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(54) Title: USE OF PET FILM PRIMED WITH POLYALLYLAMINE COATINGS IN LAMINATED GLASS GLAZING CONSTRUCTIONS

(57) Abstract: The present invention is a laminate comprising at least one layer of an polyallylamine-based coating that is in direct contact with at least one other polymeric layer.



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TITLE**Use of PET Film Primed With Polyallylamine Coatings In
Laminated Glass Glazing Constructions**5 **BACKGROUND OF THE INVENTION****Field of the Invention**

This invention relates to laminates used in
glazing applications. This invention particularly
relates to a process for improving adhesion between
10 layers in glazing laminates.

Description of the Related Art

Polyethylene terephthalate (PET) film can be used
as a laminate layer in laminated glazing products. In
such laminate products, the PET layer can be in contact
15 with other polymeric layers of the laminate. Such
commercial laminates as SENTRYGLAS™, and SPALLSHIELD™
products, which are laminate combinations of PVB and
polyvinyl butyral available from DuPont, are examples.
Imbedded film applications (for example, MET is PET
20 imbedded between layers of PVB) are still other
examples.

Glass/plastic laminates (that is, laminates having
glass on one outer side and a hard plastic or
hardcoated plastic on the other outer side) made using
25 PVB interlayer with a PET film outer layer can be quite
compressible because of the soft underlying PVB
interlayer. Such laminates are vulnerable to gouges and
impressions when hard objects impact them or are
pressed against them for some time. If the impressions
30 are deep, they can become permanent and this mars the
appearance of glazing using such glass plastic
laminates.

Harder interlayers would make the plastic side of glass/plastic laminates harder and less prone to gouging and pressure-induced impressions. However, use of such harder interlayers has been prevented by the lack of a sufficiently adherable PET film. For example, PET film treated by electrical discharge, various plasma treatments, or flame treatment does not adhere well to harder interlayers such as ionoplast sheeting, for example DuPont's SENTRYGLAS™-PLUS (SGP) interlayer.

To obtain the PET laminates such as those described hereinabove, it can be necessary to flame treat the PET layer under controlled conditions to enhance its adhesion to PVB on one side and to a hardcoat such as a polysiloxane abrasion resistant coating (PARC) on the other side. The adhesion strength, as measured by the 90-degree angle peel test, averages about 10 lb/inch. The flame treatment is done in a separate operation from the PET film casting. U.S. Pat. No. 5,415,942 describes a hydroxy-acrylic hydrosol primer coating that, when applied to one side of a PET film, greatly improves adhesion of the PARC. However it does not improve adhesion of the PET to the PVB interlayer. Therefore the primed film still needs to be flame treated on the non-primed side.

Also, the adhesion between PVB and ionoplast resins is poor, and so laminates having these two polymer interlayers in contact are not viable for many of the applications in which these interlayer materials find use.

It can be desirable to have a primer that can improve adhesion of PET to PVB and/or ionoplast resins,

and also improve adhesion between PVB and ionoplast resins.

SUMMARY OF THE INVENTION

In one aspect the present invention is a laminate comprising at least one layer of an polyallylamine-based coating that is adjacent to and in direct contact with at least one other polymeric layer comprising a polymer selected from the group consisting of: PET; PVB; ionoplast resin; polyurethanes; polyvinyl chlorides; polycarbonates; polyacetals; ethylene acid copolymers (which are inclusive of ethylene acid terpolymers); polyolefins, including polyethylenes and polypropylenes.

In another aspect, the present invention is a laminate comprising: a three-layer laminate structure comprising (1) a PET layer that is in contact with (2) a polyester film comprising a polyallylamine-based coating on each of its two surfaces, wherein the second surface is in direct contact with (3) a polyvinyl butyral (PVB) layer.

In another aspect, the present invention is a laminate comprising: a laminate structure comprising (1) an ionoplast resin layer that is in contact with (2) a polyvinyl butyral (PVB) layer, wherein the peel strength is at least 10 lb/inch between the ionoplast and the PVB layers and wherein at least one of the polymer layers comprises a polyester film comprising a polyallylamine-based coating on each of its two surfaces.

In another aspect, the present invention is a glass laminate comprising a three-layer laminate structure comprising: (1) a polymer selected from the

group consisting of polyethylene terphthalate (PET); polyvinylbutyral (PVB); and ethylene acid copolymer ionomer (ionoplast resin), said polymer being in contact with (2) an polyallylamine-based coating that is in contact with (3) a polymer selected from the group consisting of PET; PVB; ionoplast resin; polyurethanes; polyvinyl chlorides; polycarbonates; polyacetals; ethylene acid copolymers (which are inclusive of ethylene acid terpolymers); polyolefins, including polyethylenes and polypropylenes.

In another aspect, the present invention is a process for preparing a laminate comprising the steps of: (1) applying a polyester film having a coating of polyallylamine-based polymer (PRIMER) to at least one surface of a polymer selected from the group consisting of: polyethylene terphthalate (PET); polyvinylbutyral (PVB); and ethylene acid copolymer ionomer (ionoplast resin); and (2) contacting the coated polyallylamine coated surface with at least one polymeric layer selected from a polymer in the group consisting of: PET; PVB; ionoplast resin; polyurethanes; polyvinyl chlorides; polycarbonates; polyacetals; ethylene acid copolymers (which are inclusive of ethylene acid terpolymers); polyolefins, including polyethylenes and polypropylenes wherein the PRIMER is applied in-line with the polymer sheet, and wherein the PRIMER has been heated to a temperature above about 170°C and stretched before application to the polymer surface.

DETAILED DESCRIPTION OF THE INVENTION

In one embodiment, the present invention is a polymer which has adhered to at least one of its surfaces a polyester (PET) layer wherein the PET has a

coating of a polyallylamine-based primer applied to at least one of its surfaces, preferably to both surfaces of the PET. The primer and its application to the PET polymeric layer are described in U.S. Pat. Nos. 5,411,845; 5,770,312; 5,690,994; and 5,698,329. Generally, the PET film is extruded and cast as a film by conventional methods, and the polyallylamine coating is applied to the PET film either before stretching or between the machine direction stretching and transverse direction stretching operations, and/or after the two stretching operations and heat setting in the stenter oven. It is preferable that the coating be applied before the transverse stretching operation so that the coated PET web is heated under restraint to a temperature of about 220°C in the stenter oven in order to cure the polyallylamine to the PET surface. In addition to this cured coating, an additional polyallylamine coating can be applied on it after the stretching and stenter oven heat setting in order to obtain a thicker overall coating. The coated PET treated in this general manner is the primer (PRIMER) used herein to enhance the adhesion between dissimilar polymeric layers in a laminate construction.

Adhesive strength in a laminate of the present invention is determined by the 90° peel test. The adhesive strength between dissimilar polymer layers in the present invention can be about zero (0) to about less than 10 lb/inch without any treatment to enhance adhesion, and with flame treatment the adhesive strength can be improved to about 10 lb/inch. Using a PRIMER as described herein can improve the peel

strength to at least about 10 lb/in, and preferably to at least 15 lb/inch.

Suitable polymers useful in a laminate of the present invention include, for example: PET; PVB; 5 ionoplast resins, which are ethylene acid copolymer ionomers; polyurethanes; polyvinyl chlorides; polycarbonates; polyacetals; ethylene acid copolymers (which are inclusive of ethylene acid terpolymers); polyolefins, including polyethylenes and 10 polypropylenes. Preferred for use herein are polymers that are transparent, or that can be made to be transparent, such that they are suitable for use in glazing end-use applications. Particularly preferred for use herein are PET, PVB, and ionoplast resins.

15 PVB is a commercially available product that can be obtained from E.I. DuPont de Nemours and Company (DuPont) under the tradename of Butacite®. Ionoplast resins suitable for use herein are copolymers (inclusive of terpolymers) of ethylene and unsaturated 20 carboxylic acids wherein at least a portion of the acid groups in the copolymer have been neutralized to the salt form of the acid. Extruded sheets of ionoplast resin suitable for use in the present invention can be obtained from DuPont under the trade name of 25 SentryGlass® Plus (SGP).

Polyester films (PET) are well-known polymer films that can also be obtained commercially from DuPont. PET suitable for use herein can additionally comprise a hardcoat such as an abrasion resistant polysiloxane 30 material or an oligomeric coating as described in U.S. Application Serial No. 60/499949 on one of its surfaces. The polysiloxane coated PET can be obtained

commercially from DuPont. In laminates of PET and other polymers such as PVB and SGP, it can be conventional to enhance the adhesion of the PET to the other polymers by some treatment step such as a flame
5 treatment. In the practice of the present invention, adhesion of PET to any of the other polymers can be improved by applying the PRIMER to either surface of the dissimilar polymers prior to laminating the layers using conventional laminating methods. Use of the
10 PRIMER to improve the adhesion to PVB can eliminate the need for a flame treatment to obtain suitable adhesion between these polymers, for example.

In another preferred embodiment, the adhesion between PVB and ionoplast resin can be greatly improved
15 by applying the PRIMER to the surface of either polymer layer prior to lamination. A laminate can be constructed wherein ionoplast resin and PVB are adhered using the PRIMER and thus provide a
[Glass/PVB/PRIMER/ionoplast/PRIMER/PVB/Glass] laminate,
20 for example, having enhanced penetration resistance relative to conventional Glass/PVB/Glass laminates, without losing the desirable properties of the conventional PVB glass laminates.

Laminated polymer layers comprising the PRIMER can
25 be used in the construction of other multilayer laminates. For example, the laminate constructions obtained from PET/PRIMER/PVB can be laminated to glass, or between other polymeric layers, or a combination thereof. A PET layer can comprise a hardcoat on its
30 surface, and thus be used in glass/plastic product applications such as where Spallshield® or SentryGlass® laminated products find use. Alternatively, the

lamine can be imbedded between other polymeric
lamine layers without the hardcoat on the surface of
the PET. The PRIMER adheres very well to both PVB
resins and ionoplast resins, and this makes possible
5 its use with either interlayer in glass plastic
glazing.

In one embodiment, the PRIMER can be used to
adhere PVB having a low plasticizer content, and thus
higher modulus, to "normal" PVB or to other polymeric
10 interlayer materials as defined herein.

Generally, laminates of the present invention can
be useful in architectural as well as in vehicular
applications. For example, the laminates of the
present invention can be useful as windows in
15 buildings, doors, shelves, display cabinets,
partitions, as hurricane windows, bullet-resistant
glazings, sidelites and windshields in automobiles,
windows in planes and trains, and other applications
where laminated glazings can be used.

20 EXAMPLES

The Examples and Comparative Examples are
presented for illustrative purposes only, and are not
intended to limit the scope of the present invention in
any manner.

25 Example 1

Four PET films primed in-line with three different
primer coatings along with a flame treated PET film as
control, were laminated to glass with the primed sides
against high adhesion grade BUTACITE™ BE-1028 PVB
30 sheeting. The PET films were then tested for peel
adhesion strength against the PVB sheeting. These
samples were laminated to glass using an air autoclave

at a temperature of 135°C held for 30 minutes at a pressure of 17 atmospheres. The samples were vacuum bagged to remove air from between the PET and PVB and glass layers. A glass cover plate was used to maintain optical flatness and to insure complete contact between all layers. This cover plate was removed from the PET side of each laminate after the autoclaving step.

The primed films were various grades of polyester films. The PET film used for the PRIMER was primed in-line on both sides with a crosslinked polyallylamine coating, the second PET film used as a comparative (PETC1) was primed on one side in-line with a crosslinked acrylic hydrosol coating containing acrylamide functionality, and two other comparative PET films (PETC2 and PETC3) primed in-line on one side with a crosslinked 2-hydroxyethylacrylate functionalized acrylic hydrosol coating, available from DuPont, both single coating and stretched and double coated.

The flame treated control film was PETC4, and is the same PET film base as used in the PETC2 and PETC3 primed examples, except that instead of priming it was flame treated in a separate operation from the film making process, i.e. not flame treated in-line.

The finished laminates were clear and suitable for 90 degree angle peel testing. The laminate structure was: PET/PVB/GLASS.

The laminates were peeled at a 90-degree angle using an INSTRUMENTORS, Inc., Model SP-102B-3M90 SLIP/PEEL Tester. The laminates were peeled at rates of 1 inch and 2 inches per minute. The peel test results are tabulated below:

Table 1

PET FILM TYPE 90 Degree Peel Strength (lb/inch)

	^a Flame Treated (PETC4)	10.2
5	^a Acrylamide primed (PETC1)	0.2
	^a Hydroxyacrylic Single Primed (PETC2)	0.0
	^a Hydroxyacrylic Double Primed (PETC3)	0.0
	^b Polyallylamine Primed (PRIMER)	>50.0

10 ^aNot an example of the present invention.
^bExceeded load cell capability, i.e. did not peel at all.

15 The only primer that enhanced adhesion between the PET film and PVB sheeting was the polyallylamine. The adhesion was too high to measure.

Example 2

20 This example is the same as Example 1, but with these changes: (1) 95 mil thick SENTRYGLAS™-PLUS ionoplast sheeting was used as the interlayer instead of PVB, and (2) PRIMER and PETC4 were the only PET films tested. The 90-degree peel results are tabulated below:

Table 2

PET Film Type 90 Degree Angle Peel Strength (lb/inch)

25	^a PETC4	0.062
	PRIMER	>48.7

30 ^aNot an example of the present invention.

35 The adhesion between the polyallylamine primed PET film and the SGP resin sheet exceeded the capacity of the peel tester load cell. The result reported is the limit of the load cell.

Example 3

40 Laminated glass panels imbedding PET films were made and tested for compressive shear strength. The structures tested were these:

Structure A:
GLASS/PVB/PET/PVB/GLASS (PVB layers 30 mils thick)

- 5 Structure B:
GLASS/PVB/PET/PVB/PET/PVB/GLASS (PVB layers each 15
mils thick)

Two PET films were tested for compressive shear
10 strength (CSS): (1) PETC4 (7 mil thick), and (2) 6.50
mil thick PRIMER film.

The compressive shear strengths of the laminates
described herein were determined using the method
described in WO9961243(A1) and detailed here. 1"x1"
15 (25 mm x 25 mm) chips are sawed from the laminate and
conditioned in a room controlled at $23^{\circ}\text{C} \pm 2^{\circ}\text{C}$ and $50\% \pm 1\%$
relative humidity for one hour prior to testing. The
chip to be tested was placed in the apparatus. A
cross-head is lowered at the rate of 0.1 inch per
20 minute (2.5 mm per minute) until it contacts the upper
piece of the device. As the cross-head continues to
travel downward, it causes adhesive failure in the
chip. The compressive shear strength of the chip is
the shear stress required to cause adhesive failure.
25 The precision of this test is such that one standard
deviation is typically 6% of the average result of six
chips.

Controls were also tested, and these used the same
thicknesses of PVB but with no imbedded PET films.
30 These laminates were also measured for haze and
transmission in the visible region. The test results
are tabulated below:

		Table 3		
Laminate Structure		Haze (%)	T _{vis} (%)	CSS (psi)
5	a, ¹ Glass/60milPVB/glass	0.38	90.1	2,310
	a, ² A	0.78	89.4	722
	^b A	0.95	88.9	3,170
10	a, ¹ Glass/45milPVB/glass	0.36	90.2	1,714
	a, ² B	0.94	8.5	614
	^b B	1.48	82.8	2,388

^aNot an example of the present invention.
^bPRIMER
¹No PET present in laminate.
²PETC4

The use of the polyallylamine primer on both sides of the PET films greatly improved the laminate shear strength over that seen with flame treated PET film and even over that seen in laminates made without any imbedded film.

Example 4

Imbedded film laminates with the structure given below were made using an autoclave cycle of 135C at 200 psi for 30 minutes with the use of vacuum bags:

GLASS/INTERLAYER/FILM/INTERLAYER/GLASS

The films used were PRIMER film (primed on both sides) and PETC4, flame treated on both sides. Interlayers used were BE-1028 BUTACITE™ PVB and SENTRYGLAS™-PLUS ionoplast, both mixed and as sole types in the laminates. The interlayer sheets were 30 mils thick and the films were 6.5 - 7.0 mils thick.

The laminates were evaluated for compressive shear strength, haze, transmission, and color. The results are given below:

Table 4

	<u>Laminate Structure</u>			<u>Haze (%)</u>	<u>T_{vis} (%)</u>	<u>CSS (psi)</u>
	<u>Color</u>					
	<u>L*</u>	<u>b*</u>	<u>YID</u>			
5	^a G/PVB/PVB/G			0.53	90.6	3,581
	95.61	1.13	0.64			
	^a G/PVB/PET/PVB/G			0.74	89.5	1,380
	95.15	1.55	1.41			
10	G/PVB/PR*/PVB/G			0.92	89.1	3,900
	94.94	1.89	2.00			
	^a G/SGP/SGP/G			1.43	90.1	4,040
	95.31	0.97	0.49			
	^a G/SGP/PET/SGP/G			1.69	89.4	3,867
15	94.94	1.38	1.20			
	G/SGP/PR*/SGP/G			1.97	89.2	4,365
	94.80	1.63	1.69			
	^a G/SGP/PVB/G			1.19	90.2	372
	95.36	1.03	0.50			
20	^a G/SGP/PET/PVB/G			1.29	89.3	1,812
	94.97	1.51	1.38			
	G/SGP/PR*/PVB/G			1.46	89.0	1,793
	94.83	1.81	1.91			

25

^aNot an example of the present invention.

Notes: G = GLASS (90 mils thick and annealed); PET = flame treated 7.0 mil thick PET film (PETC4)

PR* = PET film primed on both sides with polyallylamine crosslinked coating (PRIMER).

30

Comments on the data in Table 4
PVB/SGP/film hybrid laminates:

The data show the poor adhesion between PVB and
5 SGP where the CSS was only 372 psi and the shearing
took place at the interface between the PVB and the
SGP. Both the PETC4 and PRIMER films improved the CSS
about equally. The shearing took place at the
10 glass/SGP interface for the PRIMER laminates and at the
PET/SGP for the PETC4 laminates.

PVB/film laminates:

Using the imbedded PRIMER film apparently
increases the CSS and using the flame treated PET film
15 reduces the CSS relative to using no intermediate layer
between the PVB.

SGP/film laminates:

The shearing took place at the SGP-to-glass interfaces.
20

Example 5

SENTRYGLAS™/SPALLSHIELD™ laminates were made using
flame treated PET film and PRIMER films by coating each
25 film on one side with polysiloxane abrasion resistant
hardcoat followed by lamination to glass in an
autoclave at 135°C for 30 minutes at a pressure of 17
atmospheres using vacuum bags.

A polysiloxane abrasion resistant coating (PARC)
30 solution was made by the technique described in U.S.
Pat. No. 5,069,942 and was coated onto the films using
a "RESOURCE I" bench top lab coater (sold by BYK-
Gardner, Inc.) fitted with a #16 wire-wound coating rod
which gave a PARC coating measuring about 2.5 microns
35 in dried thickness. The coating was allowed to dry at
room temperature, and then the coated films were

laminated to glass using an air autoclave and a removable coverplate that acted to insure optically flat laminates. The interlayer materials used were 30 mil SENTRYGLAS™-PLUS ionoplast and 30 mil BUTACITE™
5 PVB.

The product laminates were measured for optical properties and abrasion resistance using the Taber Abrader (ANSI Z26.1 Standard, Test No. 34) method. The laminates were then immersed in boiling water for 6
10 hours followed by testing again for optical properties (ASTM D 1003-61), PARC adhesion (D 3359 - 87), micro-blistering, and PET-to-interlayer adhesion (peel testing). The results are tabulated below in Table 5.

Table 5

Construction	Treat- Ment ^a	PET peel Strength (lb/inch)	Gloss 20°	ΔHaze (%)	T _{vis} (%)	YID Haze	Taber Abrasion (%)	PARC Adhes. Retention (%)	Blisters (no./cm ² / dia mm)
¹ G/PVB/PET	(1)	10.2	87.6	0.85	92.3	1.35	1.8	100	none
	(2)	0.0	-	1.03	92.3	1.32	-	94	240/.08
G/PVB/PR*	(1)	>50	88.8	0.98	91.8	1.89	1.5	100	none
	(2)	>50	-	1.28	92.2	1.79	-	100	65/.11
¹ G/SGP/PET	(1)	0.06	90.4	1.02	92.3	1.18	0.8	100	none
	(2)	0.0	-	7.76	83.4	1.03	-	100	340/.08
G/SGP/PR*	(1)	>50	88.7	1.28	91.9	1.64	1.4	100	none
	(2)	>50	-	2.47	89.1	4.62	-	100	52/.14

^a(1) = As made; (2) = 6-hour boil.

¹Not an example of the present invention.

G = 90 mil annealed glass; PET = flame treated PET film, 7.0 mils thick (PETC4)

PR* = PET film primed on both sides with polyallylamine coating (PRIMER).

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15

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Example 6

Two laminates were made with 6.5 mil PRIMER film:
(A) structure "A" used 30 mil BUTACITE™ PVB sheeting
5 and the 6.5 mil primed PET, and (B) structure "B" was
made using 60 mil SENTRYGLAS™-PLUS ionoplast interlayer
and the 6.5 mil primed PET. Both laminates were made
with the GLASS/INTERLAYER/PET construction and a
removable cover plate of 90 mil glass was used against
10 the plastic side of the laminates to give it an
optically flat surface. The laminates were vacuum
bagged followed by heating in an autoclave at 135°C for
30 minutes at temperature and 200 psi pressure.

These laminates were tested for pressure-induced
15 impressions by pressing against them a weighted steel
stylus having a spherical head with a radius of 0.50
mm. The stylus was pressed normal against the plastic
sides of the two samples at a given weight for 1
minute, and then the stylus was removed and the
20 laminates were allowed to sit at room temperature
(73°F) for one hour before measuring the depths of the
resulting impressions. The impression depths were
measured by measuring the width of the circular shaped
impressions and then calculating the depth assuming
25 this impression width was the chord on a circle
measuring 1.00 mm in diameter (the diameter of the
spherical stylus head).

The results are tabulated in Table 6. Neither
laminates suffered lasting impressions at a weight of
30 246 grams, but with a weight of 501 grams both
developed measurable impressions, but the one on the
laminates using the ionoplast interlayer was not visible
to the unaided eye whereas the one on the laminates

using PVB interlayer was visible. As the weight on the stylus was increased, the impressions became deeper and more visible, but two differences were noted in the way the two laminates behaved: (1) the laminates with PVB
5 interlayer depressed more deeply at any given weight than those with SGP interlayer, and (2) the laminates with PVB interlayer took the circular stylus impression, but they also formed very broad depressions surrounding them; i.e. the surface formed wide
10 impressions with a center core impression from the stylus itself, while the laminates containing the SGP interlayer only deformed at the stylus location with no broad ancillary surrounding depression.

The laminates using SGP ionoplast resin interlayer
15 were much harder and more resistant to deformation than those using the softer PVB interlayer.

Table 6
Impressibility of SPALLSHIELD™ Laminates using PVB and
SGP as Interlayers

Weight on Stylus (grams)	Impression Depth (mm)	
	SGP Interlayer	PVB Interlayer
246	0.0000	0.0000
501	0.0098	0.0180
647	0.0122	0.0289
787	0.0173	0.0382
884	0.0199	0.0430
980	0.0227	0.0526

5 **Example 7**

The use of polyallylamine primed PET film in SP/SG laminates allows the use of SGP as the interlayer instead of PVB, and, as described above, it gives a
10 harder plastic side to the laminates that is more resistant to dents and dings from rough handling. But it also gives a stiffer laminate post breakage, and so should perform well in the hurricane test from both the impact and pressure cycling aspects.

15 Two SGP based SP/SG laminates were tested for impact performance using a bull-nosed pendulum impactor that weighed 70.12 lbs. The nose is of steel and is hemispheric with a 3" diameter rounded head. The 12" X 12" laminates were securely fastened in a vertical
20 steel frame with rubber gasketing. Impact energy is determined by the height of the impactor above the center of the laminate at the release point. The impactor height was increased until it fully penetrated the laminate and this was the Height reported in the
25 Table below, and the penetration energy (reported in the Table below) was calculated using this height and the weight of the impactor.

The two SGP-based laminates used 60 mil SENTRYGLAS™-PLUS interlayer. One used 7.0 mil thick

CRONAR™ 732C film that was flame treated, and the other one used 6.5 mil PRIMER film that was primed in-line with polyallylamine coating. The results are shown in Table 7.

5

Table 7
Pendulum Impact Test Results on Glass/Plastic Laminates
and Hybrid Laminates Containing Different PET Films and
Either SGP and/or PVB Interlayers

Sample	Laminate Construction	PET Film Type	PVB Type	Ionoplast (SGP)	Energy (ft-lbs)	Ht (ft)
AA ^a	GLASS/PVB/PET	PETC4 ¹	BE-1030 ³	none	1.92	135
BB ^a	GLASS/PVB/PET	PETC5 ²	BE-1030 ³	none	1.92	135
CC	GLASS/PVB/PET	PRIMER ⁴	BE-1030 ³	none	2	140
DD ^a	GLASS/SGP/PET	PETC4 ¹	none	60 mil	2.58	181
EE	GLASS/SGP/PET	PRIMER ⁴	none	60 mil	3.75	263
GG	GLASS/PVB/PET/SGP/PET	PRIMER ⁴	BE-1030 ³	60 mil	>5.75	>403
HH ^a	GLASS/PVB/SGP/PVB/GLASS	none	BE-1030 (30 mil)	60 mil	4.08 ⁵	286
JJ ^a	GLASS/PVB/PET/SGP/PET/PVB/GLASS	PETC4 ¹	BE-1030 (30 mil)	60 mil	4.75	333
KK	GLASS/PVB/PET/SGP/PET/PVB/GLASS	PRIMER ⁴	BE-1030 (30 mil)	60 mil	4.67	327

- 5 ¹7 mil thick film that has standard flame treatment on both sides.
²7 mils thick and has no surface treatment for adhesion improvement.
³BE-1030 is high adhesion grade PVB available from DuPont.
⁴6.5 mils thick and primed in-line.
10 ⁵Laminate suffered massive delamination between PVB and SGP interlayers.
^aNot an example of the present invention.

Example 8

- 15 Polyallylamine primed PET film also makes possible hybrid SP/SG laminate structures wherein SGP and PVB can be used in the same laminate with the primed film acting as the adhesive layer attaching them strongly together. The PET also adds its high strength and
20 stiffness to the total structure as well. Such a structure is included in the table used in Example 7 as Sample "GG". This structure could not be penetrated below 400 ft-lbs, and was not penetrated in this test.

25

CLAIMS**WHAT IS CLAIMED IS:**

1. A laminate comprising at least one layer of a polyester film that has been coated with an polyallylamine polymeric coating (PRIMER) that is adjacent to, and in direct contact with, at least one other polymeric layer comprising a polymer selected from the group consisting of: PET; PVB; ionoplast resin; polyurethanes; polyvinyl chlorides; polycarbonates; polyacetals; ethylene acid copolymers (which are inclusive of ethylene acid terpolymers); polyolefins, including polyethylenes and polypropylenes.
2. The laminate of Claim 1 wherein the PRIMER has been heated to a temperature above about 190°C and stretched prior to application to the other polymer.
3. The laminate of Claim 2 wherein the other polymer in direct contact with the PRIMER is PVB.
4. The laminate of Claim 2 wherein the other polymer in direct contact with the PRIMER is an ionoplast resin.
5. The laminate of Claim 2 wherein the PRIMER is in direct contact with two of the other polymers, wherein the two other polymers are not the same polymer type.
6. The laminate of Claim 5 wherein at least one of the two other polymers in direct contact with the PRIMER is PET.
7. The laminate of Claim 6 wherein the other polymer in direct contact with the PRIMER is PVB.

8. The laminate of Claim 6 wherein the other polymer in direct contact with the PRIMER is an ionoplast resin.

5 9. The laminate of Claim 5 wherein the two other polymers in direct contact with the PRIMER are PVB and an ionoplast resin.

10 10. The laminate of Claim 6 wherein the PET in direct contact with the PRIMER comprises on its other surface a polysiloxane abrasion resistant coating (PARC).

11. The laminate of Claim 10 wherein the other polymer in direct contact with the PRIMER is PVB.

15 12. The laminate of Claim 10 wherein the other polymer in direct contact with the PRIMER is an ionoplast resin.

13. A laminate comprising: (1) a first polymer layer that is in contact with (2) a polyester film that has been coated with an polyallylamine coating (PRIMER), wherein the PRIMER is additionally in direct contact with (3) a second polymer layer, wherein the second polymer is additionally in direct contact with (4) a second PRIMER layer, wherein the second PRIMER is additionally in direct contact with (5) a third polymer layer.

25 14. The laminate of Claim 13 wherein the first, second and third polymers are polymers selected from the group consisting of: PET; PVB; ionoplast resin; polyurethanes; polyvinyl chlorides; polycarbonates; polyacetals; ethylene acid copolymers (which are inclusive of ethylene acid terpolymers); polyolefins, 30 including polyethylenes and polypropylenes, and wherein

the first and third polymers are not the same polymer type as the second polymer.

15. The laminate of Claim 14 wherein the first polymer is PET.

5 16. The laminate of Claim 15 wherein the first and the third polymers are each PET.

17. The laminate of Claim 16 wherein either the first or third polymers further comprises a polysiloxane abrasion resistant coat on the surface that is not in direct contact with the PRIMER.

10 18. The laminate of Claim 14 wherein the second polymer is PET.

19. The laminate of Claim 18 wherein the first and third polymers are the same polymer type.

15 20. The laminate of Claim 19 wherein the first polymer is an ionoplast resin.

21. The laminate of Claim 19 wherein the third polymer is PVB.

22. The laminate of Claim 14 wherein the first and third polymers are the same, and wherein neither the first or the second polymer is PET.

23. The laminate of Claim 22 wherein the first polymer is PVB.

24. The laminate of Claim 22 wherein the first polymer is an ionoplast resin.

25. The laminate of Claim 14 wherein the first and third polymers are different, and wherein neither the first or the second polymer is PET.

26. A laminate comprising: (1) an ionoplast resin layer that is in direct contact with (2) a polyester film that has been coated with an polyallylamine coating (PRIMER), wherein the PRIMER is additionally in

direct contact with (3) a polyvinyl butyral (PVB) layer, wherein the peel strength is at least 10 lb/inch for the laminate.

27. A process for preparing a laminate comprising
5 the steps of: (1) applying a polyester film having a coating of polyallylamine-based polymer (PRIMER) to at least one surface of a polymer selected from the group consisting of polyethylene terphthalate (PET); polyvinylbutyral (PVB); and ethylene acid copolymer
10 ionomer (ionoplast resin) and (2) contacting the coated polyallylamine coated surface with at least one polymeric layer selected from a polymer in the group consisting of: PET; PVB; ionoplast resin; polyurethanes; polyvinyl chlorides; polycarbonates;
15 polyacetals; ethylene acid copolymers (which are inclusive of ethylene acid terpolymers); polyolefins, including polyethylenes and polypropylenes wherein the PRIMER is applied in-line with the polymer sheet, and wherein the PRIMER has been heated to a temperature
20 above about 170°C and stretched before application to the polymer surface.

28. An article comprising a laminate of Claim 1.

29. The article of Claim 28 wherein the article
is an article selected from articles in the group
25 consisting of: automobiles, windows, display cabinets, trains, airplanes, boats, buildings, stairs, ceilings, walls, and skylights.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US2004/042266

A. CLASSIFICATION OF SUBJECT MATTER		
IPC 7	B32B27/08 B29C55/14	B32B17/10 C08J5/12 C08J7/04 C08F126/02
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)		
IPC 7	G02B A61L G03C B32B C08J C08F B29C	
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used)		
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C. DOCUMENTS CONSIDERED TO BE RELEVANT		
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<input checked="" type="checkbox"/> Further documents are listed in the continuation of box C. <input checked="" type="checkbox"/> Patent family members are listed in annex.		
* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "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) "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 "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 "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 "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. "&" document member of the same patent family		
Date of the actual completion of the international search		Date of mailing of the international search report
8 April 2005		19/04/2005
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016		Authorized officer Lindner, T

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
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