored under a nitrogen blanket.

EXAMPLE 3

This example 3 describes the preparation of an unsaturated polyurethane (UPU) to be blended with a polyol and/or a polyamine to form Part B.

Formulation:

Unsaturated Polyurethane (UPU)

	Methyl Methacrylate, MMA	48.0	pbw
5	Hydroquinone, HQ	0.008	
	p-Benzoquinone, BQ	0.008	
	Hydroxyethyl Methacrylate, HEMA	9.6	
	Rubinol F428 ethylene oxide capped triol (Hydroxyl No 28)	29.3	
	Rubinate M polydiphenylmethane diisocyanate	11.5	
	Dibutyl tin dilaurate	0.68	
	MMA	<u>0.86</u>	
		99.96	

10

Procedure

MMA and HEMA were charged. Hydroquinone (HQ) and p-benzoquinone (BQ) were added and stirred until homogeneous. Rubinol F428, an ethylene oxide capped polyether triol with a hydroxyl number of 28

15 was charged. The moisture content was less than 600 ppm. Rubinate M was charged and stirring continued. Dibutyl tin dilaurate predissolved in MMA was charged. The reaction was stirred and continued for 90 minutes.

EXAMPLE 4

20 This example 4 describes the preparation of another unsaturated polymer similar to the unsaturated polyester (UPE) chemistry used to bind glass fibers for the manufacture of watercraft.

Unsaturated Polyester UPE

25

Diethylene glycol	467.2 pbw
Dipropylene glycol	31.1
Maleic anhydride	99.3
Isophthalic acid	536.3
Styrene	538.0
Monotertiary butyl hydroquinone	0.193
Methanol	0.772

5

Procedure

Diethylene glycol and dipropylene glycol were charged and heated to 140°C under an inert blanket. Maleic anhydride and isophthalic acid were added and heat to 210°C. The reaction continued until a viscosity at 28% styrene of 10 13-15 stokes. Styrene and monotertiary butyl hydroquinone dissolved in methanol were added. The product was cooled to 170°C and discharged.

EXAMPLE 5

This example 5 describes the preparation of a polyol / polyamine / 15 unsaturated polymer Part B to cure a polyisocyanate such as Example 1 polyisocyanate 4495.

Curative 4600

20	PeP 550 Propoxylated pentaerythritol (Hydroxyl Number 450, MW 500)	2.67 pbw
	ET 3500 Propoxylated glycerin (OH# 48, MW 3500)	10.98
	Ethacure 100 Diethyltoluene diamine	2.72
25	Example 3 unsaturated polyurethane	43.59
	Methyl methacrylate (MMA)	8.38

	Diallyl Phthalate (DAP)	6.70
	Cabosil TS720 treated fumed silica	7.54
5	Moisture scavenger Molecular Sieves 5A powder	0.42
	StanTone 6783 green dye	0.17
	Dimethyl aniline (DMA)	0.59
10	Dabco T1 Dibutyl tin diacetate	<u>0.059</u>
		83.819

15

Procedure

PeP550, ET3500, Ethacure 100, Modar 839 and DAP were charged and stirred to mix thoroughly. Half the required Cabosil TS720 was added. When the mixture was still quite fluid Molecular Sieves 5A, StanTone 6783, DMA and Dabco T1 were added. Under a nitrogen blanket, finish adding the remaining Cabosil TS720. When the filler was thoroughly wetted and dispersed the mixture was degassed. When full vacuum was achieved degassing continued for 20 minutes before discharge. The product was stored under an air atmosphere.

25

EXAMPLE 6

This example 6 illustrates the adhesion performance of an unsaturated polyurethane plus polyurethane hybrid adhesive 4606 by mixing Polyisocyanate 4495 of Example 1 with Curative 4600 of Example 5. After curing at room temperature on Arctic Cat, Inc., Thief River Falls, MN 56701, fiberglass reinforced polyester substrate or Arctic Cat, Inc. cold pressed FRP

30

or Mercury Marine FRP, adhesion strength as high as 610 psi with 98% fiber tear was observed. The adhesive also possessed excellent sag resistance by showing no slump when dispensed on a vertical surface. It had a bondability time of 5.75 minutes and developed a strength of 127 psi after 30
5 minutes at room temperature. (Table 1)

Table 1. Adhesion Performance of Acrylated Polyurethane / Polyurethane Hybrid Adhesive

Adhesive Ex. 6	4606
Polyisocyanate Ex. 1	4495
Curative Ex. 5	4600
Mix Ratio, wt	19/100
Bondability, min	5.75
Vertical Cardboard	no slump
Button Sag, inch	0.10
Heat Rise, °C/min	101/6.7
Green Strength	30 min @ RT 127(5/0) 40 min @ RT 149(100/0)
Crosspeel, psi(%FT):	
ARCTCO FRP Plaque	<u>After 7days@RT</u> 281(100/0) 163(100/0) 276(100/0) 267(100/0) <u>610(90/10)</u>
Average	319(98/2)
ARCTCO FRP Hull Part	<u>7d@RT</u> 225(100/0) 235(100/0) 227(100/0) 230(100/0) <u>279(100/0)</u>
Avg	239(100/0)
ARCTCO Cold Press	<u>7d@RT</u> 332(25/0) 276(95/5) 176(90/0)

Adhesive Ex. 6	4606
	267(40/0) <u>191(90/0)</u> 248(68/1)
Mercury Marine	<u>7d@RT</u> 268(100/0) 375(100/0) 225(100/0) 335(100/0) <u>307(100/0)</u> 302(100/0)
Stress-Strain:	
Ultimate Tensile, psi	2420
Ultimate elongation, %	46

EXAMPLE 7

This example 7 illustrates the adhesion performance of an unsaturated
 5 polyurethane and polyurethane prepolymer hybrid adhesive on FRP.

Table 2. Performance of a Prepolymer / Acrylated Polyurethane / Polyurethane Hybrid Adhesive

Adhesive Ex 7	4333
Prepolymer:	4211
Ashland Pliogrip 9400, %	25.68
Luperco ATC, %	6.42
CURATIVE:	4324
PeP 550, %	2.42
ET 3500, %	9.97
DETDA, %	2.47
Example 3, Unsaturated Polyurethane, %	44.23
DAP, %	5.44
Aerosil 200, %	2.72
Mol Sieves 5A, %	0.34
DMA, %	0.25
Dabco T1, %	0.041
Mix Ratio, wt	47.3/100
Bondability, min	7
Button Sag, inch	<0.25
Crosspeel, psi(%FT):	
ARCTCO	<u>7d@RT</u>
Original	182(100/0)
	320(100/0)
	245(100/0)
	262(100/0)
	<u>259(100/0)</u>
	254(100/0)
ARCTCO	<u>7d@RT</u>
Cold Press	512(50/0)
	487(40/0)
	375(50/0)
	425(70/0)
	<u>479(75/0)</u>

	456(57/0)
Stress-Strain:	
<i>Ultimate Tensile, psi</i>	2600
<i>Ultimate Elong, %</i>	64

EXAMPLE 8

This example 8 illustrates the adhesion performance of an unsaturated polyester, unsaturated polyurethane and polyurethane hybrid adhesive on FRP.

Table 3. Performance of a Unsaturated Polyester / Acrylated Polyurethane / Polyurethane Hybrid Adhesive

Adhesive Ex 8	4344
PolyNCO:	4323
Rubinate 9310, %	10.90
Mistron RCS, %	0.87
Aerosil 200, %	0.26
Mol Sieves 5A, %	0.086
Luperco ATC, %	5.19
CURATIVE:	4338
PeP 550, %	2.54
ET 3500, %	10.45
DETDA, %	2.58
UPU in Example 3, %	38.04
UPE in Example 4, %	19.02
DAP, %	6.62
Aerosil 200, %	2.48
Mol Sieves 5A, %	0.41
DMA, %	0.50
Dabco T1, %	0.049
Mix Ratio, wt	20.9/100

Bondability, min	9
Heat Rise, °C/min	not done
Button Sag, inch	0.25
Squeeze out	TF
Trimmability	yes
Green Strength	30' 117(0/100) 45' 258(30/70)
Crosspeel, psi(%FT):	
ARCTCO FRP Plaque	<u>7d@RT</u> 289(100/0) 227(100/0) 235(100/0) 345(100/0) <u>254(1000)</u> 270(100/0)
Stress-Strain:	
Ultimate Tensile, psi	2160
Ultimate Elongation, %	20

Example 9

This example 9 illustrates the formulation of polyols with peroxide to form Part
5 A and unsaturated polymer and polyisocyanate to form Part B.

Table 4. Performance of Polyol-Peroxide / Acrylated Polyurethane-
Polyisocyanate Hybrid Adhesives.

Adhesive	4122	4123	4124	4125	4126	4127
PeP 550, g	20.02	13.33	10.01			
Curative 4002, g*				35.16	23.44	17.58
Luperco ATC, g	1.00	1.00	1.00	1.00	1.00	1.00
DMA, gram	0.10 g	0.10 g	0.10	0.10 g	0.07 g	0.07
UPU Example 3, g	50.00	66.67	75.00	50.00	66.67	75.00
Rubinate 9310, g	29.98	20.00	14.99	14.84	9.89	7.42
Open Time, min	2	4	10	4.5	6	10-30
Squeeze Out	Tack-free	Tack-free	Tack-free	Tack-free	Tack-free	Tack-free
Crosspeel, psi(%FT):						
ARCTCO	<u>7d@RT</u>					
	273(100/0)	<u>7d@RT</u>	<u>7d@RT</u>	<u>6d@RT</u>	<u>6d@RT</u>	<u>7d@RT</u>
	<u>14d@RT</u>	324(10/90)	189(100/0)	405(100/0)	189(100/0)	326(100/0)
	340(0/100)	355(30/70)	221(95/5)	334(100/0)	336(100/0)	366(100/0)
	290(10/90)	376(5/95)	221(100/0)	392(100/0)	363(100/0)	429(100/0)
	<u>382(0/100)</u>	<u>256(25/75)</u>	<u>171(100/0)</u>	<u>368(100/0)</u>	<u>240(100/0)</u>	<u>349(100/0)</u>
	337(3/97)	328(18/82)	210(99/1)	375(100/0)	313(100/0)	368(100/0)

*Curative 4002 is prepared by reacting the polyols PolyTHF250 (275.00 pbw) and TMP (35.76 pbw) with Mondur MRS polyisocyanate (133.00) before the addition of Luperco ATC (443.76 pbw).

Example 10

- 5 This example 10 illustrates the use of benzoylperoxide (BPO) / dimethylaniline (DMA) or methylethylketone peroxide (DDM9) / cobalt naphthenlate to cure unsaturated polymer and polyurethane hybrid adhesives.

Table 5. Peroxide Curing of Hybrid Adhesives

ADHESIVE	4118 112795	4086 110895	4086 110995
PLIOGRIP 9400, g	26.24	19.69	19.69
UPU Example 3, g	66.67	50.00	50.00
DMA, g	—	—	0.10
6% Cobalt Naph* g	0.72	0.60	—
Methyl Ethyl Ketone Peroxide, g	1.80	1.50	—
Luperco ATC, g	—	—	5.0
UPE Example 4, g		25.00	25.00
PeP 550, g	7.09	5.31	5.31
Mix Ratio, wt		3.1/1.0	2.0/1.0
Bondability Time, min	22	>120	77
Crosspeel, psi(%FT):			
ARCTCO FRP Plaque	<u>7d@RT</u>	<u>7d@RT</u>	<u>8d@RT</u>
	360(100/0)	337(60/40)	299(95/5)
	181(100/0)	250(40/60)	266(95/5)
	326(100/0)	<u>19d@RT</u>	291(100/0)
	<u>397(100/0)</u>	310(100/0)	<u>313(95/5)</u>
	316(100/0)	273(75/25)	292(96/4)

*OM Group, Inc., Outokumpu Chemicals. Mooney Chemicals Inc.

Vasset S.A. Cleveland, Ohio.

Example 11

This example 11 illustrates the use of diallyl phthalate (DAP) to achieve
 5 flexibility in unsaturated polymer / polyurethane hybrid adhesives. Ultimate
 elongation values as high as 85% as measured in the stress-strain test of the
 neat adhesives were observed.

Table 6. Diallyl phthalate (DAP) as an Effective Promotor of Flexibility for

10 Unsaturated Polymer / Polyurethane Hybrid Adhesives

Adhesive	4134	4234
<i>PolyNCO:</i>		4228
PG 9400, %	24.15	
Rubinate 9310, %		8.85
UPU Example 3, %		59.69
DAP, %		6.24
Mistron RCS, %		none
Aerosil 200, %		2.73
Mol Sieves 5A, %		0.39
Luperco ATC, %	0.92	
DMA, %		0.090
<i>CURATIVE</i>		4198
PolyTHF 250* %		6.29
PeP 550, %	6.53	
Trimethylolpropane, %		0.40
Rubinate 9310, %		2.56
Mondur MRS, %		---
Mistron RCS, %		1.76
UPU Example 3, %	61.37	---
DAP, %	6.93	
DMA, %	0.092	1.76
Luperco ATC, %		11.00

Mix Ratio, wt	33.5/100	350/100
Bondability, min	29	~28
Green Strength		20' 190(2/98) 30' 326(75/25)
Crosspeel, psi(%FT):		
ARCTCO FRP Plaque	<u>7d@RT</u> 264(75/25) 314(100/0) 213(25/75) <u>396(40/60)</u>	<u>7d@RT</u> 251(100/0) 386(100/0) 282(100/0) 240(100/0) <u>432(100/0)</u>
Avg	297(60/40)	318(100/0)
Stress-Strain:		
Ultimate Tensile, psi	3350	3120
Ultimate Elongation, %	59	85

*Polytetramethylene ether glycol, MW 250.

Review of the Table 6 data shows that diallyl phthalate was very
 5 effective for promoting high ultimate elongation values of 59 to 85% for both
 unsaturated polyurethane / polyurethane prepolymer and unsaturated
 polyurethane / polyisocyanate adhesives.

Example 11a

10 This example illustrates the use of an epoxy resin such as Epon 826 to
 achieve flexibility in unsaturated polymer / polyurethane hybrid

adhesives. Ultimate elongation value of 63% as measured in the stress-strain test of the neat adhesive was observed.

Table 6a. Epoxy Resin as an Effective Promotor of Flexibility for Unsaturated

5

Polymer / Polyurethane Hybrid Adhesives

ADHESIVE	4637
PolyNCO	4631
Rubinate 9310, %	10.32
Molecular Sieves 5A, %	0.21
EPON 826, % *	3.19
Aerosil R972, %	1.26
Luperco ATC, %	6.38
CURATIVE	4595
Pep 550, %	2.62
ET 3500, %	10.76
DETDA, %	2.66
UPU in Example 3, %	34.64
Methyl Methacrylate, %	15.40
DAP, %	3.85
Cabosil TS720, %	7.57
Molecular Sieves 5A, %	0.38
StanTone 6783, %	0.15
DMA, %	0.54
Luperco ATC, %	0.054
Mix Ratio, wt	27/100
Bondability, min	5
Vertical Cardboard	Very good non sag
Hear Rise, °C/min	91/5.5
Green Strength	20' 305(90/0/0) 30' 241(15/85/0)
Crosspeel, psi (%FT) ARCTCO FRP Plaque	4dRT 373 (100/0) 310 (100/0) 307 (100/0) 145 (100/0) <u>275 (100/0)</u> 282 (100/0)
ARCTCO FRP Hull, white	4dRT 278(100/0)

	294(100/0) 277 (100/0) 182(100/0) <u>212(100/0)</u> 250(100/0)
ARCTCO Cold Press	7d@RT 290(30/0) 214(50/0) 120(0/0) <u>384(50/0)</u> 242(31/0)
Mercury Marine FRP	4d@RT 326(100/0) 291(100/0) 355(100/0) 285(100/0) <u>393(100/0)</u> 330(100/0)
Stress Strain:	
Ultimate Tensile, psi	3640
Ultimate Elongation, %	63

*EPON 826 epoxy resin is the product of epichlorshydrin and bisphenol A available from Shell.

Example 12

5 This example 12 illustrates the humidity resistance of the unsaturated polymer / polyurethane hybrid adhesives. Tables 7, 8 and 9 show adhesives retaining as much as 100% of the adhesion to FRP after exposure to 100% relative humidity at 100°F (38°C) for 4 and 8 weeks.

10

Table 7. Formulations of Unsaturated Polyurethane Polymer
/Polyurethane Hybrid Adhesives.

Adhesive	4233	4221	4159
<i>Part A</i>	<i>Polyisocyanate +</i>	<i>Unsaturated</i>	<i>Prepolymer</i>
	<i>Polyurethane</i>		
Polyisocyanate	4216	4205	4141
Rubinate 9310, %	11.95	7.91	
UPU Example 3, %	40.26	53.30	
Mistron RCS, %	14.85	15.58	
Aerosil 200, %	---	0.77	
Mol Sieves 5A, %	0.33	0.23	
DMA, %	0.097	0.10	
PLIOGRIP 9400, %	---	---	19.27
Luperco ATC, %	---	---	0.73
PART B:	4158	4198	4128
UPU Example 3, %			48.99
PeP550, %			5.21
DMA, %			0.073
PolyTHF 250, %	9.71	6.32	
TMP, %	0.61	0.40	
Rubinate 9310, %	---	2.57	
Mondur MRS, %	3.65	---	
Mistron RCS, %	2.28	1.77	25.72
Luperco ATC, %	16.25	11.05	
Mix Ratio, wt	208/100	≈353/100	25/100
Bondability, min	3	6	25
Heat Rise, °C/min	141/6	157/7	39/10
Squeeze out	Tack Free	TF	TF
Trimmability	yes/<8 min	yes/≤10 min	yes
Green Strength	10' 227(2/98) 20' 335(70/30)	9' 90(0/90) 12' 227(10/90)	
Stress-Strain:			
Ultimate Tensile, psi	2060	3270	
Ultimate Elongation, %	20	23	

Table 8. Humidity Resistance of Unsaturated Polyurethane

Polymer/Polyurethane Hybrid Adhesives from Table 7

Adhesive	4233	4221	4159
Chemistry	Polyisocyanate /	Unsaturated Polyurethane	Prepolymer / Unsaturated Polyurethane
Crosspeel, psi(%FT/CF):			
ARCTCO FRP Plaque	<u>7d@RT</u> 352(100/0) 317(100/0) 280(100/0) 293(100/0) <u>218(100/0)</u> 292(100/0)	<u>7d@RT</u> 305(95/5/0) 320(100/0/0) 238(100/0/0) 262(100/0/0) <u>247(95/5/0)</u> 274(100/0)	<u>7d@RT</u> 254(60/40) 498(98/2) 296(35/65) 389(90/10) 264(80/20) 393(85/15) 394(90/10) 299(90/10) 333(65/35) <u>320(100/0)</u> 344(79/21)
ARCTCO FRP Plaque 2 weeks 100%RH/100°F Tested <u>wet /</u> <u>warm</u>			278(95/5) 226(100/0) 338(100/0) 242(100/0) <u>202(100/0)</u> 257(99/1)
ARCTCO FRP Plaque 4 weeks 100%RH/100°F Tested <u>wet /</u> <u>warm</u>	450(100/0) 381(100/0) 386(100/0) 377(100/0) <u>244(100/0)</u> 368(100/0)	275(100/0) 300(100/0) 318(100/0) 402(100/0) <u>296(100/0)</u> 318(100/0)	353(1000) 371(100/0) 313(100/0) 294(100/0) <u>314(100/0)</u> 329(100/0)

Avg			
ARCTCO FRP	326(100/0)	290(100/0)	223(100/0)
Plaque	341(100/0)	285(100/0)	229(100/0)
8 weeks	415(100/0)	274(100/0)	320(100/0)
100%RH/100°F	355(50/50)	392(1000)	253(100/0)
Tested <u>wet /</u>	<u>400(70/30)</u>	<u>310(100/0)</u>	<u>168(100/0)</u>
<u>warm</u>	367(84/16)	310(100/0)	239(100/0)

Table 9. Humidity Resistance of Adhesive 4606 in Table 1, Example 6

Crosspeel	7 days @ RT	After 8 weeks / 100%RH/100°F
ARCTCO FRP <u>Plaque</u> Avg standard deviation	272(100/0) 14(8/0)	284(100/0) 22(0/0)
ARCTCO <u>white FRP</u> <u>Plaque</u>	225(100/0) 52(5/0)	235(100/0) 27(0/0)
ARCTCO FRP <u>Hull</u> <u>Parts</u>	429(100/0) 90(28/0)	294(100/0) 124(2/0)
ARCTCO <u>white Hull</u> <u>Parts</u>	226(100/0) 55(13/0)	206(100/0) 38(0/0)
ARCTCO Cold Press	342(88/0) 34(10/0)	307(82/0) 26(27/0)
Mercury Marine	278(100/0) 31(11/0)	294(100/0) 18(0/0)

5

Review of Tables 7, 8 and 9 reveals that some adhesives of this invention provide laminates having humidity resistance whether the adhesives are Part A polyisocyanate plus unsaturated polyurethane;- Part B polyol plus peroxide or Part A polyisocyanate plus peroxide - Part B polyol plus unsaturated

10 polyurethane.

I Claim:

1. A two component structural adhesive composition for substrates requiring no surface pretreatment and curable at ambient temperatures comprising either:

a) a first component mixture of polyisocyanate and peroxide and a second component mixture of polyol or polyamine or combinations thereof, and unsaturated polymer.

or

b) a first component mixture of polyisocyanate and unsaturated polymer, a second component mixture of polyol and peroxide.

2. The adhesive of claim 1 wherein said peroxide is benzoyl peroxide.

3. The adhesive of claim 1 further comprising diallyl phthalate.

4. The adhesive of Claim 1 wherein said polyisocyanate is polymeric methylene diphenyl polyisocyanate, said polyol is a mixture of propoxylated pentaerythritol and propoxylated glycerin, said polyamine is diethyl toluene diamine, and said unsaturated polymer comprises unsaturated polyurethane or unsaturated polyester or combinations thereof.

5. The adhesive of Claim 1 wherein said substrates are selected from the group of fiberglass reinforced plastic, metal and wood.
6. The adhesive of Claim 1 wherein said substrates are fiberglass reinforced plastic.
7. A laminate of two substrates having no surface pretreatment adhered together by the cured residue of a two component adhesive mixed before application to one of said substrates, said adhesive comprising polyisocyanate,
polyol or polyamine or mixtures thereof,
unsaturated polyurethane or
unsaturated polyester or mixtures thereof,
and peroxide.
8. The laminate of claim 7 wherein said polyisocyanate and said peroxide are provided in a first component mixture and said polyol or polyamine and said unsaturated polymer provided in a second component mixture,
9. The laminate of claim 7 wherein said polyol and said peroxide are provided in a first component mixture and said polyisocyanate and said unsaturated polyurethane or said unsaturated polyester are provided in a second component mixture.

10. The laminate of claim 7 displaying, when disrupted, tearing of said fiber glass reinforced plastic substrate and continuing integrity of said cured adhesive residue.
11. The laminate of Claim 7 wherein said polyisocyanate is polymeric methylene diphenyl polyisocyanate, said polyol is a mixture of propoxylated pentaerythritol and propoxylated glycerin, said polyamine is diethyl toluene diamine, and said unsaturated polymer comprises unsaturated polyurethane or unsaturated polyester or combinations thereof.
12. The laminate of Claim 7 wherein said substrates are selected from the group of fiberglass reinforced plastic, metal and wood.
13. The laminate of Claim 7 wherein substrates are fiberglass reinforced plastic.
14. The method of making a laminate of a first untreated substrate and a second substrate adhered together with a structural adhesive comprising a peroxide curable unsaturated polymer in combination with a polyurethane or polyurethaneurethane, such adhesive having room temperature curable property, variable open time, sag resistance on a vertical surface, tack free squeeze-out along the bondline, trimmable squeeze-out along the bondline, fast green strength development, at least 20% ultimate elongation, humidity resistance, and low temperature resistance, comprising the steps of applying to said first

- substrate an adhesive composition comprising a mixture of a first component a) polyisocyanate and peroxide and a second component b) unsaturated polymer and polyol or polyamine or mixtures thereof.
15. The method of claim 17 wherein the equivalent ratio of polyisocyanate: polyol plus polyamine is 0.8 to 1.8:1.
 16. The method of claim 17 comprising 15 to 50 parts by weight of said first component and 50 to 85 parts by weight of said second component.
 17. The method of claim 17 wherein said first component comprises polyisocyanate and unsaturated polymer and said second component comprises polyol and peroxide.
 18. The method of Claim 17 wherein the equivalent ratio of polyisocyanate:polyol is 0.8 to 1.8:1.
 19. The method of Claim 17 wherein said polyisocyanate is polymeric methylene diphenyl polyisocyanate, said polyol is a mixture of propoxylated pentaerythritol and propoxylated glycerin, said polyamine is diethyl toluene diamine, and said unsaturated polymer comprises unsaturated polyurethane or unsaturated polyester or mixtures thereof.
 20. The method of Claim 17 wherein said substrates are selected from the group of fiberglass reinforced plastic, metal and wood.

21. The method of Claim 17 wherein said substrates are fiberglass reinforced plastic.
22. An adhesive composition for substrates requiring no surface pretreatment comprising polyisocyanate, peroxide, polyol, unsaturated polymer, and optionally polyamine.
23. The adhesive of Claim 25 wherein said peroxide is tertiary butyl perbenzoate.
24. The adhesive of Claim 25 wherein said substrates are selected from the group of fiberglass reinforced plastic, metal and wood.
25. The adhesive of Claim 25 wherein said substrates are fiberglass reinforced plastic.
26. The adhesive of Claim 1 further comprising epoxy resin.
27. The laminate of Claim 7 wherein said adhesive further comprises epoxy resin.
28. The method of Claim 14 wherein said adhesive further comprises epoxy resin.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US98/01793

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :Please See Extra Sheet.

US CL :Please See Extra Sheet.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 524/589, 590; 525/123, 131, 455; 428/423.1; 156/330, 331.4, 331.7

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
NONE

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X ----- Y	US 4,439,576 A (O'CONNER et al.) 27 March 1984, See entire document.	1-28 ----- 1-28
X -- Y	US 4,584,325 A (SMITH) 22 April 1986, See entire document.	1-28 ----- 1-28
X -- Y	US 5,272,204 A (AKIMOTO et al.) 21 December 1993, See the entire document.	1-28 ----- 1-28
X -- Y	US 5,212,210 A (HALM) 18 May 1993, See entire document.	1-28 ----- 1-28



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
A document defining the general state of the art which is not considered to be of particular relevance	*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
B earlier document published on or after the international filing date	*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*g* document member of the same patent family
O document referring to an oral disclosure, use, exhibition or other means	
P document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

16 APRIL 1998

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INTERNATIONAL SEARCH REPORT

 International application No.
 PCT/US98/01793

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X --- Y	US 5,447,921 A (BORDEN et al.) 05 September 1995, See the entire document.	1-28 ----- 1-28
X --- Y	US 4,816,535 A (BOWERS et al.) 28 March 1989, See the entire document.	1-28 ----- 1-28
X -- Y	US 4,822,849 A (VANDERLAAN) 18 April 1989, See the entire document.	1-28 ----- 1-28
X -- Y	US 4,835,012 A (SAUR) 30 May 1989, See the entire document.	1-28 ----- 1-28
X -- Y	US 4,452,964 A (SARACSAN) 05 June 1984, See the entire document.	1-28 ----- 1-28
X -- Y	US 4,581,384 A (MARION) 08 April 1986, See the entire document.	1-28 ----- 1-28
X -- Y	US 3,945,875 A (JACKSON) 23 March 1976, See the entire document.	1-28 ----- 1-28
X -- Y	US 4,443,518 A (MARTINS et al.) 17 April 1984, See the entire document.	1-28 ----- 1-28

INTERNATIONAL SEARCH REPORT

International application No.
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A. CLASSIFICATION OF SUBJECT MATTER:

IPC (6):

C08J 3/00; C08K 3/20; C08L 75/00; C09J 4/00, 101/00, 201/00; B32B 27/00, 27/40; C08F 8/00, 8/30, 283/04

A. CLASSIFICATION OF SUBJECT MATTER:

US CL :

524/589, 590; 525/123, 131, 455; 428/423.1; 156/330, 331.4, 331.7